



ARKANSAS  
Department of Environmental Quality

March 27, 2009

Charlie Clark  
VP of HR & Government Affairs  
Cross Oil Refining & Marketing, Inc.  
484 East 6th Street  
Smackover, AR 71762

Dear Mr. Clark:

The enclosed Permit No. 1227-AR-16 is your authority to construct, operate, and maintain the equipment and/or control apparatus as set forth in your application initially received on 11/20/2008.

After considering the facts and requirements of A.C.A. §8-4-101 et seq., and implementing regulations, I have determined that Permit No. 1227-AR-16 for the construction, operation and maintenance of an air pollution control system for Cross Oil Refining & Marketing, Inc. be issued and effective on the date specified in the permit, unless a Commission review has been properly requested under §2.1.14 of Regulation No. 8, Arkansas Department of Pollution Control & Ecology Commission's Administrative Procedures, within thirty (30) days after service of this decision.

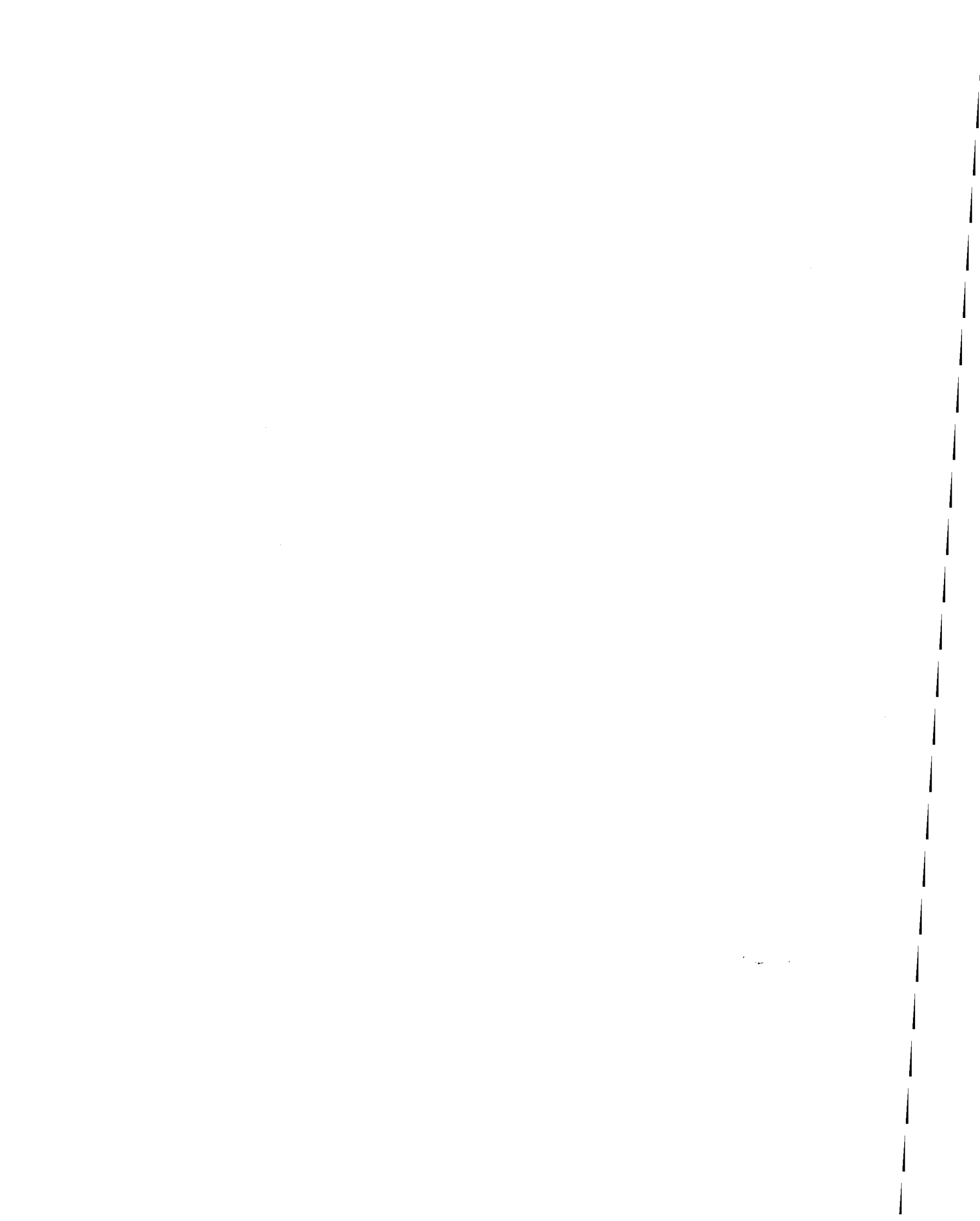
All persons submitting written comments during this thirty (30) day period, and all other persons entitled to do so, may request an adjudicatory hearing and Commission review on whether the decision of the Director should be reversed or modified. Such a request shall be in the form and manner required by §2.1.14 of Regulation No. 8.

Sincerely,

A handwritten signature in black ink, appearing to read "Mike Bates", is written over a horizontal line.

Mike Bates  
Chief, Air Division

Enclosure



# ADEQ MINOR SOURCE AIR PERMIT


Permit No. : 1227-AR-16

IS ISSUED TO:

Cross Oil Refining & Marketing, Inc.  
484 East 6th Street  
Smackover, AR 71762  
Union County  
AFIN: 70-00039

THIS PERMIT IS THE ABOVE REFERENCED PERMITTEE'S AUTHORITY TO CONSTRUCT, MODIFY, OPERATE, AND/OR MAINTAIN THE EQUIPMENT AND/OR FACILITY IN THE MANNER AS SET FORTH IN THE DEPARTMENT'S MINOR SOURCE AIR PERMIT AND THE APPLICATION. THIS PERMIT IS ISSUED PURSUANT TO THE PROVISIONS OF THE ARKANSAS WATER AND AIR POLLUTION CONTROL ACT (ARK. CODE ANN. SEC. 8-4-101 *ET SEQ.*) AND THE REGULATIONS PROMULGATED THEREUNDER, AND IS SUBJECT TO ALL LIMITS AND CONDITIONS CONTAINED HEREIN.

Signed:

  
Mike Bates  
Chief, Air Division

March 27, 2009  
Date

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#### List of Acronyms and Abbreviations

A.C.A.	Arkansas Code Annotated
AFIN	ADEQ Facility Identification Number
CFR	Code of Federal Regulations
CO	Carbon Monoxide
HAP	Hazardous Air Pollutant
lb/hr	Pound Per Hour
No.	Number
NO <sub>x</sub>	Nitrogen Oxide
PM	Particulate Matter
PM <sub>10</sub>	Particulate Matter Smaller Than Ten Microns
SO <sub>2</sub>	Sulfur Dioxide
Tpy	Tons Per Year
UTM	Universal Transverse Mercator
VOC	Volatile Organic Compound

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Section I: FACILITY INFORMATION

PERMITTEE:	Cross Oil Refining & Marketing, Inc.
AFIN:	70-00039
PERMIT NUMBER:	1227-AR-16
FACILITY ADDRESS:	484 East 6th Street Smackover, AR 71762
MAILING ADDRESS:	484 East 6th Street Smackover, AR 71762
COUNTY:	Union County
CONTACT NAME:	Charlie Clark
CONTACT POSITION:	VP of HR & Government Affairs
TELEPHONE NUMBER:	870-881-8700
REVIEWING ENGINEER:	Parviz Mokhtari
UTM North South (Y):	Zone 15: 3691692.87 m
UTM East West (X):	Zone 15: 526334.70 m

## Section II: INTRODUCTION

### Summary of Permit Activity

Cross Oil Refining and Marketing, Inc. (Cross Oil) operates an oil refinery at 484 East Sixth Street, in Smackover, Union County, Arkansas, 71762. Cross Oil submitted a De Minimis application to make the following changes:

- Install fourteen (14) onsite lube oil storage tanks #229, #230, #231, #232, #233, #332, #333, #334, #335, #336, #337, #338, #339, and #340 at SN-27.
- Allow the distillate to be loaded at the Asphalt Tank Car Loading Rack SN-32.

There will not be an increase in lube oil throughput as a result of the additional storage tanks because the tanks are being installed to allow for reduced throughput at other lube oil tanks. The introduction of distillate to SN-32 will result in an increase of 1,500,000 gallons per year of distillate. The permitted emissions will increase 1.3 ton per year (tpy) of VOC, 0.02 tpy of 2,2,4-Trimethylpentane, 0.14 tpy of Benzene, 0.01 tpy Cumene, 0.02 tpy of Hexane, 0.07 tpy of Toluene, and 0.03 tpy of Xylene.

Although the lube oil tanks #333, #334, #335, #336, #337, #338, #339, and #340 are greater than 75 cubic meters (19813 gallons), the vapor pressure of the lube oil 1.33 kPa is below the NSPS threshold of 3.5 kPa, therefore, the lube oil tanks are not subject to any other requirements of Subpart Kb.

### Process Description:

Cross Oil is a refinery that processes crude oil into naphtha, diesel fuel, lube oils, and asphalt. crude oil is charged from storage and is preheated with heat exchangers. Water is added to the crude oil to aid in removing salts. The crude passes through a series of electrostatic desalting units which separates the saltwater from the crude. From the desalters, the crude is heated through a series of heat exchangers and then through the Crude Charge Heater (SN-01). Finally, the crude is sent to the first atmospheric distillation tower where the oil is separated into naphtha, diesel fuel, No. 2 lube oil, No. 3 lube oil, and No. 4 lube oil.

Naphtha and other non-condensable gases flow overhead from the atmospheric tower. The naphtha is cooled in a condenser and then flows to an accumulator from which the liquid is pumped back to the tower as reflux. Excess naphtha product is drawn off of the accumulator, and then pumped to product storage for sales. Diesel fuel and Lube Oils No. 2, 3, and 4 are drawn off of the side of the tower, routed through strippers to remove non-condensable gases, and then pumped through heat exchangers and on to storage for product sales.

The bottoms stream off of the atmospheric tower is pumped through the Vacuum Tower Charge Heater (SN-02) before being charged to the vacuum distillation column. The reduced crude is

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separated in the vacuum tower to produce the heavier grades of lube oil, Nos. 7, 9, 10, and 11. The vacuum tower bottoms are asphalt flux, which is pumped through heat exchangers to storage for sales or for further processing in an asphalt blowstill.

Flux is charged from storage through the Asphalt Blowstill Charge Heater (SN-03) to one of two blowstills. While the flux is being pumped into the blowstill, air is blown into the bottom of the still through a distribution header. The air oxidizes the flux causing it to polymerize and thus increases the melting point and hardness of the asphalt. Oxygen, nitrogen, volatile organic compounds (VOC), and sulfur dioxide (SO<sub>2</sub>) are produced as byproducts of the operation. These byproducts are routed through an incinerator and the waste heat boiler (SN-04) before being vented to the atmosphere. The asphalt product is loaded into trucks at one of the two asphalt loading racks (SN-15 and SN-16) or loaded into tank cars at the Asphalt/Distillate Tank Car Loading Rack (SN-32).

The lube oils produced by both atmospheric and vacuum distillation are further processed in a set of heater exchangers and then are passed to the hydrotreaters. The oils are heated with heat exchangers and two hydrotreaters, the Hydrotreater Charge Heater (SN-07) and Lube Charge Pre-Heater (SN-30), before being pumped into the top of the reactor. The hot lube oils combine with hydrogen at the top of the reactor before passing through a catalyst bed. Sulfur in the oil reacts with the hydrogen to form hydrogen sulfide gas. The hydrogen sulfide gas also saturates the aromatic compounds in the oil, removes heavy metals, and converts some of the nitrogen to ammonia.

The reactor effluent flows to a high pressure separator where the excess hydrogen, hydrogen sulfide, and ammonia gases flash off. From the high pressure separator, the oil flows to a low pressure separator where additional light ends flash off. The oil then flows to a lube oil stripper where the remaining hydrogen sulfide is removed by steam stripping. The Lube Stripper Reboiler (SN-12) supplies heat to the lube oil stripper. From the lube oil stripper, the oil flows to a vacuum lube stripper where any entrained water is vacuum stripped from the product. The bottoms from the vacuum stripper are routed to finished lube storage for blending and sales. The finished lube products are loaded at one of the three lube oil loading racks (SN-17, SN-18 and SN-21). Cross Oil also operates Lube Oil and Additive Loading Rack (SN-33) that transfers the contents back and forth between rail cars and truck cars.

The waste gas from the high pressure separator is routed to a caustic scrubber where the gas enters the bottom of the column. The gas flows countercurrent to a caustic solution, which removes the hydrogen sulfide in the gas. The waste gas from the low pressure separator is combined with the gases from the lube stripper and the lube vacuum stripper. The combined gas stream is then treated in a two stage caustic scrubber system. The clean hydrogen gas from the scrubbers is then sent back to the hydrotreater reactor.

The primary hydrogen is supplied to the hydrotreater by a steam/methane reformer. Natural gas is compressed and heated in a preheat exchanger, and combined with steam. The mixture is charged to the Hydrogen Plant Heater (SN-08) where it passes over a nickel catalyst and reacts to produce hydrogen and carbon oxides. The gases leaving the reactor are routed to a shift

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converter which contains an iron-chromium catalyst. Most of the carbon monoxide (CO) in the gas is converted to carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>). The CO<sub>2</sub> and H<sub>2</sub> gas then flow to a pressure swing absorption (PSA) system where the CO<sub>2</sub> and other impurities are removed.

Steam is produced in a boiler and a cogeneration unit at the facility. The cogeneration unit (SN-25) has a gas-fired turbine, which along with the boiler, uses natural gas as fuel.

### Regulations

The following table contains the regulations applicable to this permit.

Regulations	
Arkansas Air Pollution Control Code, Regulation 18, effective January 25, 2009	
Regulations of the Arkansas Plan of Implementation for Air Pollution Control, Regulation 19, effective January 25, 2009	
All Sources	Arkansas Air Pollution Control Code, Regulation 18, effective January 25, 2009
All Sources	Regulations of the Arkansas Plan of Implementation for Air Pollution Control, Regulation 19, effective January 25, 2009
SN-27	40 CFR Part 60, Subpart Ka – <i>Standards of Performance for Storage Vessels for Petroleum Liquids for which Construction, Reconstruction, or Modification commenced after May 18, 1978, and prior to July 23, 1984</i>  40 CFR Part 60, Subpart Kb – <i>Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984</i>
SN-25	40 CFR Part 60, Subpart GG – <i>Stationary Gas Turbines</i>
All Sources	40 CFR Part 61, Subpart FF – <i>National Emission Standards for Hazardous Air Pollutants, Benzene Waste Operations</i>

Subpart FF applies because Cross Oil is a petroleum refinery. The boiler SN-26 was manufactured in 1971 and is therefore not subject to the requirements of NSPS Subpart Dc. The reformer SN-08 burns pipeline quality gas so it is not subject to 40 CFR Part 60, Subpart J – *Standards of Performance for Petroleum Refineries*.

40 CFR Part 60, Subpart Kb applies for SN-27 distillate oil tank (Tank #319) because the storage capacity is in excess of 75 cubic meters (19813 gallons) and has a vapor pressure greater than 3.5 kilopascal (kPa). Although the lube oil tanks #026p, #027p, #028p, #029p (1,182 barrel), #031p, #032p, #229, #230, #231, #232, #233, #332, #333, #334, #335, #336, #337, #338, #339, and #340 are greater than 75 cubic meters (19813 gallons), the vapor pressure of the lube oil (1.33

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kPa) is below the NSPS threshold of 3.5 kPa, therefore, the lube oil tanks are not subject to any other requirements of Subpart Kb.

40 CFR Part 60 Subpart GGG – Standards Performance for Equipment Leaks of VOC in Petroleum Refineries. This regulation applies to certain compressors and other equipment in VOC service installed after January 4, 1983. The permittee consultant's letter dated April 25, 2007 states that all compressors installed after the effective date are in hydrogen service and are not in VOC service. Therefore, no compressors at this facility are subject to Subpart GGG.

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### Total Allowable Emissions

The following table is a summary of emissions from the facility. This table, in itself, is not an enforceable condition of the permit.

TOTAL ALLOWABLE EMISSIONS		
Pollutant	Emission Rates	
	lb/hr	tpy
PM	11.4	47.4
PM <sub>10</sub>	11.4	47.4
SO <sub>2</sub>	2.7	8.4
VOC	52.1	66.1
CO	21.8	93.0
NO <sub>x</sub>	25.8	81.6*
2,2,4-Trimethylpentane	0.20	0.13
Benzene	1.48	3.65
Cumene	0.06	0.09
Ethylbenzene	0.14	0.35
Hexane	5.37	8.69
Naphthalene	0.01	0.01
Phenol	0.01	0.01
Styrene	0.01	0.01
Toluene	0.91	1.63
Xylene	0.36	0.70

\* Includes 53 tpy emission bubble for SN-01, SN-25, and SN-26

### Section III: PERMIT HISTORY

- 1227-A Issued on December 9, 1991, this was the first operating permit for CORC. This permit included the inclusion of a recently installed naphtha storage tank.
- 1227-AR-1 This modification, issued on July 14, 1992, covered the installation of a lube-oil stripper/reboiler/heater at the facility.
- 1227-AR-2 Issued on November 20, 1992, this permit allowed the installation of a replacement boiler. The installation of the replacement boiler classified the facility as a major source subject to Title V permitting since NO<sub>x</sub> emissions exceeded 100 tons per year.
- 1227-AR-3 This permit was issued on August 5, 1997 due to an emissions inventory that discovered that the facility did not have actual emissions greater than the major source threshold. Therefore, Cross Oil Refining and Marketing, Inc. was removed from major source status. Additionally, a cogeneration unit and the #4 boiler were added as sources at the facility.
- 1227-AR-4 This modification was issued on June 29, 2000 and covers the relocation of a 94.3 MMBTU/hr natural gas fired boiler to the facility. Several boilers at the plant had reached the end of their useful life. This new boiler incorporates a low NO<sub>x</sub> burner and flue gas recirculation to minimize emissions. Additionally, it was planned that a duct burner would work in conjunction with a cogeneration unit, but the duct burner was never installed and is being removed from the permit and the cogeneration unit calculations adjusted accordingly. In order for CORC to install the duct burner, a new application must be submitted. Also, the existing #3 Boiler (SN-06) has been retired from operation and so the emissions from this source have been removed.
- 1227-AR-5 This permit was issued on April 29, 2002 and addressed a proposal to make the following changes to some storage tanks:
1. Two tanks which stored lube oil product were destroyed in a fire in 1999 and have not yet been replaced. The refinery plans to move two existing identical tanks to replace these tanks. These tanks will be designated as #328 and #329. Both tanks have a capacity of 1,000 barrels each (42,000 gallons) and will be subject to the record keeping provisions of 40 CFR Part 60, Subpart Kb, since they will store organic liquids;
  2. Two tanks (#330 and #331), which will store lube oil product, are planned for installation. The tanks have a capacity of 10,000 barrels each (420,000 gallons) and will be subject to record keeping provisions of 40 CFR 60, Subpart Kb, since they will store organic liquids;
  3. Two tanks (#332 and #333), which will store lube oil product, are planned for installation. The tanks have a capacity of 500 barrels each (21,000 gallon) and will be subject to the record keeping provisions of 40 CFR 60, Subpart Kb, since they will store organic liquids; and



4. One existing tank (#284), which is currently permitted to store lube oil, will be removed from service.

The total emissions VOC from the six tanks amounted to less than 0.02 tons annually.

1227-AR-6 This permit was issued on August 2, 2002 and addressed the following modifications to the facility:

1. Tank #329 was recently permitted as a lube oil storage tank. This tank will be equipped with an internal floating roof and will store naphtha. The tank will be subject to the provisions of NSPS Subpart Kb. A floating roof meeting the requirements of 40 CFR 60.112b (a) (1) will be installed;
2. The existing naphtha tank #206 will be converted to a lube oil storage tank. It was constructed in 1980 and will not be modified with this project. Therefore, the tank will not be subject to NSPS Subpart Kb after the change of service;
3. Tanks #291 and #292 will be changing service from diesel to lube oil storage. The tanks were constructed in 1980. Therefore, the tanks will not be subject to NSPS Subpart Kb after the change of service; and
4. Tank #113 is currently permitted as a crude oil storage tank subject to NSPS Subpart Ka. It will be changing service to store Cross Oil's B Series lube oil (a mixture of lube oil and diesel). The tank was constructed in 1980. Therefore, the tank will not be subject to NSPS Subpart Kb (or NSPS Subpart Ka due to the low vapor pressure of the lube oil) after the change of service.

The above changes in tank service resulted in a decrease in VOC emissions of 2.9 tons per year. Without considering the reduction in emissions due to the change in service of the tanks, the total increase associated with this project is 0.74 tons VOC per year.

1227-AR-7 This permit was issued on October 29, 2002 and addressed the following modifications to the permit:

1. Addition of six tanks (001 through 006), which will store lube oil product, are planned for installation. The tanks have a capacity of 15,250 gallons each and will be subject to the record keeping provisions of 40 CFR 60, Subpart Kb, since they will store organic liquids; and
2. Addition of three tanks (007 through 009), which will store lube oil product, are planned for installation. The tanks have a capacity of 2,000 gallons each and will not be subject to the record keeping provisions of 40 CFR 60, Subpart K.

The above changes resulted in an increase of VOC emissions of 0.2 tons per year.

1227-AR-8 This permit was issued on May 30, 2003 and allowed the facility to modify its

existing permitted emission rates based upon emission factors, physical property data, facility operating conditions, and revised emissions modeling. In addition, the facility proposed to include hazardous air pollutant (HAP) emissions, which were not included in permit 1227-AR-7, to permit emissions from offsite storage tanks, and to correct opacity limits. No production increases were proposed. The proposed changes resulted in an increase of 0.7 tons per year of SO<sub>2</sub> emissions, 31.0 tons per year of CO emissions, and 15.8 tons per year of HAP emissions.

- 1227-AR-9 This permit was issued on April 19, 2004, and it allowed the facility to install two new 3,500 gallon lube oil storage tanks (#010p and #011p). The proposed change resulted in no production and negligible annual emissions increases.
- 1227-AR-10 This permit was issued September 28, 2004. CORC's proposal included the installation of one new 21,000 gallon reclaimed oil storage tank, one new 42,000 gallon reclaimed oil storage tank, and six new 16,800 gallon lube oil storage tanks. In addition to installing the new storage tanks, Cross Oil requested to remove #500, re-designate #332 as #500, and to re-designate #312 and #333 as #512 and #513, respectively.
- 1227-AR-11 This permit was issued April 11, 2005. The permit revision contained the following changes: converted two tanks containing asphalt to lube oil (Tank #223 and #224); added a new lube oil tank (Tank #331); converted a tank currently containing lube oil to naptha (Tank #312); corrected the current tank numbering by shifting Tank #012P though #017P each up one number, resulting in Tank #013P through #018P; added two new lube oil tanks (Tanks #012P and #019P of SN-27); added a seasonal 50 horsepower (0.125 MMBTU/hr) low pressure boiler as an insignificant activity; added a pre-heat lube charge heater, with a design rating of 6.0 MMBTU/hr (SN-30) with low NO<sub>x</sub> burners; added 7 heat exchangers (no source number) to the process in order to increase efficiency and reduce reliance on the crude heaters; and removed the crude oil throughput limit. Total annual emission increases were 0.2 ton/yr PM/PM<sub>10</sub>, 0.1 ton/yr SO<sub>2</sub>, 0.4 ton/yr VOC, 1.3 ton/yr NO<sub>x</sub>, and 2.2 ton/yr CO.
- 1227-AR-12 This permit was issued on September 23, 2005. The facility modified their permit in order to increase the annual asphalt throughput at the Blow Still Incinerator Waste Heat Boiler (SN-04) and to remove the testing requirements for SO<sub>2</sub> at the Cogeneration Unit (SN-25), which is a natural gas source. Annual particulate emissions increased by 14.6 tons/year as a result of the asphalt throughput.
- 1227-AR-12 This permit was issued on October 24, 2006. The permit revision contained the following changes:
- Installation of five 700 barrel (29,400 gallon) lube oil storage tanks at SN-27 – Tanks #020p, #022p, #023p, #024p, and #025p;
  - Install one 500 barrel (21,000 gallon) lube oil storage tank at SN-27 – Tank #021p;

- Remove the 1000 barrel (42,000 gallon) reclaimed oil storage tank and replace it with a 400 barrel (16,800 gallon) reclaimed oil storage tank at SN-27 – Tank #503;
- Correct the permitted HAP lb/hr emission rate limits for the Diesel/Naphtha/Kerosene Loading Rack (SN-14);
- Correct various typographical errors; and
- Install one 5,000 barrel (210,000 gallon) lube oil storage tank at SN-27 – Tank #030p.

The total permitted annual emission rate increases were: 0.1 tpy NO<sub>x</sub>, 0.01 tpy cumene, 0.01 tpy phenol, and 0.01 tpy toluene.

1227-AR-13 This permit was issued October 26, 2006. The permit revision contained the following changes:

Cross Oil's proposal included the installation of five 700 barrel (29,400 gallons) lube oil storage tanks at SN-27 (Tanks #020p, #022p, #023p, #024p, and #025p), install one 500 barrel (21,000 gallons) lube oil storage tank at SN-27 (Tank #021p), Install one 5,000 barrel (210,000 gallons) lube oil storage tank at SN-27 (Tank #030p), and remove the 1000 barrel (42,000 gallon) reclaimed oil storage tank and replace it with a 400 barrel (16,800 gallon) reclaimed oil storage tank at SN-27 (Tank #503). In addition, the facility requested the permitted HAP lb/hr emission rate limits to be corrected for the Diesel/Naphtha/Kerosene Loading Rack (SN-14), and to correct various typographical errors. The typographical errors included adding SN-23's VOC emissions back to Specific Condition #1; adding naphthalene to the Total Allowable Emissions Table; and correcting the VOC, NO<sub>x</sub>, and toluene total emission rates in the Total Allowable Emissions Table.

The total permitted annual emission rate increases include: 0.1 tpy NO<sub>x</sub>, 0.01 tpy cumene, 0.01 tpy phenol, and 0.01 tpy toluene.

1227-AR-14 This permit was issued August 27, 2007. The permit revision contained the following changes:

- Installation of Six (6) lube oil storage tanks at SN-27 with the following storage capacities: Tanks #026p (1,182 barrel), #027p (1,049 barrel), #028p (862 barrel), #029p (1,182 barrel), #031p (1,182 barrel), #032p (1,049 barrel);
- Installation of one 1,000 barrel distillate oil storage tank (Tank #319) at SN-27;
- Removing of the 1000 barrel reclaimed oil storage tank and replacing it with a 400 barrel reclaimed oil storage tank at SN-27 – Tank #504;
- Installation of four (4) 280 barrel reclaimed oil storage tanks at SN-27; Tanks #514, #515, #516, and #517;
- Add an asphalt tank car loading rack;
- Add a distillate lube oil loading rack; and

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- Revise insignificant activity list in the existing permit.

Cross Oil also submitted a DeMinimis application to perform the necessary piping modifications to allow for pipeline quality natural gas to be fired at Blow Still Incinerator Waste Heat Boiler (SN-04), Lube Stripper Reboiler (SN-12), and Lube Charge Heater (SN-30); to include use of mixed gas at the Crude Charge Heater (SN-01), Vacuum Tower Charge Heater (SN-02), the Asphalt Below Charge Heater (SN-03), and the Lube Precharge Heater (SN-07); to make necessary improvement to NASH plant to ensure the sulfur content in the waste gas produced onsite remain below 0.1 gr/dscf; and to change the source descriptions for SN-07 to the "Lube Precharge Heater" and SN-30 to the "Lube Charge Heater".

The permitted emission increases were due to these modifications: 3.8 tons per year (tpy) PM/PM10, 5.8 tpy SO<sub>2</sub>, 1.1 tpy VOC, 0.01 tpy 2,2,4-trimethylpentane, 0.18 tpy benzene, 0.01 tpy cumene, 0.01 tpy ethylbenzene, 0.34 tpy hexane, 0.06 tpy toluene, and 0.04 tpy xylene.

1227-AR-15 This permit was issued January 26, 2009. This permitting action was necessary to:

- Add two (2) 400 barrel asphalt plasticizer tanks #227 and #228 at SN-27,
- Replace three (3) 280 barrel reclaimed oil storage tanks #514, #515, and #516 (previously permitted) with three (3) reclaimed oil tanks of different size (400 barrel) and throughput at SN-27,
- Remove the 280 barrel reclaimed oil storage tank #517 at SN-27,
- Add a lube oil and additive loading/unloading rack (SN-33), and
- Add a lube oil packaging operation into insignificant activities list.

The permitted emission increased due to this De Minimis modification is 0.2 tons per year (tpy) VOC. The new tanks #227, #228, #514, #515, and #516 are not subject to 40 CFR 60 Subpart Ka and Kb.

Also, Cross Oil submitted another DeMinimis application on September 3, 2008 to modify its existing minor source to address the throughput at the Distillate Lube Oil Truck Loading Rack and associated storage tanks:

- Increase the throughput at the distillate lube oil storage tank (Tank # 319) from 1,302,000 gal/yr to 2,730,000 gal/yr.
- Increase the throughput at the Distillate Lube Oil loading Rack SN-31.
- Add a condition to address the throughput and tracking for the gasoline tank at SN-27.
- Record keeping requirements for SN-31 and SN-32 have been added to the permit.

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The permitted emissions for SN-31 increased by: 1.2 tons per year (tpy) VOC, Benzene 0.15 tpy, Ethylbenzene 0.02 tpy, Hexane 0.3 tpy, Toluene 0.05, and Xylene 0.03 tpy.

Additionally, Cross Oil submitted a summary of all of the tanks with the revised capacities, turnovers, and emissions for Onsite Storage Tanks SN-27, Sandyland Storage Tanks SN-28, and Miller's Storage Tanks SN-29 by email dated June 26, 2008. Due to this revision the emission limits for these sources were decreased. The overall permitted emissions decreased due to this DeMinimis modification by: 16.2 tpy VOC, 2,2,4-Trimethylpentane 0.06 tpy, Benzene 0.6 tpy, Cumene 0.02 tpy, Ethylbenzene 0.04 tpy, Hexane 1.02 tpy, Toluene 0.48, and Xylene 0.17 tpy.

## Section IV: EMISSION UNIT INFORMATION

## Specific Conditions

1. The permittee shall not exceed the emission rates set forth in the following table.  
 [Regulation 19, §19.501 et seq., and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

SN	Description	Pollutant	lb/hr	tpy
01	Crude Charge Heater	PM <sub>10</sub>	0.3	1.0
		SO <sub>2</sub>	0.9	4.0
		VOC	0.2	0.8
		CO	2.6	11.1
		NO <sub>x</sub>	2.8	*
02	Vacuum Tower Charge Heater	PM <sub>10</sub>	0.1	0.3
		SO <sub>2</sub>	0.3	1.1
		VOC	0.1	0.2
		CO	0.8	3.3
		NO <sub>x</sub>	0.9	3.9
03	Asphalt Blow Still Charge Heater	PM <sub>10</sub>	0.1	0.3
		SO <sub>2</sub>	0.3	0.3
		VOC	0.1	0.2
		CO	0.7	2.9
		NO <sub>x</sub>	0.8	3.5
04	Blow Still Incinerator Waste Heat Boiler	PM <sub>10</sub>	8.5	37.0
		SO <sub>2</sub>	0.1	0.1
		VOC	0.1	0.4
		CO	1.2	5.0
		NO <sub>x</sub>	1.4	5.9
05	Boiler #1	Retired		
06	Boiler #3	Retired		
07	Lube Precharge Heater	PM <sub>10</sub>	0.1	0.2
		SO <sub>2</sub>	0.2	0.8
		VOC	0.1	0.2
		CO	0.5	2.2
		NO <sub>x</sub>	0.6	2.6
08	Hydrogen Plant Heater/Reactor	PM <sub>10</sub>	0.3	1.0
		SO <sub>2</sub>	0.1	0.1
		VOC	0.2	0.8
		CO	2.6	11.1
		NO <sub>x</sub>	1.3	5.6
09	High Pressure Flare	PM <sub>10</sub>	0.1	0.1
		SO <sub>2</sub>	0.1	0.1

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SN	Description	Pollutant	lb/hr	tpy
		VOC	0.1	0.1
		CO	0.1	0.1
		NO <sub>x</sub>	0.1	0.1
10	Low Pressure Flare	PM <sub>10</sub>	0.1	0.1
		SO <sub>2</sub>	0.1	0.1
		VOC	0.1	0.1
		CO	0.1	0.1
		NO <sub>x</sub>	0.1	0.1
11	Naphtha Storage Tank	Retired		
12	Lube Stripper Reboiler	PM <sub>10</sub>	0.1	0.5
		SO <sub>2</sub>	0.1	0.1
		VOC	0.1	0.4
		CO	1.1	4.7
		NO <sub>x</sub>	1.3	5.6
13	Boiler #2	Retired		
14	Diesel/Naphtha/Kerosene Loading Rack	VOC	37.4	4.1
15	Asphalt Truck Loading Rack #1	VOC	0.1	0.1
16	Asphalt Truck Loading Rack #2	VOC	0.1	0.1
17	Lube Oil Truck Loading Rack	VOC	0.1	0.1
18	Lube Oil Truck Loading Rack	VOC	0.1	0.1
21	Lube Oil Rail Car Loading Rack	VOC	0.2	0.2
23	Fugitive Emissions	VOC	3.6	15.7
24	Wastewater Emissions	VOC	2.0	8.6
25	Cogeneration Unit	PM <sub>10</sub>	0.6	2.5
		SO <sub>2</sub>	0.1	0.3
		VOC	0.7	2.8
		CO	5.5	23.8
		NO <sub>x</sub>	12.3	*
26	Boiler #4	PM <sub>10</sub>	1.0	4.2
		SO <sub>2</sub>	0.3	1.3
		VOC	0.4	1.7
		CO	6.1	26.5
		NO <sub>x</sub>	3.8	*
27	Onsite Storage Tanks (152 Tanks) Tanks Subject to 40 CFR Part 60, Subpart Ka: 113, 197, 287, 288, 289, 290, 296, 297, 298,	VOC	1.0	4.2

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SN	Description	Pollutant	lb/hr	tpy
	299, 312, 313, 314, 315, 206, 266, 291, 292, 329 and Tank Subject to 40 CFR Part 60, Subpart Kb: Tank #319 The Lube Oil Tanks #229, #230, #231, #232, #233, #332, #333, #334, #335, #336, #337, #338, #339, and #340 are in excess of 19,813 gallons, the vapor pressure of the lube oil is less than 3.5 kPa , therefore, these tanks are not subject to NSPS Subpart Kb.			
28	Sandyland Storage Tanks Tank #104, #110, #111  Tanks Subject to 40 CFR Part 60, Subpart Ka: #111	VOC	3.6	15.7
29	Miller's Storage Tanks Tank #114 and #115	VOC	1.3	5.4
30	Lube Charge Heater	PM <sub>10</sub> SO <sub>2</sub> VOC CO NO <sub>x</sub>	0.1 0.1 0.1 0.5 0.3	0.2 0.1 0.1 2.2 1.3
31	Distillate Lube Oil Truck loading Rack	VOC	0.57	2.5
32	Asphalt/Distillate Tank Car Loading Rack	VOC	3.7	1.4
33	Lube oil/additive Loading/Unloading	VOC	0.1	0.1

\* Single emission bubble for NO<sub>x</sub> is 53 tpy for SN-01, 25, and 26

- The permittee shall not exceed the emission rates set forth in the following table.  
 [Regulation 18, §18.801 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

SN	Description	Pollutant	lb/hr	tpy
01	Crude Charge Heater	PM	0.3	1.0
02	Vacuum Tower Charge Heater	PM	0.1	0.3
03	Asphalt Blow Still Charge Heater	PM	0.1	0.3
04	Blow Still Incinerator Waste Heat Boiler	PM	8.5	37.0



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SN	Description	Pollutant	lb/hr	tpy
05	Boiler #1	Retired		
06	Boiler #3	Retired		
07	Lube Precharge Heater	PM	0.1	0.2
08	Hydrogen Plant Heater/Reactor	PM	0.3	1.0
09	High Pressure Flare	PM	0.1	0.1
10	Low Pressure Flare	PM	0.1	0.1
11	Naphtha Storage Tank	Retired		
12	Lube Stripper Reboiler	PM	0.1	0.5
13	Boiler #2	Retired		
14	Diesel/Naphtha/Kerosene Loading Rack	2,2,4-Trimethylpentane	0.14	0.04
		Benzene	0.40	0.63
		Cumene	0.02	0.03
		Ethylbenzene	0.05	0.08
		Hexane	3.84	2.33
		Naphthalene	0.01	0.01
		Phenol	0.01	0.01
		Styrene	0.01	0.01
		Toluene	0.49	0.47
		Xylene	0.15	0.24
17	Lube Oil Truck Loading Rack	Benzene	0.01	0.01
		Hexane	0.01	0.01
18	Lube Oil Truck Loading Rack	Benzene	0.01	0.01
		Hexane	0.01	0.01
21	Lube Oil Rail Car Loading Rack	Benzene	0.04	0.05
		Hexane	0.06	0.06
		Toluene	0.02	0.02
23	Fugitive Emissions	Benzene	0.49	2.15
		Cumene	0.01	0.03
		Ethylbenzene	0.04	0.18
		Hexane	0.72	3.12
		Toluene	0.18	0.79
		Xylene	0.07	0.27
24	Wastewater Emissions	Hexane	0.06	0.24
25	Cogeneration Unit	PM	0.6	2.5
26	Boiler #4	PM	1.0	4.2

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SN	Description	Pollutant	lb/hr	tpy
27	<p>Onsite Storage Tanks (152 Tanks)</p> <p>Tanks Subject to 40 CFR Part 60, Subpart Ka: 113, 197, 287, 288, 289, 290, 296, 297, 298, 299, 312, 313, 314, 315, 206, 266, 291, 292, 329 and Tank Subject to 40 CFR Part 60, Subpart Kb: Tank #319</p> <p>The Lube Oil Tanks (#229, #230, #231, #232, #233, #332, #333, #334, #335, #336, #337, #338, #339, and #340) are in excess of 19,813 gallons, the vapor pressure of the lube oil is less than 3.5 kPa , therefore, these tanks are not subject to NSPS Subpart Kb.</p>	<p>2,2,4-Trimethylpentane</p> <p>Benzene</p> <p>Cumene</p> <p>Ethylbenzene</p> <p>Hexane</p> <p>Toluene</p> <p>Xylene</p>	<p>0.01</p> <p>0.04</p> <p>0.01</p> <p>0.01</p> <p>0.09</p> <p>0.02</p> <p>0.01</p>	<p>0.02</p> <p>0.14</p> <p>0.01</p> <p>0.02</p> <p>0.39</p> <p>0.07</p> <p>0.03</p>
28	<p>Sandyland Storage Tanks Tank #104, #110, #111</p> <p>Tanks Subject to 40 CFR Part 60, Subpart Ka: #111</p>	<p>2,2,4-Trimethylpentane</p> <p>Benzene</p> <p>Ethylbenzene</p> <p>Hexane</p> <p>Toluene</p> <p>Xylene</p>	<p>0.01</p> <p>0.03</p> <p>0.01</p> <p>0.26</p> <p>0.02</p> <p>0.01</p>	<p>0.04</p> <p>0.13</p> <p>0.01</p> <p>1.20</p> <p>0.08</p> <p>0.04</p>
29	<p>Miller's Storage Tanks Tank #114 and #115</p>	<p>2,2,4-Trimethylpentane</p> <p>Benzene</p> <p>Ethylbenzene</p> <p>Hexane</p> <p>Toluene</p> <p>Xylene</p>	<p>0.01</p> <p>0.01</p> <p>0.01</p> <p>0.09</p> <p>0.01</p> <p>0.01</p>	<p>0.02</p> <p>0.05</p> <p>0.01</p> <p>0.38</p> <p>0.03</p> <p>0.02</p>
30	Lube Charge Heater	PM	0.1	0.2
31	Distillate Lube Oil Truck loading Rack	<p>2,2,4-Trimethylpentane</p> <p>Benzene</p> <p>Cumene</p> <p>Ethylbenzene</p> <p>Hexane</p> <p>Toluene</p> <p>Xylene</p>	<p>0.01</p> <p>0.07</p> <p>0.01</p> <p>0.01</p> <p>0.14</p> <p>0.03</p> <p>0.02</p>	<p>0.01</p> <p>0.31</p> <p>0.01</p> <p>0.03</p> <p>0.61</p> <p>0.11</p> <p>0.06</p>
SN-32	Asphalt/Distillate Tank Car Loading Rack	<p>Benzene</p> <p>Cumene</p> <p>Ethylbenzene</p> <p>Hexane</p> <p>Toluene</p> <p>Xylene</p>	<p>0.45</p> <p>0.02</p> <p>0.04</p> <p>0.90</p> <p>0.16</p> <p>0.09</p>	<p>0.17</p> <p>0.01</p> <p>0.02</p> <p>0.34</p> <p>0.06</p> <p>0.04</p>

3. Visible emissions may not exceed the limits specified in the following table of this permit as measured by EPA Reference Method 9. [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

SN	Limit	Regulatory Citation
01, 02, 03, 04, 07, 08, 12, 25, 26, 30	5%	§18.501
14, 15, 16, 17, 18, and 21	20%	§19.503

4. The permittee will not cause or permit the emission of air contaminants, including odors or water vapor and including an air contaminant whose emission is not otherwise prohibited by Regulation #18, if the emission of the air contaminant constitutes air pollution within the meaning of A.C.A. §8-4-303. [§18.801 of Regulation 18, and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-31]
5. The permittee will not conduct operations in such a manner as to unnecessarily cause air contaminants and other pollutants to become airborne. [§18.901 of Regulation 18, and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]

#### SN-01, SN-25, and SN-26 Conditions

6. The permittee shall not emit more than 53 tons of NO<sub>x</sub> at SN-01, SN-25, and SN-26 combined per consecutive 12 month period. NO<sub>x</sub> emissions shall be calculated by monitoring fuel inlet flow to all three sources and applying the following emission factors, unless the Department determines that testing results or other credible evidence indicate that other factors should be used: [Regulation 19 §19.705 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

**Table 6 – NO<sub>x</sub> Emission Factors for SN-01, SN-25, and SN-26**

Source Number	Emission Factor*	Emission Factor Source
SN-01	(92.4 lb NO <sub>x</sub> ) / (10 <sup>6</sup> ft <sup>3</sup> natural gas)	Stack Test
SN-25, Cogeneration Unit	(184.6 lb NO <sub>x</sub> ) / (10 <sup>6</sup> ft <sup>3</sup> natural gas)	Vendor Data
SN-26	(40 lb NO <sub>x</sub> ) / (10 <sup>6</sup> ft <sup>3</sup> natural gas)	Vendor Data

\*Emission factors are calculated based on heat value of 1020 Btu/ scfm for natural gas.

7. The permittee shall maintain monthly records of fuel usage and NO<sub>x</sub> emissions for sources SN-01, SN-25, and SN-26 which demonstrates compliance with Specific Condition #6. Records shall be updated by the fifteenth day of the month following the month to which the records pertain. A twelve month rolling total and each individual month's data shall be kept on site, and shall be made available to Department personnel

upon request. [Regulation 19 §19.705 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

8. The permittee shall install and maintain dedicated meters on the natural gas piping which feeds each emission unit specified in Specific Condition #6. [Regulation 19 §19.703 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

#### **SN-04 Condition**

9. The permittee shall maintain monthly records providing PM emissions from asphalt blowing at the Blow Still Incinerator Waste Heat Boiler. These emissions shall be calculated using the production rate multiplied by the PM emission factor of 0.81 lb/ton of asphalt. These records shall include ton per year PM calculations and thus demonstrate compliance with the limits in Specific Condition #1. Records shall be updated by the fifteenth day of the month following the month to which the records pertain. A twelve month rolling total and each individual month's data shall be kept on site, and shall be made available to Department personnel upon request. [Regulation 19 §19.705 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

#### **SN-09 and SN-10 Conditions**

10. The permittee shall report an upset condition any time that the flares are used. The permittee shall report the upset (by telephone, facsimile, or overnight delivery) to the Department by the end of the next business day after the occurrence or the discovery of the occurrence. The permittee shall submit to the Department, within five business days after the occurrence or the discovery of the occurrence, a full, written report of such occurrence, including a statement of all known causes and of the scheduling and nature of the actions to be taken to minimize or eliminate future occurrences, including, but not limited to, action to reduce the frequency of occurrence of such conditions, to minimize the amount by which said limits are exceeded, and to reduce the length of time for which said limits are exceeded. If the information is included in the initial report, it need not be submitted again. [Regulation 19 §19.601 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

#### **SN-14 through SN-21 Conditions**

11. The permittee shall maintain monthly records providing VOC and HAP emissions from the loading of diesel, naphtha, kerosene, asphalt, and lube oil at the loading racks. These records shall include ton per year VOC and HAP calculations and thus demonstrate compliance with the VOC limits in Specific Condition #1 and the HAP limits in Specific Condition #2. A record of VOC and HAPs calculations for each one of the loading/unloading racks must be presented in a similar format to the spread sheet in the Attachment F. Records shall be updated by the fifteenth day of the month following the month to which the records pertain. A twelve month rolling total and each individual month's data shall be kept on site, and shall be made available to Department personnel

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upon request. [Regulation 19 §19.705 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

### **SN-27 Onsite Storage Tanks**

12. The permittee shall not process more than 24,066 gallons per year of gasoline in gasoline tank located at the Onsite Storage Tanks (SN-27) in any consecutive 12 month period. [§19.705 of Regulation 19 and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]
13. The permittee shall maintain monthly records which demonstrate compliance with Specific Condition # 12. These records shall include the gallons per month of gasoline received. These records shall also include the cumulative 12 month rolling totals of liquid received for each tank. Records shall be updated by the fifteenth day of the month following the month for which the records pertain. These records shall be kept on site, and shall be made available to Department personnel upon request. [§19.705 of Regulation 19 and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]
14. The permittee shall store lube oil or a liquid with maximum true vapor pressure less than 3.5 kPa include storage tanks #229, #230, #231, #232, #233, #332, #333, #334, #335, #336, #337, #338, #339, and #340. [§19.304 of Regulation 19 and 40 CFR Part 60, Subpart Kb, §60.110b(b)]

**NSPS Kb Conditions:** Tank #319 (distillate oil storage tank) is Subject to 40 CFR Part 60, Subpart Kb:

15. SN-27 (Tank #39) shall meet all applicable requirements of 40 CFR Part 60, Subpart Kb (Appendix D) - *Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984*. These requirements include, but are not limited to the following: [§19.304 of Regulation 19 and 40 CFR Part 60, Subpart Kb]
  - a. The owner or operator shall keep copies of all records required by § 60.116b, except for the record required by paragraph of §60.116b(b), for at least 2 years. The record required by paragraph (b) of §60.116b will be kept for the life of the source.
  - b. The owner or operator of each storage vessel as specified in §60.110b(a) shall keep readily accessible records showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel.
  - c. The owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure greater than or equal to 3.5 kPa or with a design capacity greater than or equal to 75 m<sup>3</sup> but less than 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure greater than or equal to 15.0 kPa shall maintain a record of the VOL stored, the

period of storage, and the maximum true vapor pressure of that VOL during the respective storage period.

- d. The owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure that is normally less than 5.2 kPa or with a design capacity greater than or equal to 75 m<sup>3</sup> but less than 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure that is normally less than 27.6 kPa shall notify the Administrator within 30 days when the maximum true vapor pressure of the liquid exceeds the respective maximum true vapor vapor pressure values for each volume range.
- e. Available data on the storage temperature may be used to determine the maximum true vapor pressure as determined below.
  - (1) For vessels operated above or below ambient temperatures, the maximum true vapor pressure is calculated based upon the highest expected calendar-month average of the storage temperature. For vessels operated at ambient temperatures, the maximum true vapor pressure is calculated based upon the maximum local monthly average ambient temperature as reported by the National Weather Service.
  - (2) For refined petroleum products the vapor pressure may be obtained by the following:
    - i. Available data on the Reid vapor pressure and the maximum expected storage temperature based on the highest expected calendar-month average temperature of the stored product may be used to determine the maximum true vapor pressure from nomographs contained in API Bulletin 2517 (incorporated by reference—see §60.17), unless the Administrator specifically requests that the liquid be sampled, the actual storage temperature determined, and the Reid vapor pressure determined from the sample(s).
    - ii. The true vapor pressure of each type of crude oil with a Reid vapor pressure less than 13.8 kPa or with physical properties that preclude determination by the recommended method is to be determined from available data and recorded if the estimated maximum true vapor pressure is greater than 3.5 kPa.

**SN-31, SN-32, and SN-33**

- 16. The permittee shall maintain monthly records providing VOC and HAPs emissions from the Distillate Lube Oil Truck loading Rack SN-31, Asphalt Tank Car Loading Rack SN-32, and Loading/Unloading of Lube Oil and Additive Rack SN-33. These VOC and HAPs records shall include ton per year VOC and HAPs calculations and thus demonstrate compliance with the VOC and HAPs limits in Specific Condition #1 and #2. A record of VOC and HAPs calculations for each one of the loading/unloading racks must be presented in a similar format to the spread sheet in the Attachment F. Records

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shall be updated by the fifteenth day of the month following the month to which the records pertain. A twelve month rolling total and each individual month's data shall be kept on site, and shall be made available to Department personnel upon request. [Regulation 19 §19.705 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

### **NSPS GG Conditions**

17. The cogeneration unit (SN-25) is an affected source of 40 CFR Part 60, Subpart GG (Appendix B) – Standards of Performance for Stationary Gas Turbines. [Regulation 19 §19.304 and 40 CFR Part 60, Subpart GG]
  - a. The turbine shall not discharge any gases which contain nitrogen oxides in excess of 209 ppm by volume at 15 percent oxygen on a dry basis. [40 CFR Part 60, Subpart GG, §60.332 (a) (2)]
  - b. The turbine is exempt from Specific Condition #17(a) when ice fog is deemed a traffic hazard by the owner or operator of the gas turbine. [40 CFR Part 60, Subpart GG, §60.332 (f)]
  - c. The cogeneration unit shall only be fired with pipeline quality natural gas. [Regulation No. 19 §19.705, A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311, and 40 CFR 70.6]
  - d. No owner or operator shall burn in any stationary gas turbine any fuel which contains sulfur in excess of 0.8 percent by weight. [40 CFR Part 60, Subpart GG, §60.332 (b)]
  - e. Analysis for fuel sulfur content of the natural gas shall be conducted using one of the approved ASTM reference methods for the measurement of sulfur in gaseous fuels, or an approved alternative method. The approved reference methods are: ASTM D1072-80; ASTM D3031-81; ASTM D3246-81; and ASTM D4084-82 as referenced in 40 CFR 60.335 (b) (2). [40 CFR Part 60, Subpart GG, §60.335 (d)]
  - f. The fuel supply shall be initially sampled daily for a period of two weeks to establish that the pipeline quality natural gas fuel supply is low in sulfur content. [Regulation No. 19 §19.705, A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311, and 40 CFR 70.6]
  - g. After the monitoring required in Specific Condition #17 (e), sulfur monitoring shall be conducted twice monthly for six months. If this monitoring shows little variability in the fuel sulfur content, and indicates consistent compliance with 40 CFR 60.333, then sulfur monitoring shall be conducted once per quarter for six quarters. [40 CFR Part 60, Subpart GG, §60.335 (d)]

- h. If after the monitoring required in Specific Condition #17 (f), the sulfur content of the fuel shows little variability and, calculated as sulfur dioxide, represents consistent compliance with the sulfur dioxide emission limits specified under 40 CFR 60, Subpart GG, §60.333, sample analysis shall be conducted twice per annum. This monitoring shall be conducted during the first and third quarters of each calendar year. [40 CFR 60, Subpart GG, §60.333]
- i. Should any sulfur analysis as required in Specific Condition #17(f) or (g) indicate noncompliance with 40 CFR 60, Subpart GG, §60.333, the owner or operator shall notify ADEQ of such excess emissions and the custom schedule shall be re-examined. Sulfur monitoring shall be conducted weekly during the interim period when this custom schedule is being re-examined. [Regulation No. 19 §19.303 and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]
- j. If there is a change in fuel supply (supplier), the fuel shall be sampled daily for a period of two weeks to re-establish for the record that the fuel supply is low in sulfur content. If the fuel supply's low sulfur content is re-established, then the custom fuel monitoring schedule can be resumed. [Regulation No. 19 §19.705, 40 CFR Part 52, Subpart E, and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]
- k. Records of sample analysis and fuel supply pertinent to this custom schedule shall be retained for a period of three years, and be available for inspection. [Regulation No. 19 §19.705, 40 CFR Part 52, Subpart E, and A.C.A. §8-4-203 as referenced by §8-4-304 and §8-4-311]
- l. Any one hour period during which the average water-to-fuel ratio, as measured by the continuous monitoring system, falls below the water-to-fuel ratio determined to demonstrate compliance with §60.332 by the performance test required in §60.8 or any period during which the fuel-bound nitrogen of the fuel is greater than the maximum nitrogen content allowed by the fuel-bound nitrogen allowance used during the performance test required in §60.8 shall be recorded. Each record entry shall include the average water-to-fuel ratio, average fuel consumption, ambient conditions gas turbine load, and nitrogen content of the fuel during the period of excess emissions, and the graphs or figures developed under §60.335(a). These records shall be retained for a period of five years, and be available for inspection. [40 CFR Part 60, Subpart GG, §60.334]
- m. Records shall be kept of any daily period during which the sulfur content of the fuel being fired in the gas turbine exceeds 0.8 percent. These records shall be retained for a period of five years, and be available for inspection. [40 CFR Part 60, Subpart GG, §60.334]
- n. Records shall be kept for each period which Specific Condition #17 (b) applies. For each period the ambient conditions existing during the period, the date and



time the air pollution control system was deactivated, and the date and time the air pollution control system was reactivated shall be recorded. These records shall be retained for a period of five years, and be available for inspection. [40 CFR Part 60, Subpart GG, §60.334]

- o. The permittee shall perform an initial test of NO<sub>x</sub> and SO<sub>2</sub> to verify emissions. EPA Method 20 shall be used to determine the nitrogen oxides and oxygen concentrations. The span values shall be 300 ppm of nitrogen oxide and 21 percent oxygen. NO<sub>x</sub> emissions shall be determined at each of the load conditions specified in §60.335(c) (2). The testing shall be coordinated in advance with the Compliance Inspector Supervisor. This initial test was performed in March 2005. [40 CFR Part 60, Subpart GG, §60.335]
18. The permittee shall test NO<sub>x</sub> emissions once every five years to verify that the unit is operating within permitted limits. The permittee shall utilize the procedure outlined in 40 CFR Part 60, Subpart GG §60.335 and as previously conducted in the initial test required by Specific Condition #17(o). The testing shall be coordinated in advance with the Compliance Inspector Supervisor. [Regulation No. 19 §19.702, 40 CFR Part 52, Subpart E and 40 CFR Part 60, Subpart GG, §60.335]

#### NSPS Ka Conditions

19. The onsite storage tanks of SN-27 which are subject to provisions for 40 CFR Part 60, Subpart Ka (Appendix A) and their requirements are listed in the following table. [Regulation No. 19 §19.304 and 40 CFR Part 60, Subpart Ka]

**Table 7 – Storage Tanks Subject 40 CFR Part 60, Subpart Ka**

Tank	Contents	NSPS Requirement
113, 197, 287, 288, 289, 290, 296, 297, 298, 299, 313, 314, 315	Lube Oils	Pursuant to 40 CFR 60.115a (a), maintain a record of the petroleum liquid stored, the period of storage, and the maximum true vapor pressure of that liquid during the respective storage period.
206, 266, 291, 292	Diesel	
329, 312	Naphtha	
111	Crude	

#### NESHAP FF Conditions

20. The facility is an affected source according to 40 CFR Part 61, Subpart FF (Appendix C) – *National Emission Standard for Benzene Waste Operations*. [Regulation No. 19 §19.304 and 40 CFR Part 61, Subpart FF]
  - a. The owner and operator shall determine the total annual benzene quantity from facility waste by the procedures outlined in §61.355 (a). [40 CFR Part 61, Subpart FF, §61.355]

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- b. The facility shall comply with all record keeping requirements outlined in §61.356 (b). [40 CFR Part 61, Subpart FF, §61.355 (a)]
- c. The facility shall submit reports to the Department by following the procedures of §61.357 (a) (1)-(4). In cases where the total annual benzene quantity is less than 1 Mg/yr [as determined in Specific Condition #20 (a)], reports will comply with §61.357 (b). In cases where the total annual benzene quantity is greater than 1 Mg/yr but less than 10 Mg/yr, reports will comply with §61.357 (c). And when the total annual benzene quantity is greater than 10 Mg/yr, reports will comply with §61.357 (d). [40 CFR Part 61, Subpart FF, §61.357]

The facility is an affected source according to 40 CFR Part 61, Subpart FF – *National Emission Standards for Hazardous Air Pollutants, Benzene Waste Operations*

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Section V: INSIGNIFICANT ACTIVITIES

The Department deems the following types of activities or emissions as insignificant on the basis of size, emission rate, production rate, or activity in accordance with Group A of the Insignificant Activities list found in Regulation 18 and 19 Appendix A. Insignificant activity emission determinations rely upon the information submitted by the permittee in an application dated November 29, 2004, February 23, 2007, and October 16, 2007.

Description	Category
50 horsepower (0.125 MMBTU/hr) Low Pressure Boiler	Group A, No. 1
Recycle Water Evaporators (2)	Group A, No. 13
Packaging operation	Group A, No. 13

Section VI: GENERAL CONDITIONS

1. Any terms or conditions included in this permit that specify and reference Arkansas Pollution Control & Ecology Commission Regulation 18 or the Arkansas Water and Air Pollution Control Act (A.C.A. §8-4-101 et seq.) as the sole origin of and authority for the terms or conditions are not required under the Clean Air Act or any of its applicable requirements, and are not federally enforceable under the Clean Air Act. Arkansas Pollution Control & Ecology Commission Regulation 18 was adopted pursuant to the Arkansas Water and Air Pollution Control Act (A.C.A. §8-4-101 et seq.). Any terms or conditions included in this permit that specify and reference Arkansas Pollution Control & Ecology Commission Regulation 18 or the Arkansas Water and Air Pollution Control Act (A.C.A. §8-4-101 et seq.) as the origin of and authority for the terms or conditions are enforceable under this Arkansas statute.
2. This permit does not relieve the owner or operator of the equipment and/or the facility from compliance with all applicable provisions of the Arkansas Water and Air Pollution Control Act and the regulations promulgated under the Act. [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
3. The permittee shall notify the Department in writing within thirty (30) days after commencement of construction, completion of construction, first operation of equipment and/or facility, and first attainment of the equipment and/or facility target production rate. [Regulation 19, §19.704 and/or A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
4. Construction or modification must commence within eighteen (18) months from the date of permit issuance. [Regulation 19, §19.410(B) and/or Regulation 18, §18.309(B) and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
5. The permittee must keep records for five years to enable the Department to determine compliance with the terms of this permit such as hours of operation, throughput, upset conditions, and continuous monitoring data. The Department may use the records, at the discretion of the Department, to determine compliance with the conditions of the permit. [Regulation 19, §19.705 and/or Regulation 18, §18.1004 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
6. A responsible official must certify any reports required by any condition contained in this permit and submit any reports to the Department at the address below. [Regulation 19, §19.705 and/or Regulation 18, §18.1004 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

Arkansas Department of Environmental Quality  
Air Division  
ATTN: Compliance Inspector Supervisor

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5301 Northshore Drive  
North Little Rock, AR 72118-5317

7. The permittee shall test any equipment scheduled for testing, unless stated in the Specific Conditions of this permit or by any federally regulated requirements, within the following time frames: (1) newly constructed or modified equipment within sixty (60) days of achieving the maximum production rate, but no later than 180 days after initial start up of the permitted source or (2) existing equipment already operating according to the time frames set forth by the Department. The permittee must notify the Department of the scheduled date of compliance testing at least fifteen (15) days in advance of such test. The permittee must submit compliance test results to the Department within thirty (30) days after the completion of testing. [Regulation 19, §19.702 and/or Regulation 18, §18.1002 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
8. The permittee shall provide: [Regulation 19, §19.702 and/or Regulation 18, §18.1002 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
  - a. Sampling ports adequate for applicable test methods;
  - b. Safe sampling platforms;
  - c. Safe access to sampling platforms; and
  - d. Utilities for sampling and testing equipment
9. The permittee shall operate equipment, control apparatus and emission monitoring equipment within their design limitations. The permittee shall maintain in good condition at all times equipment, control apparatus and emission monitoring equipment. [Regulation 19, §19.303 and/or Regulation 18, §18.1104 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
10. If the permittee exceeds an emission limit established by this permit, the permittee will be deemed in violation of said permit and will be subject to enforcement action. The Department may forego enforcement action for emissions exceeding any limits established by this permit provided the following requirements are met: [Regulation 19, §19.601 and/or Regulation 18, §18.1101 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
  - a. The permittee demonstrates to the satisfaction of the Department that the emissions resulted from an equipment malfunction or upset and are not the result of negligence or improper maintenance, and the permittee took all reasonable measures to immediately minimize or eliminate the excess emissions.
  - b. The permittee reports the occurrence or upset or breakdown of equipment (by telephone, facsimile, or overnight delivery) to the Department by the end of the next business day after the occurrence or the discovery of the occurrence.
  - c. The permittee must submit to the Department, within five business days after the occurrence or the discovery of the occurrence, a full, written report of such occurrence, including a statement of all known causes and of the scheduling and

nature of the actions to be taken to minimize or eliminate future occurrences, including, but not limited to, action to reduce the frequency of occurrence of such conditions, to minimize the amount by which said limits are exceeded, and to reduce the length of time for which said limits are exceeded. If the information is included in the initial report, the information need not be submitted again.

11. The permittee shall allow representatives of the Department upon the presentation of credentials: [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
  - a. To enter upon the permittee's premises, or other premises under the control of the permittee, where an air pollutant source is located or in which any records are required to be kept under the terms and conditions of this permit;
  - b. To have access to and copy any records required to be kept under the terms and conditions of this permit, or the Act;
  - c. To inspect any monitoring equipment or monitoring method required in this permit;
  - d. To sample any emission of pollutants; and
  - e. To perform an operation and maintenance inspection of the permitted source.
12. The Department issued this permit in reliance upon the statements and presentations made in the permit application. The Department has no responsibility for the adequacy or proper functioning of the equipment or control apparatus. [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
13. The Department may revoke or modify this permit when, in the judgment of the Department, such revocation or modification is necessary to comply with the applicable provisions of the Arkansas Water and Air Pollution Control Act and the regulations promulgated the Arkansas Water and Air Pollution Control Act. [Regulation 19, §19.410(A) and/or Regulation 18, §18.309(A) and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
14. This permit may be transferred. An applicant for a transfer must submit a written request for transfer of the permit on a form provided by the Department and submit the disclosure statement required by Arkansas Code Annotated §8-1-106 at least thirty (30) days in advance of the proposed transfer date. The permit will be automatically transferred to the new permittee unless the Department denies the request to transfer within thirty (30) days of the receipt of the disclosure statement. The Department may deny a transfer on the basis of the information revealed in the disclosure statement or other investigation or, deliberate falsification or omission of relevant information. [Regulation 19, §19.407(B) and/or Regulation 18, §18.307(B) and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
15. This permit shall be available for inspection on the premises where the control apparatus is located. [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]

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16. This permit authorizes only those pollutant emitting activities addressed herein. [A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
17. This permit supersedes and voids all previously issued air permits for this facility. [Regulation 18 and 19 and A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311]
18. The permittee must pay all permit fees in accordance with the procedures established in Regulation No. 9. [A.C.A §8-1-105(c)]
19. The permittee may request in writing and at least 15 days in advance of the deadline, an extension to any testing, compliance or other dates in this permit. No such extensions are authorized until the permittee receives written Department approval. The Department may grant such a request, at its discretion in the following circumstances:
  - a. Such an extension does not violate a federal requirement;
  - b. The permittee demonstrates the need for the extension; and
  - c. The permittee documents that all reasonable measures have been taken to meet the current deadline and documents reasons it cannot be met.

[Regulation 18, §18.314(A), Regulation 19, §19.416(A), A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311, and 40 CFR Part 52, Subpart E]

20. The permittee may request in writing and at least 30 days in advance, temporary emissions and/or testing that would otherwise exceed an emission rate, throughput requirement, or other limit in this permit. No such activities are authorized until the permittee receives written Department approval. Any such emissions shall be included in the facilities total emissions and reported as such. The Department may grant such a request, at its discretion under the following conditions:
  - a. Such a request does not violate a federal requirement;
  - b. Such a request is temporary in nature;
  - c. Such a request will not result in a condition of air pollution;
  - d. The request contains such information necessary for the Department to evaluate the request, including but not limited to, quantification of such emissions and the date/time such emission will occur;
  - e. Such a request will result in increased emissions less than five tons of any individual criteria pollutant, one ton of any single HAP and 2.5 tons of total HAPs; and
  - f. The permittee maintains records of the dates and results of such temporary emissions/testing.

[Regulation 18, §18.314(B), Regulation 19, §19.416(B), A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311, and 40 CFR Part 52, Subpart E]

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21. The permittee may request in writing and at least 30 days in advance, an alternative to the specified monitoring in this permit. No such alternatives are authorized until the permittee receives written Department approval. The Department may grant such a request, at its discretion under the following conditions:
  - a. The request does not violate a federal requirement;
  - b. The request provides an equivalent or greater degree of actual monitoring to the current requirements; and
  - c. Any such request, if approved, is incorporated in the next permit modification application by the permittee.

[Regulation 18, §18.314(C), Regulation 19, §19.416(C), A.C.A. §8-4-203 as referenced by A.C.A. §8-4-304 and §8-4-311, and 40 CFR Part 52, Subpart E]



## **APPENDIX A**

40 CFR Part 60, Subpart Ka

*Standards of Performance for Storage Vessels for Petroleum Liquids for which Construction, Reconstruction, or Modification commenced after May 18, 1978, and prior to July 23, 1984*



## e-CFR Data is current as of October 28, 2008

### Title 40: Protection of Environment

#### PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

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### Subpart Ka—Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After May 18, 1978, and Prior to July 23, 1984

#### § 60.110a Applicability and designation of affected facility.

(a) *Affected facility.* Except as provided in paragraph (b) of this section, the affected facility to which this subpart applies is each storage vessel with a storage capacity greater than 151,416 liters (40,000 gallons) that is used to store petroleum liquids for which construction is commenced after May 18, 1978.

(b) Each petroleum liquid storage vessel with a capacity of less than 1,589,873 liters (420,000 gallons) used for petroleum or condensate stored, processed, or treated prior to custody transfer is not an affected facility and, therefore, is exempt from the requirements of this subpart.

(c) *Alternative means of compliance* —(1) *Option to comply with part 65.* Owners or operators may choose to comply with 40 CFR part 65, subpart C, to satisfy the requirements of §§60.112a through 60.114a for storage vessels that are subject to this subpart that store petroleum liquids that, as stored, have a maximum true vapor pressure equal to or greater than 10.3 kPa (1.5 psia). Other provisions applying to owners or operators who choose to comply with 40 CFR part 65 are provided in 40 CFR 65.1.

(2) *Part 60, subpart A.* Owners or operators who choose to comply with 40 CFR part 65, subpart C, must also comply with §§60.1, 60.2, 60.5, 60.6, 60.7(a)(1) and (4), 60.14, 60.15, and 60.16 for those storage vessels. All sections and paragraphs of subpart A of this part that are not mentioned in this paragraph (c)(2) do not apply to owners or operators of storage vessels complying with 40 CFR part 65, subpart C, except that provisions required to be met prior to implementing 40 CFR part 65 still apply. Owners and operators who choose to comply with 40 CFR part 65, subpart C, must comply with 40 CFR part 65, subpart A.

[45 FR 23379, Apr. 4, 1980, as amended at 65 FR 78275, Dec. 14, 2000]

#### § 60.111a Definitions.

In addition to the terms and their definitions listed in the Act and subpart A of this part the following definitions apply in this subpart:

(a) *Storage vessel* means each tank, reservoir, or container used for the storage of petroleum liquids, but does not include:

(1) Pressure vessels which are designed to operate in excess of 204.9 kPa (15 psig) without emissions to the atmosphere except under emergency conditions.

(2) Subsurface caverns or porous rock reservoirs, or

(3) Underground tanks if the total volume of petroleum liquids added to and taken from a tank annually does not exceed twice the volume of the tank.

(b) *Petroleum liquids* means petroleum, condensate, and any finished or intermediate products manufactured in a petroleum refinery but does not mean Nos. 2 through 6 fuel oils as specified in ASTM D396–78, 89, 90, 92, 96, or 98, gas turbine fuel oils Nos. 2–GT through 4–GT as specified in ASTM D2880–78 or 96, gas turbine fuel oils Nos. 2–GT through 4–GT as specified in ASTM D2880–78 or 96, or diesel fuel oils Nos. 2–D and 4–D as specified in ASTM D975–78, 96, or 98a. (These three methods are incorporated by reference—see §60.17.)

(c) *Petroleum refinery* means each facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through distillation of petroleum or through redistillation, cracking, extracting, or reforming of unfinished petroleum derivatives.

(d) *Petroleum* means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

(e) *Condensate* means hydrocarbon liquid separated from natural gas which condenses due to changes in the temperature or pressure, or both, and remains liquid at standard conditions.

(f) *True vapor pressure* means the equilibrium partial pressure exerted by a petroleum liquid such as determined in accordance with methods described in American Petroleum Institute Bulletin 2517, Evaporation Loss from External Floating-Roof Tanks, Second Edition, February 1980 (incorporated by reference—see §60.17).

(g) *Reid vapor pressure* is the absolute vapor pressure of volatile crude oil and nonviscous petroleum liquids, except liquefied petroleum gases, as determined by ASTM D323–82 or 94 (incorporated by reference—see §60.17).

(h) *Liquid-mounted seal* means a foam or liquid-filled primary seal mounted in contact with the liquid between the tank wall and the floating roof continuously around the circumference of the tank.

(i) *Metallic shoe seal* includes but is not limited to a metal sheet held vertically against the tank wall by springs or weighted levers and is connected by braces to the floating roof. A flexible coated fabric (envelope) spans the annular space between the metal sheet and the floating roof.

(j) *Vapor-mounted seal* means a foam-filled primary seal mounted continuously around the circumference of the tank so there is an annular vapor space underneath the seal. The annular vapor space is bounded by the bottom of the primary seal, the tank wall, the liquid surface, and the floating roof.

(k) *Custody transfer* means the transfer of produced petroleum and/or condensate, after processing and/or treating in the producing operations, from storage tanks or automatic transfer facilities to pipelines or any other forms of transportation.

[45 FR 23379, Apr. 4, 1980, as amended at 48 FR 3737, Jan. 27, 1983; 52 FR 11429, Apr. 8, 1987; 65 FR 61756, Oct. 17, 2000]

#### **§ 60.112a Standard for volatile organic compounds (VOC).**

(a) The owner or operator of each storage vessel to which this subpart applies which contains a petroleum liquid which, as stored, has a true vapor pressure equal to or greater than 10.3 kPa (1.5 psia) but not greater than 76.6 kPa (11.1 psia) shall equip the storage vessel with one of the following:

(1) An external floating roof, consisting of a pontoon-type or double-deck-type cover that rests on the surface of the liquid contents and is equipped with a closure device between the tank wall and the roof edge. Except as provided in paragraph (a)(1)(ii)(D) of this section, the closure device is to consist of two seals, one above the other. The lower seal is referred to as the primary seal and the upper seal is referred to as the secondary seal. The roof is to be floating on the liquid at all times (i.e., off the roof leg supports) except during initial fill and when the tank is completely emptied and subsequently refilled. The process of emptying and refilling when the roof is resting on the leg supports shall be continuous and shall be accomplished as rapidly as possible.

(i) The primary seal is to be either a metallic shoe seal, a liquid-mounted seal, or a vapor-mounted seal. Each seal is to meet the following requirements:

(A) The accumulated area of gaps between the tank wall and the metallic shoe seal or the liquid-mounted seal shall not exceed 212 cm<sup>2</sup> per meter of tank diameter (10.0 in<sup>2</sup> per ft of tank diameter) and the width of any portion of any gap shall not exceed 3.81 cm (1 1/2 in).

(B) The accumulated area of gaps between the tank wall and the vapor-mounted seal shall not exceed 21.2 cm<sup>2</sup> per meter of tank diameter (1.0 in<sup>2</sup> per ft of tank diameter) and the width of any portion of any gap shall not exceed 1.27 cm (1/2 in).

(C) One end of the metallic shoe is to extend into the stored liquid and the other end is to extend a minimum vertical distance of 61 cm (24 in) above the stored liquid surface.

(D) There are to be no holes, tears, or other openings in the shoe, seal fabric, or seal envelope.

(ii) The secondary seal is to meet the following requirements:

(A) The secondary seal is to be installed above the primary seal so that it completely covers the space between the roof edge and the tank wall except as provided in paragraph (a)(1)(ii)(B) of this section.

(B) The accumulated area of gaps between the tank wall and the secondary seal used in combination with a metallic shoe or liquid-mounted primary seal shall not exceed 21.2 cm<sup>2</sup> per meter of tank diameter (1.0 in<sup>2</sup> per ft. of tank diameter) and the width of any portion of any gap shall not exceed 1.27 cm (1/2 in.). There shall be no gaps between the tank wall and the secondary seal used in combination with a vapor-mounted primary seal.

(C) There are to be no holes, tears or other openings in the seal or seal fabric.

(D) The owner or operator is exempted from the requirements for secondary seals and the secondary seal gap criteria when performing gap measurements or inspections of the primary seal.

(iii) Each opening in the roof except for automatic bleeder vents and rim space vents is to provide a projection below the liquid surface. Each opening in the roof except for automatic bleeder vents, rim space vents and leg sleeves is to be equipped with a cover, seal or lid which is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use or as described in paragraph (a)(1)(iv) of this section. Automatic bleeder vents are to be closed at all times when the roof is floating, except when the roof is being floated off or is being landed on the roof leg supports. Rim vents are to be set to open when the roof is being floated off the roof legs supports or at the manufacturer's recommended setting.

(iv) Each emergency roof drain is to be provided with a slotted membrane fabric cover that covers at least 90 percent of the area of the opening.

(2) A fixed roof with an internal floating type cover equipped with a continuous closure device between the tank wall and the cover edge. The cover is to be floating at all times, (i.e., off the leg supports) except during initial fill and when the tank is completely emptied and subsequently refilled. The process of emptying and refilling when the cover is resting on the leg supports shall be continuous and shall be accomplished as rapidly as possible. Each opening in the cover except for automatic bleeder vents and the rim space vents is to provide a projection below the liquid surface. Each opening in the cover except for automatic bleeder vents, rim space vents, stub drains and leg sleeves is to be equipped with a cover, seal, or lid which is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use. Automatic bleeder vents are to be closed at all times when the cover is floating except when the cover is being floated off or is being landed on the leg supports. Rim vents are to be set to open only when the cover is being floated off the leg supports or at the manufacturer's recommended setting.

(3) A vapor recovery system which collects all VOC vapors and gases discharged from the storage vessel, and a vapor return or disposal system which is designed to process such VOC vapors and gases so as to reduce their emission to the atmosphere by at least 95 percent by weight.

(4) A system equivalent to those described in paragraphs (a)(1), (a)(2), or (a)(3) of this section as provided in §60.114a.

(b) The owner or operator of each storage vessel to which this subpart applies which contains a petroleum liquid which, as stored, has a true vapor pressure greater than 76.6 kPa (11.1 psia), shall equip the storage vessel with a vapor recovery system which collects all VOC vapors and gases discharged from the storage vessel, and a vapor return or disposal system which is designed to process such VOC vapors and gases so as to reduce their emission to the atmosphere by at least 95 percent by weight.

[45 FR 23379, Apr. 4, 1980, as amended at 45 FR 83229, Dec. 18, 1980]

### **§ 60.113a Testing and procedures.**

(a) Except as provided in §60.8(b) compliance with the standard prescribed in §60.112a shall be determined as follows or in accordance with an equivalent procedure as provided in §60.114a.

(1) The owner or operator of each storage vessel to which this subpart applies which has an external floating roof shall meet the following requirements:

(i) Determine the gap areas and maximum gap widths between the primary seal and the tank wall and between the secondary seal and the tank wall according to the following frequency:

(A) For primary seals, gap measurements shall be performed within 60 days of the initial fill with petroleum liquid and at least once every five years thereafter. All primary seal inspections or gap measurements which require the removal or dislodging of the secondary seal shall be accomplished as rapidly as possible and the secondary seal shall be replaced as soon as possible.

(B) For secondary seals, gap measurements shall be performed within 60 days of the initial fill with petroleum liquid and at least once every year thereafter.

(C) If any storage vessel is out of service for a period of one year or more, subsequent refilling with petroleum liquid shall be considered initial fill for the purposes of paragraphs (a)(1)(i)(A) and (a)(1)(i)(B) of this section.

(D) Keep records of each gap measurement at the plant for a period of at least 2 years following the date of measurement. Each record shall identify the vessel on which the measurement was performed and shall contain the date of the seal gap measurement, the raw data obtained in the measurement process required by paragraph (a)(1)(ii) of this section and the calculation required by paragraph (a)(1)(iii) of this section.

(E) If either the seal gap calculated in accord with paragraph (a)(1)(iii) of this section or the measured maximum seal gap exceeds the limitations specified by §60.112a of this subpart, a report shall be furnished to the Administrator within 60 days of the date of measurements. The report shall identify the vessel and list each reason why the vessel did not meet the specifications of §60.112a. The report shall also describe the actions necessary to bring the storage vessel into compliance with the specifications of §60.112a.

(ii) Determine gap widths in the primary and secondary seals individually by the following procedures:

(A) Measure seal gaps, if any, at one or more floating roof levels when the roof is floating off the roof leg supports.

(B) Measure seal gaps around the entire circumference of the tank in each place where a 1/8 inch diameter uniform probe passes freely (without forcing or binding against seal) between the seal and the tank wall and measure the circumferential distance of each such location.

(C) The total surface area of each gap described in paragraph (a)(1)(ii)(B) of this section shall be determined by using probes of various widths to accurately measure the actual distance from the tank wall to the seal and multiplying each such width by its respective circumferential distance.

(iii) Add the gap surface area of each gap location for the primary seal and the secondary seal individually. Divide the sum for each seal by the nominal diameter of the tank and compare each ratio to the appropriate ratio in the standard in §60.112a(a)(1)(i) and §60.112a(a)(1)(ii).

(iv) Provide the Administrator 30 days prior notice of the gap measurement to afford the Administrator the opportunity to have an observer present.

(2) The owner or operator of each storage vessel to which this subpart applies which has a vapor recovery and return or disposal system shall provide the following information to the Administrator on or before the date on which construction of the storage vessel commences:

(i) Emission data, if available, for a similar vapor recovery and return or disposal system used on the same type of storage vessel, which can be used to determine the efficiency of the system. A complete description of the emission measurement method used must be included.

(ii) The manufacturer's design specifications and estimated emission reduction capability of the system.

(iii) The operation and maintenance plan for the system.

(iv) Any other information which will be useful to the Administrator in evaluating the effectiveness of the system in reducing VOC emissions.

[45 FR 23379, Apr. 4, 1980, as amended at 52 FR 11429, Apr. 8, 1987]

## **§ 60.114a Alternative means of emission limitation.**

(a) If, in the Administrator's judgment, an alternative means of emission limitation will achieve a reduction in emissions at least equivalent to the reduction in emissions achieved by any requirement in §60.112a, the Administrator will publish in the Federal Register a notice permitting the use of the alternative means for purposes of compliance with that requirement.

(b) Any notice under paragraph (a) of this section will be published only after notice and an opportunity for a hearing.

(c) Any person seeking permission under this section shall submit to the Administrator a written application including:

(1) An actual emissions test that uses a full-sized or scale-model storage vessel that accurately collects and measures all VOC emissions from a given control device and that accurately simulates wind and accounts for other emission variables such as temperature and barometric pressure.

(2) An engineering evaluation that the Administrator determines is an accurate method of determining equivalence.

(d) The Administrator may condition the permission on requirements that may be necessary to ensure operation and maintenance to achieve the same emissions reduction as specified in §60.112a.

(e) The primary vapor-mounted seal in the "Volume-Maximizing Seal" manufactured by R.F.I. Services Corporation is approved as equivalent to the vapor-mounted seal required by §60.112a(a)(1)(i) and must meet the gap criteria specified in §60.112a(a)(1)(i)(B). There shall be no gaps between the tank wall and any secondary seal used in conjunction with the primary seal in the "Volume-Maximizing Seal".

[52 FR 11429, Apr. 8, 1987]

#### **§ 60.115a Monitoring of operations.**

(a) Except as provided in paragraph (d) of this section, the owner or operator subject to this subpart shall maintain a record of the petroleum liquid stored, the period of storage, and the maximum true vapor pressure of that liquid during the respective storage period.

(b) Available data on the typical Reid vapor pressure and the maximum expected storage temperature of the stored product may be used to determine the maximum true vapor pressure from nomographs contained in API Bulletin 2517, unless the Administrator specifically requests that the liquid be sampled, the actual storage temperature determined, and the Reid vapor pressure determined from the sample(s).

(c) The true vapor pressure of each type of crude oil with a Reid vapor pressure less than 13.8 kPa (2.0 psia) or whose physical properties preclude determination by the recommended method is to be determined from available data and recorded if the estimated true vapor pressure is greater than 6.9 kPa (1.0 psia).

(d) The following are exempt from the requirements of this section:

(1) Each owner or operator of each storage vessel storing a petroleum liquid with a Reid vapor pressure of less than 6.9 kPa (1.0 psia) provided the maximum true vapor pressure does not exceed 6.9 kPa (1.0 psia).

(2) The owner or operator of each storage vessel equipped with a vapor recovery and return or disposal system in accordance with the requirements of §60.112a(a)(3) and (b), or a closed vent system and control device meeting the specifications of 40 CFR 65.42(b)(4), (b)(5), or (c).

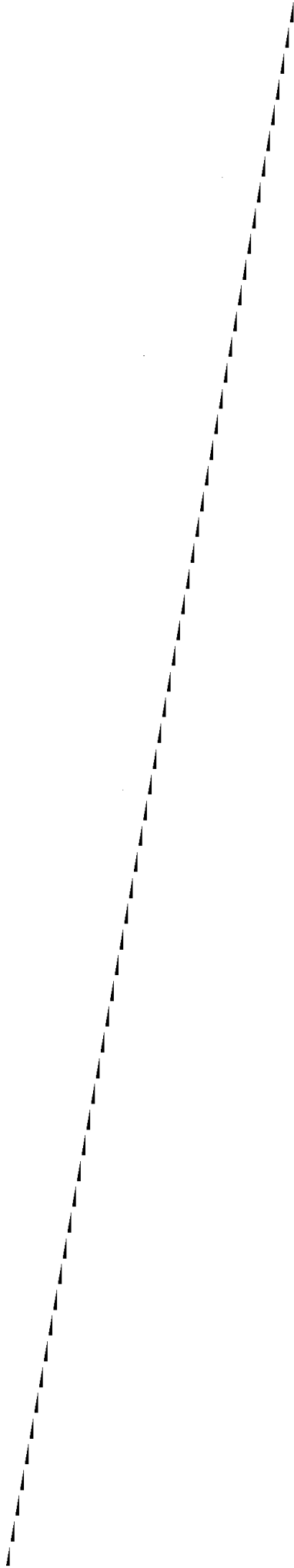
[45 FR 23379, Apr. 4, 1980, as amended at 65 FR 78275, Dec. 14, 2000]

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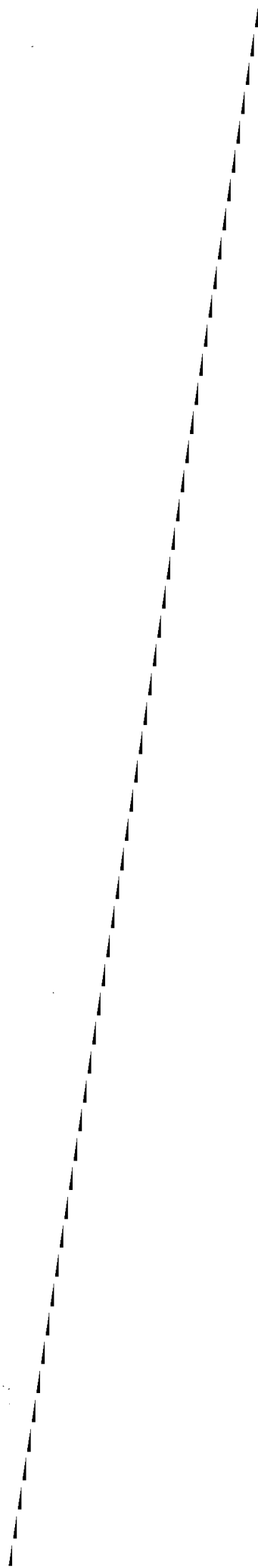
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## **APPENDIX B**

**40 CFR Part 60, Subpart GG Stationary Gas Turbines**



# e-CFR Data is current as of October 28, 2008

## Title 40: Protection of Environment

### PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

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#### Subpart GG—Standards of Performance for Stationary Gas Turbines

##### § 60.330 Applicability and designation of affected facility.

(a) The provisions of this subpart are applicable to the following affected facilities: All stationary gas turbines with a heat input at peak load equal to or greater than 10.7 gigajoules (10 million Btu) per hour, based on the lower heating value of the fuel fired.

(b) Any facility under paragraph (a) of this section which commences construction, modification, or reconstruction after October 3, 1977, is subject to the requirements of this part except as provided in paragraphs (e) and (j) of §60.332.

[44 FR 52798, Sept. 10, 1979, as amended at 52 FR 42434, Nov. 5, 1987; 65 FR 61759, Oct. 17, 2000]

##### § 60.331 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

(a) *Stationary gas turbine* means any simple cycle gas turbine, regenerative cycle gas turbine or any gas turbine portion of a combined cycle steam/electric generating system that is not self propelled. It may, however, be mounted on a vehicle for portability.

(b) *Simple cycle gas turbine* means any stationary gas turbine which does not recover heat from the gas turbine exhaust gases to preheat the inlet combustion air to the gas turbine, or which does not recover heat from the gas turbine exhaust gases to heat water or generate steam.

(c) *Regenerative cycle gas turbine* means any stationary gas turbine which recovers heat from the gas turbine exhaust gases to preheat the inlet combustion air to the gas turbine.

(d) *Combined cycle gas turbine* means any stationary gas turbine which recovers heat from the gas turbine exhaust gases to heat water or generate steam.

(e) *Emergency gas turbine* means any stationary gas turbine which operates as a mechanical or electrical power source only when the primary power source for a facility has been rendered inoperable by an emergency situation.

(f) *Ice fog* means an atmospheric suspension of highly reflective ice crystals.

(g) *ISO standard day conditions* means 288 degrees Kelvin, 60 percent relative humidity and 101.3 kilopascals pressure.

(h) *Efficiency* means the gas turbine manufacturer's rated heat rate at peak load in terms of heat input per unit of power output based on the lower heating value of the fuel.

(i) *Peak load* means 100 percent of the manufacturer's design capacity of the gas turbine at ISO standard day conditions.

(j) *Base load* means the load level at which a gas turbine is normally operated.

(k) *Fire-fighting turbine* means any stationary gas turbine that is used solely to pump water for extinguishing fires.

(l) *Turbines employed in oil/gas production or oil/gas transportation* means any stationary gas turbine used to provide power to extract crude oil/natural gas from the earth or to move crude oil/natural gas, or products refined from these substances through pipelines.

(m) A *Metropolitan Statistical Area or MSA* as defined by the Department of Commerce.

(n) *Offshore platform gas turbines* means any stationary gas turbine located on a platform in an ocean.

(o) *Garrison facility* means any permanent military installation.

(p) *Gas turbine model* means a group of gas turbines having the same nominal air flow, combustor inlet pressure, combustor inlet temperature, firing temperature, turbine inlet temperature and turbine inlet pressure.

(q) *Electric utility stationary gas turbine* means any stationary gas turbine constructed for the purpose of supplying more than one-third of its potential electric output capacity to any utility power distribution system for sale.

(r) *Emergency fuel* is a fuel fired by a gas turbine only during circumstances, such as natural gas supply curtailment or breakdown of delivery system, that make it impossible to fire natural gas in the gas turbine.

(s) *Unit operating hour* means a clock hour during which any fuel is combusted in the affected unit. If the unit combusts fuel for the entire clock hour, it is considered to be a full unit operating hour. If the unit combusts fuel for only part of the clock hour, it is considered to be a partial unit operating hour.

(t) *Excess emissions* means a specified averaging period over which either:

(1) The NO<sub>x</sub> emissions are higher than the applicable emission limit in §60.332;

(2) The total sulfur content of the fuel being combusted in the affected facility exceeds the limit specified in §60.333; or

(3) The recorded value of a particular monitored parameter is outside the acceptable range specified in the parameter monitoring plan for the affected unit.

(u) *Natural gas* means a naturally occurring fluid mixture of hydrocarbons ( e.g. , methane, ethane, or propane) produced in geological formations beneath the Earth's surface that maintains a gaseous state at standard atmospheric temperature and pressure under ordinary conditions. Natural gas contains 20.0 grains or less of total sulfur per 100 standard cubic feet. Equivalents of this in other units are as follows: 0.068 weight percent total sulfur, 680 parts per million by weight (ppmw) total sulfur, and 338 parts per million by volume (ppmv) at 20 degrees Celsius total sulfur. Additionally, natural gas must either be composed of at least 70 percent methane by volume or have a gross calorific value between 950 and 1100 British thermal units (Btu) per standard cubic foot. Natural gas does not include the following gaseous fuels: landfill gas, digester gas, refinery gas, sour gas, blast furnace gas, coal-derived gas, producer gas, coke oven gas, or any gaseous fuel produced in a process which might result in highly variable sulfur content or heating value.

(v) *Duct burner* means a device that combusts fuel and that is placed in the exhaust duct from another source, such as a stationary gas turbine, internal combustion engine, kiln, etc., to allow the firing of additional fuel to heat the exhaust gases before the exhaust gases enter a heat recovery steam generating unit.

(w) *Lean premix stationary combustion turbine* means any stationary combustion turbine where the air and fuel are thoroughly mixed to form a lean mixture for combustion in the combustor. Mixing may occur before or in the combustion chamber. A unit which is capable of operating in both lean premix and diffusion flame modes is considered a lean premix stationary combustion turbine when it is in the lean premix mode, and it is considered a diffusion flame stationary combustion turbine when it is in the diffusion flame mode.

(x) *Diffusion flame stationary combustion turbine* means any stationary combustion turbine where fuel and air are injected at the combustor and are mixed only by diffusion prior to ignition. A unit which is capable of operating in both lean premix and diffusion flame modes is considered a lean premix stationary combustion turbine when it is in the lean premix mode, and it is considered a diffusion flame stationary combustion turbine when it is in the diffusion flame mode.

(y) *Unit operating day* means a 24-hour period between 12:00 midnight and the following midnight during which any fuel is combusted at any time in the unit. It is not necessary for fuel to be combusted continuously for the entire 24-hour period.

**§ 60.332 Standard for nitrogen oxides.**

(a) On and after the date on which the performance test required by §60.8 is completed, every owner or operator subject to the provisions of this subpart as specified in paragraphs (b), (c), and (d) of this section shall comply with one of the following, except as provided in paragraphs (e), (f), (g), (h), (i), (j), (k), and (l) of this section.

(1) No owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any stationary gas turbine, any gases which contain nitrogen oxides in excess of:

$$STD = 0.0075 \frac{(14.4)}{Y} + F$$

where:

STD = allowable ISO corrected (if required as given in §60.335(b)(1)) NO<sub>x</sub>emission concentration (percent by volume at 15 percent oxygen and on a dry basis),

Y = manufacturer's rated heat rate at manufacturer's rated load (kilojoules per watt hour) or, actual measured heat rate based on lower heating value of fuel as measured at actual peak load for the facility. The value of Y shall not exceed 14.4 kilojoules per watt hour, and

F = NO<sub>x</sub>emission allowance for fuel-bound nitrogen as defined in paragraph (a)(4) of this section.

(2) No owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any stationary gas turbine, any gases which contain nitrogen oxides in excess of:

$$STD = 0.0150 \frac{(14.4)}{Y} + F$$

where:

STD = allowable ISO corrected (if required as given in §60.335(b)(1)) NO<sub>x</sub>emission concentration (percent by volume at 15 percent oxygen and on a dry basis),

Y = manufacturer's rated heat rate at manufacturer's rated peak load (kilojoules per watt hour), or actual measured heat rate based on lower heating value of fuel as measured at actual peak load for the facility. The value of Y shall not exceed 14.4 kilojoules per watt hour, and

F = NO<sub>x</sub>emission allowance for fuel-bound nitrogen as defined in paragraph (a)(4) of this section.

(3) The use of F in paragraphs (a)(1) and (2) of this section is optional. That is, the owner or operator may choose to apply a NO<sub>x</sub>allowance for fuel-bound nitrogen and determine the appropriate F-value in accordance with paragraph (a)(4) of this section or may accept an F-value of zero.

(4) If the owner or operator elects to apply a NO<sub>x</sub>emission allowance for fuel-bound nitrogen, F shall be defined according to the nitrogen content of the fuel during the most recent performance test required under §60.8 as follows:

Fuel-bound nitrogen (percent by weight)	F (NO <sub>x</sub> percent by volume)
N ≤ .015	0

$0.015 < N \leq 0.1$	$0.04 (N)$
$0.1 < N \leq 0.25$	$0.004 + 0.0067(N - 0.1)$
$N > 0.25$	$0.005$

Where:

N = the nitrogen content of the fuel (percent by weight).

or:

Manufacturers may develop and submit to EPA custom fuel-bound nitrogen allowances for each gas turbine model they manufacture. These fuel-bound nitrogen allowances shall be substantiated with data and must be approved for use by the Administrator before the initial performance test required by §60.8. Notices of approval of custom fuel-bound nitrogen allowances will be published in the Federal Register.

(b) Electric utility stationary gas turbines with a heat input at peak load greater than 107.2 gigajoules per hour (100 million Btu/hour) based on the lower heating value of the fuel fired shall comply with the provisions of paragraph (a)(1) of this section.

(c) Stationary gas turbines with a heat input at peak load equal to or greater than 10.7 gigajoules per hour (10 million Btu/hour) but less than or equal to 107.2 gigajoules per hour (100 million Btu/hour) based on the lower heating value of the fuel fired, shall comply with the provisions of paragraph (a)(2) of this section.

(d) Stationary gas turbines with a manufacturer's rated base load at ISO conditions of 30 megawatts or less except as provided in §60.332(b) shall comply with paragraph (a)(2) of this section.

(e) Stationary gas turbines with a heat input at peak load equal to or greater than 10.7 gigajoules per hour (10 million Btu/hour) but less than or equal to 107.2 gigajoules per hour (100 million Btu/hour) based on the lower heating value of the fuel fired and that have commenced construction prior to October 3, 1982 are exempt from paragraph (a) of this section.

(f) Stationary gas turbines using water or steam injection for control of NO<sub>x</sub> emissions are exempt from paragraph (a) when ice fog is deemed a traffic hazard by the owner or operator of the gas turbine.

(g) Emergency gas turbines, military gas turbines for use in other than a garrison facility, military gas turbines installed for use as military training facilities, and fire fighting gas turbines are exempt from paragraph (a) of this section.

(h) Stationary gas turbines engaged by manufacturers in research and development of equipment for both gas turbine emission control techniques and gas turbine efficiency improvements are exempt from paragraph (a) on a case-by-case basis as determined by the Administrator.

(i) Exemptions from the requirements of paragraph (a) of this section will be granted on a case-by-case basis as determined by the Administrator in specific geographical areas where mandatory water restrictions are required by governmental agencies because of drought conditions. These exemptions will be allowed only while the mandatory water restrictions are in effect.

(j) Stationary gas turbines with a heat input at peak load greater than 107.2 gigajoules per hour that commenced construction, modification, or reconstruction between the dates of October 3, 1977, and January 27, 1982, and were required in the September 10, 1979, Federal Register (44 FR 52792) to comply with paragraph (a)(1) of this section, except electric utility stationary gas turbines, are exempt from paragraph (a) of this section.

(k) Stationary gas turbines with a heat input greater than or equal to 10.7 gigajoules per hour (10 million Btu/hour) when fired with natural gas are exempt from paragraph (a)(2) of this section when being fired with an emergency fuel.

(l) Regenerative cycle gas turbines with a heat input less than or equal to 107.2 gigajoules per hour (100 million Btu/hour) are exempt from paragraph (a) of this section.

[44 FR 52798, Sept. 10, 1979, as amended at 47 FR 3770, Jan. 27, 1982; 65 FR 61759, Oct. 17, 2000; 69 FR 41359, July 8, 2004]

### **§ 60.333 Standard for sulfur dioxide.**

On and after the date on which the performance test required to be conducted by §60.8 is completed, every owner or operator subject to the provision of this subpart shall comply with one or the other of the following conditions:

(a) No owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any stationary gas turbine any gases which contain sulfur dioxide in excess of 0.015 percent by volume at 15 percent oxygen and on a dry basis.

(b) No owner or operator subject to the provisions of this subpart shall burn in any stationary gas turbine any fuel which contains total sulfur in excess of 0.8 percent by weight (8000 ppmw).

[44 FR 52798, Sept. 10, 1979, as amended at 69 FR 41360, July 8, 2004]

### **§ 60.334 Monitoring of operations.**

(a) Except as provided in paragraph (b) of this section, the owner or operator of any stationary gas turbine subject to the provisions of this subpart and using water or steam injection to control NO<sub>x</sub> emissions shall install, calibrate, maintain and operate a continuous monitoring system to monitor and record the fuel consumption and the ratio of water or steam to fuel being fired in the turbine.

(b) The owner or operator of any stationary gas turbine that commenced construction, reconstruction or modification after October 3, 1977, but before July 8, 2004, and which uses water or steam injection to control NO<sub>x</sub> emissions may, as an alternative to operating the continuous monitoring system described in paragraph (a) of this section, install, certify, maintain, operate, and quality-assure a continuous emission monitoring system (CEMS) consisting of NO<sub>x</sub> and O<sub>2</sub> monitors. As an alternative, a CO<sub>2</sub> monitor may be used to adjust the measured NO<sub>x</sub> concentrations to 15 percent O<sub>2</sub> by either converting the CO<sub>2</sub> hourly averages to equivalent O<sub>2</sub> concentrations using Equation F-14a or F-14b in appendix F to part 75 of this chapter and making the adjustments to 15 percent O<sub>2</sub>, or by using the CO<sub>2</sub> readings directly to make the adjustments, as described in Method 20. If the option to use a CEMS is chosen, the CEMS shall be installed, certified, maintained and operated as follows:

(1) Each CEMS must be installed and certified according to PS 2 and 3 (for diluent) of 40 CFR part 60, appendix B, except the 7-day calibration drift is based on unit operating days, not calendar days. Appendix F, Procedure 1 is not required. The relative accuracy test audit (RATA) of the NO<sub>x</sub> and diluent monitors may be performed individually or on a combined basis, *i.e.*, the relative accuracy tests of the CEMS may be performed either:

(i) On a ppm basis (for NO<sub>x</sub>) and a percent O<sub>2</sub> basis for oxygen; or

(ii) On a ppm at 15 percent O<sub>2</sub> basis; or

(iii) On a ppm basis (for NO<sub>x</sub>) and a percent CO<sub>2</sub> basis (for a CO<sub>2</sub> monitor that uses the procedures in Method 20 to correct the NO<sub>x</sub> data to 15 percent O<sub>2</sub>).

(2) As specified in §60.13(e)(2), during each full unit operating hour, each monitor must complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each 15-minute quadrant of the hour, to validate the hour. For partial unit operating hours, at least one valid data point must be obtained for each quadrant of the hour in which the unit operates. For unit operating hours in which required quality assurance and maintenance activities are performed on the CEMS, a minimum of two valid data points (one in each of two quadrants) are required to validate the hour.

(3) For purposes of identifying excess emissions, CEMS data must be reduced to hourly averages as specified in §60.13(h).

(i) For each unit operating hour in which a valid hourly average, as described in paragraph (b)(2) of this section, is obtained for both NO<sub>x</sub> and diluent, the data acquisition and handling system must calculate and record the hourly NO<sub>x</sub> emissions in the units of the applicable NO<sub>x</sub> emission standard under §60.332(a), *i.e.*, percent NO<sub>x</sub> by volume, dry basis, corrected to 15 percent O<sub>2</sub> and International Organization for Standardization (ISO) standard conditions (if required as given in §60.335(b)(1)). For any hour in which the hourly average O<sub>2</sub> concentration exceeds 19.0 percent O<sub>2</sub>, a diluent cap value of 19.0 percent O<sub>2</sub> may be used in the emission calculations.

(ii) A worst case ISO correction factor may be calculated and applied using historical ambient data. For the purpose of this calculation, substitute the maximum humidity of ambient air ( $H_o$ ), minimum ambient temperature ( $T_a$ ), and minimum combustor inlet absolute pressure ( $P_o$ ) into the ISO correction equation.

(iii) If the owner or operator has installed a NO<sub>x</sub>CEMS to meet the requirements of part 75 of this chapter, and is continuing to meet the ongoing requirements of part 75 of this chapter, the CEMS may be used to meet the requirements of this section, except that the missing data substitution methodology provided for at 40 CFR part 75, subpart D, is not required for purposes of identifying excess emissions. Instead, periods of missing CEMS data are to be reported as monitor downtime in the excess emissions and monitoring performance report required in §60.7(c).

(c) For any turbine that commenced construction, reconstruction or modification after October 3, 1977, but before July 8, 2004, and which does not use steam or water injection to control NO<sub>x</sub>emissions, the owner or operator may, but is not required to, for purposes of determining excess emissions, use a CEMS that meets the requirements of paragraph (b) of this section. Also, if the owner or operator has previously submitted and received EPA, State, or local permitting authority approval of a procedure for monitoring compliance with the applicable NO<sub>x</sub>emission limit under §60.332, that approved procedure may continue to be used.

(d) The owner or operator of any new turbine constructed after July 8, 2004, and which uses water or steam injection to control NO<sub>x</sub>emissions may elect to use either the requirements in paragraph (a) of this section for continuous water or steam to fuel ratio monitoring or may use a NO<sub>x</sub>CEMS installed, certified, operated, maintained, and quality-assured as described in paragraph (b) of this section.

(e) The owner or operator of any new turbine that commences construction after July 8, 2004, and which does not use water or steam injection to control NO<sub>x</sub>emissions, may, but is not required to, elect to use a NO<sub>x</sub>CEMS installed, certified, operated, maintained, and quality-assured as described in paragraph (b) of this section. Other acceptable monitoring approaches include periodic testing approved by EPA or the State or local permitting authority or continuous parameter monitoring as described in paragraph (f) of this section.

(f) The owner or operator of a new turbine that commences construction after July 8, 2004, which does not use water or steam injection to control NO<sub>x</sub>emissions may, but is not required to, perform continuous parameter monitoring as follows:

(1) For a diffusion flame turbine without add-on selective catalytic reduction controls (SCR), the owner or operator shall define at least four parameters indicative of the unit's NO<sub>x</sub>formation characteristics and shall monitor these parameters continuously.

(2) For any lean premix stationary combustion turbine, the owner or operator shall continuously monitor the appropriate parameters to determine whether the unit is operating in low-NO<sub>x</sub>mode.

(3) For any turbine that uses SCR to reduce NO<sub>x</sub>emissions, the owner or operator shall continuously monitor appropriate parameters to verify the proper operation of the emission controls.

(4) For affected units that are also regulated under part 75 of this chapter, if the owner or operator elects to monitor NO<sub>x</sub>emission rate using the methodology in appendix E to part 75 of this chapter, or the low mass emissions methodology in §75.19 of this chapter, the requirements of this paragraph (f) may be met by performing the parametric monitoring described in section 2.3 of appendix E or in §75.19(c)(1)(iv)(H) of this chapter.

(g) The steam or water to fuel ratio or other parameters that are continuously monitored as described in paragraphs (a), (d) or (f) of this section shall be monitored during the performance test required under §60.8, to establish acceptable values and ranges. The owner or operator may supplement the performance test data with engineering analyses, design specifications, manufacturer's recommendations and other relevant information to define the acceptable parametric ranges more precisely. The owner or operator shall develop and keep on-site a parameter monitoring plan which explains the procedures used to document proper operation of the NO<sub>x</sub>emission controls. The plan shall include the parameter(s) monitored and the acceptable range(s) of the parameter(s) as well as the basis for designating the parameter(s) and acceptable range(s). Any supplemental data such as engineering analyses, design specifications, manufacturer's recommendations and other relevant information shall be included in the monitoring plan. For affected units that are also subject to part 75 of this chapter and that use the low mass emissions methodology in §75.19 of this chapter or the NO<sub>x</sub>emission measurement methodology in appendix E to part 75, the owner or operator may meet the requirements of this paragraph by developing and keeping on-site (or at a central location for unmanned facilities) a quality-assurance plan, as described in §75.19 (e)(5) or in section 2.3 of appendix E and section 1.3.6 of appendix B to part 75 of this chapter.

(h) The owner or operator of any stationary gas turbine subject to the provisions of this subpart:



(1) Shall monitor the total sulfur content of the fuel being fired in the turbine, except as provided in paragraph (h)(3) of this section. The sulfur content of the fuel must be determined using total sulfur methods described in §60.335(b)(10). Alternatively, if the total sulfur content of the gaseous fuel during the most recent performance test was less than 0.4 weight percent (4000 ppmw), ASTM D4084–82, 94, D5504–01, D6228–98, or Gas Processors Association Standard 2377–86 (all of which are incorporated by reference—see §60.17), which measure the major sulfur compounds may be used; and

(2) Shall monitor the nitrogen content of the fuel combusted in the turbine, if the owner or operator claims an allowance for fuel bound nitrogen ( *i.e.* , if an F-value greater than zero is being or will be used by the owner or operator to calculate STD in §60.332). The nitrogen content of the fuel shall be determined using methods described in §60.335(b)(9) or an approved alternative.

(3) Notwithstanding the provisions of paragraph (h)(1) of this section, the owner or operator may elect not to monitor the total sulfur content of the gaseous fuel combusted in the turbine, if the gaseous fuel is demonstrated to meet the definition of natural gas in §60.331(u), regardless of whether an existing custom schedule approved by the administrator for subpart GG requires such monitoring. The owner or operator shall use one of the following sources of information to make the required demonstration:

(i) The gas quality characteristics in a current, valid purchase contract, tariff sheet or transportation contract for the gaseous fuel, specifying that the maximum total sulfur content of the fuel is 20.0 grains/100 scf or less; or

(ii) Representative fuel sampling data which show that the sulfur content of the gaseous fuel does not exceed 20 grains/100 scf. At a minimum, the amount of fuel sampling data specified in section 2.3.1.4 or 2.3.2.4 of appendix D to part 75 of this chapter is required.

(4) For any turbine that commenced construction, reconstruction or modification after October 3, 1977, but before July 8, 2004, and for which a custom fuel monitoring schedule has previously been approved, the owner or operator may, without submitting a special petition to the Administrator, continue monitoring on this schedule.

(i) The frequency of determining the sulfur and nitrogen content of the fuel shall be as follows:

(1) *Fuel oil.* For fuel oil, use one of the total sulfur sampling options and the associated sampling frequency described in sections 2.2.3, 2.2.4.1, 2.2.4.2, and 2.2.4.3 of appendix D to part 75 of this chapter ( *i.e.* , flow proportional sampling, daily sampling, sampling from the unit's storage tank after each addition of fuel to the tank, or sampling each delivery prior to combining it with fuel oil already in the intended storage tank). If an emission allowance is being claimed for fuel-bound nitrogen, the nitrogen content of the oil shall be determined and recorded once per unit operating day.

(2) *Gaseous fuel.* Any applicable nitrogen content value of the gaseous fuel shall be determined and recorded once per unit operating day. For owners and operators that elect not to demonstrate sulfur content using options in paragraph (h)(3) of this section, and for which the fuel is supplied without intermediate bulk storage, the sulfur content value of the gaseous fuel shall be determined and recorded once per unit operating day.

(3) *Custom schedules.* Notwithstanding the requirements of paragraph (i)(2) of this section, operators or fuel vendors may develop custom schedules for determination of the total sulfur content of gaseous fuels, based on the design and operation of the affected facility and the characteristics of the fuel supply. Except as provided in paragraphs (i)(3)(i) and (i)(3)(ii) of this section, custom schedules shall be substantiated with data and shall be approved by the Administrator before they can be used to comply with the standard in §60.333.

(i) The two custom sulfur monitoring schedules set forth in paragraphs (i)(3)(i)(A) through (D) and in paragraph (i)(3)(ii) of this section are acceptable, without prior Administrative approval:

(A) The owner or operator shall obtain daily total sulfur content measurements for 30 consecutive unit operating days, using the applicable methods specified in this subpart. Based on the results of the 30 daily samples, the required frequency for subsequent monitoring of the fuel's total sulfur content shall be as specified in paragraph (i)(3)(i)(B), (C), or (D) of this section, as applicable.

(B) If none of the 30 daily measurements of the fuel's total sulfur content exceeds 0.4 weight percent (4000 ppmw), subsequent sulfur content monitoring may be performed at 12 month intervals. If any of the samples taken at 12-month intervals has a total sulfur content between 0.4 and 0.8 weight percent (4000 and 8000 ppmw), follow the procedures in paragraph (i)(3)(i)(C) of this section. If any measurement exceeds 0.8 weight percent (8000 ppmw), follow the procedures in paragraph (i)(3)(i)(D) of this section.

(C) If at least one of the 30 daily measurements of the fuel's total sulfur content is between 0.4 and 0.8 weight percent (4000 and 8000 ppmw), but none exceeds 0.8 weight percent (8000 ppmw), then:

( 1 ) Collect and analyze a sample every 30 days for three months. If any sulfur content measurement exceeds 0.8 weight percent (8000 ppmw), follow the procedures in paragraph (i)(3)(i)(D) of this section. Otherwise, follow the procedures in paragraph (i)(3)(i)(C)( 2 ) of this section.

( 2 ) Begin monitoring at 6-month intervals for 12 months. If any sulfur content measurement exceeds 0.8 weight percent (8000 ppmw), follow the procedures in paragraph (i)(3)(i)(D) of this section. Otherwise, follow the procedures in paragraph (i)(3)(i)(C)( 3 ) of this section.

( 3 ) Begin monitoring at 12-month intervals. If any sulfur content measurement exceeds 0.8 weight percent (8000 ppmw), follow the procedures in paragraph (i)(3)(i)(D) of this section. Otherwise, continue to monitor at this frequency.

(D) If a sulfur content measurement exceeds 0.8 weight percent (8000 ppmw), immediately begin daily monitoring according to paragraph (i)(3)(i)(A) of this section. Daily monitoring shall continue until 30 consecutive daily samples, each having a sulfur content no greater than 0.8 weight percent (8000 ppmw), are obtained. At that point, the applicable procedures of paragraph (i)(3)(i)(B) or (C) of this section shall be followed.

(ii) The owner or operator may use the data collected from the 720-hour sulfur sampling demonstration described in section 2.3.6 of appendix D to part 75 of this chapter to determine a custom sulfur sampling schedule, as follows:

(A) If the maximum fuel sulfur content obtained from the 720 hourly samples does not exceed 20 grains/100 scf ( i.e. , the maximum total sulfur content of natural gas as defined in §60.331(u)), no additional monitoring of the sulfur content of the gas is required, for the purposes of this subpart.

(B) If the maximum fuel sulfur content obtained from any of the 720 hourly samples exceeds 20 grains/100 scf, but none of the sulfur content values (when converted to weight percent sulfur) exceeds 0.4 weight percent (4000 ppmw), then the minimum required sampling frequency shall be one sample at 12 month intervals.

(C) If any sample result exceeds 0.4 weight percent sulfur (4000 ppmw), but none exceeds 0.8 weight percent sulfur (8000 ppmw), follow the provisions of paragraph (i)(3)(i)(C) of this section.

(D) If the sulfur content of any of the 720 hourly samples exceeds 0.8 weight percent (8000 ppmw), follow the provisions of paragraph (i)(3)(i)(D) of this section.

(j) For each affected unit that elects to continuously monitor parameters or emissions, or to periodically determine the fuel sulfur content or fuel nitrogen content under this subpart, the owner or operator shall submit reports of excess emissions and monitor downtime, in accordance with §60.7(c). Excess emissions shall be reported for all periods of unit operation, including startup, shutdown and malfunction. For the purpose of reports required under §60.7(c), periods of excess emissions and monitor downtime that shall be reported are defined as follows:

(1) Nitrogen oxides.

(i) For turbines using water or steam to fuel ratio monitoring:

(A) An excess emission shall be any unit operating hour for which the average steam or water to fuel ratio, as measured by the continuous monitoring system, falls below the acceptable steam or water to fuel ratio needed to demonstrate compliance with §60.332, as established during the performance test required in §60.8. Any unit operating hour in which no water or steam is injected into the turbine shall also be considered an excess emission.

(B) A period of monitor downtime shall be any unit operating hour in which water or steam is injected into the turbine, but the essential parametric data needed to determine the steam or water to fuel ratio are unavailable or invalid.

(C) Each report shall include the average steam or water to fuel ratio, average fuel consumption, ambient conditions (temperature, pressure, and humidity), gas turbine load, and (if applicable) the nitrogen content of the fuel during each excess emission. You do not have to report ambient conditions if you opt to use the worst case ISO correction factor as specified in §60.334(b)(3)(ii), or if you are not using the ISO correction equation under the provisions of §60.335(b)(1).

(ii) If the owner or operator elects to take an emission allowance for fuel bound nitrogen, then excess emissions and periods of monitor downtime are as described in paragraphs (j)(1)(ii)(A) and (B) of this section.

(A) An excess emission shall be the period of time during which the fuel-bound nitrogen (N) is greater than the value measured during the performance test required in §60.8 and used to determine the allowance. The excess emission begins on the date and hour of the sample which shows that N is greater than the performance test value, and ends with the date and hour of a subsequent sample which shows a fuel nitrogen content less than or equal to the performance test value.

(B) A period of monitor downtime begins when a required sample is not taken by its due date. A period of monitor downtime also begins on the date and hour that a required sample is taken, if invalid results are obtained. The period of monitor downtime ends on the date and hour of the next valid sample.

(iii) For turbines using NO<sub>x</sub> and diluent CEMS:

(A) An hour of excess emissions shall be any unit operating hour in which the 4-hour rolling average NO<sub>x</sub> concentration exceeds the applicable emission limit in §60.332(a)(1) or (2). For the purposes of this subpart, a "4-hour rolling average NO<sub>x</sub> concentration" is the arithmetic average of the average NO<sub>x</sub> concentration measured by the CEMS for a given hour (corrected to 15 percent O<sub>2</sub> and, if required under §60.335(b)(1), to ISO standard conditions) and the three unit operating hour average NO<sub>x</sub> concentrations immediately preceding that unit operating hour.

(B) A period of monitor downtime shall be any unit operating hour in which sufficient data are not obtained to validate the hour, for either NO<sub>x</sub> concentration or diluent (or both).

(C) Each report shall include the ambient conditions (temperature, pressure, and humidity) at the time of the excess emission period and (if the owner or operator has claimed an emission allowance for fuel bound nitrogen) the nitrogen content of the fuel during the period of excess emissions. You do not have to report ambient conditions if you opt to use the worst case ISO correction factor as specified in §60.334(b)(3)(ii), or if you are not using the ISO correction equation under the provisions of §60.335(b)(1).

(iv) For owners or operators that elect, under paragraph (f) of this section, to monitor combustion parameters or parameters that document proper operation of the NO<sub>x</sub> emission controls:

(A) An excess emission shall be a 4-hour rolling unit operating hour average in which any monitored parameter does not achieve the target value or is outside the acceptable range defined in the parameter monitoring plan for the unit.

(B) A period of monitor downtime shall be a unit operating hour in which any of the required parametric data are either not recorded or are invalid.

(2) Sulfur dioxide. If the owner or operator is required to monitor the sulfur content of the fuel under paragraph (h) of this section:

(i) For samples of gaseous fuel and for oil samples obtained using daily sampling, flow proportional sampling, or sampling from the unit's storage tank, an excess emission occurs each unit operating hour included in the period beginning on the date and hour of any sample for which the sulfur content of the fuel being fired in the gas turbine exceeds 0.8 weight percent and ending on the date and hour that a subsequent sample is taken that demonstrates compliance with the sulfur limit.

(ii) If the option to sample each delivery of fuel oil has been selected, the owner or operator shall immediately switch to one of the other oil sampling options (i.e., daily sampling, flow proportional sampling, or sampling from the unit's storage tank) if the sulfur content of a delivery exceeds 0.8 weight percent. The owner or operator shall continue to use one of the other sampling options until all of the oil from the delivery has been combusted, and shall evaluate excess emissions according to paragraph (j)(2)(i) of this section. When all of the fuel from the delivery has been burned, the owner or operator may resume using the as-delivered sampling option.

(iii) A period of monitor downtime begins when a required sample is not taken by its due date. A period of monitor downtime also begins on the date and hour of a required sample, if invalid results are obtained. The period of monitor downtime shall include only unit operating hours, and ends on the date and hour of the next valid sample.

(3) *Ice fog*. Each period during which an exemption provided in §60.332(f) is in effect shall be reported in writing to the Administrator quarterly. For each period the ambient conditions existing during the period, the date and time the air pollution control system was deactivated, and the date and time the air pollution control system was reactivated shall be reported. All quarterly reports shall be postmarked by the 30th day following the end of each calendar quarter.

(4) *Emergency fuel.* Each period during which an exemption provided in §60.332(k) is in effect shall be included in the report required in §60.7(c). For each period, the type, reasons, and duration of the firing of the emergency fuel shall be reported.

(5) All reports required under §60.7(c) shall be postmarked by the 30th day following the end of each 6-month period.

[44 FR 52798, Sept. 10, 1979, as amended at 47 FR 3770, Jan. 27, 1982; 65 FR 61759, Oct. 17, 2000; 69 FR 41360, July 8, 2004; 71 FR 9457, Feb. 24, 2006]

## **§ 60.335 Test methods and procedures.**

(a) The owner or operator shall conduct the performance tests required in §60.8, using either

(1) EPA Method 20,

(2) ASTM D6522–00 (incorporated by reference, see §60.17), or

(3) EPA Method 7E and either EPA Method 3 or 3A in appendix A to this part, to determine NO<sub>x</sub> and diluent concentration.

(4) Sampling traverse points are to be selected following Method 20 or Method 1, (non-particulate procedures) and sampled for equal time intervals. The sampling shall be performed with a traversing single-hole probe or, if feasible, with a stationary multi-hole probe that samples each of the points sequentially. Alternatively, a multi-hole probe designed and documented to sample equal volumes from each hole may be used to sample simultaneously at the required points.

(5) Notwithstanding paragraph (a)(4) of this section, the owner or operator may test at few points than are specified in Method 1 or Method 20 if the following conditions are met:

(i) You may perform a stratification test for NO<sub>x</sub> and diluent pursuant to

(A) [Reserved]

(B) The procedures specified in section 6.5.6.1(a) through (e) appendix A to part 75 of this chapter.

(ii) Once the stratification sampling is completed, the owner or operator may use the following alternative sample point selection criteria for the performance test:

(A) If each of the individual traverse point NO<sub>x</sub> concentrations, normalized to 15 percent O<sub>2</sub>, is within ±10 percent of the mean normalized concentration for all traverse points, then you may use 3 points (located either 16.7, 50.0, and 83.3 percent of the way across the stack or duct, or, for circular stacks or ducts greater than 2.4 meters (7.8 feet) in diameter, at 0.4, 1.2, and 2.0 meters from the wall). The 3 points shall be located along the measurement line that exhibited the highest average normalized NO<sub>x</sub> concentration during the stratification test; or

(B) If each of the individual traverse point NO<sub>x</sub> concentrations, normalized to 15 percent O<sub>2</sub>, is within ±5 percent of the mean normalized concentration for all traverse points, then you may sample at a single point, located at least 1 meter from the stack wall or at the stack centroid.

(6) Other acceptable alternative reference methods and procedures are given in paragraph (c) of this section.

(b) The owner or operator shall determine compliance with the applicable nitrogen oxides emission limitation in §60.332 and shall meet the performance test requirements of §60.8 as follows:

(1) For each run of the performance test, the mean nitrogen oxides emission concentration (NO<sub>xo</sub>) corrected to 15 percent O<sub>2</sub> shall be corrected to ISO standard conditions using the following equation. Notwithstanding this requirement, use of the ISO correction equation is optional for: Lean premix stationary combustion turbines; units used in association with heat recovery steam generators (HRSG) equipped with duct burners; and units equipped with add-on emission control devices:

$$NO_x = (NO_{xo})(P_r/P_o)^{0.5} e^{19 (Ho - 0.00633)(288^\circ K/T_a)^{1.53}}$$

Where:

$\text{NO}_x$  = emission concentration of  $\text{NO}_x$  at 15 percent  $\text{O}_2$  and ISO standard ambient conditions, ppm by volume, dry basis,

$\text{NO}_{x0}$  = mean observed  $\text{NO}_x$  concentration, ppm by volume, dry basis, at 15 percent  $\text{O}_2$ ,

$P_r$  = reference combustor inlet absolute pressure at 101.3 kilopascals ambient pressure, mm Hg,

$P_o$  = observed combustor inlet absolute pressure at test, mm Hg,

$H_o$  = observed humidity of ambient air, g  $\text{H}_2\text{O}$ /g air,

$e$  = transcendental constant, 2.718, and

$T_a$  = ambient temperature, °K.

(2) The 3-run performance test required by §60.8 must be performed within  $\pm 5$  percent at 30, 50, 75, and 90-to-100 percent of peak load or at four evenly-spaced load points in the normal operating range of the gas turbine, including the minimum point in the operating range and 90-to-100 percent of peak load, or at the highest achievable load point if 90-to-100 percent of peak load cannot be physically achieved in practice. If the turbine combusts both oil and gas as primary or backup fuels, separate performance testing is required for each fuel. Notwithstanding these requirements, performance testing is not required for any emergency fuel (as defined in §60.331).

(3) For a combined cycle turbine system with supplemental heat (duct burner), the owner or operator may elect to measure the turbine  $\text{NO}_x$  emissions after the duct burner rather than directly after the turbine. If the owner or operator elects to use this alternative sampling location, the applicable  $\text{NO}_x$  emission limit in §60.332 for the combustion turbine must still be met.

(4) If water or steam injection is used to control  $\text{NO}_x$  with no additional post-combustion  $\text{NO}_x$  control and the owner or operator chooses to monitor the steam or water to fuel ratio in accordance with §60.334(a), then that monitoring system must be operated concurrently with each EPA Method 20, ASTM D6522-00 (incorporated by reference, see §60.17), or EPA Method 7E run and shall be used to determine the fuel consumption and the steam or water to fuel ratio necessary to comply with the applicable §60.332  $\text{NO}_x$  emission limit.

(5) If the owner operator elects to claim an emission allowance for fuel bound nitrogen as described in §60.332, then concurrently with each reference method run, a representative sample of the fuel used shall be collected and analyzed, following the applicable procedures described in §60.335(b)(9). These data shall be used to determine the maximum fuel nitrogen content for which the established water (or steam) to fuel ratio will be valid.

(6) If the owner or operator elects to install a CEMS, the performance evaluation of the CEMS may either be conducted separately (as described in paragraph (b)(7) of this section) or as part of the initial performance test of the affected unit.

(7) If the owner or operator elects to install and certify a  $\text{NO}_x$  CEMS under §60.334(e), then the initial performance test required under §60.8 may be done in the following alternative manner:

(i) Perform a minimum of 9 reference method runs, with a minimum time per run of 21 minutes, at a single load level, between 90 and 100 percent of peak (or the highest physically achievable) load.

(ii) Use the test data both to demonstrate compliance with the applicable  $\text{NO}_x$  emission limit under §60.332 and to provide the required reference method data for the RATA of the CEMS described under §60.334(b).

(iii) The requirement to test at three additional load levels is waived.

(8) If the owner or operator elects under §60.334(f) to monitor combustion parameters or parameters indicative of proper operation of  $\text{NO}_x$  emission controls, the appropriate parameters shall be continuously monitored and recorded during each run of the initial performance test, to establish acceptable operating ranges, for purposes of the parameter monitoring plan for the affected unit, as specified in §60.334(g).

(9) To determine the fuel bound nitrogen content of fuel being fired (if an emission allowance is claimed for fuel bound nitrogen), the owner or operator may use equipment and procedures meeting the requirements of:

(i) For liquid fuels, ASTM D2597–94 (Reapproved 1999), D6366–99, D4629–02, D5762–02 (all of which are incorporated by reference, see §60.17); or

(ii) For gaseous fuels, shall use analytical methods and procedures that are accurate to within 5 percent of the instrument range and are approved by the Administrator.

(10) If the owner or operator is required under §60.334(i)(1) or (3) to periodically determine the sulfur content of the fuel combusted in the turbine, a minimum of three fuel samples shall be collected during the performance test. Analyze the samples for the total sulfur content of the fuel using:

(i) For liquid fuels, ASTM D129–00, D2622–98, D4294–02, D1266–98, D5453–00 or D1552–01 (all of which are incorporated by reference, see §60.17); or

(ii) For gaseous fuels, ASTM D1072–80, 90 (Reapproved 1994); D3246–81, 92, 96; D4468–85 (Reapproved 2000); or D6667–01 (all of which are incorporated by reference, see §60.17). The applicable ranges of some ASTM methods mentioned above are not adequate to measure the levels of sulfur in some fuel gases. Dilution of samples before analysis (with verification of the dilution ratio) may be used, subject to the prior approval of the Administrator.

(11) The fuel analyses required under paragraphs (b)(9) and (b)(10) of this section may be performed by the owner or operator, a service contractor retained by the owner or operator, the fuel vendor, or any other qualified agency.

(c) The owner or operator may use the following as alternatives to the reference methods and procedures specified in this section:

(1) Instead of using the equation in paragraph (b)(1) of this section, manufacturers may develop ambient condition correction factors to adjust the nitrogen oxides emission level measured by the performance test as provided in §60.8 to ISO standard day conditions.

[69 FR 41363, July 8, 2004, as amended at 71 FR 9458, Feb. 24, 2006]

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## **APPENDIX C**

40 CFR Part 61, Subpart FF

*National Emission Standards for Hazardous Air Pollutants, Benzene Waste Operations*





## e-CFR Data is current as of October 28, 2008

### Title 40: Protection of Environment

#### PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

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### Subpart FF—National Emission Standard for Benzene Waste Operations

**Source:** 55 FR 8346, Mar. 7, 1990, unless otherwise noted.

#### § 61.340 Applicability.

(a) The provisions of this subpart apply to owners and operators of chemical manufacturing plants, coke by-product recovery plants, and petroleum refineries.

(b) The provisions of this subpart apply to owners and operators of hazardous waste treatment, storage, and disposal facilities that treat, store, or dispose of hazardous waste generated by any facility listed in paragraph (a) of this section. The waste streams at hazardous waste treatment, storage, and disposal facilities subject to the provisions of this subpart are the benzene-containing hazardous waste from any facility listed in paragraph (a) of this section. A hazardous waste treatment, storage, and disposal facility is a facility that must obtain a hazardous waste management permit under subtitle C of the Solid Waste Disposal Act.

(c) At each facility identified in paragraph (a) or (b) of this section, the following waste is exempt from the requirements of this subpart:

(1) Waste in the form of gases or vapors that is emitted from process fluids:

(2) Waste that is contained in a segregated stormwater sewer system.

(d) At each facility identified in paragraph (a) or (b) of this section, any gaseous stream from a waste management unit, treatment process, or wastewater treatment system routed to a fuel gas system, as defined in §61.341, is exempt from this subpart. No testing, monitoring, recordkeeping, or reporting is required under this subpart for any gaseous stream from a waste management unit, treatment process, or wastewater treatment unit routed to a fuel gas system.

[55 FR 8346, Mar. 7, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3095, Jan. 7, 1993; 67 FR 68531, Nov. 12, 2002]

#### § 61.341 Definitions.

*Benzene concentration* means the fraction by weight of benzene in a waste as determined in accordance with the procedures specified in §61.355 of this subpart.

*Car-seal* means a seal that is placed on a device that is used to change the position of a valve (e.g., from opened to closed) in such a way that the position of the valve cannot be changed without breaking the seal.

*Chemical manufacturing plant* means any facility engaged in the production of chemicals by chemical, thermal, physical, or biological processes for use as a product, co-product, by-product, or intermediate including but not limited to industrial organic chemicals, organic pesticide products, pharmaceutical preparations, paint and allied products, fertilizers, and agricultural chemicals. Examples of chemical manufacturing plants include facilities at which process units are operated to produce one or more of the following chemicals: benzenesulfonic acid, benzene, chlorobenzene, cumene, cyclohexane, ethylene, ethylbenzene, hydroquinone, linear alkylbenzene, nitrobenzene, resorcinol, sulfolane, or styrene.

*Closed-vent system* means a system that is not open to the atmosphere and is composed of piping, ductwork, connections, and, if necessary, flow inducing devices that transport gas or vapor from an emission source to a control device.

*Coke by-product recovery plant* means any facility designed and operated for the separation and recovery of coal tar derivatives (by-products) evolved from coal during the coking process of a coke oven battery.

*Container* means any portable waste management unit in which a material is stored, transported, treated, or otherwise handled. Examples of containers are drums, barrels, tank trucks, barges, dumpsters, tank cars, dump trucks, and ships.

*Control device* means an enclosed combustion device, vapor recovery system, or flare.

*Cover* means a device or system which is placed on or over a waste placed in a waste management unit so that the entire waste surface area is enclosed and sealed to minimize air emissions. A cover may have openings necessary for operation, inspection, and maintenance of the waste management unit such as access hatches, sampling ports, and gauge wells provided that each opening is closed and sealed when not in use. Example of covers include a fixed roof installed on a tank, a lid installed on a container, and an air-supported enclosure installed over a waste management unit.

*External floating roof* means a pontoon-type or double-deck type cover with certain rim sealing mechanisms that rests on the liquid surface in a waste management unit with no fixed roof.

*Facility* means all process units and product tanks that generate waste within a stationary source, and all waste management units that are used for waste treatment, storage, or disposal within a stationary source.

*Fixed roof* means a cover that is mounted on a waste management unit in a stationary manner and that does not move with fluctuations in liquid level.

*Floating roof* means a cover with certain rim sealing mechanisms consisting of a double deck, pontoon single deck, internal floating cover or covered floating roof, which rests upon and is supported by the liquid being contained, and is equipped with a closure seal or seals to close the space between the roof edge and unit wall.

*Flow indicator* means a device which indicates whether gas flow is present in a line or vent system.

*Fuel gas system* means the offsite and onsite piping and control system that gathers gaseous streams generated by facility operations, may blend them with sources of gas, if available, and transports the blended gaseous fuel at suitable pressures for use as fuel in heaters, furnaces, boilers, incinerators, gas turbines, and other combustion devices located within or outside the facility. The fuel is piped directly to each individual combustion device, and the system typically operates at pressures over atmospheric.

*Individual drain system* means the system used to convey waste from a process unit, product storage tank, or waste management unit to a waste management unit. The term includes all process drains and common junction boxes, together with their associated sewer lines and other junction boxes, down to the receiving waste management unit.

*Internal floating roof* means a cover that rests or floats on the liquid surface inside a waste management unit that has a fixed roof.

*Liquid-mounted seal* means a foam or liquid-filled primary seal mounted in contact with the liquid between the waste management unit wall and the floating roof continuously around the circumference.

*Loading* means the introduction of waste into a waste management unit but not necessarily to complete capacity (also referred to as filling).

*Maximum organic vapor pressure* means the equilibrium partial pressure exerted by the waste at the temperature equal to the highest calendar-month average of the waste storage temperature for waste stored above or below the ambient temperature or at the local maximum monthly average temperature as reported by the National Weather Service for waste stored at the ambient temperature, as determined:

- (1) In accordance with §60.17(c); or
- (2) As obtained from standard reference texts; or
- (3) In accordance with §60.17(a)(37); or
- (4) Any other method approved by the Administrator.

*No detectable emissions* means less than 500 parts per million by volume (ppmv) above background levels, as measured by a detection instrument reading in accordance with the procedures specified in §61.355(h) of this subpart.

*Oil-water separator* means a waste management unit, generally a tank or surface impoundment, used to separate oil from water. An oil-water separator consists of not only the separation unit but also the forebay and other separator basins, skimmers, weirs, grit chambers, sludge hoppers, and bar screens that are located directly after the individual drain system and prior to additional treatment units such as an air flotation unit, clarifier, or biological treatment unit. Examples of an oil-water separator include an API separator, parallel-plate interceptor, and corrugated-plate interceptor with the associated ancillary equipment.

*Petroleum refinery* means any facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through the distillation of petroleum, or through the redistillation, cracking, or reforming of unfinished petroleum derivatives.

*Petroleum* means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

*Point of waste generation* means the location where the waste stream exits the process unit component or storage tank prior to handling or treatment in an operation that is not an integral part of the production process, or in the case of waste management units that generate new wastes after treatment, the location where the waste stream exits the waste management unit component.

*Process unit* means equipment assembled and connected by pipes or ducts to produce intermediate or final products. A process unit can be operated independently if supplied with sufficient fuel or raw materials and sufficient product storage facilities.

*Process unit turnaround* means the shutting down of the operations of a process unit, the purging of the contents of the process unit, the maintenance or repair work, followed by restarting of the process.

*Process unit turnaround waste* means a waste that is generated as a result of a process unit turnaround.

*Process wastewater* means water which comes in contact with benzene during manufacturing or processing operations conducted within a process unit. Process wastewater is not organic wastes, process fluids, product tank drawdown, cooling tower blowdown, steam trap condensate, or landfill leachate.

*Process wastewater stream* means a waste stream that contains only process wastewater.

*Product tank* means a stationary unit that is designed to contain an accumulation of materials that are fed to or produced by a process unit, and is constructed primarily of non-earthen materials (e.g., wood, concrete, steel, plastic) which provide structural support.

*Product tank drawdown* means any material or mixture of materials discharged from a product tank for the purpose of removing water or other contaminants from the product tank.

*Safety device* means a closure device such as a pressure relief valve, frangible disc, fusible plug, or any other type of device which functions exclusively to prevent physical damage or permanent deformation to a unit or its air emission control equipment by venting gases or vapors directly to the atmosphere during unsafe conditions resulting from an unplanned, accidental, or emergency event. For the purpose of this subpart, a safety device is not used for routine venting of gases or vapors from the vapor headspace underneath a cover such as during filling of the unit or to adjust the pressure in this vapor headspace in response to normal daily diurnal ambient temperature fluctuations. A safety device is designed to remain in a closed position during normal operations and open only when the internal pressure, or another relevant parameter, exceeds the device threshold setting applicable to the air emission control equipment as determined by the owner or operator based on manufacturer recommendations, applicable regulations, fire protection and prevention codes, standard engineering codes and practices, or other requirements for the safe handling of flammable, ignitable, explosive, reactive, or hazardous materials.

*Segregated stormwater sewer system* means a drain and collection system designed and operated for the sole purpose of collecting rainfall runoff at a facility, and which is segregated from all other individual drain systems.

*Sewer line* means a lateral, trunk line, branch line, or other enclosed conduit used to convey waste to a downstream waste management unit.

*Slop oil* means the floating oil and solids that accumulate on the surface of an oil-water separator.

*Sour water stream* means a stream that:

- (1) Contains ammonia or sulfur compounds (usually hydrogen sulfide) at concentrations of 10 ppm by weight or more;
- (2) Is generated from separation of water from a feed stock, intermediate, or product that contained ammonia or sulfur compounds; and
- (3) Requires treatment to remove the ammonia or sulfur compounds.

*Sour water stripper* means a unit that:

- (1) Is designed and operated to remove ammonia or sulfur compounds (usually hydrogen sulfide) from sour water streams;
- (2) Has the sour water streams transferred to the stripper through hard piping or other enclosed system; and
- (3) Is operated in such a manner that the offgases are sent to a sulfur recovery unit, processing unit, incinerator, flare, or other combustion device.

*Surface impoundment* means a waste management unit which is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although it may be lined with man-made materials), which is designed to hold an accumulation of liquid wastes or waste containing free liquids, and which is not an injection well. Examples of surface impoundments are holding, storage, settling, and aeration pits, ponds, and lagoons.

*Tank* means a stationary waste management unit that is designed to contain an accumulation of waste and is constructed primarily of nonearthen materials (e.g., wood, concrete, steel, plastic) which provide structural support.

*Treatment process* means a stream stripping unit, thin-film evaporation unit, waste incinerator, or any other process used to comply with §61.348 of this subpart.

*Vapor-mounted seal* means a foam-filled primary seal mounted continuously around the perimeter of a waste management unit so there is an annular vapor space underneath the seal. The annular vapor space is bounded by the bottom of the primary seal, the unit wall, the liquid surface, and the floating roof.

*Waste* means any material resulting from industrial, commercial, mining or agricultural operations, or from community activities that is discarded or is being accumulated, stored, or physically, chemically, thermally, or biologically treated prior to being discarded, recycled, or discharged.

*Waste management unit* means a piece of equipment, structure, or transport mechanism used in handling, storage, treatment, or disposal of waste. Examples of a waste management unit include a tank, surface impoundment, container, oil-water separator, individual drain system, steam stripping unit, thin-film evaporation unit, waste incinerator, and landfill.

*Waste stream* means the waste generated by a particular process unit, product tank, or waste management unit. The characteristics of the waste stream (e.g., flow rate, benzene concentration, water content) are determined at the point of waste generation. Examples of a waste stream include process wastewater, product tank drawdown, sludge and slop oil removed from waste management units, and landfill leachate.

*Wastewater treatment system* means any component, piece of equipment, or installation that receives, manages, or treats process wastewater, product tank drawdown, or landfill leachate prior to direct or indirect discharge in accordance with the National Pollutant Discharge Elimination System permit regulations under 40 CFR part 122. These systems typically include individual drain systems, oil-water separators, air flotation units, equalization tanks, and biological treatment units.

*Water seal controls* means a seal pot, p-leg trap, or other type of trap filled with water (e.g., flooded sewers that maintain water levels adequate to prevent air flow through the system) that creates a water barrier between the sewer line and the atmosphere. The water level of the seal must be maintained in the vertical leg of a drain in order to be considered a water seal.

[55 FR 8346, Mar. 7, 1990; 55 FR 12444, Apr. 3, 1990, as amended at 58 FR 3095, Jan. 7, 1993; 67 FR 68531, Nov. 12, 2002]

## **§ 61.342 Standards: General.**

(a) An owner or operator of a facility at which the total annual benzene quantity from facility waste is less than 10 megagrams per year (Mg/yr) (11 ton/yr) shall be exempt from the requirements of paragraphs (b) and (c) of this section. The total annual benzene quantity from facility waste is the sum of the annual benzene quantity for each waste stream at the facility that has a flow-weighted annual average water content greater than 10 percent or that is mixed with water, or other wastes, at any time and the mixture has an annual average water content greater than 10 percent. The benzene quantity in a waste stream is to be counted only once without multiple counting if other waste streams are mixed with or generated from the original waste stream. Other specific requirements for calculating the total annual benzene waste quantity are as follows:

(1) Wastes that are exempted from control under §§61.342(c)(2) and 61.342(c)(3) are included in the calculation of the total annual benzene quantity if they have an annual average water content greater than 10 percent, or if they are mixed with water or other wastes at any time and the mixture has an annual average water content greater than 10 percent.

(2) The benzene in a material subject to this subpart that is sold is included in the calculation of the total annual benzene quantity if the material has an annual average water content greater than 10 percent.

(3) Benzene in wastes generated by remediation activities conducted at the facility, such as the excavation of contaminated soil, pumping and treatment of groundwater, and the recovery of product from soil or groundwater, are not included in the calculation of total annual benzene quantity for that facility. If the facility's total annual benzene quantity is 10 Mg/yr (11 ton/yr) or more, wastes generated by remediation activities are subject to the requirements of paragraphs (c) through (h) of this section. If the facility is managing remediation waste generated offsite, the benzene in this waste shall be included in the calculation of total annual benzene quantity in facility waste, if the waste streams have an annual average water content greater than 10 percent, or if they are mixed with water or other wastes at any time and the mixture has an annual average water content greater than 10 percent.

(4) The total annual benzene quantity is determined based upon the quantity of benzene in the waste before any waste treatment occurs to remove the benzene except as specified in §61.355(c)(1)(i) (A) through (C).

(b) Each owner or operator of a facility at which the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr) as determined in paragraph (a) of this section shall be in compliance with the requirements of paragraphs (c) through (h) of this section no later than 90 days following the effective date, unless a waiver of compliance has been obtained under §61.11, or by the initial startup for a new source with an initial startup after the effective date.

(1) The owner or operator of an existing source unable to comply with the rule within the required time may request a waiver of compliance under §61.10.

(2) As part of the waiver application, the owner or operator shall submit to the Administrator a plan under §61.10(b)(3) that is an enforceable commitment to obtain environmental benefits to mitigate the benzene emissions that result from extending the compliance date. The plan shall include the following information:

(i) A description of the method of compliance, including the control approach, schedule for installing controls, and quantity of the benzene emissions that result from extending the compliance date;

(ii) If the control approach involves a compliance strategy designed to obtain integrated compliance with multiple regulatory requirements, a description of the other regulations involved and their effective dates; and

(iii) A description of the actions to be taken at the facility to obtain mitigating environmental benefits, including how the benefits will be obtained, the schedule for these actions, and an estimate of the quantifiable benefits that directly result from these actions.

(c) Each owner or operator of a facility at which the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr) as determined in paragraph (a) of this section shall manage and treat the facility waste as follows:

(1) For each waste stream that contains benzene, including (but not limited to) organic waste streams that contain less than 10 percent water and aqueous waste streams, even if the wastes are not discharged to an individual drain system, the owner or operator shall:

(i) Remove or destroy the benzene contained in the waste using a treatment process or wastewater treatment system that complies with the standards specified in §61.348 of this subpart.

(ii) Comply with the standards specified in §§61.343 through 61.347 of this subpart for each waste management unit that receives or manages the waste stream prior to and during treatment of the waste stream in accordance with paragraph (c)(1)(i) of this section.

(iii) Each waste management unit used to manage or treat waste streams that will be recycled to a process shall comply with the standards specified in §§61.343 through 61.347. Once the waste stream is recycled to a process, including to a tank used for the storage of production process feed, product, or product intermediates, unless this tank is used primarily for the storage of wastes, the material is no longer subject to paragraph (c) of this section.

(2) A waste stream is exempt from paragraph (c)(1) of this section provided that the owner or operator demonstrates initially and, thereafter, at least once per year that the flow-weighted annual average benzene concentration for the waste stream is less than 10 ppmw as determined by the procedures specified in §61.355(c)(2) or §61.355(c)(3).

(3) A waste stream is exempt from paragraph (c)(1) of this section provided that the owner or operator demonstrates initially and, thereafter, at least once per year that the conditions specified in either paragraph (c)(3)(i) or (c)(3)(ii) of this section are met.

(i) The waste stream is process wastewater that has a flow rate less than 0.02 liters per minute (0.005 gallons per minute) or an annual wastewater quantity of less than 10 Mg/yr (11 ton/yr); or

(ii) All of the following conditions are met:

(A) The owner or operator does not choose to exempt process wastewater under paragraph (c)(3)(i) of this section,

(B) The total annual benzene quantity in all waste streams chosen for exemption in paragraph (c)(3)(ii) of this section does not exceed 2.0 Mg/yr (2.2 ton/yr) as determined in the procedures in §61.355(j), and

(C) The total annual benzene quantity in a waste stream chosen for exemption, including process unit turnaround waste, is determined for the year in which the waste is generated.

(d) As an alternative to the requirements specified in paragraphs (c) and (e) of this section, an owner or operator of a facility at which the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr) as determined in paragraph (a) of this section may elect to manage and treat the facility waste as follows:

(1) The owner or operator shall manage and treat facility waste other than process wastewater in accordance with the requirements of paragraph (c)(1) of this section.

(2) The owner or operator shall manage and treat process wastewater in accordance with the following requirements:

(i) Process wastewater shall be treated to achieve a total annual benzene quantity from facility process wastewater less than 1 Mg/yr (1.1 ton/yr). Total annual benzene from facility process wastewater shall be determined by adding together the annual benzene quantity at the point of waste generation for each untreated process wastewater stream plus the annual benzene quantity exiting the treatment process for each process wastewater stream treated in accordance with the requirements of paragraph (c)(1)(i) of this section.

(ii) Each treated process wastewater stream identified in paragraph (d)(2)(i) of this section shall be managed and treated in accordance with paragraph (c)(1) of this section.

(iii) Each untreated process wastewater stream identified in paragraph (d)(2)(i) of this section is exempt from the requirements of paragraph (c)(1) of this section.

(e) As an alternative to the requirements specified in paragraphs (c) and (d) of this section, an owner or operator of a facility at which the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr) as determined in paragraph (a) of this section may elect to manage and treat the facility waste as follows:

(1) The owner or operator shall manage and treat facility waste with a flow-weighted annual average water content of less than 10 percent in accordance with the requirements of paragraph (c)(1) of this section; and

(2) The owner or operator shall manage and treat facility waste (including remediation and process unit turnaround waste) with a flow-weighted annual average water content of 10 percent or greater, on a volume basis as total water, and each

waste stream that is mixed with water or wastes at any time such that the resulting mixture has an annual water content greater than 10 percent, in accordance with the following:

(i) The benzene quantity for the wastes described in paragraph (e)(2) of this section must be equal to or less than 6.0 Mg/yr (6.6 ton/yr), as determined in §61.355(k). Wastes as described in paragraph (e)(2) of this section that are transferred offsite shall be included in the determination of benzene quantity as provided in §61.355(k). The provisions of paragraph (f) of this section shall not apply to any owner or operator who elects to comply with the provisions of paragraph (e) of this section.

(ii) The determination of benzene quantity for each waste stream defined in paragraph (e)(2) of this section shall be made in accordance with §61.355(k).

(f) Rather than treating the waste onsite, an owner or operator may elect to comply with paragraph (c)(1)(i) of this section by transferring the waste offsite to another facility where the waste is treated in accordance with the requirements of paragraph (c)(1)(i) of this section. The owner or operator transferring the waste shall:

(1) Comply with the standards specified in §§61.343 through 61.347 of this subpart for each waste management unit that receives or manages the waste prior to shipment of the waste offsite.

(2) Include with each offsite waste shipment a notice stating that the waste contains benzene which is required to be managed and treated in accordance with the provisions of this subpart.

(g) Compliance with this subpart will be determined by review of facility records and results from tests and inspections using methods and procedures specified in §61.355 of this subpart.

(h) Permission to use an alternative means of compliance to meet the requirements of §§61.342 through 61.352 of this subpart may be granted by the Administrator as provided in §61.353 of this subpart.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3095, Jan. 7, 1993; 65 FR 62159, 62160, Oct. 17, 2000]

#### **§ 61.343 Standards: Tanks.**

(a) Except as provided in paragraph (b) of this section and in §61.351, the owner or operator must meet the standards in paragraph (a)(1) or (2) of this section for each tank in which the waste stream is placed in accordance with §61.342 (c)(1)(ii). The standards in this section apply to the treatment and storage of the waste stream in a tank, including dewatering.

(1) The owner or operator shall install, operate, and maintain a fixed-roof and closed-vent system that routes all organic vapors vented from the tank to a control device.

(i) The fixed-roof shall meet the following requirements:

(A) The cover and all openings (e.g., access hatches, sampling ports, and gauge wells) shall be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.

(B) Each opening shall be maintained in a closed, sealed position (e.g., covered by a lid that is gasketed and latched) at all times that waste is in the tank except when it is necessary to use the opening for waste sampling or removal, or for equipment inspection, maintenance, or repair.

(C) If the cover and closed-vent system operate such that the tank is maintained at a pressure less than atmospheric pressure, then paragraph (a)(1)(i)(B) of this section does not apply to any opening that meets all of the following conditions:

( 1 ) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

( 2 ) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h); and

( 3 ) The pressure is monitored continuously to ensure that the pressure in the tank remains below atmospheric pressure.

(ii) The closed-vent system and control device shall be designed and operated in accordance with the requirements of §61.349 of this subpart.

(2) The owner or operator must install, operate, and maintain an enclosure and closed-vent system that routes all organic vapors vented from the tank, located inside the enclosure, to a control device in accordance with the requirements specified in paragraph (e) of this section.

(b) For a tank that meets all the conditions specified in paragraph (b)(1) of this section, the owner or operator may elect to comply with paragraph (b)(2) of this section as an alternative to the requirements specified in paragraph (a)(1) of this section.

(1) The waste managed in the tank complying with paragraph (b)(2) of this section shall meet all of the following conditions:

(i) Each waste stream managed in the tank must have a flow-weighted annual average water content less than or equal to 10 percent water, on a volume basis as total water.

(ii) The waste managed in the tank either:

(A) Has a maximum organic vapor pressure less than 5.2 kilopascals (kPa) (0.75 pounds per square inch (psi));

(B) Has a maximum organic vapor pressure less than 27.6 kPa (4.0 psi) and is managed in a tank having design capacity less than 151 m<sup>3</sup> (40,000 gal); or

(C) Has a maximum organic vapor pressure less than 76.6 kPa (11.1 psi) and is managed in a tank having a design capacity less than 75 m<sup>3</sup> (20,000 gal).

(2) The owner or operator shall install, operate, and maintain a fixed roof as specified in paragraph (a)(1)(i).

(3) For each tank complying with paragraph (b) of this section, one or more devices which vent directly to the atmosphere may be used on the tank provided each device remains in a closed, sealed position during normal operations except when the device needs to open to prevent physical damage or permanent deformation of the tank or cover resulting from filling or emptying the tank, diurnal temperature changes, atmospheric pressure changes or malfunction of the unit in accordance with good engineering and safety practices for handling flammable, explosive, or other hazardous materials.

(c) Each fixed-roof, seal, access door, and all other openings shall be checked by visual inspection initially and quarterly thereafter to ensure that no cracks or gaps occur and that access doors and other openings are closed and gasketed properly.

(d) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, or when detectable emissions are measured, first efforts at repair shall be made as soon as practicable, but not later than 45 calendar days after identification.

(e) Each owner or operator who controls air pollutant emissions by using an enclosure vented through a closed-vent system to a control device must meet the requirements specified in paragraphs (e)(1) through (4) of this section.

(1) The tank must be located inside a total enclosure. The enclosure must be designed and operated in accordance with the criteria for a permanent total enclosure as specified in "Procedure T—Criteria for and Verification of a Permanent or Temporary Total Enclosure" in 40 CFR 52.741, appendix B. The enclosure may have permanent or temporary openings to allow worker access; passage of material into or out of the enclosure by conveyor, vehicles, or other mechanical means; entry of permanent mechanical or electrical equipment; or direct airflow into the enclosure. The owner or operator must perform the verification procedure for the enclosure as specified in section 5.0 of Procedure T initially when the enclosure is first installed and, thereafter, annually. A facility that has conducted an initial compliance demonstration and that performs annual compliance demonstrations in accordance with the requirements for Tank Level 2 control requirements 40 CFR 264.1084(i) or 40 CFR 265(i) is not required to make repeat demonstrations of initial and continuous compliance for the purposes of this subpart.

(2) The enclosure must be vented through a closed-vent system to a control device that is designed and operated in accordance with the standards for control devices specified in §61.349.



(3) Safety devices, as defined in this subpart, may be installed and operated as necessary on any enclosure, closed-vent system, or control device used to comply with the requirements of paragraphs (e)(1) and (2) of this section.

(4) The closed-vent system must be designed and operated in accordance with the requirements of §61.349.

[55 FR 8346, Mar. 7, 1990, as amended at 55 FR 18331, May 2, 1990; 58 FR 3096, Jan. 7, 1993; 67 FR 68532, Nov. 12, 2002; 68 FR 6082, Feb. 6, 2003; 68 FR 67935, Dec. 4, 2003]

#### **§ 61.344 Standards: Surface impoundments.**

(a) The owner or operator shall meet the following standards for each surface impoundment in which waste is placed in accordance with §61.342(c)(1)(ii) of this subpart:

(1) The owner or operator shall install, operate, and maintain on each surface impoundment a cover (e.g., air-supported structure or rigid cover) and closed-vent system that routes all organic vapors vented from the surface impoundment to a control device.

(i) The cover shall meet the following requirements:

(A) The cover and all openings (e.g., access hatches, sampling ports, and gauge wells) shall be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.

(B) Each opening shall be maintained in a closed, sealed position (e.g., covered by a lid that is gasketed and latched) at all times that waste is in the surface impoundment except when it is necessary to use the opening for waste sampling or removal, or for equipment inspection, maintenance, or repair.

(C) If the cover and closed-vent system operate such that the enclosure of the surface impoundment is maintained at a pressure less than atmospheric pressure, then paragraph (a)(1)(i)(B) of this section does not apply to any opening that meets all of the following conditions:

( 1 ) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

( 2 ) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart; and

( 3 ) The pressure is monitored continuously to ensure that the pressure in the enclosure of the surface impoundment remains below atmospheric pressure.

(D) The cover shall be used at all times that waste is placed in the surface impoundment except during removal of treatment residuals in accordance with 40 CFR 268.4 or closure of the surface impoundment in accordance with 40 CFR 264.228. (Note: the treatment residuals generated by these activities may be subject to the requirements of this part.)

(ii) The closed-vent system and control device shall be designed and operated in accordance with §61.349 of this subpart.

(b) Each cover seal, access hatch, and all other openings shall be checked by visual inspection initially and quarterly thereafter to ensure that no cracks or gaps occur and that access hatches and other openings are closed and gasketed properly.

(c) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, or when detectable emissions are measured, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3097, Jan. 7, 1993]

#### **§ 61.345 Standards: Containers.**

(a) The owner or operator shall meet the following standards for each container in which waste is placed in accordance with §61.342(c)(1)(ii) of this subpart:

(1) The owner or operator shall install, operate, and maintain a cover on each container used to handle, transfer, or store waste in accordance with the following requirements:

(i) The cover and all openings (e.g., bungs, hatches, and sampling ports) shall be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.

(ii) Except as provided in paragraph (a)(4) of this section, each opening shall be maintained in a closed, sealed position (e.g., covered by a lid that is gasketed and latched) at all times that waste is in the container except when it is necessary to use the opening for waste loading, removal, inspection, or sampling.

(2) When a waste is transferred into a container by pumping, the owner or operator shall perform the transfer using a submerged fill pipe. The submerged fill pipe outlet shall extend to within two fill pipe diameters of the bottom of the container while the container is being loaded. During loading of the waste, the cover shall remain in place and all openings shall be maintained in a closed, sealed position except for those openings required for the submerged fill pipe, those openings required for venting of the container to prevent physical damage or permanent deformation of the container or cover, and any openings complying with paragraph (a)(4) of this section.

(3) Treatment of a waste in a container, including aeration, thermal or other treatment, must be performed by the owner or operator in a manner such that while the waste is being treated the container meets the standards specified in paragraphs (a)(3)(i) through (iii) of this section, except for covers and closed-vent systems that meet the requirements in paragraph (a)(4) of this section.

(i) The owner or operator must either:

(A) Vent the container inside a total enclosure which is exhausted through a closed-vent system to a control device in accordance with the requirements of paragraphs (a)(3)(ii)(A) and (B) of this section; or

(B) Vent the covered or closed container directly through a closed-vent system to a control device in accordance with the requirements of paragraphs (a)(3)(ii)(B) and (C) of this section.

(ii) The owner or operator must meet the following requirements, as applicable to the type of air emission control equipment selected by the owner or operator:

(A) The total enclosure must be designed and operated in accordance with the criteria for a permanent total enclosure as specified in section 5 of the "Procedure T—Criteria for and Verification of a Permanent or Temporary Total Enclosure" in 40 CFR 52.741, appendix B. The enclosure may have permanent or temporary openings to allow worker access; passage of containers through the enclosure by conveyor or other mechanical means; entry of permanent mechanical or electrical equipment; or direct airflow into the enclosure. The owner or operator must perform the verification procedure for the enclosure as specified in section 5.0 of "Procedure T—Criteria for and Verification of a Permanent or Temporary Total Enclosure" initially when the enclosure is first installed and, thereafter, annually. A facility that has conducted an initial compliance demonstration and that performs annual compliance demonstrations in accordance with the Container Level 3 control requirements in 40 CFR 264.1086(e)(2)(i) or 40 CFR 265.1086(e)(2)(i) is not required to make repeat demonstrations of initial and continuous compliance for the purposes of this subpart.

(B) The closed-vent system and control device must be designed and operated in accordance with the requirements of §61.349.

(C) For a container cover, the cover and all openings (e.g., doors, hatches) must be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, initially and thereafter at least once per year by the methods specified in §61.355(h).

(iii) Safety devices, as defined in this subpart, may be installed and operated as necessary on any container, enclosure, closed-vent system, or control device used to comply with the requirements of paragraph (a)(3)(i) of this section.

(4) If the cover and closed-vent system operate such that the container is maintained at a pressure less than atmospheric pressure, the owner or operator may operate the system with an opening that is not sealed and kept closed at all times if the following conditions are met:

(i) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

(ii) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by methods specified in §61.355(h); and

(iii) The pressure is monitored continuously to ensure that the pressure in the container remains below atmospheric pressure.

(b) Each cover and all openings shall be visually inspected initially and quarterly thereafter to ensure that they are closed and gasketed properly.

(c) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3097, Jan. 7, 1993; 67 FR 68532, Nov. 12, 2002; 68 FR 67936, Dec. 4, 2003]

#### **§ 61.346 Standards: Individual drain systems.**

(a) Except as provided in paragraph (b) of this section, the owner or operator shall meet the following standards for each individual drain system in which waste is placed in accordance with §61.342(c)(1)(ii) of this subpart:

(1) The owner or operator shall install, operate, and maintain on each drain system opening a cover and closed-vent system that routes all organic vapors vented from the drain system to a control device.

(i) The cover shall meet the following requirements:

(A) The cover and all openings (e.g., access hatches, sampling ports) shall be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.

(B) Each opening shall be maintained in a closed, sealed position (e.g., covered by a lid that is gasketed and latched) at all times that waste is in the drain system except when it is necessary to use the opening for waste sampling or removal, or for equipment inspection, maintenance, or repair.

(C) If the cover and closed-vent system operate such that the individual drain system is maintained at a pressure less than atmospheric pressure, then paragraph (a)(1)(i)(B) of this section does not apply to any opening that meets all of the following conditions:

( 1 ) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

( 2 ) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h); and

( 3 ) The pressure is monitored continuously to ensure that the pressure in the individual drain system remains below atmospheric pressure.

(ii) The closed-vent system and control device shall be designed and operated in accordance with §61.349 of this subpart.

(2) Each cover seal, access hatch, and all other openings shall be checked by visual inspection initially and quarterly thereafter to ensure that no cracks or gaps occur and that access hatches and other openings are closed and gasketed properly.

(3) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, or when detectable emissions are measured, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

(b) As an alternative to complying with paragraph (a) of this section, an owner or operator may elect to comply with the following requirements:

- (1) Each drain shall be equipped with water seal controls or a tightly sealed cap or plug.
- (2) Each junction box shall be equipped with a cover and may have a vent pipe. The vent pipe shall be at least 90 cm (3 ft) in length and shall not exceed 10.2 cm (4 in) in diameter.
- (i) Junction box covers shall have a tight seal around the edge and shall be kept in place at all times, except during inspection and maintenance.
- (ii) One of the following methods shall be used to control emissions from the junction box vent pipe to the atmosphere:
- (A) Equip the junction box with a system to prevent the flow of organic vapors from the junction box vent pipe to the atmosphere during normal operation. An example of such a system includes use of water seal controls on the junction box. A flow indicator shall be installed, operated, and maintained on each junction box vent pipe to ensure that organic vapors are not vented from the junction box to the atmosphere during normal operation.
- (B) Connect the junction box vent pipe to a closed-vent system and control device in accordance with §61.349 of this subpart.
- (3) Each sewer line shall not be open to the atmosphere and shall be covered or enclosed in a manner so as to have no visual gaps or cracks in joints, seals, or other emission interfaces.
- (4) Equipment installed in accordance with paragraphs (b)(1), (b)(2), or (b)(3) of this section shall be inspected as follows:
- (i) Each drain using water seal controls shall be checked by visual or physical inspection initially and thereafter quarterly for indications of low water levels or other conditions that would reduce the effectiveness of water seal controls.
- (ii) Each drain using a tightly sealed cap or plug shall be visually inspected initially and thereafter quarterly to ensure caps or plugs are in place and properly installed.
- (iii) Each junction box shall be visually inspected initially and thereafter quarterly to ensure that the cover is in place and to ensure that the cover has a tight seal around the edge.
- (iv) The unburied portion of each sewer line shall be visually inspected initially and thereafter quarterly for indication of cracks, gaps, or other problems that could result in benzene emissions.
- (5) Except as provided in §61.350 of this subpart, when a broken seal, gap, crack or other problem is identified, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

[55 FR 8346, Mar. 7, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3097, Jan. 7, 1993]

#### **§ 61.347 Standards: Oil-water separators.**

- (a) Except as provided in §61.352 of this subpart, the owner or operator shall meet the following standards for each oil-water separator in which waste is placed in accordance with §61.342(c)(1)(ii) of this subpart:
- (1) The owner or operator shall install, operate, and maintain a fixed-roof and closed-vent system that routes all organic vapors vented from the oil-water separator to a control device.
- (i) The fixed-roof shall meet the following requirements:
- (A) The cover and all openings (e.g., access hatches, sampling ports, and gauge wells) shall be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.
- (B) Each opening shall be maintained in a closed, sealed position (e.g., covered by a lid that is gasketed and latched) at all times that waste is in the oil-water separator except when it is necessary to use the opening for waste sampling or removal, or for equipment inspection, maintenance, or repair.

(C) If the cover and closed-vent system operate such that the oil-water separator is maintained at a pressure less than atmospheric pressure, then paragraph (a)(1)(i)(B) of this section does not apply to any opening that meets all of the following conditions:

( 1 ) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

( 2 ) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h); and

( 3 ) The pressure is monitored continuously to ensure that the pressure in the oil-water separator remains below atmospheric pressure.

(ii) The closed-vent system and control device shall be designed and operated in accordance with the requirements of §61.349 of this subpart.

(b) Each cover seal, access hatch, and all other openings shall be checked by visual inspection initially and quarterly thereafter to ensure that no cracks or gaps occur between the cover and oil-water separator wall and that access hatches and other openings are closed and gasketed properly.

(c) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, or when detectable emissions are measured, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3098, Jan. 7, 1993]

#### **§ 61.348 Standards: Treatment processes.**

(a) Except as provided in paragraph (a)(5) of this section, the owner or operator shall treat the waste stream in accordance with the following requirements:

(1) The owner or operator shall design, install, operate, and maintain a treatment process that either:

(i) Removes benzene from the waste stream to a level less than 10 parts per million by weight (ppmw) on a flow-weighted annual average basis,

(ii) Removes benzene from the waste stream by 99 percent or more on a mass basis, or

(iii) Destroys benzene in the waste stream by incinerating the waste in a combustion unit that achieves a destruction efficiency of 99 percent or greater for benzene.

(2) Each treatment process complying with paragraphs (a)(1)(i) or (a)(1)(ii) of this section shall be designed and operated in accordance with the appropriate waste management unit standards specified in §§61.343 through 61.347 of this subpart. For example, if a treatment process is a tank, then the owner or operator shall comply with §61.343 of this subpart.

(3) For the purpose of complying with the requirements specified in paragraph (a)(1)(i) of this section, the intentional or unintentional reduction in the benzene concentration of a waste stream by dilution of the waste stream with other wastes or materials is not allowed.

(4) An owner or operator may aggregate or mix together individual waste streams to create a combined waste stream for the purpose of facilitating treatment of waste to comply with the requirements of paragraph (a)(1) of this section except as provided in paragraph (a)(5) of this section.

(5) If an owner or operator aggregates or mixes any combination of process wastewater, product tank drawdown, or landfill leachate subject to §61.342(c)(1) of this subpart together with other waste streams to create a combined waste stream for the purpose of facilitating management or treatment of waste in a wastewater treatment system, then the wastewater treatment system shall be operated in accordance with paragraph (b) of this section. These provisions apply to above-ground wastewater treatment systems as well as those that are at or below ground level.

(b) Except for facilities complying with §61.342(e), the owner or operator that aggregates or mixes individual waste streams as defined in paragraph (a)(5) of this section for management and treatment in a wastewater treatment system shall comply with the following requirements:

(1) The owner or operator shall design and operate each waste management unit that comprises the wastewater treatment system in accordance with the appropriate standards specified in §§61.343 through 61.347 of this subpart.

(2) The provisions of paragraph (b)(1) of this section do not apply to any waste management unit that the owner or operator demonstrates to meet the following conditions initially and, thereafter, at least once per year:

(i) The benzene content of each waste stream entering the waste management unit is less than 10 ppmw on a flow-weighted annual average basis as determined by the procedures specified in §61.355(c) of this subpart; and

(ii) The total annual benzene quantity contained in all waste streams managed or treated in exempt waste management units comprising the facility wastewater treatment systems is less than 1 Mg/yr (1.1 ton/yr). For this determination, total annual benzene quantity shall be calculated as follows:

(A) The total annual benzene quantity shall be calculated as the sum of the individual benzene quantities determined at each location where a waste stream first enters an exempt waste management unit. The benzene quantity discharged from an exempt waste management unit shall not be included in this calculation.

(B) The annual benzene quantity in a waste stream managed or treated in an enhanced biodegradation unit shall not be included in the calculation of the total annual benzene quantity, if the enhanced biodegradation unit is the first exempt unit in which the waste is managed or treated. A unit shall be considered enhanced biodegradation if it is a suspended-growth process that generates biomass, uses recycled biomass, and periodically removes biomass from the process. An enhanced biodegradation unit typically operates at a food-to-microorganism ratio in the range of 0.05 to 1.0 kg of biological oxygen demand per kg of biomass per day, a mixed liquor suspended solids ratio in the range of 1 to 8 grams per liter (0.008 to 0.7 pounds per liter), and a residence time in the range of 3 to 36 hours.

(c) The owner and operator shall demonstrate that each treatment process or wastewater treatment system unit, except as provided in paragraph (d) of this section, achieves the appropriate conditions specified in paragraphs (a) or (b) of this section in accordance with the following requirements:

(1) Engineering calculations in accordance with requirements specified in §61.356(e) of this subpart; or

(2) Performance tests conducted using the test methods and procedures that meet the requirements specified in §61.355 of this subpart.

(d) A treatment process or waste stream is in compliance with the requirements of this subpart and exempt from the requirements of paragraph (c) of this section provided that the owner or operator documents that the treatment process or waste stream is in compliance with other regulatory requirements as follows:

(1) The treatment process is a hazardous waste incinerator for which the owner or operator has been issued a final permit under 40 CFR part 270 and complies with the requirements of 40 CFR part 264, subpart O;

(2) The treatment process is an industrial furnace or boiler burning hazardous waste for energy recovery for which the owner or operator has been issued a final permit under 40 CFR part 270 and complies with the requirements of 40 CFR part 266, subpart D;

(3) The waste stream is treated by a means or to a level that meets benzene-specific treatment standards in accordance with the Land Disposal Restrictions under 40 CFR part 268, and the treatment process is designed and operated with a closed-vent system and control device meeting the requirements of §61.349 of this subpart;

(4) The waste stream is treated by a means or to a level that meets benzene-specific effluent limitations or performance standards in accordance with the Effluent Guidelines and Standards under 40 CFR parts 401–464, and the treatment process is designed and operated with a closed-vent system and control device meeting the requirements of §61.349 of this subpart; or

(5) The waste stream is discharged to an underground injection well for which the owner or operator has been issued a final permit under 40 CFR part 270 and complies with the requirements of 40 CFR part 122.

(e) Except as specified in paragraph (e)(3) of this section, if the treatment process or wastewater treatment system unit has any openings (e.g., access doors, hatches, etc.), all such openings shall be sealed (e.g., gasketed, latched, etc.) and kept closed at all times when waste is being treated, except during inspection and maintenance.

(1) Each seal, access door, and all other openings shall be checked by visual inspections initially and quarterly thereafter to ensure that no cracks or gaps occur and that openings are closed and gasketed properly.

(2) Except as provided in §61.350 of this subpart, when a broken seal or gasket or other problem is identified, first efforts at repair shall be made as soon as practicable, but not later than 15 calendar days after identification.

(3) If the cover and closed-vent system operate such that the treatment process and wastewater treatment system unit are maintained at a pressure less than atmospheric pressure, the owner or operator may operate the system with an opening that is not sealed and kept closed at all times if the following conditions are met:

(i) The purpose of the opening is to provide dilution air to reduce the explosion hazard;

(ii) The opening is designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h); and

(iii) The pressure is monitored continuously to ensure that the pressure in the treatment process and wastewater treatment system unit remain below atmospheric pressure.

(f) Except for treatment processes complying with paragraph (d) of this section, the Administrator may request at any time an owner or operator demonstrate that a treatment process or wastewater treatment system unit meets the applicable requirements specified in paragraphs (a) or (b) of this section by conducting a performance test using the test methods and procedures as required in §61.355 of this subpart.

(g) The owner or operator of a treatment process or wastewater treatment system unit that is used to comply with the provisions of this section shall monitor the unit in accordance with the applicable requirements in §61.354 of this subpart.

[55 FR 8346, Mar. 7, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3098, Jan. 7, 1993; 65 FR 62160, Oct. 17, 2000]

#### **§ 61.349 Standards: Closed-vent systems and control devices.**

(a) For each closed-vent system and control device used to comply with standards in accordance with §§61.343 through 61.348 of this subpart, the owner or operator shall properly design, install, operate, and maintain the closed-vent system and control device in accordance with the following requirements:

(1) The closed-vent system shall:

(i) Be designed to operate with no detectable emissions as indicated by an instrument reading of less than 500 ppmv above background, as determined initially and thereafter at least once per year by the methods specified in §61.355(h) of this subpart.

(ii) Vent systems that contain any bypass line that could divert the vent stream away from a control device used to comply with the provisions of this subpart shall install, maintain, and operate according to the manufacturer's specifications a flow indicator that provides a record of vent stream flow away from the control device at least once every 15 minutes, except as provided in paragraph (a)(1)(ii)(B) of this section.

(A) The flow indicator shall be installed at the entrance to any bypass line that could divert the vent stream away from the control device to the atmosphere.

(B) Where the bypass line valve is secured in the closed position with a car-seal or a lock-and-key type configuration, a flow indicator is not required.

(iii) All gauging and sampling devices shall be gas-tight except when gauging or sampling is taking place.

(iv) For each closed-vent system complying with paragraph (a) of this section, one or more devices which vent directly to the atmosphere may be used on the closed-vent system provided each device remains in a closed, sealed position during normal operations except when the device needs to open to prevent physical damage or permanent deformation of the closed-vent system resulting from malfunction of the unit in accordance with good engineering and safety practices for handling flammable, explosive, or other hazardous materials.

(2) The control device shall be designed and operated in accordance with the following conditions:

(i) An enclosed combustion device (e.g., a vapor incinerator, boiler, or process heater) shall meet one of the following conditions:

(A) Reduce the organic emissions vented to it by 95 weight percent or greater;

(B) Achieve a total organic compound concentration of 20 ppmv (as the sum of the concentrations for individual compounds using Method 18) on a dry basis corrected to 3 percent oxygen; or

(C) Provide a minimum residence time of 0.5 seconds at a minimum temperature of 760 °C (1,400 °F). If a boiler or process heater issued as the control device, then the vent stream shall be introduced into the flame zone of the boiler or process heater.

(ii) A vapor recovery system (e.g., a carbon adsorption system or a condenser) shall recover or control the organic emissions vented to it with an efficiency of 95 weight percent or greater, or shall recover or control the benzene emissions vented to it with an efficiency of 98 weight percent or greater.

(iii) A flare shall comply with the requirements of 40 CFR 60.18.

(iv) A control device other than those described in paragraphs (a)(2) (i) through (iii) of this section may be used provided that the following conditions are met:

(A) The device shall recover or control the organic emissions vented to it with an efficiency of 95 weight percent or greater, or shall recover or control the benzene emissions vented to it with an efficiency of 98 weight percent or greater.

(B) The owner or operator shall develop test data and design information that documents the control device will achieve an emission control efficiency of either 95 percent or greater for organic compounds or 98 percent or greater for benzene.

(C) The owner or operator shall identify:

( 1 ) The critical operating parameters that affect the emission control performance of the device;

( 2 ) The range of values of these operating parameters that ensure the emission control efficiency specified in paragraph (a)(2)(iv)(A) of this section is maintained during operation of the device; and

( 3 ) How these operating parameters will be monitored to ensure the proper operation and maintenance of the device.

(D) The owner or operator shall submit the information and data specified in paragraphs (a)(2)(iv) (B) and (C) of this section to the Administrator prior to operation of the alternative control device.

(E) The Administrator will determine, based on the information submitted under paragraph (a)(2)(iv)(D) of this section, if the control device subject to paragraph (a)(2)(iv) of this section meets the requirements of §61.349. The control device subject to paragraph (a)(2)(iv) of this section may be operated prior to receiving approval from the Administrator. However, if the Administrator determines that the control device does not meet the requirements of §61.349, the facility may be subject to enforcement action beginning from the time the control device began operation.

(b) Each closed-vent system and control device used to comply with this subpart shall be operated at all times when waste is placed in the waste management unit vented to the control device except when maintenance or repair of the waste management unit cannot be completed without a shutdown of the control device.

(c) An owner and operator shall demonstrate that each control device, except for a flare, achieves the appropriate conditions specified in paragraph (a)(2) of this section by using one of the following methods:



- (1) Engineering calculations in accordance with requirements specified in §61.356(f) of this subpart; or
- (2) Performance tests conducted using the test methods and procedures that meet the requirements specified in §61.355 of this subpart.
- (d) An owner or operator shall demonstrate compliance of each flare in accordance with paragraph (a)(2)(iii) of this section.
- (e) The Administrator may request at any time an owner or operator demonstrate that a control device meets the applicable conditions specified in paragraph (a)(2) of this section by conducting a performance test using the test methods and procedures as required in §61.355, and for control devices subject to paragraph (a)(2)(iv) of this section, the Administrator may specify alternative test methods and procedures, as appropriate.
- (f) Each closed-vent system and control device shall be visually inspected initially and quarterly thereafter. The visual inspection shall include inspection of ductwork and piping and connections to covers and control devices for evidence of visible defects such as holes in ductwork or piping and loose connections.
- (g) Except as provided in §61.350 of this subpart, if visible defects are observed during an inspection, or if other problems are identified, or if detectable emissions are measured, a first effort to repair the closed-vent system and control device shall be made as soon as practicable but no later than 5 calendar days after detection. Repair shall be completed no later than 15 calendar days after the emissions are detected or the visible defect is observed.
- (h) The owner or operator of a control device that is used to comply with the provisions of this section shall monitor the control device in accordance with §61.354(c) of this subpart.

[55 FR 8346, Mar. 7, 1990; 55 FR 12444, Apr. 3, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3098, Jan. 7, 1993; 65 FR 62160, Oct. 17, 2000]

#### **§ 61.350 Standards: Delay of repair.**

- (a) Delay of repair of facilities or units that are subject to the provisions of this subpart will be allowed if the repair is technically impossible without a complete or partial facility or unit shutdown.
- (b) Repair of such equipment shall occur before the end of the next facility or unit shutdown.

#### **§ 61.351 Alternative standards for tanks.**

- (a) As an alternative to the standards for tanks specified in §61.343 of this subpart, an owner or operator may elect to comply with one of the following:
- (1) A fixed roof and internal floating roof meeting the requirements in 40 CFR 60.112b(a)(1);
- (2) An external floating roof meeting the requirements of 40 CFR 60.112b (a)(2); or
- (3) An alternative means of emission limitation as described in 40 CFR 60.114b.
- (b) If an owner or operator elects to comply with the provisions of this section, then the owner or operator is exempt from the provisions of §61.343 of this subpart applicable to the same facilities.

[55 FR 8346, Mar. 7, 1990, as amended at 55 FR 37231, Sept. 10, 1990]

#### **§ 61.352 Alternative standards for oil-water separators.**

- (a) As an alternative to the standards for oil-water separators specified in §61.347 of this subpart, an owner or operator may elect to comply with one of the following:
- (1) A floating roof meeting the requirements in 40 CFR 60.693–2(a); or

(2) An alternative means of emission limitation as described in 40 CFR 60.694.

(b) For portions of the oil-water separator where it is infeasible to construct and operate a floating roof, such as over the weir mechanism, a fixed roof vented to a vapor control device that meets the requirements in §§61.347 and 61.349 of this subpart shall be installed and operated.

(c) Except as provided in paragraph (b) of this section, if an owner or operator elects to comply with the provisions of this section, then the owner or operator is exempt from the provisions in §61.347 of this subpart applicable to the same facilities.

#### **§ 61.353 Alternative means of emission limitation.**

(a) If, in the Administrator's judgment, an alternative means of emission limitation will achieve a reduction in benzene emissions at least equivalent to the reduction in benzene emissions from the source achieved by the applicable design, equipment, work practice, or operational requirements in §§61.342 through 61.349, the Administrator will publish in the Federal Register a notice permitting the use of the alternative means for purposes of compliance with that requirement. The notice may condition the permission on requirements related to the operation and maintenance of the alternative means.

(b) Any notice under paragraph (a) of this section shall be published only after public notice and an opportunity for a hearing.

(c) Any person seeking permission under this section shall collect, verify, and submit to the Administrator information showing that the alternative means achieves equivalent emission reductions.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3099, Jan. 7, 1993]

#### **§ 61.354 Monitoring of operations.**

(a) Except for a treatment process or waste stream complying with §61.348(d), the owner or operator shall monitor each treatment process or wastewater treatment system unit to ensure the unit is properly operated and maintained by one of the following monitoring procedures:

(1) Measure the benzene concentration of the waste stream exiting the treatment process complying with §61.348(a)(1)(i) at least once per month by collecting and analyzing one or more samples using the procedures specified in §61.355(c)(3).

(2) Install, calibrate, operate, and maintain according to manufacturer's specifications equipment to continuously monitor and record a process parameter (or parameters) for the treatment process or wastewater treatment system unit that indicates proper system operation. The owner or operator shall inspect at least once each operating day the data recorded by the monitoring equipment (e.g., temperature monitor or flow indicator) to ensure that the unit is operating properly.

(b) If an owner or operator complies with the requirements of §61.348(b), then the owner or operator shall monitor each wastewater treatment system to ensure the unit is properly operated and maintained by the appropriate monitoring procedure as follows:

(1) For the first exempt waste management unit in each waste treatment train, other than an enhanced biodegradation unit, measure the flow rate, using the procedures of §61.355(b), and the benzene concentration of each waste stream entering the unit at least once per month by collecting and analyzing one or more samples using the procedures specified in §61.355(c)(3).

(2) For each enhanced biodegradation unit that is the first exempt waste management unit in a treatment train, measure the benzene concentration of each waste stream entering the unit at least once per month by collecting and analyzing one or more samples using the procedures specified in §61.355(c)(3).

(c) An owner or operator subject to the requirements in §61.349 of this subpart shall install, calibrate, maintain, and operate according to the manufacturer's specifications a device to continuously monitor the control device operation as specified in the following paragraphs, unless alternative monitoring procedures or requirements are approved for that facility by the Administrator. The owner or operator shall inspect at least once each operating day the data recorded by the monitoring equipment (e.g., temperature monitor or flow indicator) to ensure that the control device is operating properly.

(1) For a thermal vapor incinerator, a temperature monitoring device equipped with a continuous recorder. The device shall have an accuracy of  $\pm 1$  percent of the temperature being monitored in  $^{\circ}\text{C}$  or  $\pm 0.5$   $^{\circ}\text{C}$ , whichever is greater. The temperature sensor shall be installed at a representative location in the combustion chamber.

(2) For a catalytic vapor incinerator, a temperature monitoring device equipped with a continuous recorder. The device shall be capable of monitoring temperature at two locations, and have an accuracy of  $\pm 1$  percent of the temperature being monitored in  $^{\circ}\text{C}$  or  $\pm 0.5$   $^{\circ}\text{C}$ , whichever is greater. One temperature sensor shall be installed in the vent stream at the nearest feasible point to the catalyst bed inlet and a second temperature sensor shall be installed in the vent stream at the nearest feasible point to the catalyst bed outlet.

(3) For a flare, a monitoring device in accordance with 40 CFR 60.18(f)(2) equipped with a continuous recorder.

(4) For a boiler or process heater having a design heat input capacity less than 44 MW ( $150 \times 10^6$  BTU/hr), a temperature monitoring device equipped with a continuous recorder. The device shall have an accuracy of  $\pm 1$  percent of the temperature being monitored in  $^{\circ}\text{C}$  or  $\pm 0.5$   $^{\circ}\text{C}$ , whichever is greater. The temperature sensor shall be installed at a representative location in the combustion chamber.

(5) For a boiler or process heater having a design heat input capacity greater than or equal to 44 MW ( $150 \times 10^6$  BTU/hr), a monitoring device equipped with a continuous recorder to measure a parameter(s) that indicates good combustion operating practices are being used.

(6) For a condenser, either:

(i) A monitoring device equipped with a continuous recorder to measure either the concentration level of the organic compounds or the concentration level of benzene in the exhaust vent stream from the condenser; or

(ii) A temperature monitoring device equipped with a continuous recorder. The device shall be capable of monitoring temperature at two locations, and have an accuracy of  $\pm 1$  percent of the temperature being monitored in  $^{\circ}\text{C}$  or  $\pm 0.5$   $^{\circ}\text{C}$ , whichever is greater. One temperature sensor shall be installed at a location in the exhaust stream from the condenser, and a second temperature sensor shall be installed at a location in the coolant fluid exiting the condenser.

(7) For a carbon adsorption system that regenerates the carbon bed directly in the control device such as a fixed-bed carbon adsorber, either:

(i) A monitoring device equipped with a continuous recorder to measure either the concentration level of the organic compounds or the benzene concentration level in the exhaust vent stream from the carbon bed; or

(ii) A monitoring device equipped with a continuous recorder to measure a parameter that indicates the carbon bed is regenerated on a regular, predetermined time cycle.

(8) For a vapor recovery system other than a condenser or carbon adsorption system, a monitoring device equipped with a continuous recorder to measure either the concentration level of the organic compounds or the benzene concentration level in the exhaust vent stream from the control device.

(9) For a control device subject to the requirements of §61.349(a)(2)(iv), devices to monitor the parameters as specified in §61.349(a)(2)(iv)(C).

(d) For a carbon adsorption system that does not regenerate the carbon bed directly on site in the control device (e.g., a carbon canister), either the concentration level of the organic compounds or the concentration level of benzene in the exhaust vent stream from the carbon adsorption system shall be monitored on a regular schedule, and the existing carbon shall be replaced with fresh carbon immediately when carbon breakthrough is indicated. The device shall be monitored on a daily basis or at intervals no greater than 20 percent of the design carbon replacement interval, whichever is greater. As an alternative to conducting this monitoring, an owner or operator may replace the carbon in the carbon adsorption system with fresh carbon at a regular predetermined time interval that is less than the carbon replacement interval that is determined by the maximum design flow rate and either the organic concentration or the benzene concentration in the gas stream vented to the carbon adsorption system.

(e) An alternative operation or process parameter may be monitored if it can be demonstrated that another parameter will ensure that the control device is operated in conformance with these standards and the control device's design specifications.

(f) Owners or operators using a closed-vent system that contains any bypass line that could divert a vent stream from a control device used to comply with the provisions of this subpart shall do the following:

(1) Visually inspect the bypass line valve at least once every month, checking the position of the valve and the condition of the car-seal or closure mechanism required under §61.349(a)(1)(ii) to ensure that the valve is maintained in the closed position and the vent stream is not diverted through the bypass line.

(2) Visually inspect the readings from each flow monitoring device required by §61.349(a)(1)(ii) at least once each operating day to check that vapors are being routed to the control device as required.

(g) Each owner or operator who uses a system for emission control that is maintained at a pressure less than atmospheric pressure with openings to provide dilution air shall install, calibrate, maintain, and operate according to the manufacturer's specifications a device equipped with a continuous recorder to monitor the pressure in the unit to ensure that it is less than atmospheric pressure.

[55 FR 8346, Mar. 7, 1990, as amended at 58 FR 3099, Jan. 7, 1993; 65 FR 62160, Oct. 17, 2000]

### **§ 61.355 Test methods, procedures, and compliance provisions.**

(a) An owner or operator shall determine the total annual benzene quantity from facility waste by the following procedure:

(1) For each waste stream subject to this subpart having a flow-weighted annual average water content greater than 10 percent water, on a volume basis as total water, or is mixed with water or other wastes at any time and the resulting mixture has an annual average water content greater than 10 percent as specified in §61.342(a), the owner or operator shall:

(i) Determine the annual waste quantity for each waste stream using the procedures specified in paragraph (b) of this section.

(ii) Determine the flow-weighted annual average benzene concentration for each waste stream using the procedures specified in paragraph (c) of this section.

(iii) Calculate the annual benzene quantity for each waste stream by multiplying the annual waste quantity of the waste stream times the flow-weighted annual average benzene concentration.

(2) Total annual benzene quantity from facility waste is calculated by adding together the annual benzene quantity for each waste stream generated during the year and the annual benzene quantity for each process unit turnaround waste annualized according to paragraph (b)(4) of this section.

(3) If the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr), then the owner or operator shall comply with the requirements of §61.342 (c), (d), or (e).

(4) If the total annual benzene quantity from facility waste is less than 10 Mg/yr (11 ton/yr) but is equal to or greater than 1 Mg/yr (1.1 ton/yr), then the owner or operator shall:

(i) Comply with the recordkeeping requirements of §61.356 and reporting requirements of §61.357 of this subpart; and

(ii) Repeat the determination of total annual benzene quantity from facility waste at least once per year and whenever there is a change in the process generating the waste that could cause the total annual benzene quantity from facility waste to increase to 10 Mg/yr (11 ton/yr) or more.

(5) If the total annual benzene quantity from facility waste is less than 1 Mg/yr (1.1 ton/yr), then the owner or operator shall:

(i) Comply with the recordkeeping requirements of §61.356 and reporting requirements of §61.357 of this subpart; and

(ii) Repeat the determination of total annual benzene quantity from facility waste whenever there is a change in the process generating the waste that could cause the total annual benzene quantity from facility waste to increase to 1 Mg/yr (1.1 ton/yr) or more.

(6) The benzene quantity in a waste stream that is generated less than one time per year, except as provided for process unit turnaround waste in paragraph (b)(4) of this section, shall be included in the determination of total annual benzene quantity from facility waste for the year in which the waste is generated unless the waste stream is otherwise excluded from the determination of total annual benzene quantity from facility waste in accordance with paragraphs (a) through (c) of this section. The benzene quantity in this waste stream shall not be annualized or averaged over the time interval between the activities that resulted in generation of the waste, for purposes of determining the total annual benzene quantity from facility waste.

(b) For purposes of the calculation required by paragraph (a) of this section, an owner or operator shall determine the annual waste quantity at the point of waste generation, unless otherwise provided in paragraphs (b) (1), (2), (3), and (4) of this section, by one of the methods given in paragraphs (b) (5) through (7) of this section.

(1) The determination of annual waste quantity for sour water streams that are processed in sour water strippers shall be made at the point that the water exits the sour water stripper.

(2) The determination of annual waste quantity for wastes at coke by-product plants subject to and complying with the control requirements of §61.132, 61.133, 61.134, or 61.139 of subpart L of this part shall be made at the location that the waste stream exits the process unit component or waste management unit controlled by that subpart or at the exit of the ammonia still, provided that the following conditions are met:

(i) The transfer of wastes between units complying with the control requirements of subpart L of this part, process units, and the ammonia still is made through hard piping or other enclosed system.

(ii) The ammonia still meets the definition of a sour water stripper in §61.341.

(3) The determination of annual waste quantity for wastes that are received at hazardous waste treatment, storage, or disposal facilities from offsite shall be made at the point where the waste enters the hazardous waste treatment, storage, or disposal facility.

(4) The determination of annual waste quantity for each process unit turnaround waste generated only at 2 year or greater intervals, may be made by dividing the total quantity of waste generated during the most recent process unit turnaround by the time period (in the nearest tenth of a year) between the turnaround resulting in generation of the waste and the most recent preceding process turnaround for the unit. The resulting annual waste quantity shall be included in the calculation of the annual benzene quantity as provided in paragraph (a)(1)(iii) of this section for the year in which the turnaround occurs and for each subsequent year until the unit undergoes the next process turnaround. For estimates of total annual benzene quantity as specified in the 90-day report, required under §61.357(a)(1), the owner or operator shall estimate the waste quantity generated during the most recent turnaround, and the time period between turnarounds in accordance with good engineering practices. If the owner or operator chooses not to annualize process unit turnaround waste, as specified in this paragraph, then the process unit turnaround waste quantity shall be included in the calculation of the annual benzene quantity for the year in which the turnaround occurs.

(5) Select the highest annual quantity of waste managed from historical records representing the most recent 5 years of operation or, if the facility has been in service for less than 5 years but at least 1 year, from historical records representing the total operating life of the facility;

(6) Use the maximum design capacity of the waste management unit; or

(7) Use measurements that are representative of maximum waste generation rates.

(c) For the purposes of the calculation required by §§61.355(a) of this subpart, an owner or operator shall determine the flow-weighted annual average benzene concentration in a manner that meets the requirements given in paragraph (c)(1) of this section using either of the methods given in paragraphs (c)(2) and (c)(3) of this section.

(1) The determination of flow-weighted annual average benzene concentration shall meet all of the following criteria:

(i) The determination shall be made at the point of waste generation except for the specific cases given in paragraphs (c)(1)(i)(A) through (D) of this section.

(A) The determination for sour water streams that are processed in sour water strippers shall be made at the point that the water exits the sour water stripper.

(B) The determination for wastes at coke by-product plants subject to and complying with the control requirements of §61.132, 61.133, 61.134, or 61.139 of subpart L of this part shall be made at the location that the waste stream exits the process unit component or waste management unit controlled by that subpart or at the exit of the ammonia still, provided that the following conditions are met:

( 1 ) The transfer of wastes between units complying with the control requirements of subpart L of this part, process units, and the ammonia still is made through hard piping or other enclosed system.

( 2 ) The ammonia still meets the definition of a sour water stripper in §61.341.

(C) The determination for wastes that are received from offsite shall be made at the point where the waste enters the hazardous waste treatment, storage, or disposal facility.

(D) The determination of flow-weighted annual average benzene concentration for process unit turnaround waste shall be made using either of the methods given in paragraph (c)(2) or (c)(3) of this section. The resulting flow-weighted annual average benzene concentration shall be included in the calculation of annual benzene quantity as provided in paragraph (a)(1)(iii) of this section for the year in which the turnaround occurs and for each subsequent year until the unit undergoes the next process unit turnaround.

(ii) Volatilization of the benzene by exposure to air shall not be used in the determination to reduce the benzene concentration.

(iii) Mixing or diluting the waste stream with other wastes or other materials shall not be used in the determination—to reduce the benzene concentration.

(iv) The determination shall be made prior to any treatment of the waste that removes benzene, except as specified in paragraphs (c)(1)(i)(A) through (D) of this section.

(v) For wastes with multiple phases, the determination shall provide the weighted-average benzene concentration based on the benzene concentration in each phase of the waste and the relative proportion of the phases.

(2) *Knowledge of the waste.* The owner or operator shall provide sufficient information to document the flow-weighted annual average benzene concentration of each waste stream. Examples of information that could constitute knowledge include material balances, records of chemicals purchases, or previous test results provided the results are still relevant to the current waste stream conditions. If test data are used, then the owner or operator shall provide documentation describing the testing protocol and the means by which sampling variability and analytical variability were accounted for in the determination of the flow-weighted annual average benzene concentration for the waste stream. When an owner or operator and the Administrator do not agree on determinations of the flow-weighted annual average benzene concentration based on knowledge of the waste, the procedures under paragraph (c)(3) of this section shall be used to resolve the disagreement.

(3) Measurements of the benzene concentration in the waste stream in accordance with the following procedures:

(i) Collect a minimum of three representative samples from each waste stream. Where feasible, samples shall be taken from an enclosed pipe prior to the waste being exposed to the atmosphere.

(ii) For waste in enclosed pipes, the following procedures shall be used:

(A) Samples shall be collected prior to the waste being exposed to the atmosphere in order to minimize the loss of benzene prior to sampling.

(B) A static mixer shall be installed in the process line or in a by-pass line unless the owner or operator demonstrates that installation of a static mixer in the line is not necessary to accurately determine the benzene concentration of the waste stream.

(C) The sampling tap shall be located within two pipe diameters of the static mixer outlet.

(D) Prior to the initiation of sampling, sample lines and cooling coil shall be purged with at least four volumes of waste.

(E) After purging, the sample flow shall be directed to a sample container and the tip of the sampling tube shall be kept below the surface of the waste during sampling to minimize contact with the atmosphere.

(F) Samples shall be collected at a flow rate such that the cooling coil is able to maintain a waste temperature less than 10 °C (50 °F).

(G) After filling, the sample container shall be capped immediately (within 5 seconds) to leave a minimum headspace in the container.

(H) The sample containers shall immediately be cooled and maintained at a temperature below 10 °C (50 °F) for transfer to the laboratory.

(iii) When sampling from an enclosed pipe is not feasible, a minimum of three representative samples shall be collected in a manner to minimize exposure of the sample to the atmosphere and loss of benzene prior to sampling.

(iv) Each waste sample shall be analyzed using one of the following test methods for determining the benzene concentration in a waste stream:

(A) Method 8020, Aromatic Volatile Organics, in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication No. SW-846 (incorporation by reference as specified in §61.18 of this part);

(B) Method 8021, Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication No. SW-846 (incorporation by reference as specified in §61.18 of this part);

(C) Method 8240, Gas Chromatography/Mass Spectrometry for Volatile Organics in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication No. SW-846 (incorporation by reference as specified in §61.18 of this part);

(D) Method 8260, Gas Chromatography/Mass Spectrometry for Volatile Organics: Capillary Column Technique in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication No. SW-846 (incorporation by reference as specified in §61.18 of this part);

(E) Method 602, Purgeable Aromatics, as described in 40 CFR part 136, appendix A, Test Procedures for Analysis of Organic Pollutants, for wastewaters for which this is an approved EPA methods; or

(F) Method 624, Purgeables, as described in 40 CFR part 136, appendix A, Test Procedures for Analysis of Organic Pollutants, for wastewaters for which this is an approved EPA method.

(v) The flow-weighted annual average benzene concentration shall be calculated by averaging the results of the sample analyses as follows:

$$\bar{C} = \frac{1}{Q_t} \times \sum_{i=1}^n (Q_i)(C_i)$$

Where:

C=Flow-weighted annual average benzene concentration for waste stream, ppmw.

Q<sub>t</sub>=Total annual waste quantity for waste stream, kg/yr (lb/yr).

n=Number of waste samples (at least 3).

Q<sub>i</sub>=Annual waste quantity for waste stream represented by C<sub>i</sub>, kg/yr (lb/yr).

C<sub>i</sub>=Measured concentration of benzene in waste sample i, ppmw.

(d) An owner or operator using performance tests to demonstrate compliance of a treatment process with §61.348 (a)(1)(i) shall measure the flow-weighted annual average benzene concentration of the waste stream exiting the treatment process

by collecting and analyzing a minimum of three representative samples of the waste stream using the procedures in paragraph (c)(3) of this section. The test shall be conducted under conditions that exist when the treatment process is operating at the highest inlet waste stream flow rate and benzene content expected to occur. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a test. The owner or operator shall record all process information as is necessary to document the operating conditions during the test.

(e) An owner or operator using performance tests to demonstrate compliance of a treatment process with §61.348(a)(1)(ii) of this subpart shall determine the percent reduction of benzene in the waste stream on a mass basis by the following procedure:

(1) The test shall be conducted under conditions that exist when the treatment process is operating at the highest inlet waste stream flow rate and benzene content expected to occur. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a test. The owner or operator shall record all process information as is necessary to document the operating conditions during the test.

(2) All testing equipment shall be prepared and installed as specified in the appropriate test methods.

(3) The mass flow rate of benzene entering the treatment process ( $E_b$ ) shall be determined by computing the product of the flow rate of the waste stream entering the treatment process, as determined by the inlet flow meter, and the benzene concentration of the waste stream, as determined using the sampling and analytical procedures specified in paragraph (c)(2) or (c)(3) of this section. Three grab samples of the waste shall be taken at equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs conducted over a 3-hour period. The mass flow rate of benzene entering the treatment process is calculated as follows:

$$E_b = \frac{K}{n \times 10^6} \left[ \sum_{i=1}^n V_i C_i \right]$$

Where:

$E_b$  = Mass flow rate of benzene entering the treatment process, kg/hr (lb/hr).

$K$  = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

$V_i$  = Average volume flow rate of waste entering the treatment process during each run  $i$ , m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

$C_i$  = Average concentration of benzene in the waste stream entering the treatment process during each run  $i$ , ppmw.

$n$  = Number of runs.

$10^6$  = Conversion factor for ppmw.

(4) The mass flow rate of benzene exiting the treatment process ( $E_a$ ) shall be determined by computing the product of the flow rate of the waste stream exiting the treatment process, as determined by the outlet flow meter or the inlet flow meter, and the benzene concentration of the waste stream, as determined using the sampling and analytical procedures specified in paragraph (c)(2) or (c)(3) of this section. Three grab samples of the waste shall be taken at equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs conducted over the same 3-hour period at which the mass flow rate of benzene entering the treatment process is determined. The mass flow rate of benzene exiting the treatment process is calculated as follows:

$$E_a = \frac{K}{n \times 10^6} \left[ \sum_{i=1}^n V_i C_i \right]$$

Where:



$E_a$  = Mass flow rate of benzene exiting the treatment process, kg/hr (lb/hr).

$K$  = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

$V_i$  = Average volume flow rate of waste exiting the treatment process during each run  $i$ , m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

$C_i$  = Average concentration of benzene in the waste stream exiting the treatment process during each run  $i$ , ppmw.

$n$  = Number of runs.

$10^6$  = Conversion factor for ppmw.

(f) An owner or operator using performance tests to demonstrate compliance of a treatment process with §61.348(a)(1)(iii) of this subpart shall determine the benzene destruction efficiency for the combustion unit by the following procedure:

(1) The test shall be conducted under conditions that exist when the combustion unit is operating at the highest inlet waste stream flow rate and benzene content expected to occur. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a test. The owner or operator shall record all process information necessary to document the operating conditions during the test.

(2) All testing equipment shall be prepared and installed as specified in the appropriate test methods.

(3) The mass flow rate of benzene entering the combustion unit shall be determined by computing the product of the flow rate of the waste stream entering the combustion unit, as determined by the inlet flow meter, and the benzene concentration of the waste stream, as determined using the sampling procedures in paragraph (c)(2) or (c)(3) of this section. Three grab samples of the waste shall be taken at equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs conducted over a 3-hour period. The mass flow rate of benzene into the combustion unit is calculated as follows:

$$E_b = \frac{K}{n \times 10^6} \left[ \sum_{i=1}^n V_i C_i \right]$$

Where:

$E_b$  = Mass flow rate of benzene entering the combustion unit, kg/hr (lb/hr).

$K$  = Density of the waste stream, kg/m<sup>3</sup> (lb/ft<sup>3</sup>).

$V_i$  = Average volume flow rate of waste entering the combustion unit during each run  $i$ , m<sup>3</sup>/hr (ft<sup>3</sup>/hr).

$C_i$  = Average concentration of benzene in the waste stream entering the combustion unit during each run  $i$ , ppmw.

$n$  = Number of runs.

$10^6$  = Conversion factor for ppmw.

(4) The mass flow rate of benzene exiting the combustion unit exhaust stack shall be determined as follows:

(i) The time period for the test shall not be less than 3 hours during which at least 3 stack gas samples are collected and be the same time period at which the mass flow rate of benzene entering the treatment process is determined. Each

sample shall be collected over a 1-hour period (e.g., in a tedlar bag) to represent a time-integrated composite sample and each 1-hour period shall correspond to the periods when the waste feed is sampled.

(ii) A run shall consist of a 1-hour period during the test. For each run:

(A) The reading from each measurement shall be recorded;

(B) The volume exhausted shall be determined using Method 2, 2A, 2C, or 2D from appendix A of 40 CFR part 60, as appropriate.

(C) The average benzene concentration in the exhaust downstream of the combustion unit shall be determined using Method 18 from appendix A of 40 CFR part 60.

(iii) The mass of benzene emitted during each run shall be calculated as follows:

$$M_i = D_b V C (10^{-6})$$

Where:

$M_i$  = Mass of benzene emitted during run i, kg (lb).

$V$  = Volume of air-vapor mixture exhausted at standard conditions,  $m^3$  ( $ft^3$ ).

$C$  = Concentration of benzene measured in the exhaust, ppmv.

$D_b$  = Density of benzene,  $3.24 \text{ kg}/m^3$  ( $0.202 \text{ lb}/ft^3$ ).

$10^6$  = Conversion factor for ppmv.

(iv) The benzene mass emission rate in the exhaust shall be calculated as follows:

$$E_a = \left( \sum_{i=1}^n M_i \right) / T$$

Where:

$E_a$  = Mass flow rate of benzene emitted from the combustion unit, kg/hr (lb/hr).

$M_i$  = Mass of benzene emitted from the combustion unit during run i, kg (lb).

$T$  = Total time of all runs, hr.

$n$  = Number of runs.

(5) The benzene destruction efficiency for the combustion unit shall be calculated as follows:

$$R = \frac{E_b - E_a}{E_b} \times 100$$

Where:

R = Benzene destruction efficiency for the combustion unit, percent.

$E_b$  = Mass flow rate of benzene entering the combustion unit, kg/hr (lb/hr).

$E_a$  = Mass flow rate of benzene emitted from the combustion unit, kg/hr (lb/hr).

(g) An owner or operator using performance tests to demonstrate compliance of a wastewater treatment system unit with §61.348(b) shall measure the flow-weighted annual average benzene concentration of the wastewater stream where the waste stream enters an exempt waste management unit by collecting and analyzing a minimum of three representative samples of the waste stream using the procedures in paragraph (c)(3) of this section. The test shall be conducted under conditions that exist when the wastewater treatment system is operating at the highest inlet wastewater stream flow rate and benzene content expected to occur. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a test. The owner or operator shall record all process information as is necessary to document the operating conditions during the test.

(h) An owner or operator shall test equipment for compliance with no detectable emissions as required in §§61.343 through 61.347, and §61.349 of this subpart in accordance with the following requirements:

(1) Monitoring shall comply with Method 21 from appendix A of 40 CFR part 60.

(2) The detection instrument shall meet the performance criteria of Method 21.

(3) The instrument shall be calibrated before use on each day of its use by the procedures specified in Method 21.

(4) Calibration gases shall be:

(i) Zero air (less than 10 ppm of hydrocarbon in air); and

(ii) A mixture of methane or n-hexane and air at a concentration of approximately, but less than, 10,000 ppm methane or n-hexane.

(5) The background level shall be determined as set forth in Method 21.

(6) The instrument probe shall be traversed around all potential leak interfaces as close as possible to the interface as described in Method 21.

(7) The arithmetic difference between the maximum concentration indicated by the instrument and the background level is compared to 500 ppm for determining compliance.

(i) An owner or operator using a performance test to demonstrate compliance of a control device with either the organic reduction efficiency requirement or the benzene reduction efficiency requirement specified under §61.349(a)(2) shall use the following procedures:

(1) The test shall be conducted under conditions that exist when the waste management unit vented to the control device is operating at the highest load or capacity level expected to occur. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a test. The owner or operator shall record all process information necessary to document the operating conditions during the test.

(2) Sampling sites shall be selected using Method 1 or 1A from appendix A of 40 CFR part 60, as appropriate.

(3) The mass flow rate of either the organics or benzene entering and exiting the control device shall be determined as follows:

(i) The time period for the test shall not be less than 3 hours during which at least 3 stack gas samples are collected. Samples of the vent stream entering and exiting the control device shall be collected during the same time period. Each sample shall be collected over a 1-hour period (e.g., in a tedlar bag) to represent a time-integrated composite sample.

(ii) A run shall consist of a 1-hour period during the test. For each run:

(A) The reading from each measurement shall be recorded;

(B) The volume exhausted shall be determined using Method 2, 2A, 2C, or 2D from appendix A of 40 CFR part 60, as appropriate;

(C) The organic concentration or the benzene concentration, as appropriate, in the vent stream entering and exiting the control shall be determined using Method 18 from appendix A of 40 CFR part 60.

(iii) The mass of organics or benzene entering and exiting the control device during each run shall be calculated as follows:

$$M_{aj} = \frac{K_1 V_{aj}}{10^6} \left( \sum_{i=1}^n C_{ai} MW_i \right)$$

$$M_{bj} = \frac{K_1 V_{bj}}{10^6} \left( \sum_{i=1}^n C_{bi} MW_i \right)$$

$M_{aj}$  = Mass of organics or benzene in the vent stream entering the control device during run j, kg (lb).

$M_{bj}$  = Mass of organics or benzene in the vent stream exiting the control device during run j, kg (lb).

$V_{aj}$  = Volume of vent stream entering the control device during run j, at standard conditions,  $m^3$  ( $ft^3$ ).

$V_{bj}$  = Volume of vent stream exiting the control device during run j, at standard conditions,  $m^3$  ( $ft^3$ ).

$C_{ai}$  = Organic concentration of compound i or the benzene concentration measured in the vent stream entering the control device as determined by Method 18, ppm by volume on a dry basis.

$C_{bi}$  = Organic concentration of compound i or the benzene concentration measured in the vent stream exiting the control device as determined by Method 18, ppm by volume on a dry basis.

$MW_i$  = Molecular weight of organic compound i in the vent stream, or the molecular weight of benzene, kg/kg-mol (lb/lb-mole).

$n$  = Number of organic compounds in the vent stream; if benzene reduction efficiency is being demonstrated, then  $n=1$ .

$K_1$  = Conversion factor for molar volume at standard conditions (293 K and 760 mm Hg (527 R and 14.7 psia))

$$= 0.0416 \text{ kg-mol/m}^3 \text{ (0.00118 lb-mol/ft}^3 \text{)}$$

$10^{-6}$  = Conversion factor for ppmv.

(iv) The mass flow rate of organics or benzene entering and exiting the control device shall be calculated as follows:

$$E_a = \left( \sum_{j=1}^n M_{aj} \right) / T$$

$$E_b = \left( \sum_{j=1}^n M_{bj} \right) / T$$

Where:

$E_a$  = Mass flow rate of organics or benzene entering the control device, kg/hr (lb/hr).

$E_b$  = Mass flow rate of organics or benzene exiting the control device, kg/hr (lb/hr).

$M_{aj}$  = Mass of organics or benzene in the vent stream entering the control device during run j, kg (lb).

$M_{bj}$  = Mass of organics or benzene in the vent stream exiting the control device during run j, kg (lb).

T = Total time of all runs, hr.

n = Number of runs.

(4) The organic reduction efficiency or the benzene reduction efficiency for the control device shall be calculated as follows:

$$R = \frac{E_a - E_b}{E_a} \times 100$$

Where:

R = Total organic reduction of efficiency or benzene reduction efficiency for the control device, percent.

$E_b$  = Mass flow rate of organics or benzene entering the control device, kg/hr (lb/hr).

$E_a$  = Mass flow rate of organic or benzene emitted from the control device, kg/hr (lb/hr).

(j) An owner or operator shall determine the benzene quantity for the purposes of the calculation required by §61.342 (c)(3)(ii)(B) according to the provisions of paragraph (a) of this section, except that the procedures in paragraph (a) of this section shall also apply to wastes with a water content of 10 percent or less.

(k) An owner or operator shall determine the benzene quantity for the purposes of the calculation required by §61.342(e)(2) by the following procedure:

(1) For each waste stream that is not controlled for air emissions in accordance with §61.343, 61.344, 61.345, 61.346, 61.347, or 61.348(a), as applicable to the waste management unit that manages the waste, the benzene quantity shall be determined as specified in paragraph (a) of this section, except that paragraph (b)(4) of this section shall not apply, i.e., the waste quantity for process unit turnaround waste is not annualized but shall be included in the determination of benzene quantity for the year in which the waste is generated for the purposes of the calculation required by §61.342(e)(2).

(2) For each waste stream that is controlled for air emissions in accordance with §61.343, 61.344, 61.345, 61.346, 61.347, or 61.348(a), as applicable to the waste management unit that manages the waste, the determination of annual waste quantity and flow-weighted annual average benzene concentration shall be made at the first applicable location as described in paragraphs (k)(2)(i), (k)(2)(ii), and (k)(2)(iii) of this section and prior to any reduction of benzene concentration through volatilization of the benzene, using the methods given in (k)(2)(iv) and (k)(2)(v) of this section.

(i) Where the waste stream enters the first waste management unit not complying with §§61.343, 61.344, 61.345, 61.346, 61.347, and 61.348(a) that are applicable to the waste management unit,

(ii) For each waste stream that is managed or treated only in compliance with §§61.343 through 61.348(a) up to the point of final direct discharge from the facility, the determination of benzene quantity shall be prior to any reduction of benzene concentration through volatilization of the benzene, or

(iii) For wastes managed in units controlled for air emissions in accordance with §§61.343, 61.344, 61.345, 61.346, 61.347, and 61.348(a), and then transferred offsite, facilities shall use the first applicable offsite location as described in paragraphs (k)(2)(i) and (k)(2)(ii) of this section if they have documentation from the offsite facility of the benzene quantity at this location. Facilities without this documentation for offsite wastes shall use the benzene quantity determined at the point where the transferred waste leaves the facility.

(iv) Annual waste quantity shall be determined using the procedures in paragraphs (b)(5), (6), or (7) of this section, and

(v) The flow-weighted annual average benzene concentration shall be determined using the procedures in paragraphs (c)(2) or (3) of this section.

(3) The benzene quantity in a waste stream that is generated less than one time per year, including process unit turnaround waste, shall be included in the determination of benzene quantity as determined in paragraph (k)(6) of this section for the year in which the waste is generated. The benzene quantity in this waste stream shall not be annualized or averaged over the time interval between the activities that resulted in generation of the waste for purposes of determining benzene quantity as determined in paragraph (k)(6) of this section.

(4) The benzene in waste entering an enhanced biodegradation unit, as defined in §61.348(b)(2)(ii)(B), shall not be included in the determination of benzene quantity, determined in paragraph (k)(6) of this section, if the following conditions are met:

(i) The benzene concentration for each waste stream entering the enhanced biodegradation unit is less than 10 ppmw on a flow-weighted annual average basis, and

(ii) All prior waste management units managing the waste comply with §§61.343, 61.344, 61.345, 61.346, 61.347 and 61.348(a).

(5) The benzene quantity for each waste stream in paragraph (k)(2) of this section shall be determined by multiplying the annual waste quantity of each waste stream times its flow-weighted annual average benzene concentration.

(6) The total benzene quantity for the purposes of the calculation required by §61.342(e)(2) shall be determined by adding together the benzene quantities determined in paragraphs (k)(1) and (k)(5) of this section for each applicable waste stream.

(7) If the benzene quantity determined in paragraph (6) of this section exceeds 6.0 Mg/yr (6.6 ton/yr) only because of multiple counting of the benzene quantity for a waste stream, the owner or operator may use the following procedures for the purposes of the calculation required by §61.342(e)(2):

(i) Determine which waste management units are involved in the multiple counting of benzene;

(ii) Determine the quantity of benzene that is emitted, recovered, or removed from the affected units identified in paragraph (k)(7)(i) of this section, or destroyed in the units if applicable, using either direct measurements or the best available estimation techniques developed or approved by the Administrator.

(iii) Adjust the benzene quantity to eliminate the multiple counting of benzene based on the results from paragraph (k)(7)(ii) of this section and determine the total benzene quantity for the purposes of the calculation required by §61.342(e)(2).

(iv) Submit in the annual report required under §61.357(a) a description of the methods used and the resulting calculations for the alternative procedure under paragraph (k)(7) of this section, the benzene quantity determination from paragraph (k)(6) of this section, and the adjusted benzene quantity determination from paragraph (k)(7)(iii) of this section.

[55 FR 8346, Mar. 7, 1990; 55 FR 12444, Apr. 3, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3099, Jan. 7, 1993; 65 FR 62160, Oct. 17, 2000]

#### **§ 61.356 Recordkeeping requirements.**

(a) Each owner or operator of a facility subject to the provisions of this subpart shall comply with the recordkeeping requirements of this section. Each record shall be maintained in a readily accessible location at the facility site for a period not less than two years from the date the information is recorded unless otherwise specified.

(b) Each owner or operator shall maintain records that identify each waste stream at the facility subject to this subpart, and indicate whether or not the waste stream is controlled for benzene emissions in accordance with this subpart. In addition the owner or operator shall maintain the following records:

(1) For each waste stream not controlled for benzene emissions in accordance with this subpart, the records shall include all test results, measurements, calculations, and other documentation used to determine the following information for the waste stream: waste stream identification, water content, whether or not the waste stream is a process wastewater stream, annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity.

(2) For each waste stream exempt from §61.342(c)(1) in accordance with §61.342(c)(3), the records shall include:

(i) All measurements, calculations, and other documentation used to determine that the continuous flow of process wastewater is less than 0.02 liters (0.005 gallons) per minute or the annual waste quantity of process wastewater is less than 10 Mg/yr (11 ton/yr) in accordance with §61.342(c)(3)(i), or

(ii) All measurements, calculations, and other documentation used to determine that the sum of the total annual benzene quantity in all exempt waste streams does not exceed 2.0 Mg/yr (2.2 ton/yr) in accordance with §61.342(c)(3)(ii).

(3) For each facility where process wastewater streams are controlled for benzene emissions in accordance with §61.342(d) of this subpart, the records shall include for each treated process wastewater stream all measurements, calculations, and other documentation used to determine the annual benzene quantity in the process wastewater stream exiting the treatment process.

(4) For each facility where waste streams are controlled for benzene emissions in accordance with §61.342(e), the records shall include for each waste stream all measurements, including the locations of the measurements, calculations, and other documentation used to determine that the total benzene quantity does not exceed 6.0 Mg/yr (6.6 ton/yr).

(5) For each facility where the annual waste quantity for process unit turnaround waste is determined in accordance with §61.355(b)(5), the records shall include all test results, measurements, calculations, and other documentation used to determine the following information: identification of each process unit at the facility that undergoes turnarounds, the date of the most recent turnaround for each process unit, identification of each process unit turnaround waste, the water content of each process unit turnaround waste, the annual waste quantity determined in accordance with §61.355(b)(5), the range of benzene concentrations in the waste, the annual average flow-weighted benzene concentration of the waste, and the annual benzene quantity calculated in accordance with §61.355(a)(1)(iii) of this section.

(6) For each facility where wastewater streams are controlled for benzene emissions in accordance with §61.348(b)(2), the records shall include all measurements, calculations, and other documentation used to determine the annual benzene content of the waste streams and the total annual benzene quantity contained in all waste streams managed or treated in exempt waste management units.

(c) An owner or operator transferring waste off-site to another facility for treatment in accordance with §61.342(f) shall maintain documentation for each offsite waste shipment that includes the following information: Date waste is shipped offsite, quantity of waste shipped offsite, name and address of the facility receiving the waste, and a copy of the notice sent with the waste shipment.

(d) An owner or operator using control equipment in accordance with §§61.343 through 61.347 shall maintain engineering design documentation for all control equipment that is installed on the waste management unit. The documentation shall

be retained for the life of the control equipment. If a control device is used, then the owner or operator shall maintain the control device records required by paragraph (f) of this section.

(e) An owner or operator using a treatment process or wastewater treatment system unit in accordance with §61.348 of this subpart shall maintain the following records. The documentation shall be retained for the life of the unit.

(1) A statement signed and dated by the owner or operator certifying that the unit is designed to operate at the documented performance level when the waste stream entering the unit is at the highest waste stream flow rate and benzene content expected to occur.

(2) If engineering calculations are used to determine treatment process or wastewater treatment system unit performance, then the owner or operator shall maintain the complete design analysis for the unit. The design analysis shall include for example the following information: Design specifications, drawings, schematics, piping and instrumentation diagrams, and other documentation necessary to demonstrate the unit performance.

(3) If performance tests are used to determine treatment process or wastewater treatment system unit performance, then the owner or operator shall maintain all test information necessary to demonstrate the unit performance.

(i) A description of the unit including the following information: type of treatment process; manufacturer name and model number; and for each waste stream entering and exiting the unit, the waste stream type (e.g., process wastewater, sludge, slurry, etc.), and the design flow rate and benzene content.

(ii) Documentation describing the test protocol and the means by which sampling variability and analytical variability were accounted for in the determination of the unit performance. The description of the test protocol shall include the following information: sampling locations, sampling method, sampling frequency, and analytical procedures used for sample analysis.

(iii) Records of unit operating conditions during each test run including all key process parameters.

(iv) All test results.

(4) If a control device is used, then the owner or operator shall maintain the control device records required by paragraph (f) of this section.

(f) An owner or operator using a closed-vent system and control device in accordance with §61.349 of this subpart shall maintain the following records. The documentation shall be retained for the life of the control device.

(1) A statement signed and dated by the owner or operator certifying that the closed-vent system and control device is designed to operate at the documented performance level when the waste management unit vented to the control device is or would be operating at the highest load or capacity expected to occur.

(2) If engineering calculations are used to determine control device performance in accordance with §61.349(c), then a design analysis for the control device that includes for example:

(i) Specifications, drawings, schematics, and piping and instrumentation diagrams prepared by the owner or operator, or the control device manufacturer or vendor that describe the control device design based on acceptable engineering texts. The design analysis shall address the following vent stream characteristics and control device operating parameters:

(A) For a thermal vapor incinerator, the design analysis shall consider the vent stream composition, constituent concentrations, and flow rate. The design analysis shall also establish the design minimum and average temperature in the combustion zone and the combustion zone residence time.

(B) For a catalytic vapor incinerator, the design analysis shall consider the vent stream composition, constituent concentrations, and flow rate. The design analysis shall also establish the design minimum and average temperatures across the catalyst bed inlet and outlet.

(C) For a boiler or process heater, the design analysis shall consider the vent stream composition, constituent concentrations, and flow rate. The design analysis shall also establish the design minimum and average flame zone temperatures, combustion zone residence time, and description of method and location where the vent stream is introduced into the flame zone.



(D) For a flare, the design analysis shall consider the vent stream composition, constituent concentrations, and flow rate. The design analysis shall also consider the requirements specified in 40 CFR 60.18.

(E) For a condenser, the design analysis shall consider the vent stream composition, constituent concentration, flow rate, relative humidity, and temperature. The design analysis shall also establish the design outlet organic compound concentration level or the design outlet benzene concentration level, design average temperature of the condenser exhaust vent stream, and the design average temperatures of the coolant fluid at the condenser inlet and outlet.

(F) For a carbon adsorption system that regenerates the carbon bed directly on-site in the control device such as a fixed-bed adsorber, the design analysis shall consider the vent stream composition, constituent concentration, flow rate, relative humidity, and temperature. The design analysis shall also establish the design exhaust vent stream organic compound concentration level or the design exhaust vent stream benzene concentration level, number and capacity of carbon beds, type and working capacity of activated carbon used for carbon beds, design total steam flow over the period of each complete carbon bed regeneration cycle, duration of the carbon bed steaming and cooling/drying cycles, design carbon bed temperature after regeneration, design carbon bed regeneration time, and design service life of carbon.

(G) For a carbon adsorption system that does not regenerate the carbon bed directly on-site in the control device, such as a carbon canister, the design analysis shall consider the vent stream composition, constituent concentration, flow rate, relative humidity, and temperature. The design analysis shall also establish the design exhaust vent stream organic compound concentration level or the design exhaust vent stream benzene concentration level, capacity of carbon bed, type and working capacity of activated carbon used for carbon bed, and design carbon replacement interval based on the total carbon working capacity of the control device and source operating schedule.

(H) For a control device subject to the requirements of §61.349(a)(2)(iv), the design analysis shall consider the vent stream composition, constituent concentration, and flow rate. The design analysis shall also include all of the information submitted under §61.349 (a)(2)(iv).

(ii) [Reserved]

(3) If performance tests are used to determine control device performance in accordance with §61.349(c) of this subpart:

(i) A description of how it is determined that the test is conducted when the waste management unit or treatment process is operating at the highest load or capacity level. This description shall include the estimated or design flow rate and organic content of each vent stream and definition of the acceptable operating ranges of key process and control parameters during the test program.

(ii) A description of the control device including the type of control device, control device manufacturer's name and model number, control device dimensions, capacity, and construction materials.

(iii) A detailed description of sampling and monitoring procedures, including sampling and monitoring locations in the system, the equipment to be used, sampling and monitoring frequency, and planned analytical procedures for sample analysis.

(iv) All test results.

(g) An owner or operator shall maintain a record for each visual inspection required by §§61.343 through 61.347 of this subpart that identifies a problem (such as a broken seal, gap or other problem) which could result in benzene emissions. The record shall include the date of the inspection, waste management unit and control equipment location where the problem is identified, a description of the problem, a description of the corrective action taken, and the date the corrective action was completed.

(h) An owner or operator shall maintain a record for each test of no detectable emissions required by §§61.343 through 61.347 and §61.349 of this subpart. The record shall include the following information: date the test is performed, background level measured during test, and maximum concentration indicated by the instrument reading measured for each potential leak interface. If detectable emissions are measured at a leak interface, then the record shall also include the waste management unit, control equipment, and leak interface location where detectable emissions were measured, a description of the problem, a description of the corrective action taken, and the date the corrective action was completed.

(i) For each treatment process and wastewater treatment system unit operated to comply with §61.348, the owner or operator shall maintain documentation that includes the following information regarding the unit operation:

(1) Dates of startup and shutdown of the unit.

(2) If measurements of waste stream benzene concentration are performed in accordance with §61.354(a)(1) of this subpart, the owner or operator shall maintain records that include date each test is performed and all test results.

(3) If a process parameter is continuously monitored in accordance with §61.354(a)(2) of this subpart, the owner or operator shall maintain records that include a description of the operating parameter (or parameters ) to be monitored to ensure that the unit will be operated in conformance with these standards and the unit's design specifications, and an explanation of the criteria used for selection of that parameter (or parameters). This documentation shall be kept for the life of the unit.

(4) If measurements of waste stream benzene concentration are performed in accordance with §61.354(b), the owner or operator shall maintain records that include the date each test is performed and all test results.

(5) Periods when the unit is not operated as designed.

(j) For each control device, the owner or operator shall maintain documentation that includes the following information regarding the control device operation:

(1) Dates of startup and shutdown of the closed-vent system and control device.

(2) A description of the operating parameter (or parameters ) to be monitored to ensure that the control device will be operated in conformance with these standards and the control device's design specifications and an explanation of the criteria used for selection of that parameter (or parameters). This documentation shall be kept for the life of the control device.

(3) Periods when the closed-vent system and control device are not operated as designed including all periods and the duration when:

(i) Any valve car-seal or closure mechanism required under §61.349(a)(1)(ii) is broken or the by-pass line valve position has changed.

(ii) The flow monitoring devices required under §61.349(a)(1)(ii) indicate that vapors are not routed to the control device as required.

(4) If a thermal vapor incinerator is used, then the owner or operator shall maintain continuous records of the temperature of the gas stream in the combustion zone of the incinerator and records of all 3-hour periods of operation during which the average temperature of the gas stream in the combustion zone is more than 28 °C (50 °F) below the design combustion zone temperature.

(5) If a catalytic vapor incinerator is used, then the owner or operator shall maintain continuous records of the temperature of the gas stream both upstream and downstream of the catalyst bed of the incinerator, records of all 3-hour periods of operation during which the average temperature measured before the catalyst bed is more than 28 °C (50 °F) below the design gas stream temperature, and records of all 3-hour periods of operation during which the average temperature difference across the catalyst bed is less than 80 percent of the design temperature difference.

(6) If a boiler or process heater is used, then the owner or operator shall maintain records of each occurrence when there is a change in the location at which the vent stream is introduced into the flame zone as required by §61.349(a)(2)(i)(C). For a boiler or process heater having a design heat input capacity less than 44 MW (150 × 106 BTU/hr), the owner or operator shall maintain continuous records of the temperature of the gas stream in the combustion zone of the boiler or process heater and records of all 3-hour periods of operation during which the average temperature of the gas stream in the combustion zone is more than 28 °C (50 °F) below the design combustion zone temperature. For a boiler or process heater having a design heat input capacity greater than or equal to 44 MW (150 × 106 BTU/hr), the owner or operator shall maintain continuous records of the parameter(s) monitored in accordance with the requirements of §61.354(c)(5).

(7) If a flare is used, then the owner or operator shall maintain continuous records of the flare pilot flame monitoring and records of all periods during which the pilot flame is absent.

(8) If a condenser is used, then the owner or operator shall maintain records from the monitoring device of the parameters selected to be monitored in accordance with §61.354(c)(6). If concentration of organics or concentration of benzene in the control device outlet gas stream is monitored, then the owner or operator shall record all 3-hour periods of operation during which the concentration of organics or the concentration of benzene in the exhaust stream is more than 20 percent greater than the design value. If the temperature of the condenser exhaust stream and coolant fluid is monitored, then the owner or operator shall record all 3-hour periods of operation during which the temperature of the condenser exhaust vent stream is more than 6 °C (11 °F) above the design average exhaust vent stream temperature, or the temperature of the

coolant fluid exiting the condenser is more than 6 °C (11 °F) above the design average coolant fluid temperature at the condenser outlet.

(9) If a carbon adsorber is used, then the owner or operator shall maintain records from the monitoring device of the concentration of organics or the concentration of benzene in the control device outlet gas stream. If the concentration of organics or the concentration of benzene in the control device outlet gas stream is monitored, then the owner or operator shall record all 3-hour periods of operation during which the concentration of organics or the concentration of benzene in the exhaust stream is more than 20 percent greater than the design value. If the carbon bed regeneration interval is monitored, then the owner or operator shall record each occurrence when the vent stream continues to flow through the control device beyond the predetermined carbon bed regeneration time.

(10) If a carbon adsorber that is not regenerated directly on site in the control device is used, then the owner or operator shall maintain records of dates and times when the control device is monitored, when breakthrough is measured, and shall record the date and time then the existing carbon in the control device is replaced with fresh carbon.

(11) If an alternative operational or process parameter is monitored for a control device, as allowed in §61.354(e) of this subpart, then the owner or operator shall maintain records of the continuously monitored parameter, including periods when the device is not operated as designed.

(12) If a control device subject to the requirements of §61.349(a)(2)(iv) is used, then the owner or operator shall maintain records of the parameters that are monitored and each occurrence when the parameters monitored are outside the range of values specified in §61.349(a)(2)(iv)(C), or other records as specified by the Administrator.

(k) An owner or operator who elects to install and operate the control equipment in §61.351 of this subpart shall comply with the recordkeeping requirements in 40 CFR 60.115b.

(l) An owner or operator who elects to install and operate the control equipment in §61.352 of this subpart shall maintain records of the following:

(1) The date, location, and corrective action for each visual inspection required by 40 CFR 60.693–2(a)(5), during which a broken seal, gap, or other problem is identified that could result in benzene emissions.

(2) Results of the seal gap measurements required by 40 CFR 60.693–2(a).

(m) If a system is used for emission control that is maintained at a pressure less than atmospheric pressure with openings to provide dilution air, then the owner or operator shall maintain records of the monitoring device and records of all periods during which the pressure in the unit is operated at a pressure that is equal to or greater than atmospheric pressure.

(n) Each owner or operator using a total enclosure to comply with control requirements for tanks in §61.343 or the control requirements for containers in §61.345 must keep the records required in paragraphs (n)(1) and (2) of this section. Owners or operators may use records as required in 40 CFR 264.1089(b)(2)(iv) or 40 CFR 265.1090(b)(2)(iv) for a tank or as required in 40 CFR 264.1089(d)(1) or 40 CFR 265.1090(d)(1) for a container to meet the recordkeeping requirement in paragraph (n)(1) of this section. The owner or operator must make the records of each verification of a total enclosure available for inspection upon request.

(1) Records of the most recent set of calculations and measurements performed to verify that the enclosure meets the criteria of a permanent total enclosure as specified in "Procedure T—Criteria for and Verification of a Permanent or Temporary Total Enclosure" in 40 CFR 52.741, appendix B;

(2) Records required for a closed-vent system and control device according to the requirements in paragraphs (d) (f), and (j) of this section.

[55 FR 8346, Mar. 7, 1990; 55 FR 12444, Apr. 3, 1990; 55 FR 18331, May 2, 1990, as amended at 58 FR 3103, Jan. 7, 1993; 65 FR 62161, Oct. 17, 2000; 67 FR 68533, Nov. 12, 2002]

## **§ 61.357 Reporting requirements.**

(a) Each owner or operator of a chemical plant, petroleum refinery, coke by-product recovery plant, and any facility managing wastes from these industries shall submit to the Administrator within 90 days after January 7, 1993, or by the initial startup for a new source with an initial startup after the effective date, a report that summarizes the regulatory status of each waste stream subject to §61.342 and is determined by the procedures specified in §61.355(c) to contain benzene. Each owner or operator subject to this subpart who has no benzene onsite in wastes, products, by-products, or

intermediates shall submit an initial report that is a statement to this effect. For all other owners or operators subject to this subpart, the report shall include the following information:

- (1) Total annual benzene quantity from facility waste determined in accordance with §61.355(a) of this subpart.
- (2) A table identifying each waste stream and whether or not the waste stream will be controlled for benzene emissions in accordance with the requirements of this subpart.
- (3) For each waste stream identified as not being controlled for benzene emissions in accordance with the requirements of this subpart the following information shall be added to the table:
  - (i) Whether or not the water content of the waste stream is greater than 10 percent;
  - (ii) Whether or not the waste stream is a process wastewater stream, product tank drawdown, or landfill leachate;
  - (iii) Annual waste quantity for the waste stream;
  - (iv) Range of benzene concentrations for the waste stream;
  - (v) Annual average flow-weighted benzene concentration for the waste stream; and
  - (vi) Annual benzene quantity for the waste stream.

(4) The information required in paragraphs (a) (1), (2), and (3) of this section should represent the waste stream characteristics based on current configuration and operating conditions. An owner or operator only needs to list in the report those waste streams that contact materials containing benzene. The report does not need to include a description of the controls to be installed to comply with the standard or other information required in §61.10(a).

(b) If the total annual benzene quantity from facility waste is less than 1 Mg/yr (1.1 ton/yr), then the owner or operator shall submit to the Administrator a report that updates the information listed in paragraphs (a)(1) through (a)(3) of this section whenever there is a change in the process generating the waste stream that could cause the total annual benzene quantity from facility waste to increase to 1 Mg/yr (1.1 ton/yr) or more.

(c) If the total annual benzene quantity from facility waste is less than 10 Mg/yr (11 ton/yr) but is equal to or greater than 1 Mg/yr (1.1 ton/yr), then the owner or operator shall submit to the Administrator a report that updates the information listed in paragraphs (a)(1) through (a)(3) of this section. The report shall be submitted annually and whenever there is a change in the process generating the waste stream that could cause the total annual benzene quantity from facility waste to increase to 10 Mg/yr (11 ton/yr) or more. If the information in the annual report required by paragraphs (a)(1) through (a)(3) of this section is not changed in the following year, the owner or operator may submit a statement to that effect.

(d) If the total annual benzene quantity from facility waste is equal to or greater than 10 Mg/yr (11 ton/yr), then the owner or operator shall submit to the Administrator the following reports:

(1) Within 90 days after January 7, 1993, unless a waiver of compliance under §61.11 of this part is granted, or by the date of initial startup for a new source with an initial startup after the effective date, a certification that the equipment necessary to comply with these standards has been installed and that the required initial inspections or tests have been carried out in accordance with this subpart. If a waiver of compliance is granted under §61.11, the certification of equipment necessary to comply with these standards shall be submitted by the date the waiver of compliance expires.

(2) Beginning on the date that the equipment necessary to comply with these standards has been certified in accordance with paragraph (d)(1) of this section, the owner or operator shall submit annually to the Administrator a report that updates the information listed in paragraphs (a)(1) through (a)(3) of this section. If the information in the annual report required by paragraphs (a)(1) through (a)(3) of this section is not changed in the following year, the owner or operator may submit a statement to that effect.

(3) If an owner or operator elects to comply with the requirements of §61.342(c)(3)(ii), then the report required by paragraph (d)(2) of this section shall include a table identifying each waste stream chosen for exemption and the total annual benzene quantity in these exempted streams.

(4) If an owner or operator elects to comply with the alternative requirements of §61.342(d) of this subpart, then he shall include in the report required by paragraph (d)(2) of this section a table presenting the following information for each process wastewater stream:

(i) Whether or not the process wastewater stream is being controlled for benzene emissions in accordance with the requirements of this subpart;

(ii) For each process wastewater stream identified as not being controlled for benzene emissions in accordance with the requirements of this subpart, the table shall report the following information for the process wastewater stream as determined at the point of waste generation: annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity;

(iii) For each process wastewater stream identified as being controlled for benzene emissions in accordance with the requirements of this subpart, the table shall report the following information for the process wastewater stream as determined at the exit to the treatment process: Annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity.

(5) If an owner or operator elects to comply with the alternative requirements of §61.342(e), then the report required by paragraph (d)(2) of this section shall include a table presenting the following information for each waste stream:

(i) For each waste stream identified as not being controlled for benzene emissions in accordance with the requirements of this subpart; the table shall report the following information for the waste stream as determined at the point of waste generation: annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity;

(ii) For each waste stream identified as being controlled for benzene emissions in accordance with the requirements of this subpart; the table shall report the following information for the waste stream as determined at the applicable location described in §61.355(k)(2): Annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity.

(6) Beginning 3 months after the date that the equipment necessary to comply with these standards has been certified in accordance with paragraph (d)(1) of this section, the owner or operator shall submit quarterly to the Administrator a certification that all of the required inspections have been carried out in accordance with the requirements of this subpart.

(7) Beginning 3 months after the date that the equipment necessary to comply with these standards has been certified in accordance with paragraph (d)(1) of this section, the owner or operator shall submit a report quarterly to the Administrator that includes:

(i) If a treatment process or wastewater treatment system unit is monitored in accordance with §61.354(a)(1) of this subpart, then each period of operation during which the concentration of benzene in the monitored waste stream exiting the unit is equal to or greater than 10 ppmw.

(ii) If a treatment process or wastewater treatment system unit is monitored in accordance with §61.354(a)(2) of this subpart, then each 3-hour period of operation during which the average value of the monitored parameter is outside the range of acceptable values or during which the unit is not operating as designed.

(iii) If a treatment process or wastewater treatment system unit is monitored in accordance with §61.354(b), then each period of operation during which the flow-weighted annual average concentration of benzene in the monitored waste stream entering the unit is equal to or greater than 10 ppmw and/or the total annual benzene quantity is equal to or greater than 1.0 mg/yr.

(iv) For a control device monitored in accordance with §61.354(c) of this subpart, each period of operation monitored during which any of the following conditions occur, as applicable to the control device:

(A) Each 3-hour period of operation during which the average temperature of the gas stream in the combustion zone of a thermal vapor incinerator, as measured by the temperature monitoring device, is more than 28 °C (50 °F) below the design combustion zone temperature.

(B) Each 3-hour period of operation during which the average temperature of the gas stream immediately before the catalyst bed of a catalytic vapor incinerator, as measured by the temperature monitoring device, is more than 28 °C (50 °F) below the design gas stream temperature, and any 3-hour period during which the average temperature difference across the catalyst bed (i.e., the difference between the temperatures of the gas stream immediately before and after the

catalyst bed), as measured by the temperature monitoring device, is less than 80 percent of the design temperature difference.

(C) Each 3-hour period of operation during which the average temperature of the gas stream in the combustion zone of a boiler or process heater having a design heat input capacity less than 44 MW (150 × 106 BTU/hr), as measured by the temperature monitoring device, is more than 28 °C (50 °F) below the design combustion zone temperature.

(D) Each 3-hour period of operation during which the average concentration of organics or the average concentration of benzene in the exhaust gases from a carbon adsorber, condenser, or other vapor recovery system is more than 20 percent greater than the design concentration level of organics or benzene in the exhaust gas.

(E) Each 3-hour period of operation during which the temperature of the condenser exhaust vent stream is more than 6 °C (11 °F) above the design average exhaust vent stream temperature, or the temperature of the coolant fluid exiting the condenser is more than 6 °C (11 °F) above the design average coolant fluid temperature at the condenser outlet.

(F) Each period in which the pilot flame of a flare is absent.

(G) Each occurrence when there is a change in the location at which the vent stream is introduced into the flame zone of a boiler or process heater as required by §61.349(a)(2)(i)(C) of this subpart.

(H) Each occurrence when the carbon in a carbon adsorber system that is regenerated directly on site in the control device is not regenerated at the predetermined carbon bed regeneration time.

(I) Each occurrence when the carbon in a carbon adsorber system that is not regenerated directly on site in the control device is not replaced at the predetermined interval specified in §61.354(c) of this subpart.

(J) Each 3-hour period of operation during which the parameters monitored are outside the range of values specified in §61.349(a)(2)(iv)(C), or any other periods specified by the Administrator for a control device subject to the requirements of §61.349(a)(2)(iv).

(v) For a cover and closed-vent system monitored in accordance with §61.354(g), the owner or operator shall submit a report quarterly to the Administrator that identifies any period in which the pressure in the waste management unit is equal to or greater than atmospheric pressure.

(8) Beginning one year after the date that the equipment necessary to comply with these standards has been certified in accordance with paragraph (d)(1) of this section, the owner or operator shall submit annually to the Administrator a report that summarizes all inspections required by §§61.342 through 61.354 during which detectable emissions are measured or a problem (such as a broken seal, gap or other problem) that could result in benzene emissions is identified, including information about the repairs or corrective action taken.

(e) An owner or operator electing to comply with the provisions of §§61.351 or 61.352 of this subpart shall notify the Administrator of the alternative standard selected in the report required under §61.07 or §61.10 of this part.

(f) An owner or operator who elects to install and operate the control equipment in §61.351 of this subpart shall comply with the reporting requirements in 40 CFR 60.115b.

(g) An owner or operator who elects to install and operate the control equipment in §61.352 of this subpart shall submit initial and quarterly reports that identify all seal gap measurements, as required in 40 CFR 60.693–2(a), that are outside the prescribed limits.

[55 FR 8346, Mar. 7 1990; 55 FR 12444, Apr. 3, 1990, as amended at 55 FR 37231, Sept. 10, 1990; 58 FR 3105, Jan. 7, 1993; 65 FR 62161, Oct. 17, 2000]

## **§ 61.358 Delegation of authority.**

(a) In delegating implementation and enforcement authority to a State under section 112(d) of the Clean Air Act, the authorities contained in paragraph (b) of this section shall be retained by the Administrator and not transferred to a State.

(b) Alternative means of emission limitation under §61.353 of this subpart will not be delegated to States.

§ 61.359 [Reserved]

Appendix A to Part 61

APPENDIX A

National Emission Standards for Hazardous Air Pollutants  
Compliance Status Information

1. SOURCE REPORT

INSTRUCTIONS: Owners or operators of sources of hazardous pollutants subject to the National Emission Standards for Hazardous Air Pollutants are required to submit the information contained in Section 1 to the appropriate U.S. Environmental Protection Agency Regional Office prior to 90 days after the effective date of any standards or amendments which require the submission of such information.

A list of regional offices is provided in 161.04.

A. SOURCE INFORMATION

1. Identification/Location - Indicate the name and address of each source.

1 Region	2 State	3 County	4 Source Number	5 0 0 0	6 16	7 0 0	8 18	9 19
20 22	23 26	27	Source Name			46		
47 Street Address (Location of Plant)								
Dup 1-18 19 20 City Name 34 State 35 39								
48 Scale Regis. Number 54 55 58								
59 SIC 62 FF 64 65 77 Staff 79 80								
Dup 1-18 5 19 25 30 31 49 50								

2. Contact - Indicate the name and telephone number of the owner or operator or other responsible official whom EPA may contact concerning this report.

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Dup 1-18	4 1	19 20	21	Name			43
44	46	47	48	54	80		
3. Source Description - Briefly state the nature of the source (e.g., "Chlor-alkali Plant" or "Machine Shop").							
Dup 1-18	4 2	19 20	21	Description			50
51 Continued 79 80							
4. Alternative Mailing Address - Indicate an alternative mailing address if correspondence is to be directed to a location different than that specified above.							
Dup 1-18	4 3	19 20	21	Number Street or Box Number			65 80
Dup 1-18	4 4	19 20	21	35	37 38	41 42	44 45
5. Compliance Status - The emissions from this source can cannot meet the emission limitations contained in the National Emission Standards on or prior to 90 days after the effective date of any standards or amendments which require the submission of such information.							

Signature of Owner, Operator or Other Responsible Official

NOTE: If the emissions from the source will exceed those limits set by the National Emission Standards for Hazardous Air Pollutants, the source will be in violation and subject to Federal enforcement actions unless granted a waiver of compliance by the Administrator of the U.S. Environmental Protection Agency. The information needed for such waivers is listed in Section 11 of this form.

- B. PROCESS INFORMATION. Part B should be completed separately for each point of emission for each hazardous pollutant. [Sources subject to 61.22(i) may omit number 4. below.]

Dup 1-13	13 14	17 18	19	20	21	22	23	24	25	26	27	28	29	30	31
NEQS X Ref L3 SIP															

1. **Pollutant Emitted** - Indicate the type of hazardous pollutant emitted by the process. Indicate "AS" for asbestos, "BE" for beryllium, or "HG" for mercury.

32	33	Regulation		48	49
Pollutant					EC

2. **Process Description** - Provide a brief description of each process (e.g., "hydrogen end box" in a mercury chlor-alkali plant, "grinding machine" in a beryllium machine shop). Use additional sheets if necessary.

50	Process Description			74	80
Dup 1-18 6.1 19 20 21 50					
51				79	80
Dup 1-18 6.2 19 20 21 50					
51				79	80

3. **Amount of Pollutant** - Indicate the average weight of the hazardous material named in Item 1 which enters the process in pounds per month (based on the previous twelve months of operation).

Dup 1-18	6.3	19	20	21	27	29	lbs./mo.	36	80
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4. **Control Devices**

- a. Indicate the type of pollution control devices, if any, used to reduce the emissions from the process (e.g., venturi scrubber, baghouse, wet cyclone) and the estimated percent of the pollutant which the device removes from the process gas stream.

Dup 1-18	6.4	19	20	21	PRIMARY CONTROL DEVICE:			43
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45	Primary Device Name		64	66	70	Percent Removal Efficiency	72	79
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BT
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Dup 1-18	6.5	19	20	21	SECONDARY CONTROL DEVICES:			45
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47	Secondary Device Name		64	66	70	Percent Removal Efficiency	72	79	80
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- b. **Asbestos Emission Control Devices Only**

1. If a baghouse is specified in Item 4a, give the following information:

- The air flow permeability in cubic feet per minute per square foot of fabric area.

Air flow permeability = \_\_\_\_\_ cfm/ft<sup>2</sup>

- The pressure drop in inches water gauge across the filter at which the baghouse is operated.

Operating pressure drop = \_\_\_\_\_ inches w.g.

- If the baghouse material contains synthetic fill yarn, check whether this material is / / spun / / or not spun.

- If the baghouse utilizes a felted fabric, give the minimum thickness in inches and the density in ounces per square yard.

Thickness = \_\_\_\_\_ inches Density = \_\_\_\_\_ oz/yd<sup>2</sup>

11. If a wet collection device is specified in Item 4a, give the designed unit contacting energy in inches water gauge.

Unit contacting energy = \_\_\_\_\_ inches w.g.

- c. **DISPOSAL OF ASBESTOS-CONTAINING WASTES.** Part C should be completed separately for each asbestos-containing waste generation operation arising from sources subject to 161.22(a), (c), (e), and (h).

Dup 1-13	14	16	00	17	18	19	20	500	27	28	29	30	31
MEDS X Ref CS SIP													
A B	32	33	Regulation		48	49							
Pollutant							EC						



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1. Waste Generation - Provide a brief description of each process that generates asbestos-containing waste (e.g., disposal of control device wastes).

5J \_\_\_\_\_ Process Description \_\_\_\_\_ 79 80

2. Asbestos Concentration - Indicate the average percentage asbestos content of these materials.

Dup 1-18 6.1 \_\_\_\_\_ ASBESTOS CONCENTRATION: \_\_\_\_\_ 43 45 48  
19 20 21  
5 80  
50

3. Amount of Wastes - Indicate the average weight of asbestos-containing wastes disposed of, measured in kg/day.

Dup 1-18 6.2 \_\_\_\_\_ kg/day \_\_\_\_\_ 80  
19 20 21 27 28 36

4. Control Methods - Indicate the emission control methods used in all stages of waste disposal, from collection, processing, and packaging to transporting and deposition.

Dup 1-18 6.3 \_\_\_\_\_ Primary Control Method \_\_\_\_\_ 43  
19 20 21

45 \_\_\_\_\_ 79 80

Dup 1-18 6.4 \_\_\_\_\_ 50  
19 20 21

51 \_\_\_\_\_ 79 80

5. Waste Disposal - Indicate the type of disposal site (sanitary landfill, open, covered) or incineration site (municipal, private) where the waste is disposed of and who operates the site (company, private, municipal). State the name and location of the site (closest city or town, county, state).

Dup 1-18 6.5 \_\_\_\_\_ TYPE OF SITE: \_\_\_\_\_ 33 35 50  
19 20 21

51 \_\_\_\_\_ 79 80

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Dup 1-18 6.6 OPERATOR: 21 29 31 50  
 19 20 79 80  
 Dup 1-18 6.7 LOCATION: 21 29  
 31 70  
 71 79 80

D. WASTE DISPOSAL SITES. Part D should be completed separately for each asbestos waste disposal site subject to section 61.22(f).

Dup 1-13 14 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31  
 HEDS & Ref CS 51P  
 A B  
 32 33 Regulation 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50  
 Pollutant EC  
 WASTE DISPOSAL SITE 51 52 53 54 55 56 57 58 59 60

1. Description - Provide a brief description of the site, including its size and configuration, and the distance to the closest city or town, closest residence, and closest primary road.

Cup 1-18 6.1 SITE DESCRIPTION 21 29 31 50  
 19 20 79 80  
 Dup 1-18 6.2 DISTANCE: 21 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43  
 19 20 79 80  
 RESIDENCE: 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60  
 K M ROAD: 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75  
 K M 76 77 78 79 80

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2. Inactivation - After the site is inactivated, indicate the method or methods used to comply with the standard and send a list of the actions that will be undertaken to maintain the inactivated site.

Dup 1-18 6.8 COMPLIANCE METHOD/INACTIVE SITE: 21 29 31 50  
 19 20 79 80  
 51 52 53 54 55 56 57 58 59 60

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## II. Waiver Requests

A. *Waiver of Compliance.* Owners or operators of sources unable to operate in compliance with the National Emission Standards for Hazardous Air Pollutants prior to 90 days after the effective date of any standards or amendments which require the submission of such information may request a waiver of compliance from the Administrator of the U.S. Environmental Protection Agency for the time period necessary to install appropriate control devices or make modifications to achieve compliance. The Administrator may grant a waiver of compliance with the standard for a period not exceeding two years from the effective date of the hazardous pollutant standards, if he finds that such period is necessary for the installation of controls and that steps will be taken during the period of the waiver to assure that the health of persons will be protected from imminent endangerment.

The report information provided in Section I must accompany this application. Applications should be sent to the appropriate EPA regional office.

1. *Processes Involved* —Indicate the process or processes emitting hazardous pollutants to which emission controls are to be applied.

2. *Controls*

a. Describe the proposed type of control device to be added or modification to be made to the process to reduce the emission of hazardous pollutants to an acceptable level. (Use additional sheets if necessary.)

b. Describe the measures that will be taken during the waiver period to assure that the health of persons will be protected from imminent endangerment. (Use additional sheets if necessary.)

3. *Increments of Progress* —Specify the dates by which the following increments of progress will be met.

Date by which contracts for emission control systems or process modifications will be awarded; or date by which orders will be issued for the purchase of the component parts to accomplish emission control or process modification.

Dup 1-16      0 1 7  
17 19 53 54 55 60 61 MO/DY/YR 66 80  
Date of initiation of on-site construction or installation of  
emission control equipment or process change.

Dup 1-16      0 2 7  
17 19 53 54 55 60 61 MO/DY/YR 66 80  
Date by which on-site construction or installation of emission control  
equipment or process modification is to be completed.

Dup 1-16      0 3 7  
17 19 53 54 55 60 61 MO/DY/YR 66 80  
Date by which final compliance is to be achieved.

Dup 1-16      0 4 7  
17 19 53 54 55 60 61 MO/DY/YR 66 80

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B. *Waiver of Emission Tests.* A waiver of emission testing may be granted to owners or operators of sources subject to emission testing if, in the judgment of the Administrator of the Environmental Protection Agency the emissions from the source comply with the appropriate standard or if the owners or operators of the source have requested a waiver of compliance or have been granted a waiver of compliance.

This application should accompany the report information provided in Section I.

1. *Reason* —State the reasons for requesting a waiver of emission testing. If the reason stated is that the emissions from the source are within the prescribed limits, documentation of this condition must be attached.

\_\_\_\_\_  
Date/Signature of the owner or operator

(Sec. 114, of the Clean Air Act as amended (42 U.S.C. 7414))

[40 FR 48303, Oct. 14, 1975, as amended at 43 FR 8800, Mar. 3, 1978; 50 FR 46295, Sept. 9, 1985]

## Appendix B to Part 61—Test Methods

Method 101—Determination of particulate and gaseous mercury emissions from chlor-alkali plants (air streams)

Method 101A—Determination of particulate and gaseous mercury emissions from sewage sludge incinerators

Method 102—Determination of particulate and gaseous mercury emissions from chlor-alkali plants (hydrogen streams)

Method 103—Beryllium screening method

Method 104—Determination of beryllium emissions from stationary sources

Method 105—Determination of mercury in wastewater treatment plant sewage sludges

Method 106—Determination of vinyl chloride emissions from stationary sources

Method 107—Determination of vinyl chloride content of in-process wastewater samples, and vinyl chloride content of polyvinyl chloride resin slurry, wet cake, and latex samples

Method 107A—Determination of vinyl chloride content of solvents, resin-solvent solution, polyvinyl chloride resin, resin slurry, wet resin, and latex samples

Method 108—Determination of particulate and gaseous arsenic emissions

Method 108A—Determination of arsenic content in ore samples from nonferrous smelters

Method 108B—Determination of arsenic content in ore samples from nonferrous smelters

Method 108C—Determination of arsenic content in ore samples from nonferrous smelters (molybdenum blue photometric procedure)

Method 111—Determination of Polonium—210 emissions from stationary sources

Method 101—Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants (Air Streams)

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg)	7439-97-6	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Hg emissions, including both particulate and gaseous Hg, from chlor-alkali plants and other sources (as specified in the regulations) where the carrier-gas stream in the duct or stack is principally air.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICl) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

#### 3.0 Definitions[Reserved]

#### 4.0 Interferences

4.1 Sample Collection. Sulfur dioxide (SO<sub>2</sub>) reduces ICl and causes premature depletion of the ICl solution.

4.2 Sample Analysis.

4.2.1 ICl concentrations greater than 10<sup>-4</sup> molar inhibit the reduction of the Hg (II) ion in the aeration cell.

4.2.2 Condensation of water vapor on the optical cell windows causes a positive interference.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to tissues. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.3 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. 3 mg/m<sup>3</sup> will cause lung damage. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

## 6.0 Equipment and Supplies.

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 101–1; it is similar to the Method 5 sampling train. The following items are required for sample collection:

6.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1, 6.1.1.3, 6.1.1.4, 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature of 120 ±14 °C (248 ±25 °F) at the probe exit during sampling may be used to prevent water condensation.

**Note:** Do not use metal probe liners.

6.1.3 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, impingers that are modified by replacing the tip with a 13-mm ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask may be used.

6.1.4 Acid Trap. Mine Safety Appliances air line filter, Catalog number 81857, with acid absorbing cartridge and suitable connections, or equivalent.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000- and 100-ml.

6.2.2 Graduated Cylinder. 250-ml.

6.2.3 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.4 Funnel. Glass, to aid in sample recovery.

6.3 Sample Preparation and Analysis. The following items are needed for sample preparation and analysis:

6.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, containing a hollow-cathode mercury lamp and the optical cell described in Section 6.3.2.

6.3.2 Optical Cell. Cylindrical shape with quartz end windows and having the dimensions shown in Figure 101-2. Wind the cell with approximately 2 meters (6 ft) of 24-gauge Nichrome wire, or equivalent, and wrap with fiberglass insulation tape, or equivalent; do not let the wires touch each other.

6.3.3 Aeration Cell. Constructed according to the specifications in Figure 101-3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 101-3.

6.3.4 Recorder. Matched to output of the spectrophotometer described in Section 6.3.1.

6.3.5 Variable Transformer. To vary the voltage on the optical cell from 0 to 40 volts.

6.3.6 Hood. For venting optical cell exhaust.

6.3.7 Flow Metering Valve.

6.3.8 Rate Meter. Rotameter, or equivalent, capable of measuring to within 2 percent a gas flow of 1.5 liters/min (0.053 cfm).

6.3.9 Aeration Gas Cylinder. Nitrogen or dry, Hg-free air, equipped with a single-stage regulator.

6.3.10 Tubing. For making connections. Use glass tubing (ungreased ball and socket connections are recommended) for all tubing connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. Teflon, steel, or copper tubing may be used between the nitrogen tank and flow metering valve (Section 6.3.7), and Tygon, gum, or rubber tubing between the flow metering valve and the aeration cell.

6.3.11 Flow Rate Calibration Equipment. Bubble flow meter or wet-test meter for measuring a gas flow rate of  $1.5 \pm 0.1$  liters/min ( $0.053 \pm 0.0035$  cfm).

6.3.12 Volumetric Flasks. Class A with penny head standard taper stoppers; 100-, 250-, 500-, and 1000-ml.

6.3.13 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, and 5-ml.

6.3.14 Graduated Cylinder. 50-ml.

6.3.15 Magnetic Stirrer. General-purpose laboratory type.

6.3.16 Magnetic Stirring Bar. Teflon-coated.

6.3.17 Balance. Capable of weighing to  $\pm 0.5$  g.

6.3.18 Alternative Analytical Apparatus. Alternative systems are allowable as long as they meet the following criteria:

6.3.18.1 A linear calibration curve is generated and two consecutive samples of the same aliquot size and concentration agree within 3 percent of their average.

6.3.18.2 A minimum of 95 percent of the spike is recovered when an aliquot of a source sample is spiked with a known concentration of Hg (II) compound.

6.3.18.3 The reducing agent should be added after the aeration cell is closed.

6.3.18.4 The aeration bottle bubbler should not contain a frit.

6.3.18.5 Any Tygon tubing used should be as short as possible and conditioned prior to use until blanks and standards yield linear and reproducible results.

6.3.18.6 If manual stirring is done before aeration, it should be done with the aeration cell closed.

6.3.18.7 A drying tube should not be used unless it is conditioned as the Tygon tubing above.

## 7.0 Reagents and Standards

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society; where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 (incorporated by reference—see §61.18), Type 1. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the  $\text{KMnO}_4$  test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

7.1.2 Nitric Acid, 50 Percent (v/v). Mix equal volumes of concentrated  $\text{HNO}_3$  and water, being careful to add the acid to the water slowly.

7.1.3 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. The tester may use new silica gel as received.

7.1.4 Potassium Iodide (KI) Solution, 25 Percent. Dissolve 250 g of KI in water, and dilute to 1 liter.

7.1.5 Iodine Monochloride Stock Solution, 1.0 M. To 800 ml of 25 percent KI solution, add 800 ml of concentrated HCl. Cool to room temperature. With vigorous stirring, slowly add 135 g of potassium iodate ( $\text{KIO}_3$ ), and stir until all free iodine has dissolved. A clear orange-red solution occurs when all the  $\text{KIO}_3$  has been added. Cool to room temperature, and dilute to 1800 ml with water. Keep the solution in amber glass bottles to prevent degradation.

7.1.6 Absorbing Solution, 0.1 M ICl. Dilute 100 ml of the 1.0 M ICl stock solution to 1 liter with water. Keep the solution in amber glass bottles and in darkness to prevent degradation. This reagent is stable for at least two months.

7.2 Sample Preparation and Analysis. The following reagents and standards are required for sample preparation and analysis:

7.2.1 Reagents.

7.2.1.1 Tin (II) Solution. Prepare fresh daily, and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with water. Do not substitute  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or other strong acids for the HCl.

7.2.1.2 Sulfuric Acid, 5 Percent (v/v). Dilute 25 ml of concentrated  $\text{H}_2\text{SO}_4$  to 500 ml with water.

7.2.2 Standards

7.2.2.1 Hg Stock Solution, 1 mg Hg/ml. Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 ml of water in a 100-ml glass volumetric flask. Add 10 ml of concentrated  $\text{HNO}_3$ , and adjust the volume to exactly 100 ml with water. Mix thoroughly. This solution is stable for at least one month.

7.2.2.2 Intermediate Hg Standard Solution, 10 µg Hg/ml. Prepare fresh weekly. Pipet 5.0 ml of the Hg stock solution (Section 7.2.2.1) into a 500-ml glass volumetric flask, and add 20 ml of the 5 percent  $\text{H}_2\text{SO}_4$  solution. Dilute to exactly 500 ml with water. Thoroughly mix the solution.

7.2.2.3 Working Hg Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml of the intermediate Hg standard solution (Section 7.2.2.2) into a 250-ml volumetric glass flask. Add 10 ml of the 5 percent  $\text{H}_2\text{SO}_4$  and 2 ml of the 0.1 M ICl absorbing solution taken as a blank (Section 8.7.4.3), and dilute to 250 ml with water. Mix thoroughly.

## 8.0 Sample Collection, Preservation, Transport, and Storage

Because of the complexity of this method, testers should be trained and experienced with the test procedures to ensure reliable results. Since the amount of Hg that is collected generally is small, the method must be carefully applied to prevent contamination or loss of sample.

8.1 Pretest Preparation. Follow the general procedure outlined in Method 5, Section 8.1, except omit Sections 8.1.2 and 8.1.3.

8.2 Preliminary Determinations. Follow the general procedure outlined in Method 5, Section 8.2, with the exception of the following:

8.2.1 Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.2.2 Perform test runs such that samples are obtained over a period or periods that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, run sufficient tests for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours is recommended. In some instances, high Hg or high SO<sub>2</sub> concentrations make it impossible to sample for the desired minimum time. This is indicated by reddening (liberation of free iodine) in the first impinger. In these cases, the sample run may be divided into two or more subruns to ensure that the absorbing solution is not depleted.

8.3 Preparation of Sampling Train.

8.3.1 Clean all glassware (probe, impingers, and connectors) by rinsing with 50 percent HNO<sub>3</sub>, tap water, 0.1 M ICl, tap water, and finally deionized distilled water. Place 100 ml of 0.1 M ICl in each of the first three impingers. Take care to prevent the absorbing solution from contacting any greased surfaces. Place approximately 200 g of preweighed silica gel in the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g.

8.3.2 Install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F). Use a fiberglass string gasket if temperatures are higher. See APTD-0576 (Reference 3 in Method 5) for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.3 Assemble the train as shown in Figure 101-1, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion (see APTD-0576) to avoid the possibility of contamination by the silicone grease.

**Note:** An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

8.3.4 After the sampling train has been assembled, turn on and set the probe heating system, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

8.4 Leak-Check Procedures. Follow the leak-check procedures outlined in Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure outlined in Method 5, Section 8.5. For each run, record the data required on a data sheet such as the one shown in Figure 101-4.

8.6 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.7 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

8.7.1 Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle, and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling. Capping would create a vacuum and draw liquid out from the impingers.

8.7.2 Before moving the sampling train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.



8.7.3 Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

8.7.4 Inspect the train before and during disassembly, and note any abnormal conditions. Treat the samples as follows.

8.7.4.1 Container No. 1 (Impingers and Probe).

8.7.4.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present (e.g., see Figure 5–6 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only glass storage bottles and graduated cylinders that have been precleaned as in Section 8.3.1) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

8.7.4.1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, and probe liner as follows: Rinse these components with two 50-ml portions of 0.1 M ICl. Next, rinse the probe nozzle, fitting and liner, and each piece of connecting glassware between the probe liner and the back half of the third impinger with a maximum of 400 ml of water. Add all washings to the 1000-ml glass sample bottle containing the liquid from the first three impingers.

8.7.4.1.3 After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the liquid to determine later whether leakage occurred during transport. Label the container to identify clearly its contents.

8.7.4.2 Container No. 2 (Silica Gel). Same as Method 5, Section 8.7.6.3.

8.7.4.3 Container No. 3 (Absorbing Solution Blank). Place 50 ml of the 0.1 M ICl absorbing solution in a 100-ml sample bottle. Seal the container. Use this blank to prepare the working Hg standard solution (Section 7.2.2.3).

## 9.0 Quality Control

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4 10.2	Sampling equipment leak-checks and calibration	Ensure accuracy and precision of sampling measurements.
10.5, 10.6	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3.3	Check for matrix effects	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Before use, clean all glassware, both new and used, as follows: brush with soap and tap water, liberally rinse with tap water, soak for 1 hour in 50 percent HNO<sub>3</sub>, and then rinse with deionized distilled water.

10.2 Sampling Equipment. Calibrate the sampling equipment according to the procedures outlined in the following sections of Method 5: Section 10.1 (Probe Nozzle), Section 10.2 (Pitot Tube Assembly), Section 10.3 (Metering System), Section 10.5 (Temperature Sensors), Section 10.6 (Barometer).

10.3 Aeration System Flow Rate Meter. Assemble the aeration system as shown in Figure 101–5. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flow metering valve and

a bubble flowmeter or wet-test meter to obtain a flow rate of  $1.5 \pm 0.1$  liters/min ( $0.053 \pm 0.0035$  cfm) through the aeration cell. After the calibration of the aeration system flow rate meter is complete, remove the bubble flowmeter from the system.

10.4 Optical Cell Heating System. Using a 50-ml graduated cylinder, add 50 ml of water to the bottle section of the aeration cell, and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell and while aerating at  $1.5 \pm 0.1$  liters/min ( $0.053 \pm 0.0035$  cfm), determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

#### 10.5 Spectrophotometer and Recorder.

10.5.1 The Hg response may be measured by either peak height or peak area.

Note: The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). Therefore, to obtain reproducible results, bring all solutions to room temperature before use.

10.5.2 Set the spectrophotometer wavelength at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 50-ml graduated cylinder, add 50 ml of water to the aeration cell bottle. Add three drops of Antifoam B to the bottle, and then pipet 5.0 ml of the working Hg standard solution into the aeration cell.

Note: Always add the Hg-containing solution to the aeration cell after the 50 ml of water.

10.5.3 Place a Teflon-coated stirring bar in the bottle. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101-3) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Pipet 5 ml of tin (II) reducing solution into the aeration cell through the side arm, and immediately stopper the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

#### 10.6 Calibration Curve.

10.6.1 After setting the recorder scale, repeat the procedure in Section 10.5 using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value.

Note: To prevent Hg carryover from one sample to another, do not close the aeration cell from the optical cell until the recorder pen has returned to the baseline.)

10.6.2 It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-ml beaker containing approximately 400 ml of water. Rinse the bottle section of the aeration cell with a stream of water to remove all traces of the tin (II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with water. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) A white film appears on any inside surface of the aeration cell, (2) the calibration curve changes suddenly, or (3) the replicate samples do not yield reproducible results.

10.6.3 Subtract the average peak height (or peak area) of the blank (0.0-ml aliquot)—which must be less than 2 percent of recorder full scale—from the averaged peak heights of the 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquot standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng), and draw the best fit straight line. This line should either pass through the origin or pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

## 11.0 Analytical Procedure

11.1 Sample Loss Check. Check the liquid level in each container to see whether liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses.

11.2 Sample Preparation. Treat each sample as follows:

11.2.1 Container No. 1 (Impingers and Probe). Carefully transfer the contents of Container No. 1 into a 1000-ml volumetric flask, and adjust the volume to exactly 1000 ml with water.

11.2.2 Dilutions. Pipet a 2-ml aliquot from the diluted sample from Section 11.2.1 into a 250-ml volumetric flask. Add 10 ml of 5 percent  $\text{H}_2\text{SO}_4$ , and adjust the volume to exactly 250 ml with water. This solution is stable for at least 72 hours.

Note: The dilution factor will be 250/2 for this solution.

11.3 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.3 through 10.6.

11.3.1 Mercury Samples. Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot (1 to 5 ml) of the diluted sample (from Section 11.2.2) until two consecutive peak heights agree within 3 percent of their average value. The peak maximum of an aliquot (except the 5-ml aliquot) must be greater than 10 percent of the recorder full scale. If the peak maximum of a 1.0-ml aliquot is off scale on the recorder, further dilute the original source sample to bring the Hg concentration into the calibration range of the spectrophotometer.

11.3.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.3.3 Check for Matrix Effects (optional). Use the Method of Standard Additions as follows to check at least one sample from each source for matrix effects on the Hg results. The Method of Standard Additions procedures described on pages 9-4 and 9-5 of the section entitled "General Information" of the Perkin Elmer Corporation Atomic Absorption Spectrophotometry Manual, Number 303-0152 (Reference 16 in Section 16.0) are recommended. If the results of the Method of Standard Additions procedure used on the single source sample do not agree to within  $\pm 5$  percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

11.4 Container No. 2 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

## 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, and Isokinetic Variation. Same as Method 5, Sections 12.2 through 12.5 and 12.11, respectively.

12.2 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity  $v_g$ .

12.3 Total Mercury.

12.3.1 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the solution blank (see Section 10.6.3). Use the calibration curve and these corrected averages to determine the final total weight of Hg in ng in the aeration cell for each source sample.

12.3.2 Correct for any dilutions made to bring the sample into the working range of the spectrophotometer. Then calculate the Hg in the original solution,  $m_{Hg}$ , as follows:

$$m_{Hg} = \left[ C_{Hg(AC)} (DF) (V_f) (10^{-3}) \right] / S \quad \text{Eq. 101-1}$$

Where:

$CHg(AC)$  = Total ng of Hg in aliquot analyzed (reagent blank subtracted).

DF = Dilution factor for the Hg-containing solution (before adding to the aeration cell; e.g., DF = 250/2 if the source samples were diluted as described in Section 11.2.2).

$V_f$  = Solution volume of original sample, 1000 ml for samples diluted as described in Section 11.2.1.

$10^{-3}$  = Conversion factor,  $\mu\text{g}/\text{ng}$ .

S = Aliquot volume added to aeration cell, ml.

12.4 Mercury Emission Rate. Calculate the daily Hg emission rate, R, using Equation 101-2. For continuous operations, the operating time is equal to 86,400 seconds per day. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K m_{Hg} V_s A_s (86,400 \times 10^{-6})}{\left[ V_{m(std)} + V_{w(std)} \right] (T_s / P_s)} \quad \text{Eq. 101-2}$$

Where:

$K_1$  = 0.3858 °K/mm Hg for metric units.

$K_1$  = 17.64 °R/in. Hg for English units.

$K_3$  =  $10^{-6}$  g/ $\mu\text{g}$  for metric units.

=  $2.2046 \times 10^{-9}$  lb/ $\mu\text{g}$  for English units.

$P_s$  = Absolute stack gas pressure, mm Hg (in. Hg).

t = Daily operating time, sec/day.

$T_s$  = Absolute average stack gas temperature, °K (°R).

$V_m(std)$  = Dry gas sample volume at standard conditions, scm (scf).

$V_w(std)$  = Volume of water vapor at standard conditions, scm (scf).

12.5 Determination of Compliance. Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

### 13.0 Method Performance

The following estimates are based on collaborative tests, wherein 13 laboratories performed duplicate analyses on two Hg-containing samples from a chlor-alkali plant and on one laboratory-prepared sample of known Hg concentration. The sample concentrations ranged from 2 to 65  $\mu\text{g}$  Hg/ml.

13.1 Precision. The estimated intra-laboratory and inter-laboratory standard deviations are 1.6 and 1.8 µg Hg/ml, respectively.

13.2 Accuracy. The participating laboratories that analyzed a 64.3 µg Hg/ml (in 0.1 M ICl) standard obtained a mean of 63.7 µg Hg/ml.

13.3 Analytical Range. After initial dilution, the range of this method is 0.5 to 120 µg Hg/ml. The upper limit can be extended by further dilution of the sample.

14.0 Pollution Prevention.[Reserved]

15.0 Waste Management.[Reserved]

16.0 References

Same as Method 5, Section 17.0, References 1–3, 5, and 6, with the addition of the following:

1. Determining Dust Concentration in a Gas Stream. ASME Performance Test Code No. 27. New York, NY. 1957.
2. DeVorkin, Howard, *et al.* Air Pollution Source Testing Manual. Air Pollution Control District. Los Angeles, CA. November 1963.
3. Hatch, W.R., and W.I. Ott. Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry. *Anal. Chem.* 40:2085–87. 1968.
4. Mark, L.S. Mechanical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York, NY. 1951.
5. Western Precipitation Division of Joy Manufacturing Co. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Bulletin WP-50. Los Angeles, CA. 1968.
6. Perry, J.H. Chemical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York, NY. 1960.
7. Shigehara, R.T., W.F. Todd, and W.S. Smith. Significance of Errors in Stack Sampling Measurements. *Stack Sampling News.* 1 (3):6–18. September 1973.
8. Smith, W.S., R.T. Shigehara, and W.F. Todd. A Method of Interpreting Stack Sampling Data. *Stack Sampling News.* 1 (2):8–17. August 1973.
9. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Annual Book of ASTM Standards, Part 23. ASTM Designation D 2928–71. Philadelphia, PA 1971.
10. Vennard, J.K. Elementary Fluid Mechanics. John Wiley and Sons, Inc. New York. 1947.
11. Mitchell, W.J. and M.R. Midgett. Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants. *J. APCA.* 26 :674–677. July 1976.
12. Shigehara, R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. *Stack Sampling News.* 2 :4–11. October 1974.
13. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.
14. Klein, R. and C. Hach. Standard Additions: Uses and Limitation in Spectrophotometric Measurements. *Amer. Lab.* 9 :21. 1977.
15. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut. September 1976.

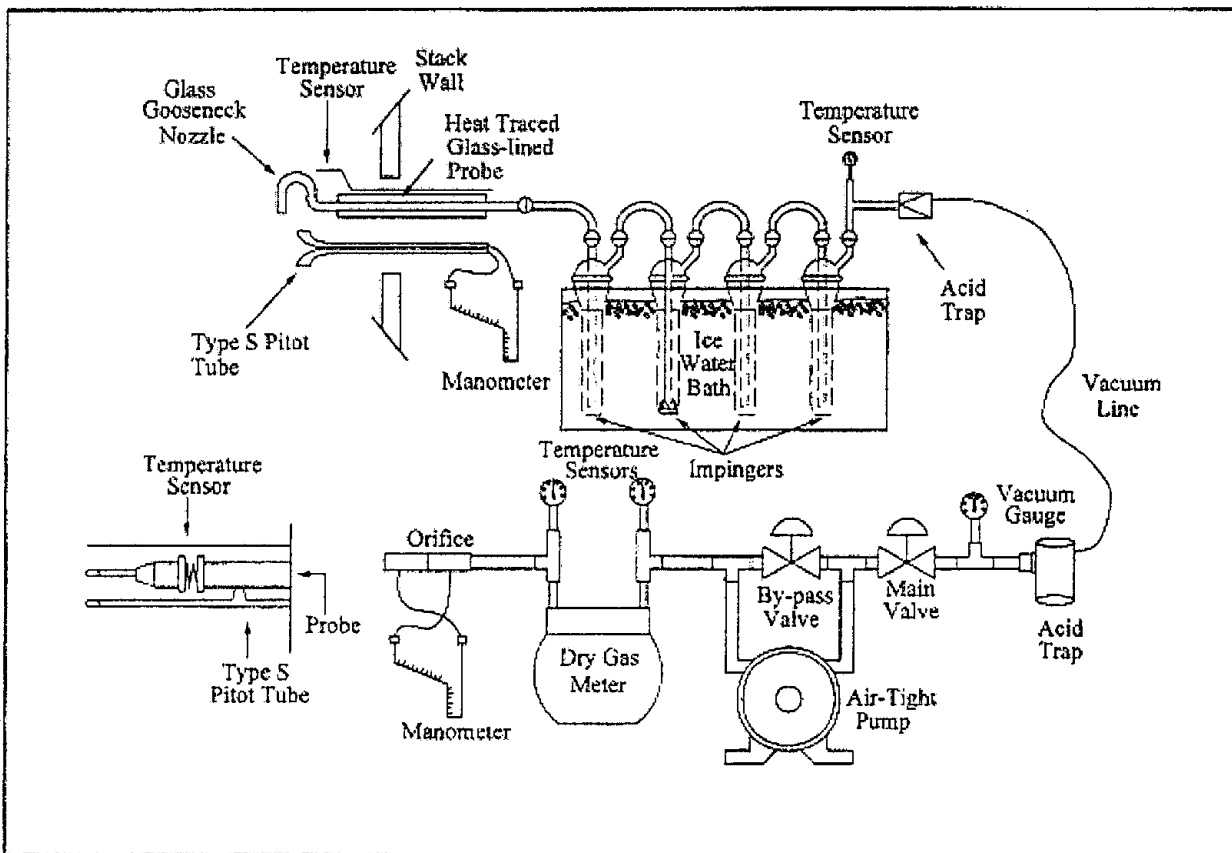


Figure 101-1. Mercury Sampling Train.

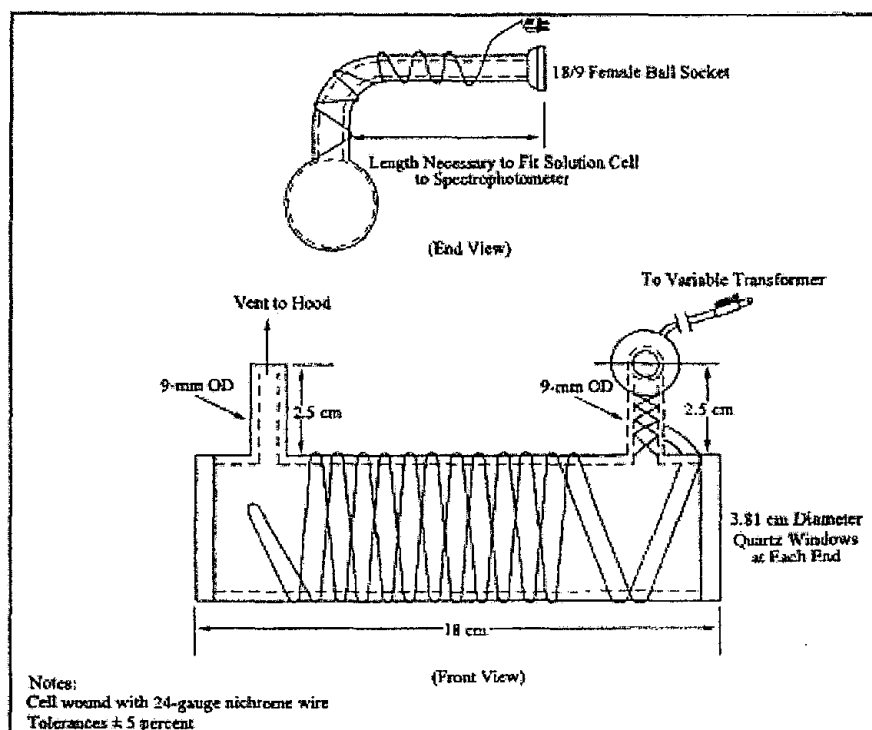


Figure 101-2. Optical Cell.

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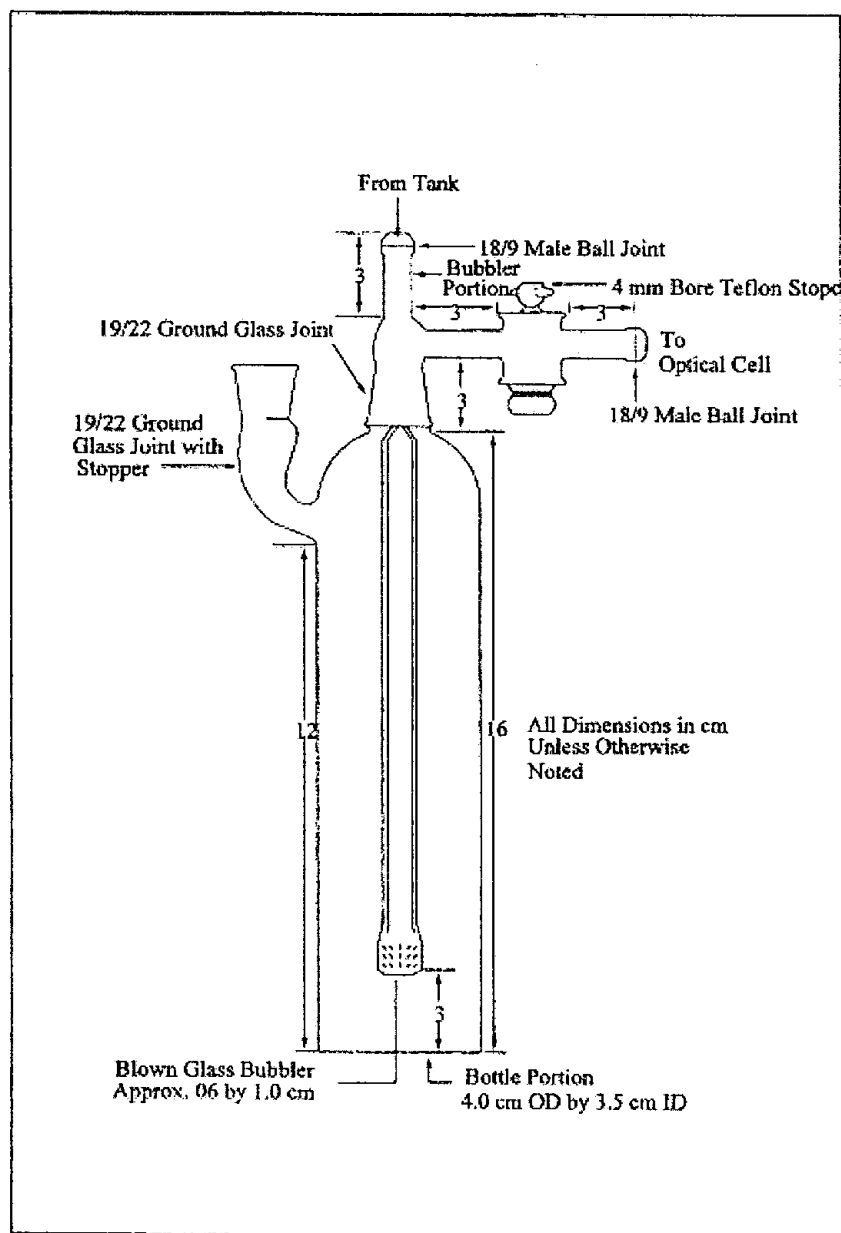


Figure 101-3. Aeration Cell.

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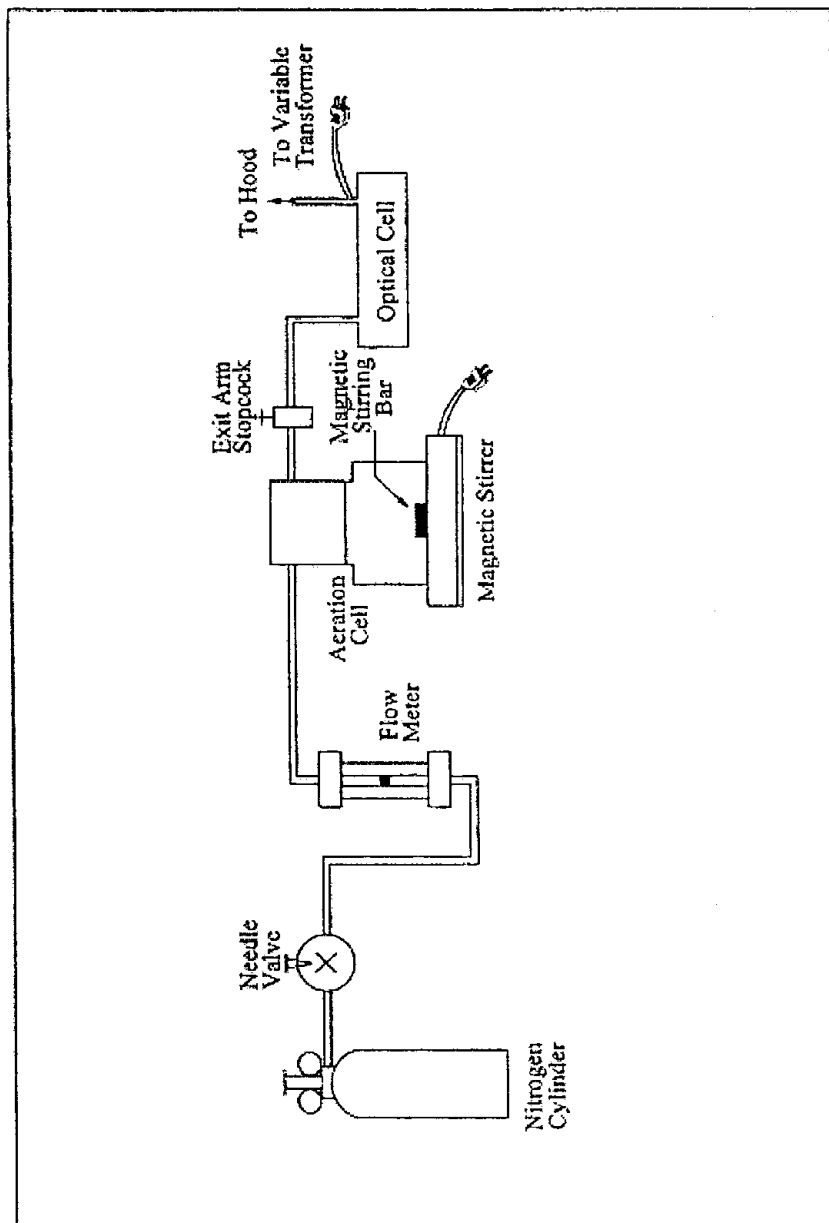


Figure 101-5. Schematic of Aeration System.

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Method 101A—Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60 and in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Methods 1, Method 2, Method 3, and Method 5 of part 60 (appendix A), and Method 101 part 61 (appendix B).

#### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg)	7439-97-6	Dependent upon spectrophotometer and recorder.

1.2 Applicability. This method is applicable for the determination of Hg emissions from sewage sludge incinerators and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and are collected in acidic potassium permanganate (KMnO<sub>4</sub>) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

#### 3.0 Definitions.[Reserved]

#### 4.0 Interferences

4.1 Sample Collection. Excessive oxidizable organic matter in the stack gas prematurely depletes the KMnO<sub>4</sub> solution and thereby prevents further collection of Hg.

4.2 Analysis. Condensation of water vapor on the optical cell windows causes a positive interference.

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.3 Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Chlorine Evolution. Hydrochloric acid reacts with KMnO<sub>4</sub> to liberate chlorine gas. Although this is a minimal concern when small quantities of HCl (5–10 ml) are used in the impinger rinse, a potential safety hazard may still exist. At sources that emit higher concentrations of oxidizable materials ( e.g., power plants), more HCl may be required to remove the larger amounts of brown deposit formed in the impingers. In such cases, the potential safety hazards due to sample container pressurization are greater, because of the larger volume of HCl rinse added to the recovered sample. These hazards are eliminated by storing and analyzing the HCl impinger wash separately from the permanganate impinger sample.

## 6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 101, Sections 6.1 and 6.2, respectively, with the following exceptions:

6.1.1 Probe Liner. Same as in Method 101, Section 6.1.2, except that if a filter is used ahead of the impingers, the probe heating system must be used to minimize the condensation of gaseous Hg.

6.1.2 Filter Holder (Optional). Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of  $120 \pm 14$  °C ( $248 \pm 25$  °F) during sampling to minimize both water and gaseous Hg condensation. A filter may also be used in cases where the stream contains large quantities of particulate matter.

6.2 Sample Analysis. Same as Method 101, Section 6.3, with the following additions and exceptions:

6.2.1 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

6.2.2 Graduated Cylinder. 25-ml.

6.2.3 Steam Bath.

6.2.4 Atomic Absorption Spectrophotometer or Equivalent. Any atomic absorption unit with an open sample presentation area in which to mount the optical cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2.5 Optical Cell. Alternatively, a heat lamp mounted above the cell or a moisture trap installed upstream of the cell may be used.

6.2.6 Aeration Cell. Alternatively, aeration cells available with commercial cold vapor instrumentation may be used.

6.2.7 Aeration Gas Cylinder. Nitrogen, argon, or dry, Hg-free air, equipped with a single-stage regulator. Alternatively, aeration may be provided by a peristaltic metering pump. If a commercial cold vapor instrument is used, follow the manufacturer's recommendations.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection and Recovery. The following reagents are required for sample collection and recovery:

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 Type 1. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the  $\text{KMnO}_4$  test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

7.1.2 Nitric Acid, 50 Percent (V/V). Mix equal volumes of concentrated  $\text{HNO}_3$  and water, being careful to add the acid to the water slowly.

7.1.3 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received.

7.1.4 Filter (Optional). Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3- $\mu\text{m}$  dioctyl phthalate smoke particles. The filter in cases where the gas stream contains large quantities of particulate matter, but blank filters should be analyzed for Hg content.

7.1.5 Sulfuric Acid, 10 Percent (V/V). Carefully add and mix 100 ml of concentrated  $\text{H}_2\text{SO}_4$  to 900 ml of water.

7.1.6 Absorbing Solution, 4 Percent  $\text{KMnO}_4$ (W/V). Prepare fresh daily. Dissolve 40 g of  $\text{KMnO}_4$  in sufficient 10 percent  $\text{H}_2\text{SO}_4$  to make 1 liter. Prepare and store in glass bottles to prevent degradation.

7.1.7 Hydrochloric Acid, 8 N. Carefully add and mix 67 ml of concentrated HCl to 33 ml of water.

7.2 Sample Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Tin (II) Solution. Prepare fresh daily, and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with water. Do not substitute  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , or other strong acids for the HCl.

7.2.3 Sodium Chloride-Hydroxylamine Solution. Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in water and dilute to 100 ml.

7.2.4 Hydrochloric Acid, 8 N. Same as Section 7.1.7.

7.2.5 Nitric Acid, 15 Percent (V/V). Carefully add 15 ml  $\text{HNO}_3$  to 85 ml of water.

7.2.6 Antifoam B Silicon Emulsion. J.T. Baker Company (or equivalent).

7.2.7 Mercury Stock Solution, 1 mg Hg/ml. Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 ml of water. Add 10 ml of concentrated  $\text{HNO}_3$ , and adjust the volume to exactly 100 ml with water. Mix thoroughly. This solution is stable for at least one month.

7.2.8 Intermediate Hg Standard Solution, 10  $\mu\text{g}/\text{ml}$ . Prepare fresh weekly. Pipet 5.0 ml of the Hg stock solution (Section 7.2.7) into a 500 ml volumetric flask, and add 20 ml of 15 percent  $\text{HNO}_3$  solution. Adjust the volume to exactly 500 ml with water. Thoroughly mix the solution.

7.2.9 Working Hg Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Hg Standard Solution" (Section 7.2.8) into a 250-ml volumetric flask. Add 5 ml of 4 percent  $\text{KMnO}_4$  absorbing solution and 5 ml of 15 percent  $\text{HNO}_3$ . Adjust the volume to exactly 250 ml with water. Mix thoroughly.

7.2.10 Potassium Permanganate, 5 Percent (W/V). Dissolve 5 g of  $\text{KMnO}_4$  in water and dilute to 100 ml.

7.2.11 Filter. Whatman No. 40, or equivalent.

## 8.0 Sample Collection, Preservation, Transport, and Storage

Same as Method 101, Section 8.0, with the exception of the following:

8.1 Preliminary Determinations. Same as Method 101, Section 8.2, except that the liberation of free iodine in the first impinger due to high Hg or sulfur dioxide concentrations is not applicable. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the  $\text{KMnO}_4$  solution. In cases where an excess of water condensation is encountered, collect two runs to make one sample, or add an extra impinger in front of the first impinger (also containing acidified  $\text{KMnO}_4$  solution).

8.2 Preparation of Sampling Train. Same as Method 101, Section 8.3, with the exception of the following:

8.2.1 In this method, clean all the glass components by rinsing with 50 percent  $\text{HNO}_3$ , tap water, 8 N HCl, tap water, and finally with deionized distilled water. Then place 50 ml of absorbing solution in the first impinger and 100 ml in each of the second and third impingers.

8.2.2 If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter, and place the gasket in the proper position to prevent the sample gas stream from bypassing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

8.3 Sampling Train Operation. In addition to the procedure outlined in Method 101, Section 8.5, maintain a temperature around the filter (if applicable) of  $120 \pm 14$  °C ( $248 \pm 25$  °F).

8.4 Sample Recovery. Same as Method 101, Section 8.7, with the exception of the following:

8.4.1 Transfer the probe, impinger assembly, and (if applicable) filter assembly to the cleanup area.

8.4.2 Treat the sample as follows:

8.4.2.1 Container No. 1 (Impinger, Probe, and Filter Holder) and, if applicable, Container No. 1A (HCl rinse).

8.4.2.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present ( e.g., see Figure 5–6 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 8.2.1.) Place the contents of the first three impingers (four if an extra impinger was added as described in Section 8.1) into a 1000-ml glass sample bottle labeled Container No. 1.

Note: If a filter is used, remove the filter from its holder as outlined under Section 8.4.3.

8.4.2.1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, front half of the filter holder (if applicable), and impingers as follows: Rinse these components with a total of 400 ml (350 ml if an extra impinger was added as described in Section 8.1) of fresh absorbing solution, carefully assuring removal of all loose particulate matter from the impingers; add all washings to the 1000 ml glass sample bottle. To remove any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of water, carefully assuring removal of all loose particulate matter from the impingers. Add this rinse to Container No. 1.

8.4.2.1.3 If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. If deposits do remain on the glassware after the water rinse, wash impinger walls and stems with 25 ml of 8 N HCl, and place the wash in a separate container labeled Container No. 1A as follows: Place 200 ml of water in a sample container labeled Container No. 1A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Pour the HCl wash carefully with stirring into Container No. 1A.

8.4.2.1.4 After all washings have been collected in the appropriate sample container(s), tighten the lid(s) on the container(s) to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to allow subsequent determination of whether leakage has occurred during transport. Label each container to identify its contents clearly.

8.4.3 Container No. 2 (Silica Gel). Same as Method 5, Section 8.7.6.3.

8.4.4 Container No. 3 (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of absorbing solution. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 100-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to identify its contents clearly. Mark the height of the fluid level to allow subsequent determination of whether leakage has occurred during transport.

8.4.5 Container No. 4 (Filter Blank). If a filter was used, treat an unused filter from the same filter lot as that used for sampling according to the procedures outlined in Section 8.4.4.

8.4.6 Container No. 5 (Absorbing Solution Blank). Place 650 ml of 4 percent  $\text{KMnO}_4$  absorbing solution in a 1000-ml sample bottle. Seal the container.

8.4.7 Container No. 6 (HCl Rinse Blank). Place 200 ml of water in a 1000-ml sample bottle, and add 25 ml of 8 N HCl carefully with stirring. Seal the container. Only one blank sample per 3 runs is required.

## 9.0 Quality Control

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak-checks and calibration	Ensure accuracy and precision of sampling measurements.
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3.3	Check for matrix effects	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

#### 10.0 Calibration and Standardization

Same as Method 101, Section 10.0, with the following exceptions:

10.1 Optical Cell Heating System Calibration. Same as in Method 101, Section 10.4, except use a 25-ml graduated cylinder to add 25 ml of water to the bottle section of the aeration cell.

#### 10.2 Spectrophotometer and Recorder Calibration.

10.2.1 The Hg response may be measured by either peak height or peak area.

**Note:** The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.

10.2.2 Set the spectrophotometer wave length at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of water to the aeration cell bottle. Add three drops of Antifoam B to the bottle, and then pipet 5.0 ml of the working Hg standard solution into the aeration cell.

**Note:** Always add the Hg-containing solution to the aeration cell after the 25 ml of water.

10.2.3 Place a Teflon-coated stirring bar in the bottle. Add 5 ml of absorbing solution to the aeration bottle, and mix well. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Add sodium chloride-hydroxylamine in 1 ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm, and immediately stopper the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

#### 11.0 Analytical Procedure

11.1 Sample Loss Check. Check the liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses.

11.2 Sample Preparation. Treat sample containers as follows:

11.2.1 Containers No. 3 and No. 4 (Filter and Filter Blank).

11.2.1.1 If a filter is used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers, and heat the beakers on a steam bath until most of the liquid has evaporated. Do not heat to dryness. Add 20 ml

of concentrated  $\text{HNO}_3$  to the beakers, cover them with a watch glass, and heat on a hot plate at 70 °C (160 °F) for 2 hours. Remove from the hot plate.

11.2.1.2 Filter the solution from digestion of the Container No. 3 contents through Whatman No. 40 filter paper, and save the filtrate for addition to the Container No. 1 filtrate as described in Section 11.2.2. Discard the filter paper.

11.2.1.3 Filter the solution from digestion of the Container No. 4 contents through Whatman No. 40 filter paper, and save the filtrate for addition to Container No. 5 filtrate as described in Section 11.2.3 below. Discard the filter paper.

11.2.2 Container No. 1 (Impingers, Probe, and Filter Holder) and, if applicable, No. 1A (HCl rinse).

11.2.2.1 Filter the contents of Container No. 1 through Whatman No. 40 filter paper into a 1 liter volumetric flask to remove the brown manganese dioxide ( $\text{MnO}_2$ ) precipitate. Save the filter for digestion of the brown  $\text{MnO}_2$  precipitate. Add the sample filtrate from Container No. 3 to the 1-liter volumetric flask, and dilute to volume with water. If the combined filtrates are greater than 1000 ml, determine the volume to the nearest ml and make the appropriate corrections for blank subtractions. Mix thoroughly. Mark the filtrate as analysis Sample No. A.1 and analyze for Hg within 48 hr of the filtration step. Place the saved filter, which was used to remove the brown  $\text{MnO}_2$  precipitate, into an appropriate sized container. In a laboratory hood, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

11.2.2.2 Filter the contents of Container 1A through Whatman No. 40 filter paper into a 500-ml volumetric flask. Then filter the digestate of the brown  $\text{MnO}_2$  precipitate from Container No. 1 through Whatman No. 40 filter paper into the same 500-ml volumetric flask, and dilute to volume with water. Mark this combined 500 ml dilute solution as analysis Sample No. A.2. Discard the filters.

11.2.3 Container No. 5 (Absorbing Solution Blank) and No. 6 (HCl Rinse Blank).

11.2.3.1 Treat Container No. 5 as Container No. 1 (as described in Section 11.2.2), except substitute the filter blank filtrate from Container No. 4 for the sample filtrate from Container No. 3, and mark as Sample A.1 Blank.

11.2.3.2 Treat Container No. 6 as Container No. 1A, (as described in Section 11.2.2, except substitute the filtrate from the digested blank  $\text{MnO}_2$  precipitate for the filtrate from the digested sample  $\text{MnO}_2$  precipitate, and mark as Sample No. A.2 Blank.

**Note:** When analyzing samples A.1 Blank and HCl A.2 Blank, always begin with 10 ml aliquots. This applies specifically to blank samples.

11.3 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Section 10.0.

11.3.1 Mercury Samples. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 11.2.2 and 11.2.3) until two consecutive peak heights agree within 3 percent of their average value. If the 10 ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0 ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

11.3.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

11.3.3 Check for Matrix Effects (optional). Same as Method 101, Section 11.3.3.

## 12.0 Data Analysis and Calculations

**Note:** Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

### 12.1 Nomenclature.



$C(\text{filtr})\text{Hg}$ = Total ng of Hg in aliquot of  $\text{KMnO}_4$  filtrate and  $\text{HNO}_3$  digestion of filter analyzed (aliquot of analysis Sample No. A.1).

$C(\text{filtr blk})\text{Hg}$ = Total ng of Hg in aliquot of  $\text{KMnO}_4$  blank and  $\text{HNO}_3$  digestion of blank filter analyzed (aliquot of analysis Sample No. A.1 blank).

$C(\text{HCl blk})\text{Hg}$ = Total ng of Hg analyzed in aliquot of the 500-ml analysis Sample No. HCl A.2 blank.

$C(\text{HCl})\text{Hg}$ = Total ng of Hg analyzed in the aliquot from the 500-ml analysis Sample No. HCl A.2.

DF = Dilution factor for the HCl-digested Hg-containing solution, Analysis Sample No. "HCl A.2."

$DF_{\text{blk}}$  = Dilution factor for the HCl-digested Hg containing solution, Analysis Sample No. "HCl A.2 blank." (Refer to sample No. "HCl A.2" dilution factor above.)

$m(\text{filtr})\text{Hg}$ = Total blank corrected  $\mu\text{g}$  of Hg in  $\text{KMnO}_4$  filtrate and  $\text{HNO}_3$  digestion of filter sample.

$m(\text{HCl})\text{Hg}$ = Total blank corrected  $\mu\text{g}$  of Hg in HCl rinse and HCl digestate of filter sample.

$m_{\text{Hg}}$  = Total blank corrected Hg content in each sample,  $\mu\text{g}$ .

S = Aliquot volume of sample added to aeration cell, ml.

$S_{\text{blk}}$  = Aliquot volume of blank added to aeration cell, ml.

$V_f(\text{blk})$ = Solution volume of blank sample, 1000 ml for samples diluted as described in Section 11.2.2.

$V_f(\text{filtr})$ = Solution volume of original sample, normally 1000 ml for samples diluted as described in Section 11.2.2.

$V_f(\text{HCl})$ = Solution volume of original sample, 500 ml for samples diluted as described in Section 11.2.1.

$10^{-3}$  = Conversion factor,  $\mu\text{g}/\text{ng}$ .

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

### 12.3 Total Mercury.

12.3.1 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the blank. Use the calibration curve and these corrected averages to determine the final total weight of Hg in ng in the aeration cell for each source sample.

12.3.2 Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m_{\text{(HCl)Hg}} = \frac{[C_{\text{(HCl)Hg}} DF]}{S} - \frac{[C_{\text{(HCl)Hg blk}} DF_{\text{blk}}]}{S_{\text{blk}}} V_f(\text{HCl}) (10^{-3}) \quad \text{Eq. 101A-1}$$

Note: This dilution factor applies only to the intermediate dilution steps, since the original sample volume  $[(V_f)_{\text{HCL}}]$  of "HCl A.2" has been factored out in the equation along with the sample aliquot (S). In Eq. 101A-1, the sample aliquot, S, is introduced directly into the aeration cell for analysis according to the procedure outlined in Section 11.3.1. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range.

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (analysis Sample No. HCl A.2 blank), or (2) 5% of the Hg content in the combined HCl rinse and digested sample (analysis Sample No. HCl A.2).

$$m_{(ftr)Hg} = \frac{[C_{(ftr)Hg} DF V_{f(ftr)}]}{S} - \frac{[C_{(ftrbk)Hg} DF_{bk} V_{f(bk)}]}{S_{bk}} \quad \text{Eq. 101A-2}$$

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (analysis Sample No. "A.1 blank"), or (2) 5% of the Hg content in the filtrate (analysis Sample No. "A.1").

$$m_{Hg} = m_{(HCl)Hg} + m_{(ftr)Hg} \quad \text{Eq. 101A-3}$$

12.3 Mercury Emission Rate. Same as Method 101, Section 12.3.

12.4 Determination of Compliance. Same as Method 101, Section 12.4.

### 13.0 Method Performance

13.1 Precision. Based on eight paired-train tests, the intra-laboratory standard deviation was estimated to be 4.8 µg/ml in the concentration range of 50 to 130 µg/m<sup>3</sup>.

13.2 Bias. [Reserved]

13.3 Range. After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

14.0 Pollution Prevention[Reserved]

15.0 Waste Management[Reserved]

### 16.0 References

Same as Section 16.0 of Method 101, with the addition of the following:

1. Mitchell, W.J., *et al.* Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-79-058. September 1979.
2. Wilshire, Frank W., *et al.* Reliability Study of the U.S. EPA's Method 101A—Determination of Particulate and Gaseous Mercury Emissions. U.S. Environmental Protection Agency. Research Triangle Park, NC. Report No. 600/D-31/219 AREAL 367, NTIS Acc No. PB91-233361.
3. Memorandum from William J. Mitchell to Roger T. Shigehara discussing the potential safety hazard in Section 7.2 of Method 101A. February 28, 1990.

17.0 Tables, Diagrams, Flowcharts, And Validation Data[Reserved]

### Method 102—Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants (Hydrogen Streams)

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part and in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough

knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 101.

#### *1.0 Scope and Application*

##### *1.1 Analytes.*

Analyte	CAS No.	Sensitivity
Mercury (Hg)	7439-97-6	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Hg emissions, including both particulate and gaseous Hg, from chlor-alkali plants and other sources (as specified in the regulations) where the carrier-gas stream in the duct or stack is principally hydrogen.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### *2.0 Summary of Method*

2.1 Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICI) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

#### *3.0 Definitions[Reserved]*

#### *4.0 Interferences*

Same as Method 101, Section 4.2.

#### *5.0 Safety*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 101, Section 5.2.

5.3 Explosive Mixtures. The sampler must conduct the source test under conditions of utmost safety because hydrogen and air mixtures are explosive. Since the sampling train essentially is leakless, attention to safe operation can be concentrated at the inlet and outlet. If a leak does occur, however, remove the meter box cover to avoid a possible explosive mixture. The following specific precautions are recommended:

5.3.1 Operate only the vacuum pump during the test. The other electrical equipment, e.g., heaters, fans, and timers, normally are not essential to the success of a hydrogen stream test.

5.3.2 Seal the sample port to minimize leakage of hydrogen from the stack.

5.3.3 Vent sampled hydrogen at least 3 m (10 ft) away from the train. This can be accomplished by attaching a 13-mm (0.50-in.) ID Tygon tube to the exhaust from the orifice meter.

Note: A smaller ID tubing may cause the orifice meter calibration to be erroneous. Take care to ensure that the exhaust line is not bent or pinched.

#### *6.0 Equipment and Supplies*

Same as Method 101, Section 6.0, with the exception of the following:

6.1 Probe Heating System. Do not use, unless otherwise specified.

6.2 Glass Fiber Filter. Do not use, unless otherwise specified.

#### 7.0 Reagents and Standards

Same as Method 101, Section 7.0.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

Same as Method 101, Section 8.0, with the exception of the following:

##### 8.1 Setting of Isokinetic Rates.

8.1.1 If a nomograph is used, take special care in the calculation of the molecular weight of the stack gas and in the setting of the nomograph to maintain isokinetic conditions during sampling (Sections 8.1.1.1 through 8.1.1.3 below).

8.1.1.1 Calibrate the meter box orifice. Use the techniques described in APTD-0576 (see Reference 9 in Section 17.0 of Method 5). Calibration of the orifice meter at flow conditions that simulate the conditions at the source is suggested. Calibration should either be done with hydrogen or with some other gas having similar Reynolds Number so that there is similarity between the Reynolds Numbers during calibration and during sampling.

8.1.1.2 The nomograph described in APTD-0576 cannot be used to calculate the C factor because the nomograph is designed for use when the stack gas dry molecular weight is  $29 \pm 4$ . Instead, the following calculation should be made to determine the proper C factor:

$$C = 0.00154 \Delta H @ C_p^2 T_m \left( P_s / P_m \right) \frac{(1 - B_{ws})^2}{(1 - B_{ws}) + 18 B_{ws}} \quad \text{Eq. 102-1}$$

Where:

$B_{ws}$  = Fraction by volume of water vapor in the stack gas.

$C_p$  = Pitot tube calibration coefficient, dimensionless.

$M_d$  = Dry molecular weight of stack gas, lb/lb-mole.

$P_s$  = Absolute pressure of stack gas, in. Hg.

$P_m$  = Absolute pressure of gas at the meter, in. Hg.

$T_m$  = Absolute temperature of gas at the orifice, °R.

$\Delta H@$  = Meter box calibration factor obtained in Section 8.1.1.1, in. H<sub>2</sub>O.

0.00154 = (in. H<sub>2</sub>O/°R).

**Note:** This calculation is left in English units, and is not converted to metric units because nomographs are based on English units.

8.1.1.3 Set the calculated C factor on the operating nomograph, and select the proper nozzle diameter and K factor as specified in APTD-0576. If the C factor obtained in Section 8.1.1.2 exceeds the values specified on the existing operating nomograph, expand the C scale logarithmically so that the values can be properly located.

8.1.2 If a calculator is used to set isokinetic rates, it is suggested that the isokinetic equation presented in Reference 13 in Section 17.0 of Method 101 be consulted.

8.2 Sampling in Small (<12-in. Diameter) Stacks. When the stack diameter (or equivalent diameter) is less than 12 inches, conventional pitot tube-probe assemblies should not be used. For sampling guidelines, see Reference 14 in Section 17.0 of Method 101.

#### 9.0 Quality Control

Same as Method 101, Section 9.0.

#### 10.0 Calibration and Standardizations

Same as Method 101, Section 10.0.

#### 11.0 Analytical Procedure

Same as Method 101, Section 11.0.

#### 12.0 Data Analysis and Calculations

Same as Method 101, Section 12.0.

#### 13.0 Method Performance

Same as Method 101, Section 13.0.

13.1 Analytical Range. After initial dilution, the range of this method is 0.5 to 120 µg Hg/ml. The upper limit can be extended by further dilution of the sample.

#### 14.0 Pollution Prevention.[Reserved]

#### 15.0 Waste Management.[Reserved]

#### 16.0 References

Same as Method 101, Section 16.0.

#### 17.0 Tables, Diagrams, Flowcharts, and Validation Data.[Reserved]

### Method 103—Beryllium Screening Method

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Beryllium (Be)	7440-41-7	Dependent upon analytical procedure used.

1.2 Applicability. This procedure details guidelines and requirements for methods acceptable for use in determining Be emissions in ducts or stacks at stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

2.1 Particulate Be emissions are withdrawn isokinetically from three points in a duct or stack and are collected on a filter. The collected sample is analyzed for Be using an appropriate technique.

## 3.0 Definitions.[Reserved]

## 4.0 Interferences.[Reserved]

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrochloric Acid (HCl). Highly corrosive and toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

## 6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the required sampling train configuration is shown in Figure 103–1 in Section 17.0. The essential components of the train are as follows:

6.1.1 Nozzle. Stainless steel, or equivalent, with sharp, tapered leading edge.

6.1.2 Probe. Sheathed borosilicate or quartz glass tubing.

6.1.3 Filter. Millipore AA, or equivalent, with appropriate filter holder that provides a positive seal against leakage from outside or around the filter. It is suggested that a Whatman 41, or equivalent, be placed immediately against the back side of the Millipore filter as a guard against breakage of the Millipore. Include the backup filter in the analysis. To be equivalent, other filters shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles, and be amenable to the Be analysis procedure. The filter efficiency tests shall be conducted in accordance with ASTM D 2986–71, 78, 95a (incorporated by reference—see §61.18). Test data from the supplier's quality control program are sufficient for this purpose.

6.1.4 Meter-Pump System. Any system that will maintain isokinetic sampling rate, determine sample volume, and is capable of a sampling rate of greater than 14 lpm (0.5 cfm).

6.2 Measurement of Stack Conditions. The following equipment is used to measure stack conditions:

6.2.1 Pitot Tube. Type S, or equivalent, with a constant coefficient ( $\pm 5$  percent) over the working range.

6.2.2 Inclined Manometer, or Equivalent. To measure velocity head to  $\pm 10$  percent of the minimum value.

6.2.3 Temperature Measuring Device. To measure stack temperature to  $\pm 1.5$  percent of the minimum absolute stack temperature.

6.2.4 Pressure Measuring Device. To measure stack pressure to  $\pm 2.5$  mm Hg (0.1 in. Hg).

6.2.5 Barometer. To measure atmospheric pressure to  $\pm 2.5$  mm Hg (0.1 in. Hg).

6.2.6 Wet and Dry Bulb Thermometers, Drying Tubes, Condensers, or Equivalent. To determine stack gas moisture content to  $\pm 1$  percent.

6.3 Sample Recovery.

6.3.1 Probe Cleaning Equipment. Probe brush or cleaning rod at least as long as probe, or equivalent. Clean cotton balls, or equivalent, should be used with the rod.

6.3.2 Leakless Glass Sample Bottles. To contain sample.

6.4 Analysis. All equipment necessary to perform an atomic absorption, spectrographic, fluorometric, chromatographic, or equivalent analysis.

## 7.0 Reagents and Standards

### 7.1 Sample Recovery.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77, 91 (incorporated by reference—see §61.18), Type 3.

7.1.2 Acetone. Reagent grade.

7.1.3 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl). Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

7.2 Analysis. Reagents and standards as necessary for the selected analytical procedure.

## 8.0 Sample Collection, Preservation, Transport, and Storage

Guidelines for source testing are detailed in the following sections. These guidelines are generally applicable; however, most sample sites differ to some degree and temporary alterations such as stack extensions or expansions often are required to insure the best possible sample site. Further, since Be is hazardous, care should be taken to minimize exposure. Finally, since the total quantity of Be to be collected is quite small, the test must be carefully conducted to prevent contamination or loss of sample.

8.1 Selection of a Sampling Site and Number of Sample Runs. Select a suitable sample site that is as close as practicable to the point of atmospheric emission. If possible, stacks smaller than one foot in diameter should not be sampled.

8.1.1 Ideal Sampling Site. The ideal sampling site is at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion or contraction. For rectangular cross sections, use Equation 103–1 in Section 12.2 to determine an equivalent diameter,  $D_e$ .

8.1.2 Alternate Sampling Site. Some sampling situations may render the above sampling site criteria impractical. In such cases, select an alternate site no less than two diameters downstream and one-half diameter upstream from any point of flow disturbance. Additional sample runs are recommended at any sample site not meeting the criteria of Section 8.1.1.

8.1.3 Number of Sample Runs Per Test. Three sample runs constitute a test. Conduct each run at one of three different points. Select three points that proportionately divide the diameter, or are located at 25, 50, and 75 percent of the diameter from the inside wall. For horizontal ducts, sample on a vertical line through the centroid. For rectangular ducts, sample on a line through the centroid and parallel to a side. If additional sample runs are performed per Section 8.1.2, proportionately divide the duct to accommodate the total number of runs.

8.2 Measurement of Stack Conditions. Using the equipment described in Section 6.2, measure the stack gas pressure, moisture, and temperature to determine the molecular weight of the stack gas. Sound engineering estimates may be made in lieu of direct measurements. Describe the basis for such estimates in the test report.

### 8.3 Preparation of Sampling Train.

8.3.1 Assemble the sampling train as shown in Figure 103–1. It is recommended that all glassware be precleaned by soaking in wash acid for two hours.

8.3.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sample rate.

### 8.4 Sampling Train Operation.

8.4.1 For each run, measure the velocity at the selected sampling point. Determine the isokinetic sampling rate. Record the velocity head and the required sampling rate. Place the nozzle at the sampling point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. At the conclusion of the test, record the sampling rate. Again measure the velocity head at the sampling point. The required isokinetic rate at the end of the period should not have deviated more than 20 percent from that originally calculated. Describe the reason for any deviation beyond 20 percent in the test report.

8.4.2 Sample at a minimum rate of 14 liters/min (0.5 cfm). Obtain samples over such a period or periods of time as are necessary to determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs so as to allow determination or calculation of the emissions that occur over the duration of the cycle. A minimum sampling time of two hours per run is recommended.

## 8.5 Sample Recovery.

8.5.1 It is recommended that all glassware be precleaned as in Section 8.3. Sample recovery should also be performed in an area free of possible Be contamination. When the sampling train is moved, exercise care to prevent breakage and contamination. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. The total amount of acetone used should be measured for accurate blank correction. Blanks can be eliminated if prior analysis shows negligible amounts.

8.5.2 Remove the filter (and backup filter, if used) and any loose particulate matter from filter holder, and place in a container.

8.5.3 Clean the probe with acetone and a brush or long rod and cotton balls. Wash into the container with the filter. Wash out the filter holder with acetone, and add to the same container.

## 9.0 Quality Control.[Reserved]

### 10.0 Calibration and Standardization

10.1 Sampling Train. As a procedural check, compare the sampling rate regulation with a dry gas meter, spirometer, rotameter (calibrated for prevailing atmospheric conditions), or equivalent, attached to the nozzle inlet of the complete sampling train.

10.2 Analysis. Perform the analysis standardization as suggested by the manufacturer of the instrument, or the procedures for the analytical method in use.

### 11.0 Analytical Procedure

Make the necessary preparation of samples and analyze for Be. Any currently acceptable method (e.g., atomic absorption, spectrographic, fluorometric, chromatographic) may be used.

### 12.0 Data Analysis and Calculations

#### 12.1 Nomenclature.

$A_s(\text{avg})$  = Stack area,  $\text{m}^2$  ( $\text{ft}^2$ ).

$L$  = Length.

$R$  = Be emission rate, g/day.

$V_s(\text{avg})$  = Average stack gas velocity, m/sec (ft/sec).

$V_{\text{total}}$  = Total volume of gas sampled,  $\text{m}^3$  ( $\text{ft}^3$ ).

$W$  = Width.

$W_t$  = Total weight of Be collected, mg.



$10^{-6}$  = Conversion factor, g/ $\mu$ g.

86,400 = Conversion factor, sec/day.

12.2 Calculate the equivalent diameter,  $D_e$ , for a rectangular cross section as follows:

$$D_e = \frac{2 \cdot L \cdot W}{L + W} \quad \text{Eq. 103-1}$$

12.3 Calculate the Be emission rate,  $R$ , in g/day for each stack using Equation 103-2. For cyclic operations, use only the time per day each stack is in operation. The total Be emission rate from a source is the summation of results from all stacks.

$$R = \frac{W_t V_{s(\text{avg})} A_s (86,400) (10^{-6})}{V_{\text{total}}} \quad \text{Eq. 103-2}$$

12.4 Test Report. Prepare a test report that includes as a minimum: A detailed description of the sampling train used, results of the procedural check described in Section 10.1 with all data and calculations made, all pertinent data taken during the test, the basis for any estimates made, isokinetic sampling calculations, and emission results. Include a description of the test site, with a block diagram and brief description of the process, location of the sample points in the stack cross section, and stack dimensions and distances from any point of disturbance.

13.0 Method Performance.[Reserved]

14.0 Pollution Prevention.[Reserved]

15.0 Waste Management.[Reserved]

16.0 References.[Reserved]

17.0 Tables, Diagrams, Flow Charts, and Validation Data

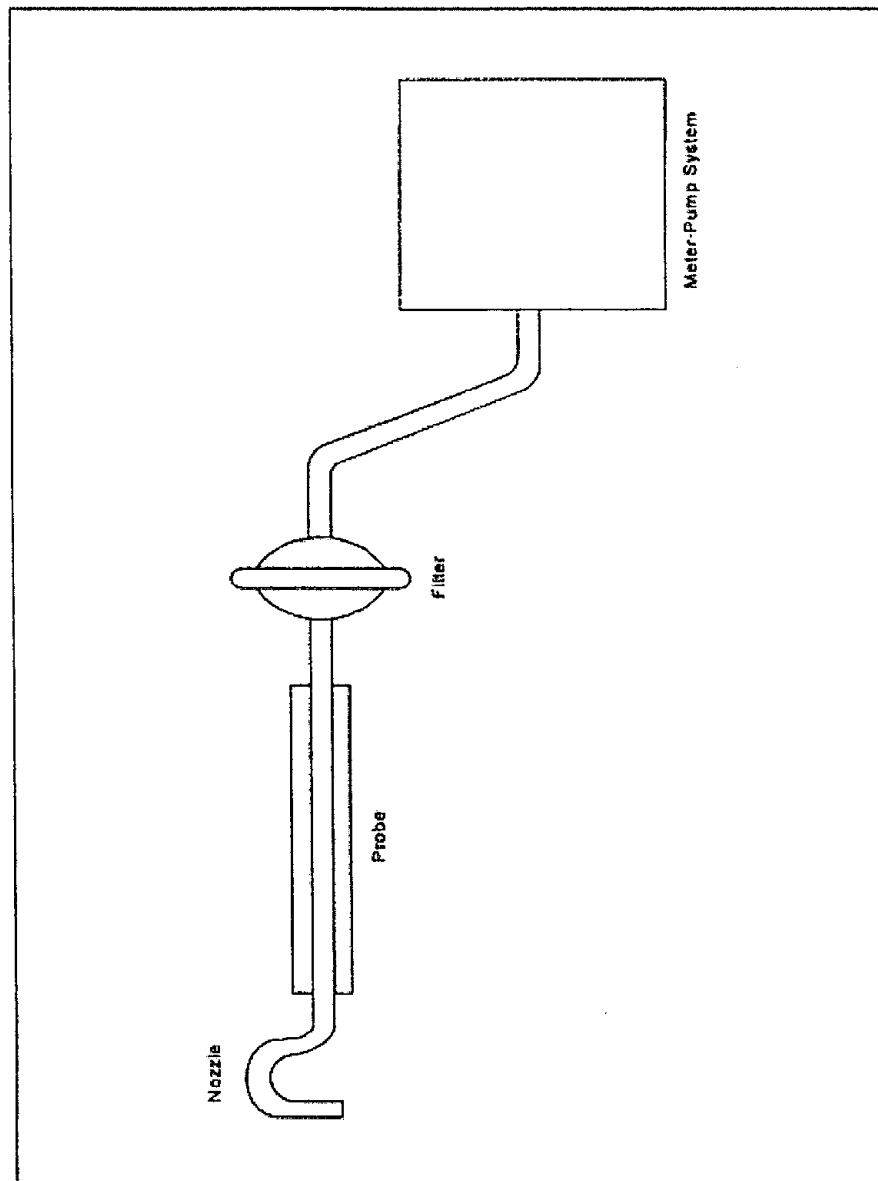


Figure 103-1. Beryllium Screening Method Sampling Train Schematic.

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#### Method 104—Determination of Beryllium Emissions From Stationary Sources

**Note:** This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5 in appendix A, part 60.

##### 1.0 Scope and Application

### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Beryllium (Be)	7440-41-7	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Be emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

1.3 Data Quality Objectives. Adherences to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 Particulate and gaseous Be emissions are withdrawn isokinetically from the source and are collected on a glass fiber filter and in water. The collected sample is digested in an acid solution and is analyzed by atomic absorption spectrophotometry.

### 3.0 Definitions[Reserved]

### 4.0 Interferences

4.1 Matrix Effects. Analysis for Be by flame atomic absorption spectrophotometry is sensitive to the chemical composition and to the physical properties ( e.g., viscosity, pH) of the sample. Aluminum and silicon in particular are known to interfere when present in appreciable quantities. The analytical procedure includes (optionally) the use of the Method of Standard Additions to check for these matrix effects, and sample analysis using the Method of Standard Additions if significant matrix effects are found to be present (see Reference 2 in Section 16.0).

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.3 Beryllium is hazardous, and precautions should be taken to minimize exposure.

### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, Section 6.1, with the exception of the following:

6.1.1 Sampling Train. Same as Method 5, Section 6.1.1, with the exception of the following:

6.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature of  $120 \pm 14$  °C ( $248 \pm 25$  °F) at the probe exit during sampling to prevent water condensation may be used.

**Note:** Do not use metal probe liners.

6.1.3 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

6.1.4 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use impingers that are modified by replacing the tip with a 13 mm-ID (0.5 in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask may be used.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe Cleaning Rod. At least as long as probe.

6.2.2 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000 ml.

6.2.3 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

6.2.4 Graduated Cylinder. 250 ml.

6.2.5 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.6 Funnel. Glass, to aid in sample recovery.

6.2.7 Plastic Jar. Approximately 300 ml.

6.3 Analysis. The following items are needed for sample analysis:

6.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, with nitrous oxide/acetylene burner.

6.3.2 Hot Plate.

6.3.3 Perchloric Acid Fume Hood.

## *7.0 Reagents and Standards*

**Note:** Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, Section 7.1, including deionized distilled water conforming to ASTM D 1193-77 or 91 (incorporated by reference—see §61.18), Type 3. The Millipore AA filter is recommended.

7.2 Sample Recovery. Same as Method 5 in appendix A, part 60, Section 7.2, with the addition of the following:

7.2.1 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl). Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

7.3 Sample Preparation and Analysis. The following reagents and standards and standards are needed for sample preparation and analysis:

7.3.1 Water. Same as in Section 7.1.

7.3.2. Perchloric Acid ( $\text{HClO}_4$ ). Concentrated (70 percent V/V).

7.3.3 Nitric Acid ( $\text{HNO}_3$ ). Concentrated.

7.3.4 Beryllium Powder. Minimum purity 98 percent.

7.3.5 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ) Solution, 12 N. Dilute 33 ml of concentrated  $\text{H}_2\text{SO}_4$  to 1 liter with water.

7.3.6 Hydrochloric Acid Solution, 25 Percent HCl (V/V).

7.3.7 Stock Beryllium Standard Solution, 10  $\mu\text{g}$  Be/ml. Dissolve 10.0 mg of Be in 80 ml of 12 N  $\text{H}_2\text{SO}_4$  in a 1000-ml volumetric flask. Dilute to volume with water. This solution is stable for at least one month. Equivalent strength Be stock solutions may be prepared from Be salts such as  $\text{BeCl}_2$  and  $\text{Be}(\text{NO}_3)_2$  (98 percent minimum purity).

7.3.8 Working Beryllium Standard Solution, 1  $\mu\text{g}$  Be/ml. Dilute a 10 ml aliquot of the stock beryllium standard solution to 100 ml with 25 percent HCl solution to give a concentration of 1 mg/ml. Prepare this dilute stock solution fresh daily.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

The amount of Be that is collected is generally small, therefore, it is necessary to exercise particular care to prevent contamination or loss of sample.

8.1 Pretest Preparation. Same as Method 5, Section 8.1, except omit Section 8.1.3.

8.2 Preliminary Determinations. Same as Method 5, Section 8.2, with the exception of the following:

8.2.1 Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.2.2 Obtain samples over a period or periods of time that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours per run is recommended.

8.3 Preparation of Sampling Train. Same as Method 5, Section 8.3, with the exception of the following:

8.3.1 Prior to assembly, clean all glassware (probe, impingers, and connectors) by first soaking in wash acid for 2 hours, followed by rinsing with water.

8.3.2 Save a portion of the water for a blank analysis.

8.3.3 Procedures relating to the use of metal probe liners are not applicable.

8.3.4 Probe and filter heating systems are needed only if water condensation is a problem. If this is the case, adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 107 °C (225 °F). If the stack gas is in excess of about 93 °C (200 °F), consideration should be given to an alternate procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. After the sampling train has been assembled, turn on and set the probe heating system, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

**Note:** An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

8.4 Leak Check Procedures, Sampling Train Operation, and Calculation of Percent Isokinetic. Same as Method 5, Sections 8.4, 8.5, and 8.6, respectively.

8.5 Sample Recovery. Same as Method 5, Section 8.7, except treat the sample as follows: Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Be contamination. Inspect the train before and during this assembly, and note any abnormal conditions. Treat the sample as follows: Disconnect the probe from the impinger train.

8.5.1 Container No. 1. Same as Method 5, Section 8.7.6.1.

8.5.2 Container No. 2. Place the contents (measured to 1 ml) of the first three impingers into a glass sample bottle. Use the procedures outlined in Section 8.7.6.2 of Method 5, where applicable, to rinse the probe nozzle, probe fitting, probe liner, filter holder, and all glassware between the filter holder and the back half of the third impinger with water. Repeat this procedure with acetone. Place both water and acetone rinse solutions in the sample bottle with the contents of the impingers.

8.5.3 Container No. 3. Same as Method 5, Section 8.7.6.3.

8.6 Blanks.

8.6.1 Water Blank. Save a portion of the water as a blank. Take 200 ml directly from the wash bottle being used and place it in a plastic sample container labeled "H<sub>2</sub>O blank."

8.6.2 Filter. Save two filters from each lot of filters used in sampling. Place these filters in a container labeled "filter blank."

8.7 Post-test Glassware Rinsing. If an additional test is desired, the glassware can be carefully double rinsed with water and reassembled. However, if the glassware is out of use more than 2 days, repeat the initial acid wash procedure.

#### 9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak checks and calibration	Ensure accuracy and precision of sampling measurements.
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminate matrix effects.
11.6	Audit sample analysis	Evaluate analyst's technique and standards preparation.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

#### 10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Preparation of Standard Solutions. Pipet 1, 3, 5, 8, and 10 ml of the 1.0 µg Be/ml working standard solution into separate 100 ml volumetric flasks, and dilute to the mark with water. The total amounts of Be in these standards are 1, 3, 5, 8, and 10 µg, respectively.

10.3 Spectrophotometer and Recorder. The Be response may be measured by either peak height or peak area. Analyze an aliquot of the 10- $\mu$ g standard at 234.8 nm using a nitrous oxide/acetylene flame. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

#### 10.4 Calibration Curve.

10.4.1 After setting the recorder scale, analyze an appropriately sized aliquot of each standard and the BLANK (see Section 11) until two consecutive peaks agree within 3 percent of their average value.

10.4.3 Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of the standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Be contamination of a reagent or carry-over of Be from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding total Be weight in the standard (in  $\mu$ g).

10.5 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (i.e., 1, 3, 5, 8, and 10  $\mu$ g Be) must be less than 7 percent for all standards.

#### 11.0 Analytical Procedure

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Container No. 2. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

11.2 Glassware Cleaning. Before use, clean all glassware according to the procedure of Section 8.3.1.

11.3 Sample Preparation. The digestion of Be samples is accomplished in part in concentrated  $\text{HClO}_4$ .

**Note:** The sample must be heated to light brown fumes after the initial  $\text{HNO}_3$  addition; otherwise, dangerous perchlorates may result from the subsequent  $\text{HClO}_4$  digestion.  $\text{HClO}_4$  should be used only under a hood.

11.3.1 Container No. 1. Transfer the filter and any loose particulate matter from Container No. 1 to a 150-ml beaker. Add 35 ml concentrated  $\text{HNO}_3$ . To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N  $\text{H}_2\text{SO}_4$  and 5 ml concentrated  $\text{HClO}_4$ .

11.3.2 Container No. 2. Place a portion of the water and acetone sample into a 150 ml beaker, and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness. Cool the residue, and add 35 ml concentrated  $\text{HNO}_3$ . To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N  $\text{H}_2\text{SO}_4$  and 5 ml concentrated  $\text{HClO}_4$ . Then proceed with step 11.3.4.

11.3.3 Final Sample Preparation. Add the sample from Section 11.3.2 to the 150-ml beaker from Section 11.3.1. Replace on a hotplate, and evaporate to dryness in a  $\text{HClO}_4$  hood. Cool the residue to room temperature, add 10.0 ml of 25 percent V/V HCl, and mix to dissolve the residue.

11.3.4 Filter and Water Blanks. Cut each filter into strips, and treat each filter individually as directed in Section 11.3.1. Treat the 200-ml water blank as directed in Section 11.3.2. Combine and treat these blanks as directed in Section 11.3.3.

11.4 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current; and adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.5 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.4 and 10.5.

11.5.1 Beryllium Samples. Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot of each sample (from Section 11.3.3) until two consecutive peak heights agree within 3 percent of their average value. The peak height of each sample must be greater than 10 percent of the recorder full scale. If the peak height of the

sample is off scale on the recorder, further dilute the original source sample to bring the Be concentration into the calibration range of the spectrophotometer.

11.5.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5.3 Check for Matrix Effects (optional). Use the Method of Standard Additions (see Reference 2 in Section 16.0) to check at least one sample from each source for matrix effects on the Be results. If the results of the Method of Standard Additions procedure used on the single source sample do not agree to within 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

11.6 Container No. 2 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

## 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

### 12.1 Nomenclature.

$K_1 = 0.3858$  °K/mm Hg for metric units.

$= 17.64$  °R/in. Hg for English units.

$K_3 = 10^{-6}$  g/ $\mu$ g for metric units.

$= 2.2046 \times 10^{-9}$  lb/ $\mu$ g for English units.

$m_{Be}$  = Total weight of beryllium in the source sample.

$P_s$  = Absolute stack gas pressure, mm Hg (in. Hg).

$t$  = Daily operating time, sec/day.

$T_s$  = Absolute average stack gas temperature, °K (°R).

$V_m(\text{std})$  = Dry gas sample volume at standard conditions, scm (scf).

$V_w(\text{std})$  = Volume of water vapor at standard conditions, scm (scf).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

12.3 Total Beryllium. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the solution blank (see Sections 11.3.4 and 11.5.2). Correcting for any dilutions if necessary, use the calibration curve and these corrected averages to determine the total weight of Be in each source sample.

12.4 Beryllium Emission Rate. Calculate the daily Hg emission rate,  $R$ , using Equation 104–1. For continuous operations, the operating time is equal to 86,400 seconds per day. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.



$$R = \frac{K_1 K_3 t m_{2e} P_s v_s A_s}{T_s \left( V_{m(s2)} + V_{w(s2)} \right)} \quad \text{Eq. 104-1}$$

12.5 Determination of Compliance. Each performance test consists of three sample runs. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all sample runs.

13.0 Method Performance.[Reserved]

14.0 Pollution Prevention.[Reserved]

15.0 Waste Management.[Reserved]

16.0 References

Same as References 1, 2, and 4–11 of Section 16.0 of Method 101 with the addition of the following:

1. Amos, M.D., and J.B. Willis. Use of High-Temperature Pre-Mixed Flames in Atomic Absorption Spectroscopy. Spectrochim. Acta. 22:1325. 1966.

2. Fleet, B., K.V. Liberty, and T. S. West. A Study of Some Matrix Effects in the Determination of Beryllium by Atomic Absorption Spectroscopy in the Nitrous Oxide-Acetylene Flame. Talanta 17:203. 1970.

17.0 Tables, Diagrams, Flowcharts, And Validation Data[Reserved]

Method 105—Determination of Mercury in Wastewater Treatment Plant Sewage Sludges

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 101 and Method 101A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg)	7439-97-6	Dependent upon spectrophotometer and recorder.

1.2 Applicability. This method is applicable for the determination of total organic and inorganic Hg content in sewage sludges.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Time-composite sludge samples are withdrawn from the conveyor belt subsequent to dewatering and before incineration or drying. A weighed portion of the sludge is digested in aqua regia and is oxidized by potassium permanganate (KMnO<sub>4</sub>). Mercury in the digested sample is then measured by the conventional spectrophotometric cold-vapor technique.

3.0 Definitions[Reserved]

#### *4.0 Interferences[Reserved]*

#### *5.0 Safety*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

#### *6.0 Equipment and Supplies*

6.1 Sample Collection and Mixing. The following items are required for collection and mixing of the sludge samples:

6.1.1 Container. Plastic, 50-liter.

6.1.2 Scoop. To remove 950-ml (1 quart.) sludge sample.

6.1.3 Mixer. Mortar mixer, wheelbarrow-type, 57-liter (or equivalent) with electricity-driven motor.

6.1.4 Blender. Waring-type, 2-liter.

6.1.5 Scoop. To remove 100-ml and 20-ml samples of blended sludge.

6.1.6 Erlenmeyer Flasks. Four, 125-ml.

6.1.7 Beakers. Glass beakers in the following sizes: 50 ml (1), 200 ml (1), 400 ml (2).

6.2 Sample Preparation and Analysis. Same as Method 101, Section 6.3, with the addition of the following:

6.2.1 Hot Plate.

6.2.2 Desiccator.

6.2.3 Filter Paper. S and S No. 588 (or equivalent).

6.2.4 Beakers. Glass beakers, 200 ml and 400 ml (2 each).

#### *7.0 Reagents and Standards*

Note: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Analysis. Same as Method 101A, Section 7.2, with the following additions and exceptions:

7.1.1 Hydrochloric Acid. The concentrated HCl specified in Method 101A, Section 7.2.4, is not required.

7.1.2 Aqua Regia. Prepare immediately before use. Carefully add one volume of concentrated HNO<sub>3</sub> to three volumes of concentrated HCl.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sludge Sampling. Withdraw equal volume increments of sludge [for a total of at least 15 liters (16 quarts)] at intervals of 30 min over an 8-hr period, and combine in a rigid plastic container.

8.2 Sludge Mixing. Transfer the entire 15-liter sample to a mortar mixer. Mix the sample for a minimum of 30 min at 30 rpm. Take six 100-ml portions of sludge, and combine in a 2-liter blender. Blend sludge for 5 min; add water as necessary to give a fluid consistency. Immediately after stopping the blender, withdraw four 20-ml portions of blended sludge, and place them in separate, tared 125-ml Erlenmeyer flasks. Reweigh each flask to determine the exact amount of sludge added.

8.3 Sample Holding Time. Samples shall be analyzed within the time specified in the applicable subpart of the regulations.

#### 9.0 Quality Control

Section	Quality control measure	Effect
10.0	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.0	Check for matrix effects	Eliminate matrix effects.

#### 10.0 Calibration and Standardization

Same as Method 101A, Section 10.2.

#### 11.0 Analytical Procedures

11.1 Solids Content of Blended Sludge. Dry one of the 20-ml blended samples from Section 8.2 in an oven at 105 °C (221 °F) to constant weight. Cool in a desiccator, weigh and record the dry weight of the sample.

#### 11.2 Aqua Regia Digestion of Blended Samples.

11.2.1 To each of the three remaining 20-ml samples from Section 8.2 add 25 ml of aqua regia, and digest the on a hot plate at low heat (do not boil) for 30 min, or until samples are a pale yellow-brown color and are void of the dark brown color characteristic of organic matter. Remove from hotplate and allow to cool.

11.2.2 Filter each digested sample separately through an S and S No. 588 filter or equivalent, and rinse the filter contents with 50 ml of water. Transfer the filtrate and filter washing to a 100-ml volumetric flask, and carefully dilute to volume with water.

11.3 Solids Content of the Sludge Before Blending. Remove two 100-ml portions of mixed sludge from the mortar mixer and place in separate, tared 400-ml beakers. Reweigh each beaker to determine the exact amount of sludge added. Dry in oven at 105 °C (221 °F) and cool in a desiccator to constant weight.

11.4 Analysis for Mercury. Analyze the three aqua regia-digested samples using the procedures outlined in Method 101A, Section 11.0.

#### 12.0 Data Analysis and Calculations

##### 12.1 Nomenclature.

$C_m$  = Concentration of Hg in the digested sample,  $\mu\text{g/g}$ .

$F_{sb}$  = Weight fraction of solids in the blended sludge.

$F_{sm}$  = Weight fraction of solids in the collected sludge after mixing.

$M$  = Hg content of the sewage sludge (on a dry basis),  $\mu\text{g/g}$ .

$m$  = Mass of Hg in the aliquot of digested sample analyzed,  $\mu\text{g}$ .

$n$  = number of digested samples (specified in Section 11.2 as three).

$V_a$  = Volume of digested sample analyzed, ml.

$V_s$  = Volume of digested sample, ml.

$W_b$  = Weight of empty sample beaker, g.

$W_{bs}$  = Weight of sample beaker and sample, g.

$W_{bd}$  = Weight of sample beaker and sample after drying, g.

$W_f$  = Weight of empty sample flask, g.

$W_{fd}$  = Weight of sample flask and sample after drying, g.

$W_{fs}$  = Weight of sample flask and sample, g.

## 12.2 Mercury Content of Digested Sample (Wet Basis).

12.2.1 For each sample analyzed for Hg content, calculate the arithmetic mean maximum absorbance of the two consecutive samples whose peak heights agree  $\pm 3$  percent of their average. Correct this average value for the contribution of the blank. Use the calibration curve and these corrected averages to determine the final Hg concentration in the solution cell for each sludge sample.

12.2.2 Calculate the average Hg concentration of the digested samples by correcting for any dilutions made to bring the sample into the working range of the spectrophotometer and for the weight of the sludge portion digested, using Equation 105-1.

$$\bar{C}_m = \sum_{i=1}^n \left[ \frac{mV_s}{V_a(W_{fs} - W_f)} \right]_i \quad \text{Eq. 105-1}$$

12.3 Solids Content of Blended Sludge. Determine the solids content of the blended sludge using Equation 105-2.

$$F_{sb} = 1 - \frac{W_{fs} - W_{fd}}{W_{fs} - W_f} \quad \text{Eq. 105-2}$$

12.4 Solids Content of Bulk Sample (before blending but, after mixing in mortar mixer). Determine the solids content of each 100 ml aliquot (Section 11.3), and average the results.

$$F_{sm} = 1 - \frac{W_{ds} - W_{dd}}{W_{ds} - W_d} \quad \text{Eq. 105-3}$$

12.5 Mercury Content of Bulk Sample (Dry Basis). Average the results from the three samples from each 8-hr composite sample, and calculate the Hg concentration of the composite sample on a dry basis.

$$M = \frac{\bar{C}_m}{F_{sd}} \quad \text{Eq. 105-4}$$

### 13.0 Method Performance

13.1 Range. The range of this method is 0.2 to 5 micrograms per gram; it may be extended by increasing or decreasing sample size.

### 14.0 Pollution Prevention.[Reserved]

### 15.0 Waste Management.[Reserved]

### 16.0 References

1. Bishop, J.N. Mercury in Sediments. Ontario Water Resources Commission. Toronto, Ontario, Canada. 1971.
2. Salma, M. Private Communication. EPA California/Nevada Basin Office. Alameda, California.
3. Hatch, W.R. and W.L. Ott. Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry. Analytical Chemistry. 40:2085. 1968.
4. Bradenberger, H., and H. Bader. The Determination of Nanogram Levels of Mercury in Solution by a Flameless Atomic Absorption Technique. Atomic Absorption Newsletter. 6:101. 1967.
5. Analytical Quality Control Laboratory (AQCL). Mercury in Sediment (Cold Vapor Technique) (Provisional Method). U.S. Environmental Protection Agency. Cincinnati, Ohio. April 1972.
6. Kopp, J.F., M.C. Longbottom, and L.B. Lobring. "Cold Vapor" Method for Determining Mercury. Journal AWWA. 64(1):20-25. 1972.
7. Manual of Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency. Cincinnati, Ohio. Publication No. EPA-624/2-74-003. December 1974. pp. 118-138.
8. Mitchell, W.J., M.R. Midgett, J. Suggs, R.J. Velton, and D. Albrink. Sampling and Homogenizing Sewage for Analysis. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Research Triangle Park, N.C. March 1979. p. 7.

### 17.0 Tables, Diagrams, Flowcharts, and Validation Data.[Reserved]

## Method 106—Determination of Vinyl Chloride Emissions From Stationary Sources

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Vinyl Chloride (CH <sub>2</sub> :CHCl)	75-01-4	Dependent upon analytical equipment.

1.2 Applicability. This method is applicable for the determination of vinyl chloride emissions from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. This method does not measure vinyl chloride contained in particulate matter.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

2.1 An integrated bag sample of stack gas containing vinyl chloride is subjected to GC analysis using a flame ionization detector (FID).

## 3.0 Definitions.[Reserved]

## 4.0 Interferences

4.1 Resolution interferences of vinyl chloride may be encountered on some sources. Therefore, the chromatograph operator should select the column and operating parameters best suited to the particular analysis requirements. The selection made is subject to approval of the Administrator. Approval is automatic, provided that confirming data are produced through an adequate supplemental analytical technique, and that the data are available for review by the Administrator. An example of this would be analysis with a different column or GC/mass spectroscopy.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Toxic Analyte. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, which is a carcinogen.

## 6.0 Equipment and Supplies

6.1 Sample Collection (see Figure 106–1). The sampling train consists of the following components:

6.1.1 Probe. Stainless steel, borosilicate glass, Teflon tubing (as stack temperature permits), or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

6.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106–1.

6.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

6.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

6.1.6 Needle Valve. To adjust sample flow rates.

6.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

6.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

6.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

6.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106–1).

6.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling training.

6.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. With FID potentiometric strip chart recorder and 1.0 to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppmv vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

6.3.2 Chromatographic Columns. Columns as listed below. Other columns may be used provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and that information is available for review confirming that there is adequate resolution of vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Procedure 1 of appendix C to this part: "Determination of Adequate Chromatographic Peak Resolution.")

6.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

6.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/100-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak T. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120 °C (250 °F).

6.3.3 Rate Meters (2). Rotameter, or equivalent, 100-ml/min capacity, with flow control valves.

6.3.4 Gas Regulators. For required gas cylinders.

6.3.5 Temperature Sensor. Accurate to  $\pm 1$  °C ( $\pm 2$  °F), to measure temperature of heated sample loop at time of sample injection.

6.3.6 Barometer. Accurate to  $\pm 5$  mm Hg, to measure atmospheric pressure around GC during sample analysis.

6.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

6.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

6.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

6.4 Calibration and Standardization.

6.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

**Note:** The following items are required only if the optional standard gas preparation procedures (Section 10.1) are followed.

6.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

6.4.3 Syringes. 0.5-ml and 50- $\mu$ l, gas tight, individually calibrated to dispense gaseous vinyl chloride.

6.4.4 Dry Gas Meter with Temperature and Pressure Gauges. Singer Model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

## 7.0 Reagents and Standards

7.1 Analysis. The following reagents are required for analysis.

7.1.1 Helium or Nitrogen. Purity 99.9995 percent or greater, for chromatographic carrier gas.

7.1.2 Hydrogen. Purity 99.9995 percent or greater.

7.1.3 Oxygen or Air. Either oxygen (purity 99.99 percent or greater) or air (less than 0.1 ppmv total hydrocarbon content), as required by detector.

7.2 Calibration. Use one of the following options: either Sections 7.2.1 and 7.2.2, or Section 7.2.3.

7.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply, rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

7.2.2 Nitrogen. Same as described in Section 7.1.1.

7.2.3 Cylinder Standards. Gas mixture standards (50-, 10-, and 5 ppmv vinyl chloride) in nitrogen cylinders may be used to directly prepare a chromatograph calibration curve as described in Section 10.3 if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better. (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf to the cylinder before shipment to the buyer.

7.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use as a minimum, a three point calibration curve. It is recommended that the manufacturer maintain (1) a high concentration calibration standard (between 50 and 100 ppmv) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppmv) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

7.2.3.2 Verification of Manufacturer's Calibration Standards. Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.2.1 or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Institute of Standards and Technology, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

7.2.4 Audit Cylinder Standards.

7.2.4.1 Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low-concentration cylinder in the range of 5 to 20 ppmv vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppmv. When available, obtain audit samples from the appropriate EPA Regional Office or from the responsible enforcement authority.

**Note:** The responsible enforcement agency should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

7.2.4.2 Alternatively, audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas meets the conditions described in Section 7.2.3, (b) the gas manufacturer certifies the audit cylinder as described in Section 7.2.3.1, and (c) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

## *8.0 Sample Collection, Preservation, Storage, and Transport*



Note: Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required.

8.1 Bag Leak-Check. The following leak-check procedure is recommended, but not required, prior to sample collection. The post-test leak-check procedure is mandatory. Connect a water manometer and pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner.

Note: An alternative leak-check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O and allow it to stand overnight. A deflated bag indicates a leak. For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8.2 Sample Collection. Assemble the sample train as shown in Figure 106-1. Join the quick connects as illustrated, and determine that all connection between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow that will fill over 50 percent of bag volume in the specific sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

8.3 Sample Storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

8.4 Post-test Bag Leak-Check. Subsequent to recovery and analysis of the sample, leak-check the sample bag according to the procedure outlined in Section 8.1.

## 9.0 Quality Control

### 9.1 Miscellaneous Quality Control

Section	Quality control measure	Effect
10.3	Chromatograph calibration	Ensure precision and accuracy of chromatograph.
11.1	Audit sample analysis	Evaluate analytical technique and standards preparation.

9.2 Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

## 10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Vinyl Chloride Standard Gas Mixtures. (Optional Procedure-delete if cylinder standards are used.) Evacuate a 16-inch square Tedlar bag that has passed a leak-check (described in Section 8.1) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250 µl of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppmv. In a like manner use the 50 µl syringe to prepare gas mixtures having 10- and 5-ppmv vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

10.2 Determination of Vinyl Chloride Retention Time. (This section can be performed simultaneously with Section 10.3.) Establish chromatograph conditions identical with those in Section 11.3. Determine proper attenuator position. Flush the sampling loop with helium or nitrogen and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 11.2, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

10.3 Preparation of Chromatograph Calibration Curve. Make a GC measurement of each gas mixture standard (described in Section 7.2.3 or 10.1) using conditions identical to those listed in Sections 11.2 and 11.3. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected ( $C_c$ ), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves.

#### 11.0 Analytical Procedure

11.1 Audit Sample Analysis. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Procedure 2 of appendix C to this part: "Procedure for Field Auditing GC Analysis."

11.2 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 1-in.  $H_2O$  pressure gauge. Maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

#### 11.3 Analysis.

11.3.1 Set the column temperature to 100 °C (210 °F) and the detector temperature to 150 °C (300 °F). When optimum hydrogen and oxygen (or air) flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the  $H_2O$  manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to vinyl chloride as determined in Section 10.2. Measure the vinyl chloride peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Measure and record the peak heights,  $H_m$ . Record  $A_m$  and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak agree within 5 percent of their average. Use the average value for these two total areas to compute the bag concentration.

11.3.2 Compare the ratio of  $H_m$  to  $A_m$  for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 6.3.2.2).

11.4 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag,  $B_{wb}$ , as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

#### 12.0 Calculations and Data Analysis

##### 12.1 Nomenclature.

$A_m$  = Measured peak area.

$A_f$  = Attenuation factor.

$B_{wb}$  = Water vapor content of the bag sample, as analyzed, volume fraction.

$C_b$  = Concentration of vinyl chloride in the bag, ppmv.

$C_c$  = Concentration of vinyl chloride in the standard sample, ppmv.

$P_i$  = Laboratory pressure at time of analysis, mm Hg.

$P_r$  = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

$T_i$  = Absolute sample loop temperature at the time of analysis, °K (°R).

$T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K (°R).

12.2 Sample Peak Area. Determine the sample peak area,  $A_c$ , as follows:

$$A_c = A_m A_f \quad \text{Eq. 106-1}$$

12.3 Vinyl Chloride Concentration. From the calibration curves prepared in Section 10.3, determine the average concentration value of vinyl chloride,  $C_c$ , that corresponds to  $A_c$ , the sample peak area. Calculate the concentration of vinyl chloride in the bag,  $C_b$ , as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r (1 - B_{wb})} \quad \text{Eq. 106-2}$$

### 13.0 Method Performance

13.1 Analytical Range. This method is designed for the 0.1 to 50 parts per million by volume (ppmv) range. However, common gas chromatograph (GC) instruments are capable of detecting 0.02 ppmv vinyl chloride. With proper calibration, the upper limit may be extended as needed.

### 14.0 Pollution Prevention, [Reserved]

### 15.0 Waste Management, [Reserved]

### 16.0 References

1. Brown D.W., E.W. Loy, and M.H. Stephenson. Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, KY. Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, GA. June 24, 1974.
2. G.D. Clayton and Associates. Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air. U.S. Environmental Protection Agency, Research Triangle Park, N.C. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1. December 13, 1974.
3. Midwest Research Institute. Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-026. May 1977.
4. Scheil, G. and M.C. Sharp. Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058. October 1978.

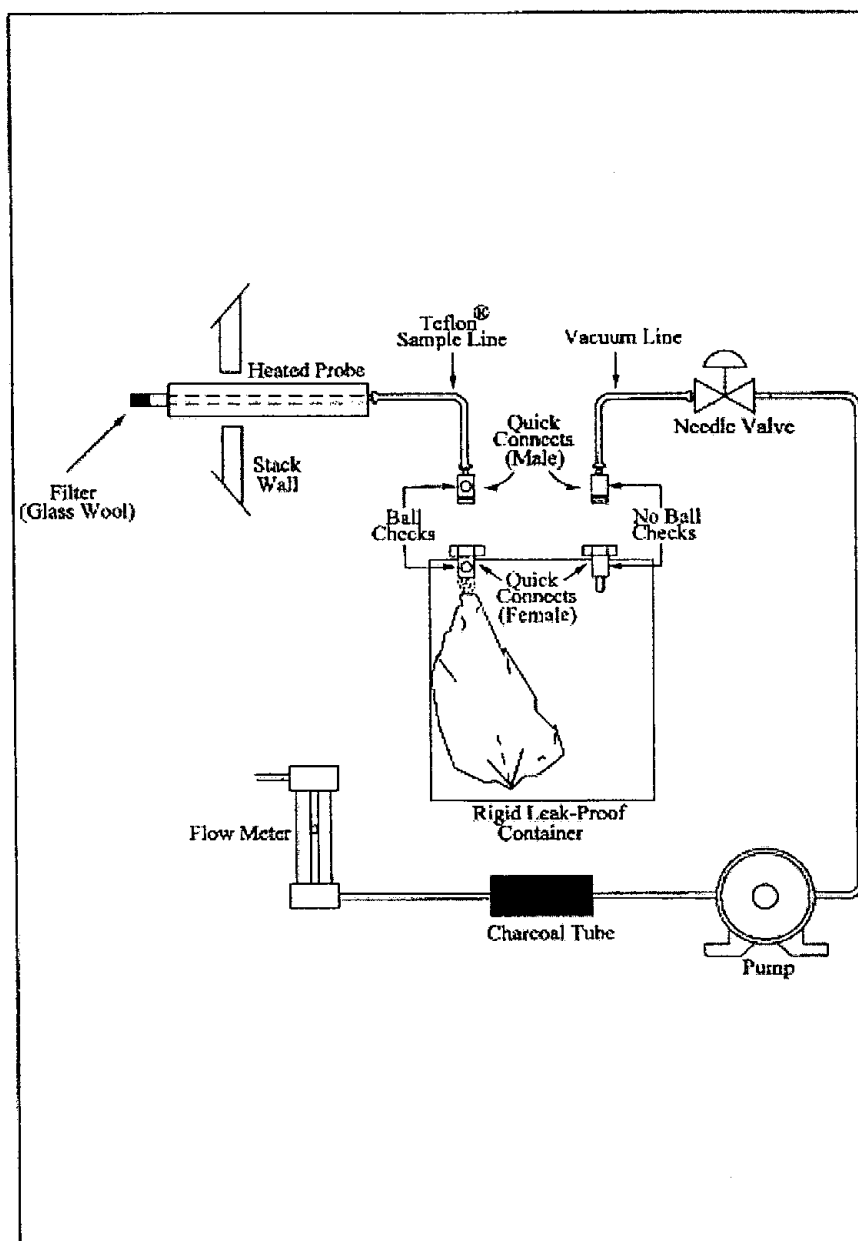


Figure 106-1. Integrated-bag sampling train.

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Method 107—Determination of Vinyl Chloride Content of In-Process Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin Slurry, Wet Cake, and Latex Samples

Note: Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106.

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Vinyl Chloride (CH <sub>2</sub> :CHCl)	75-01-4	Dependent upon analytical equipment.

1.2 Applicability. This method is applicable for the determination of the vinyl chloride monomer (VCM) content of in-process wastewater samples, and the residual vinyl chloride monomer (RCVM) content of polyvinyl chloride (PVC) resins, wet, cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from section 304(h) of the Clean Water Act, 33 U.S.C. 1251 *et seq.* (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 The basis for this method relates to the vapor equilibrium that is established at a constant known temperature in a closed system between RVCN, PVC resin, water, and air. The RVCN in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

2.2 A sample of PVC or in-process wastewater is collected in a vial or bottle and is conditioned. The headspace in the vial or bottle is then analyzed for vinyl chloride using gas chromatography with a flame ionization detector.

#### 3.0 Definitions[Reserved]

#### 4.0 Interferences

4.1 The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that confirming data are produced through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and that these data are made available for review by the Administrator.

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Toxic Analyte. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, which is a carcinogen. Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. The following equipment is required:

6.1.1 Glass bottles. 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials. Headspace vials, with Teflon-faced butyl rubber sealing discs, for water samples.

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. Headspace vials, with butyl rubber septa and aluminum caps. Silicone rubber is not acceptable.

6.2.2 Analytical Balance. Capable of determining sample weight within an accuracy of  $\pm 1$  percent.

6.2.3 Vial Sealer. To seal headspace vials.

6.2.4 Syringe. 100-ml capacity.

6.3 Analysis. The following equipment is required:

6.3.1 Headspace Sampler and Chromatograph. Capable of sampling and analyzing a constant amount of headspace gas from a sealed vial, while maintaining that vial at a temperature of  $90^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$  ( $194^{\circ}\text{F} \pm 0.9^{\circ}\text{F}$ ). The chromatograph shall be equipped with a flame ionization detector (FID). Perkin-Elmer Corporation Models F-40, F-42, F-45, HS-6, and HS-100, and Hewlett-Packard Corporation Model 19395A have been found satisfactory. Chromatograph backflush capability may be required.

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. Other columns may be used provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and information confirming that there is adequate resolution of the vinyl chloride peak are available for review. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferant peak. Calculation of area overlap is explained in Procedure 1 of appendix C to this part: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbopak B, have been found satisfactory for samples containing acetaldehyde.

6.3.3 Temperature Sensor. Range 0 to  $100^{\circ}\text{C}$  ( $32$  to  $212^{\circ}\text{F}$ ) accurate to  $0.1^{\circ}\text{C}$ .

6.3.4 Integrator-Recorder. To record chromatograms.

6.3.5 Barometer. Accurate to 1 mm Hg.

6.3.6 Regulators. For required gas cylinders.

6.3.7 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield.

## *7.0 Reagents and Standards*

7.1 Analysis. Same as Method 106, Section 7.1, with the addition of the following:

7.1.1 Water. Interference-free.

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). Cylinder standards may be used directly to prepare a chromatograph calibration curve as described in Section 10.3, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating the analytical procedure on the day of cylinder analysis. To calibrate the analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare the calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 10.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRMs) prepared by the National Institute of Standards and Technology, if such SRMs are available. The agreement between the initially determined concentration value and the verification concentration value must be within 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

## 8.0 Sample Collection, Preservation, Storage, and Transport

### 8.1 Sample Collection.

8.1.1 PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2 Water Sampling. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book.

8.2 Sample Storage. All samples must be analyzed within 24 hours of collection, and must be refrigerated during this period.

## 9.0 Quality Control

Section	Quality control measure	Effect
10.3	Chromatograph calibration	Ensure precision and accuracy of chromatograph.

## 10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100 µl or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a 1/8-in. stainless steel line from the cylinder to the vial. Do not use rubber or Tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to between 500 and 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the 1/8-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole. Prepressurization of standards is not required unless samples have been prepressurized.

10.2 Analyzer Calibration. Calibration is to be performed each 8-hour period the chromatograph is used. Alternatively, calibration with duplicate 50-, 500-, 2,000-, and 4,000-ppm standards (hereafter described as a four-point calibration) may be performed on a monthly basis, provided that a calibration confirmation test consisting of duplicate analyses of an

appropriate standard is performed once per plant shift, or once per chromatograph carousel operation (if the chromatograph operation is less frequent than once per shift). The criterion for acceptance of each calibration confirmation test is that both analyses of 500-ppm standards [2,000-ppm standards if dispersion resin (excluding latex resin) samples are being analyzed] must be within 5 percent of the most recent four-point calibration curve. If this criterion is not met, then a complete four-point calibration must be performed before sample analyses can proceed.

10.3 Preparation of Chromatograph Calibration Curve. Prepare two vials each of 50-, 500-, 2,000-, and 4,000-ppm standards. Run the calibration samples in exactly the same manner as regular samples. Plot  $A_s$ , the integrator area counts for each standard sample, versus  $C_s$ , the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

#### 11.0 Analytical Procedure

11.1 Preparation of Equipment. Install the chromatographic column and condition overnight at 160 °C (320 °F). In the first operation, Porapak columns must be purged for 1 hour at 230 °C (450 °F).

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

11.2 Flow Rate Adjustments. Adjust flow rates as follows:

11.2.1. Nitrogen Carrier Gas. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

11.2.2. Vial Prepressurizer Nitrogen.

11.2.2.1 After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2} \left[ P_1 - \frac{P_{w1} - P_{w2}}{7.50} \right] - 10kPa \quad \text{Eq. 107-1}$$

Where:

$T_1$  = Ambient temperature, °K (°R).

$T_2$  = Conditioning bath temperature, °K (°R).

$P_1$  = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

$P_{w1}$  = Water vapor pressure 525.8 mm Hg @ 90 °C.

$P_{w2}$  = Water vapor pressure 19.8 mm Hg @ 22 °C.

7.50 = mm Hg per k Pa.

10 kPa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

11.2.2.2 Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90 °C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.



11.2.3. Burner Air Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

11.2.4. Hydrogen Supply. Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35  $\pm$ 5 cc/min. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

11.3 Temperature Adjustments. Set temperatures as follows:

11.3.1. Oven (chromatograph column), 140 °C (280 °F).

11.3.2. Dosing Line, 150 °C (300 °F).

11.3.3. Injection Block, 170 °C (340 °F).

11.3.4. Sample Chamber, Water Temperature, 90 °C  $\pm$ 1.0 °C (194 °F  $\pm$ 1.8 °F).

11.4 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

11.5 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

11.6 Programming the Chromatograph. Program the chromatograph as follows:

11.6.1. I—Dosing or Injection Time. The normal setting is 2 seconds.

11.6.2. A—Analysis Time. The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.

11.6.3. B—Backflushing Time. The normal setting is double the analysis time.

11.6.4. W—Stabilization Time. The normal setting is 0.5 min to 1.0 min.

11.6.5. X—Number of Analyses Per Sample. The normal setting is one.

11.7. Sample Treatment. All samples must be recovered and analyzed within 24 hours after collection.

11.7.1 Resin Samples. The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained (within  $\pm$ 1 percent) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100 ml or about two equal drops of water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVCM. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90 °C (190 °F) bath. Do not exceed 5 hours. Prepressurization is not required if the sample weight, as analyzed, does not exceed 0.2 gram. It is also not required if solution of the prepressurization equation yields an absolute prepressurization value that is within 30 percent of the atmospheric pressure.

Note: Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

11.7.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (1 percent). All samples weighing over 0.2 gram, must be prepressurized prior to conditioning for 1 hour at 90 °C (190 °F), except as noted in Section 11.7.1. A sample of wet cake is used to determine total solids (TS). This is required for calculating the RVCM.

11.7.3 Dispersion Resin Slurry and Geon Latex Samples. The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as

possible. Determine sample weight (1 percent). Condition the vial for 1 hour at 90 °C (190 °F) in the analyzer bath. Determine the TS on the slurry sample (Section 11.10).

11.7.4 In-process Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight (1 percent). Condition the vial for 1 hour at 90 °C (190 °F) in the analyzer bath.

## 11.8 Preparation of Sample Turntable.

11.8.1 Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

11.8.1.1 Positions 1 and 2. Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

11.8.1.2 Position 3. 50-ppm standard, freshly prepared.

11.8.1.3 Position 4. 500-ppm standard, freshly prepared.

11.8.1.4 Position 5. 2000-ppm standard, freshly prepared.

11.8.1.5 Position 6. 4000-ppm standard, freshly prepared.

11.8.1.6 Position 7. Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

11.8.2 After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90 °C (190 °F) for a minimum of one hour and a maximum of five hours.

11.9 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90 °C (190 °F) for at least one hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

11.10 Determination of Total Solids. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110 °C (221 to 230 °F)). Samples must be dried to constant weight. After first weighing, return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

## 12.0 Calculations and Data Analysis

### 12.1 Nomenclature.

$A_s$  = Chromatogram area counts of vinyl chloride for the sample, area counts.

$A_s$  = Chromatogram area counts of vinyl chloride for the sample.

$C_c$  = Concentration of vinyl chloride in the standard sample, ppm.

$K_p$  = Henry's Law Constant for VCM in PVC 90 °C,  $6.52 \times 10^{-8}$  g/g/mm Hg.

$K_w$  = Henry's Law Constant for VCM in water 90 °C,  $7 \times 10^{-7}$  g/g/mm Hg.

$M_v$  = Molecular weight of VCM, 62.5 g/mole.

$m$  = Sample weight, g.

$P_a$  = Ambient atmospheric pressure, mm Hg.

$R$  = Gas constant, (62360<sup>3</sup> ml) (mm Hg)/(mole)(°K).

$R_f$  = Response factor in area counts per ppm VCM.

$R_s$  = Response factor, area counts/ppm.

$T_1$  = Ambient laboratory temperature, °K.

$TS$  = Total solids expressed as a decimal fraction.

$T_2$  = Equilibrium temperature, °K.

$V_g$  = Volume of vapor phase, ml.

$$= V_v - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$$

$V_v$  = Vial volume, <sup>3</sup> ml.

1.36 = Density of PVC at 90 °C, g/<sup>3</sup> ml.

0.9653 = Density of water at 90 °C, g/<sup>3</sup> ml.

12.2 Response Factor. If the calibration curve described in Section 10.3 passes through zero, an average response factor,  $R_f$ , may be used to facilitate computation of vinyl chloride sample concentrations.

12.2.1 To compute  $R_f$ , first compute a response factor,  $R_s$ , for each sample as follows:

$$R_s = \frac{A_s}{C_s} \quad \text{Eq. 107-2}$$

12.2.2 Sum the individual response factors, and calculate  $R_f$ . If the calibration curve does not pass through zero, use the calibration curve to determine each sample concentration.

12.3 Residual Vinyl Chloride Monomer Concentration, ( $C_{rv}$ ) or Vinyl Chloride Monomer Concentration. Calculate  $C_{rv}$  in ppm or mg/kg as follows:

$$C_{rv} = \frac{A_s P_a}{R_f T_1} \left[ \frac{M_v V_g}{Rm} + K_p (TS) T_2 K_w (1-TS) T_2 \right] \quad \text{Eq. 107-3}$$

Note: Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by  $TS$ .

### 13.0 Method Performance

13.1 Range and Sensitivity. The lower limit of detection of vinyl chloride will vary according to the sampling and chromatographic system. The system should be capable of producing a measurement for a 50-ppm vinyl chloride standard that is at least 10 times the standard deviation of the system background noise level.

13.2 An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 62.66 ppm.

#### 14.0 *Pollution Prevention[Reserved]*

#### 15.0 *Waste Management[Reserved]*

#### 16.0 *References*

1. B.F. Goodrich, Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.
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4. Berens, A.R., *et. al.* Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography. Journal of Applied Polymer Science. 19:3169–3172. 1975.
5. Mansfield, R.A. The Evaluation of Henry's Law Constant (Kp) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich. Avon Lake, Ohio. February 10, 1978.

#### 17.0 *Tables, Diagrams, Flowcharts, and Validation Data[Reserved]*

Method 107A—Determination of Vinyl Chloride Content of Solvents, Resin-Solvent Solution, Polyvinyl Chloride Resin, Resin Slurry, Wet Resin, and Latex Samples

#### *Introduction*

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) or by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

#### 1. *Applicability and Principle*

1.1 *Applicability.* This is an alternative method and applies to the measurement of the vinyl chloride content of solvents, resin solvent solutions, polyvinyl chloride (PVC) resin, wet cake slurries, latex, and fabricated resin samples. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 *et seq.*, (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 *Principle.* The basis for this method lies in the direct injection of a liquid sample into a chromatograph and the subsequent evaporation of all volatile material into the carrier gas stream of the chromatograph, thus permitting analysis of all volatile material including vinyl chloride.

#### 2. *Range and Sensitivity*

The lower limit of detection of vinyl chloride in dry PVC resin is 0.2 ppm. For resin solutions, latexes, and wet resin, this limit rises inversely as the nonvolatile (resin) content decreases.

With proper calibration, the upper limit may be extended as needed.

#### 3. *Interferences*

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride. In cases where resolution interferences are encountered, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the

Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

#### *4. Precision and Reproducibility*

A standard sample of latex containing 181.8 ppm vinyl chloride analyzed 10 times by the alternative method showed a standard deviation of 7.5 percent and a mean error of 0.21 percent.

A sample of vinyl chloride copolymer resin solution was analyzed 10 times by the alternative method and showed a standard deviation of 6.6 percent at a level of 35 ppm.

#### *5. Safety*

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with vinyl chloride monomer (VCM) air mixtures must be held to minimum. When purging is required, the vapor must be routed to outside air. Vinyl chloride, even at low-ppm levels, must never be vented inside the laboratory.

#### *6. Apparatus*

6.1 Sampling. The following equipment is required:

6.1.1 Glass Bottles. 16-oz wide mouth wide polyethylene-lined, screw-on tops.

6.1.2 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. 20-ml capacity with polycone screw caps.

6.2.2 Analytical Balance. Capable of weighing to  $\pm 0.01$  gram.

6.2.3 Syringe. 50-microliter size, with removable needle.

6.2.4 Fritted Glass Sparger. Fine porosity.

6.2.5 Aluminum Weighing Dishes.

6.2.6 Sample Roller or Shaker. To help dissolve sample.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. Hewlett Packard Model 5720A or equivalent.

6.3.2 Chromatograph Column. Stainless steel, 6.1 m by 3.2 mm, packed with 20 percent Tergitol E-35 on Chromosorb W AW 60/80 mesh. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and that he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interfering peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

6.3.3 Valco Instrument Six-Port Rotary Valve. For column back flush.

6.3.4 Septa. For chromatograph injection port.

6.3.5 Injection Port Liners. For chromatograph used.

6.3.6 Regulators. For required gas cylinders.

6.3.7 Soap Film Flowmeter. Hewlett Packard No. 0101-0113 or equivalent.

6.4 Calibration. The following equipment is required:

6.4.1 Analytical Balance. Capable of weighing to  $\pm 0.0001$  g.

6.4.2 Erlenmeyer Flask With Glass Stopper. 125 ml.

6.4.3 Pipets. 0.1, 0.5, 1, 5, 10, and 50 ml.

6.4.4 Volumetric Flasks. 10 and 100 ml.

## 7. Reagents

Use only reagents that are of chromatograph grade.

7.1 Analysis. The following items are required:

7.1.1 Hydrogen Gas. Zero grade.

7.1.2 Nitrogen Gas. Zero grade.

7.1.3 Air. Zero grade.

7.1.4 Tetrahydrofuran (THF). Reagent grade.

Analyze the THF by injecting 10 microliters into the prepared gas chromatograph. Compare the THF chromatogram with that shown in Figure 107A-1. If the chromatogram is comparable to A, the THF should be sparged with pure nitrogen for approximately 2 hours using the fritted glass sparger to attempt to remove the interfering peak. Reanalyze the sparged THF to determine whether the THF is acceptable for use. If the scan is comparable to B, the THF should be acceptable for use in the analysis.

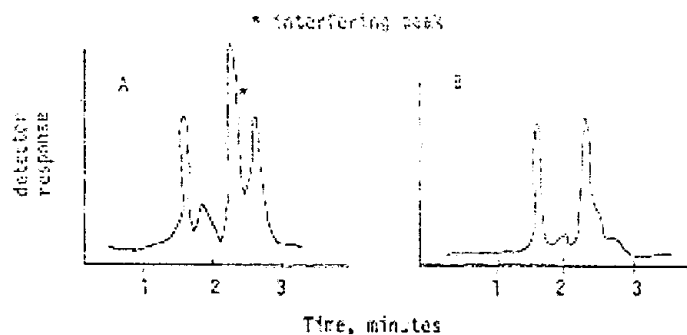


Figure 107A-1

7.1.5 N, N-Dimethylacetamide (DMAC). Spectrographic grade. For use in place of THF.

7.2 Calibration. The following item is required:

7.2.1 Vinyl Chloride 99.9 Percent. Ideal Gas Products lecture bottle, or equivalent. For preparation of standard solutions.

## 8. Procedure

8.1 Sampling. Allow the liquid or dried resin to flow from a tap on the tank, silo, or pipeline until the tap has been purged. Fill a wide-mouth pint bottle, and immediately tightly cap the bottle. Place an identifying label on each bottle and record the date, time, sample location, and material.

## 8.2 Sample Treatment. Sample must be run within 24 hours.

8.2.1 Resin Samples. Weigh  $9.00 \pm 0.01$  g of THF or DMAC in a tared 20-ml vial. Add  $1.00 \pm 0.01$  g of resin to the tared vial containing the THF or DMAC. Close the vial tightly with the screw cap, and shake or otherwise agitate the vial until complete solution of the resin is obtained. Shaking may require several minutes to several hours, depending on the nature of the resin.

8.2.2 Suspension Resin Slurry and Wet Resin Sample. Slurry must be filtered using a small Buchner funnel with vacuum to yield a wet resin sample. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration time could result in some loss of VCM. The wet resin sample is weighed into a tared 20-ml vial with THF or DMAC as described earlier for resin samples (8.2.1) and treated the same as the resin sample. A sample of the wet resin is used to determine total solids as required for calculating the residual VCM (Section 8.3.4).

8.2.3 Latex and Resin Solvent Solutions. Samples must be thoroughly mixed. Weigh  $1.00 \pm 0.01$  g of the latex or resin-solvent solution into a 20-ml vial containing  $9.00 \pm 0.01$  g of THF or DMAC as for the resin samples (8.2.1). Cap and shake until complete solution is obtained. Determine the total solids of the latex or resin solution sample (Section 8.3.4).

8.2.4 Solvents and Non-viscous Liquid Samples. No preparation of these samples is required. The neat samples are injected directly into the GC.

## 8.3 Analysis.

8.3.1 Preparation of GC. Install the chromatographic column, and condition overnight at 70 °C. Do not connect the exit end of the column to the detector while conditioning.

8.3.1.1 Flow Rate Adjustments. Adjust the flow rate as follows:

- a. Nitrogen Carrier Gas. Set regulator on cylinder to read 60 psig. Set column flow controller on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.
- b. Burner Air Supply. Set regulator on the cylinder at 40 psig. Set regulator on the chromatograph to supply air to the burner to yield a flow rate of 250 to 300 cc/min using the flowmeter.
- c. Hydrogen. Set regulator on cylinder to read 60 psig. Set regulator on the chromatograph to supply 30 to 40 cc/min using the flowmeter. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with flowmeter and record this flow.
- d. Nitrogen Back Flush Gas. Set regulator on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.

8.3.1.2 Temperature Adjustments. Set temperature as follows:

- a. Oven (chromatographic column) at 70 °C.
- b. Injection Port at 100 °C.
- c. Detector at 300 °C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions. Allow system to stabilize approximately 1 hour.

8.3.1.4 Recorder. Set pen at zero and start chart drive.

8.3.1.5 Attenuation. Set attenuation to yield desired peak height depending on sample VCM content.

## 8.3.2 Chromatographic Analyses.

a. Sample Injection. Remove needle from 50-microliter syringe. Open sample vial and draw 50-microliters of THF or DMAC sample recovery solution into the syringe. Recap sample vial. Attach needle to the syringe and while holding the syringe vertically (needle uppermost), eject 40 microliters into an absorbent tissue. Wipe needle with tissue. Now inject 10

microliters into chromatograph system. Repeat the injection until two consecutive values for the height of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two peak heights to compute the sample concentration.

b. Back Flush. After 4 minutes has elapsed after sample injection, actuate the back flush valve to purge the first 4 feet of the chromatographic column of solvent and other high boilers.

c. Sample Data. Record on the chromatograph strip chart the data from the sample label.

d. Elution Time. Vinyl chloride elutes at 2.8 minutes. Acetaldehyde elutes at 3.7 minutes. Analysis is considered complete when chart pen becomes stable. After 5 minutes, reset back flush valve and inject next sample.

### 8.3.3 Chromatograph Servicing.

a. Septum. Replace after five sample injections.

b. Sample Port Liner. Replace the sample port liner with a clean spare after five sample injections.

c. Chromatograph Shutdown. If the chromatograph has been shut down overnight, rerun one or more samples from the preceding day to test stability and precision prior to starting on the current day's work.

8.3.4 Determination of Total Solids (TS). For wet resin, resin solution, and PVC latex samples, determine the TS for each sample by accurately weighing approximately 3 to 5 grams of sample into a tared aluminum pan. The initial procedure is as follows:

a. Where water is the major volatile component: Tare the weighing dish, and add 3 to 5 grams of sample to the dish. Weigh to the nearest milligram.

b. Where volatile solvent is the major volatile component: Transfer a portion of the sample to a 20-ml screw cap vial and cap immediately. Weigh the vial to the nearest milligram. Uncap the vial and transfer a 3- to 5-gram portion of the sample to a tared aluminum weighing dish. Recap the vial and reweigh to the nearest milligram. The vial weight loss is the sample weight.

To continue, place the weighing pan in a 130 °C oven for 1 hour. Remove the dish and allow to cool to room temperature in a desiccator. Weigh the pan to the nearest 0.1 mg. Total solids is the weight of material in the aluminum pan after heating divided by the net weight of sample added to the pan originally times 100.

## 9. Calibration of the Chromatograph

9.1 Preparation of Standards. Prepare a 1 percent by weight (approximate) solution of vinyl chloride in THF or DMAC by bubbling vinyl chloride gas from a cylinder into a tared 125-ml glass-stoppered flask containing THF or DMAC. The weight of vinyl chloride to be added should be calculated prior to this operation, i.e., 1 percent of the weight of THF or DMAC contained in the tared flask. This must be carried out in a laboratory hood. Adjust the vinyl chloride flow from the cylinder so that the vinyl chloride dissolves essentially completely in the THF or DMAC and is not blown to the atmosphere. Take particular care not to volatilize any of the solution. Stopper the flask and swirl the solution to effect complete mixing. Weigh the stoppered flask to nearest 0.1 mg to determine the exact amount of vinyl chloride added.

Pipet 10 ml of the approximately 1 percent solution into a 100-ml glass-stoppered volumetric flask, and add THF or DMAC to fill to the mark. Cap the flask and invert 10 to 20 times. This solution contains approximately 1,000 ppm by weight of vinyl chloride (note the exact concentration).

Pipet 50-, 10-, 5-, 1-, 0.5-, and 0.1-ml aliquots of the approximately 1,000 ppm solution into 10 ml glass stoppered volumetric flasks. Dilute to the mark with THF or DMAC, cap the flasks and invert each 10 to 20 times. These solutions contain approximately 500, 100, 50, 10, 5, and 1 ppm vinyl chloride. Note the exact concentration of each one. These standards are to be kept under refrigeration in stoppered bottles, and must be renewed every 3 months.

### 9.2 Preparation of Chromatograph Calibration Curve.

Obtain the GC for each of the six final solutions prepared in Section 9.1 by using the procedure in Section 8.3.2. Prepare a chart plotting peak height obtained from the chromatogram of each solution versus the known concentration. Draw a straight line through the points derived by the least squares method.



## 10. Calculations

10.1 Response Factor. From the calibration curve described in Section 9.2, select the value of  $C_c$  that corresponds to  $H_c$  for each sample. Compute the response factor,  $R_f$ , for each sample as follows:

$$R_f = \frac{C_c}{H_c} \quad \text{Eq. 107A-1}$$

where:

$R_f$ =Chromatograph response factor, ppm/mm.

$C_c$ =Concentration of vinyl chloride in the standard sample, ppm.

$H_c$ =Peak height of the standard sample, mm.

10.2 Residual vinyl chloride monomer concentration ( $C_{rv}$ ) or vinyl chloride monomer concentration in resin:

$$C_{rv} = 10H_s R_f \quad \text{Eq. 107A-2}$$

Where:

$C_{rv}$ =Concentration of residual vinyl chloride monomer, ppm.

$H_s$ =Peak height of sample, mm.

$R_f$ =Chromatograph response factor.

10.3 Samples containing volatile material, i.e., resin solutions, wet resin, and latexes:

$$C_{rv} = \frac{H_s R_f (1,000)}{TS} \quad \text{Eq. 107A-3}$$

where:

$TS$ =Total solids in the sample, weight fraction.

10.4 Samples of solvents and in process wastewater:

$$C_{rv} = \frac{H_s R_f}{0.888} \quad \text{Eq. 107A-4}$$

Where:

0.888=Specific gravity of THF.

## 11. Bibliography

1. Communication from R. N. Wheeler, Jr.; Union Carbide Corporation. Part 61 National Emissions Standards for Hazardous Air Pollutants appendix B, Method 107—Alternate Method, September 19, 1977.

Method 108—Determination of Particulate and Gaseous Arsenic Emissions

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 12.

#### 1.0 Scope and Application.

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440-38-2	Lower limit 10 µg/ml or less.

1.2 Applicability. This method is applicable for the determination of inorganic As emissions from stationary sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

Particulate and gaseous As emissions are withdrawn isokinetically from the source and are collected on a glass mat filter and in water. The collected arsenic is then analyzed by means of atomic absorption spectrophotometry (AAS).

#### 3.0 Definitions.[Reserved]

#### 4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties ( e.g., viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (Section 11.5).

#### 5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Very harmful to eyes. 30% H<sub>2</sub>O<sub>2</sub> can burn skin, nose, and lungs.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 108–1; it is similar to the Method 5 sampling train of 40 CFR part 60, appendix A. The following items are required for sample collection:

6.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1 to 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.2 Impingers. Four impingers connected in series with leak-free ground-glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm ID (0.5-in.) glass tube extending to about 1.3 cm (0.5 in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip. Modifications (e.g., flexible connections between the impingers, materials other than glass, or flexible vacuum lines to connect the filter holder to the condenser) are subject to the approval of the Administrator.

6.1.3 Temperature Sensor. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F), at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 6.2.1 and 6.2.4 to 6.2.8, respectively.

6.2.2 Wash Bottles. Polyethylene (2).

6.2.3 Sample Storage Containers. Chemically resistant, polyethylene or polypropylene for glassware washes, 500- or 1000-ml.

6.3 Analysis. The following items are required for analysis:

6.3.1 Spectrophotometer. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nanometers (nm). For measuring samples having less than 10 µg As/ml, use a vapor generator accessory or a graphite furnace.

6.3.2 Recorder. To match the output of the spectrophotometer.

6.3.3 Beakers. 150 ml.

6.3.4 Volumetric Flasks. Glass 50-, 100-, 200-, 500-, and 1000-ml; and polypropylene, 50-ml.

6.3.5 Balance. To measure within 0.5 g.

6.3.6 Volumetric Pipets. 1-, 2-, 3-, 5-, 8-, and 10-ml.

6.3.7 Oven.

6.3.8 Hot Plate.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 The following reagents are required for sample collection:

7.1.1 Filters. Same as Method 5, Section 7.1.1, except that the filters need not be unreactive to SO<sub>2</sub>.

7.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.3 Water. Deionized distilled to meet ASTM D 1193–77 or 91 (incorporated by reference-see §61.18), Type 3. When high concentrations of organic matter are not expected to be present, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted.

## 7.2 Sample Recovery.

7.2.1 0.1 N NaOH. Dissolve 4.00 g of NaOH in about 500 ml of water in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Section 7.1.3.

7.3.2 Sodium Hydroxide, 0.1 N. Same as in Section 7.2.1.

7.3.3 Sodium Borohydride ( $\text{NaBH}_4$ ), 5 Percent Weight by Volume (W/V). Dissolve 50.0 g of  $\text{NaBH}_4$  in about 500 ml of 0.1 N NaOH in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with 0.1 N NaOH.

7.3.4 Hydrochloric Acid, Concentrated.

7.3.5 Potassium Iodide (KI), 30 Percent (W/V). Dissolve 300 g of KI in 500 ml of water in a 1 liter volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.3.6 Nitric Acid, Concentrated.

7.3.7 Nitric Acid, 0.8 N. Dilute 52 ml of concentrated  $\text{HNO}_3$  to exactly 1.0 liter with water.

7.3.8 Nitric Acid, 50 Percent by Volume (V/V). Add 50 ml concentrated  $\text{HNO}_3$  to 50 ml water.

7.3.9 Stock Arsenic Standard, 1 mg As/ml. Dissolve 1.3203 g of primary standard grade  $\text{As}_2\text{O}_3$  in 20 ml of 0.1 N NaOH in a 150 ml beaker. Slowly add 30 ml of concentrated  $\text{HNO}_3$ . Heat the resulting solution and evaporate just to dryness. Transfer the residue quantitatively to a 1-liter volumetric flask, and dilute to 1.0 liter with water.

7.3.10 Arsenic Working Solution, 1.0  $\mu\text{g}$  As/ml. Pipet exactly 1.0 ml of stock arsenic standard into an acid-cleaned, appropriately labeled 1-liter volumetric flask containing about 500 ml of water and 5 ml of concentrated  $\text{HNO}_3$ . Dilute to exactly 1.0 liter with water.

7.3.11 Air. Suitable quality for AAS analysis.

7.3.12 Acetylene. Suitable quality for AAS analysis.

7.3.13 Nickel Nitrate, 5 Percent Ni (W/V). Dissolve 24.780 g of nickel nitrate hexahydrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  in water in a 100-ml volumetric flask, and dilute to 100 ml with water.

7.3.14 Nickel Nitrate, 1 Percent Ni (W/V). Pipet 20 ml of 5 percent nickel nitrate solution into a 100-ml volumetric flask, and dilute to exactly 100 ml with water.

7.3.15 Hydrogen Peroxide, 3 Percent by Volume. Pipet 50 ml of 30 percent  $\text{H}_2\text{O}_2$  into a 500-ml volumetric flask, and dilute to exactly 500 ml with water.

7.3.16 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

Note: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

## 8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 8.1, except the filter need not be weighed, and the 200 ml of 0.1N NaOH and Container 4 should be tared to within 0.5 g.

8.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 8.2, except select the nozzle size to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 8.3.

8.4 Leak-Check Procedures. Same as Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5, except maintain isokinetic sampling flow rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet similar to the one shown in Figure 108-2.

8.6 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.7 Sample Recovery. Same as Method 5, Section 8.7, except that 0.1 N NaOH is used as the cleanup solvent instead of acetone and that the impinger water is treated as follows:

8.7.1 Container Number 4 (Impinger Water). Clean each of the first three impingers and connecting glassware in the following manner:

8.7.1.1 Wipe the impinger ball joints free of silicone grease, and cap the joints.

8.7.1.2 Rotate and agitate each of the first two impingers, using the impinger contents as a rinse solution.

8.7.1.3 Transfer the liquid from the first three impingers to Container Number 4. Remove the outlet ball-joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the container.

8.7.1.4 Weigh the contents of Container No. 4 to within 0.5 g. Record in the log the weight of liquid along with a notation of any color or film observed in the impinger catch. The weight of liquid is needed along with the silica gel data to calculate the stack gas moisture content.

Note: Measure and record the total amount of 0.1 N NaOH used for rinsing under Sections 8.7.1.5 and 8.7.1.6.

8.7.1.5 Pour approximately 30 ml of 0.1 NaOH into each of the first two impingers, and agitate the impingers. Drain the 0.1 N NaOH through the outlet arm of each impinger into Container Number 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

8.7.1.6 Wipe the ball joints of the glassware connecting the impingers and the back half of the filter holder free of silicone grease, and rinse each piece of glassware twice with 0.1 N NaOH; transfer this rinse into Container Number 4. (DO NOT RINSE or brush the glass-fritted filter support.) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify clearly its contents.

8.8 Blanks.

8.8.1 Sodium Hydroxide. Save a portion of the 0.1 N NaOH used for cleanup as a blank. Take 200 ml of this solution directly from the wash bottle being used and place it in a plastic sample container labeled "NaOH blank."

8.8.2 Water. Save a sample of the water, and place it in a container labeled "H<sub>2</sub>O blank."

8.8.3 Filter. Save two filters from each lot of filters used in sampling. Place these filters in a container labeled "filter blank."

9.0 *Quality Control*

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak-checks and calibration	Ensures accuracy and precision of sampling measurements.
10.4	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminates matrix effects.
11.6	Audit sample analysis	Evaluates analyst's technique and standards preparation.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

#### 10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Preparation of Standard Solutions.

10.2.1 For the high level procedure, pipet 1, 3, 5, 8, and 10 ml of the 1.0 mg As/ml stock solution into separate 100 ml volumetric flasks, each containing 5 ml of concentrated HNO<sub>3</sub>. Dilute to the mark with water.

10.2.2 For the low level vapor generator procedure, pipet 1, 2, 3, and 5 ml of 1.0 µg As/ml standard solution into separate reaction tubes. Dilute to the mark with water.

10.2.3 For the low level graphite furnace procedure, pipet 1, 5, 10 and 15 ml of 1.0 µg As/ml standard solution into separate flasks along with 2 ml of the 5 percent nickel nitrate solution and 10 ml of the 3 percent H<sub>2</sub>O<sub>2</sub> solution. Dilute to the mark with water.

10.3 Calibration Curve. Analyze a 0.8 N HNO<sub>3</sub> blank and each standard solution according to the procedures outlined in section 11.4.1. Repeat this procedure on each standard solution until two consecutive peaks agree within 3 percent of their average value. Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak height of each standard solution. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is As contamination of a reagent or carry-over of As from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total As weight in the solution.

10.4 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations ( e.g., 1, 3, 5, 8, and 10 mg As for the high-level procedure) must be less than 7 percent for all standards.

Note: For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary. In all cases, follow calibration and operational procedures in the manufacturers' instruction manual.

#### 11.0 Analytical Procedure

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Containers Number 2 and Number 4. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

## 11.2 Sample Preparation.

11.2.1 Container Number 1 (Filter). Place the filter and loose particulate matter in a 150 ml beaker. Also, add the filtered solid material from Container Number 2 (see Section 11.2.2). Add 50 ml of 0.1 N NaOH. Then stir and warm on a hot plate at low heat (do not boil) for about 15 minutes. Add 10 ml of concentrated HNO<sub>3</sub>, bring to a boil, then simmer for about 15 minutes. Filter the solution through a glass fiber filter. Wash with hot water, and catch the filtrate in a clean 150 ml beaker. Boil the filtrate, and evaporate to dryness. Cool, add 5 ml of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow to cool. Transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

### 11.2.2 Container Number 2 (Probe Wash).

11.2.2.1 Filter (using a glass fiber filter) the contents of Container Number 2 into a 200 ml volumetric flask. Combine the filtered (solid) material with the contents of Container Number 1 (Filter).

11.2.2.2 Dilute the filtrate to exactly 200 ml with water. Then pipet 50 ml into a 150 ml beaker. Add 10 ml of concentrated HNO<sub>3</sub>, bring to a boil, and evaporate to dryness. Allow to cool, add 5 ml of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow the solution to cool, transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

11.2.3 Container Number 4 (Impinger Solution). Transfer the contents of Container Number 4 to a 500 ml volumetric flask, and dilute to exactly 500-ml with water. Pipet 50 ml of the solution into a 150-ml beaker. Add 10 ml of concentrated HNO<sub>3</sub>, bring to a boil, and evaporate to dryness. Allow to cool, add 5 ml of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow the solution to cool, transfer to a 50-ml volumetric flask, dilute to volume with water, and mix well.

11.2.4 Filter Blank. Cut each filter into strips, and treat each filter individually as directed in Section 11.2.1, beginning with the sentence, "Add 50 ml of 0.1 N NaOH."

11.2.5 Sodium Hydroxide and Water Blanks. Treat separately 50 ml of 0.1 N NaOH and 50 ml water, as directed under Section 11.2.3, beginning with the sentence, "Pipet 50 ml of the solution into a 150-ml beaker."

11.3 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current. Adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.4 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.2 through 10.4.

11.4.1 Arsenic Samples. Analyze an appropriately sized aliquot of each diluted sample (from Sections 11.2.1 through 11.2.3) until two consecutive peak heights agree within 3 percent of their average value. If applicable, follow the procedures outlined in Section 11.4.1.1. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.8 N HNO<sub>3</sub> so that the final concentration falls within the range of the curve. Using the calibration curve, determine the arsenic concentration in each sample fraction.

**Note:** Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

11.4.1.1 Arsenic Determination at Low Concentration. The lower limit of flame AAS is 10 µg As/ml. If the arsenic concentration of any sample is at a lower level, use the graphite furnace or vapor generator which is available as an accessory component. Flame, graphite furnace, or vapor generators may be used for samples whose concentrations are between 10 and 30 µg/ml. Follow the manufacturer's instructions in the use of such equipment.

11.4.1.1.1 Vapor Generator Procedure. Place a sample containing between 0 and 5 µg of arsenic in the reaction tube, and dilute to 15 ml with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional atomic absorption until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 ml of concentrated HCl into each tube. Add 1 ml of 30 percent KI solution. Place the reaction tube into a 50 °C (120 °F) water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 ml of 5 percent NaBH<sub>4</sub>, and integrate the resulting spectrophotometer signal over a 30-second time period.

11.4.1.1.2 Graphite Furnace Procedure. Dilute the digested sample so that a 5 ml aliquot contains less than 1.5 µg of arsenic. Pipet 5 ml of this digested solution into a 10-ml volumetric flask. Add 1 ml of the 1 percent nickel nitrate solution,

0.5 ml of 50 percent  $\text{HNO}_3$ , and 1 ml of the 3 percent hydrogen peroxide and dilute to 10 ml with water. The sample is now ready for analysis.

11.4.1.2 Run a blank (0.8 N  $\text{HNO}_3$ ) and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.4.1.3 Determine the arsenic concentration in the filter blank (i.e., the average of the two blank values from each lot).

11.4.2 Container Number 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

11.5 Check for matrix effects on the arsenic results. Same as Method 12, Section 11.5.

11.6 Audit Sample Analysis.

11.6.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of EPA audit samples must be analyzed, subject to availability.

11.6.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

**Note:** It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.7 Audit Sample Results.

11.7.1 Calculate the audit sample concentrations in  $\text{g}/\text{m}^3$  and submit results using the instructions provided with the audit samples.

11.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.7.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.7.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

## 12.0 Data Analysis and Calculations

### 12.1 Nomenclature.

$B_{ws}$  = Water in the gas stream, proportion by volume.



$C_a$  = Concentration of arsenic as read from the standard curve,  $\mu\text{g/ml}$ .

$C_c$  = Actual audit concentration,  $\text{g/m}^3$ .

$C_d$  = Determined audit concentration,  $\text{g/m}^3$ .

$C_s$  = Arsenic concentration in stack gas, dry basis, converted to standard conditions,  $\text{g/dsm}^3$  ( $\text{gr/dscf}$ ).

$E_a$  = Arsenic mass emission rate,  $\text{g/hr}$  ( $\text{lb/hr}$ ).

$F_d$  = Dilution factor (equals 1 if the sample has not been diluted).

$I$  = Percent of isokinetic sampling.

$m_{bi}$  = Total mass of all four impingers and contents before sampling, g.

$m_{bi}$  = Total mass of all four impingers and contents after sampling, g.

$m_i$  = Total mass of arsenic collected in a specific part of the sampling train,  $\mu\text{g}$ .

$m_t$  = Total mass of arsenic collected in the sampling train,  $\mu\text{g}$ .

$T_m$  = Absolute average dry gas meter temperature (see Figure 108–2),  $^{\circ}\text{K}$  ( $^{\circ}\text{R}$ ).

$V_m$  = Volume of gas sample as measured by the dry gas meter, dry basis,  $\text{m}^3$  ( $\text{ft}^3$ ).

$V_{m(\text{std})}$  = Volume of gas sample as measured by the dry gas meter, corrected to standard conditions,  $\text{m}^3$  ( $\text{ft}^3$ ).

$V_n$  = Volume of solution in which the arsenic is contained, ml.

$V_{w(\text{std})}$  = Volume of water vapor collected in the sampling train, corrected to standard conditions,  $\text{m}^3$  ( $\text{ft}^3$ ).

$\Delta H$  = Average pressure differential across the orifice meter (see Figure 108–2), mm  $\text{H}_2\text{O}$  (in.  $\text{H}_2\text{O}$ ).

12.2 Average Dry Gas Meter Temperatures ( $T_m$ ) and Average Orifice Pressure Drop ( $\Delta H$ ). See data sheet (Figure 108–2).

12.3 Dry Gas Volume. Using data from this test, calculate  $V_{m(\text{std})}$  according to the procedures outlined in Method 5, Section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(\text{std})} = K_2 (m_{fi} - m_{di}) \quad \text{Eq. 108-1}$$

Where:

$K_2$  =  $0.001334 \text{ m}^3/\text{g}$  for metric units.

=  $0.047012 \text{ ft}^3/\text{g}$  for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad \text{Eq. 108-2}$$

## 12.6 Amount of Arsenic Collected.

12.6.1 Calculate the amount of arsenic collected in each part of the sampling train, as follows:

$$m_n = C_a F_d V_n \quad \text{Eq. 108-3}$$

12.6.2 Calculate the total amount of arsenic collected in the sampling train as follows:

$$m_t = m_{\text{filters}} + m_{\text{probe}} + m_{\text{impingers}} \quad \text{Eq. 108-4}$$

$$- m_{\text{filter blank}} - m_{\text{NaOH blank}} - m_{\text{water blank}}$$

12.7 Calculate the arsenic concentration in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_3 \left( m_t / V_{m(std)} \right) \quad \text{Eq. 108-5}$$

Where:

$K_3 = 10^{-6} \text{ g}/\mu\text{g}$  for metric units

$= 1.54 \times 10^{-5} \text{ gr}/\mu\text{g}$  for English units

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate using data obtained in this method and the equations in Sections 12.2 and 12.3 of Method 2.

12.9 Pollutant Mass Rate. Calculate the arsenic mass emission rate as follows:

$$E_a = C_s Q_{sd} \quad \text{Eq. 108-6}$$

12.10 Isokinetic Variation. Same as Method 5, Section 12.11.

## 13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS 10  $\mu\text{g As/ml}$ . The analytical procedure includes provisions for the use of a graphite furnace or vapor generator for samples with a lower arsenic concentration.

## 14.0 Pollution Prevention.[Reserved]

## 15.0 Waste Management.[Reserved]

## 16.0 References.

Same as References 1 through 9 of Method 5, Section 17.0, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. 303-0152. Norwalk, Connecticut. September 1976. pp. 5-6.

2. Standard Specification for Reagent Water. In: Annual Book of American Society for Testing and Materials Standards. Part 31: Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 40–42.

3. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

#### 17.0 Tables, Diagrams, Flowcharts, and Validation Data

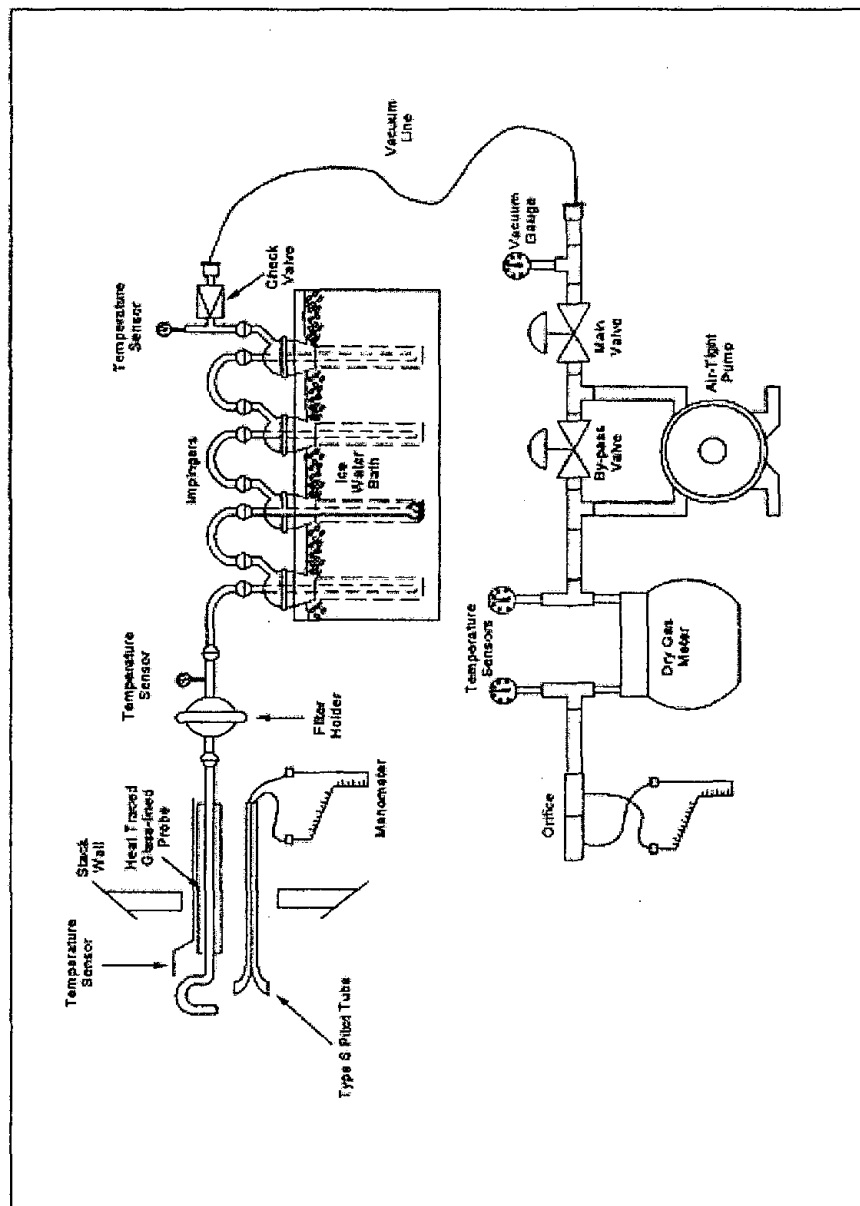


Figure 108-1. Arsenic Sampling Train

[View or download PDF](#)



Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440-38-2	Lower limit 10 µg/ml or less.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by flame atomic absorption spectrophotometry (AAS).

## 3.0 Definitions[Reserved]

## 4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties ( e.g., viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (section 11.5).

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Very harmful to eyes. 30% H<sub>2</sub>O<sub>2</sub> can burn skin, nose, and lungs.

5.2.4 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.5 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

## 6.0 Equipment and Supplies

6.1 Sample Collection and Preparation. The following items are required for sample collection and preparation:

6.1.1 Parr Acid Digestion Bomb. Stainless steel with vapor-tight Teflon cup and cover.

6.1.2 Volumetric Pipets. 2- and 5-ml sizes.

6.1.3 Volumetric Flask. 50-ml polypropylene with screw caps, (one needed per standard).

6.1.4 Funnel. Polyethylene or polypropylene.

6.1.5 Oven. Capable of maintaining a temperature of approximately 105 °C (221 °F).

6.1.6 Analytical Balance. To measure to within 0.1 mg.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer and Recorder. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm. For measuring samples having less than 10 µg As/ml, use a graphite furnace or vapor generator accessory. The recorder shall match the output of the spectrophotometer.

6.2.2 Volumetric Flasks. Class A, 50-ml (one needed per sample and blank), 500-ml, and 1-liter.

6.2.3 Volumetric Pipets. Class A, 1-, 5-, 10-, and 25-ml sizes.

#### *7.0 Reagents and Standards.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection and Preparation. The following reagents are required for sample collection and preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193–77 or 91 Type 3 (incorporated by reference—See §61.18). When high concentrations of organic matter are not expected to be present, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted. Use in all dilutions requiring water.

7.1.2 Nitric Acid Concentrated.

7.1.3 Nitric Acid, 0.5 N. In a 1-liter volumetric flask containing water, add 32 ml of concentrated  $\text{HNO}_3$  and dilute to volume with water.

7.1.4 Hydrofluoric Acid, Concentrated.

7.1.5 Potassium Chloride (KCl) Solution, 10 percent weight by volume (W/V). Dissolve 10 g KCl in water, add 3 ml concentrated  $\text{HNO}_3$ , and dilute to 100 ml.

7.1.6 Filter. Teflon filters, 3-micron porosity, 47-mm size. (Available from Millipore Co., type FS, Catalog Number FSLW04700.)

7.1.7 Sodium Borohydride ( $\text{NaBH}_4$ ), 5 Percent (W/V). Dissolve 50.0 g of  $\text{NaBH}_4$  in about 500 ml of 0.1 N NaOH in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with 0.1 N NaOH.

7.1.8 Nickel Nitrate, 5 Percent Ni (W/V). Dissolve 24.780 g of nickel nitrate hexahydrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] in water in a 100-ml volumetric flask, and dilute to 100 ml with water.

7.1.9 Nickel Nitrate, 1 Percent Ni (W/V). Pipet 20 ml of 5 percent nickel nitrate solution into a 100-ml volumetric flask, and dilute to 100 ml with water.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Sodium Hydroxide, 0.1 N. Dissolve 2.00 g of NaOH in water in a 500-ml volumetric flask. Dilute to volume with water.

7.2.3 Nitric Acid, 0.5 N. Same as in Section 7.1.3.

7.2.4 Potassium Chloride Solution, 10 percent. Same as in Section 7.1.5.

7.2.5 Hydrochloric Acid, Concentrated.

7.2.6 Potassium Iodide (KI), 30 Percent (W/V). Dissolve 300 g of KI in about 500 ml of water in a 1-liter volumetric flask. Then, dilute to exactly 1.0 liter with water.

7.2.7 Hydrogen Peroxide, 3 Percent by Volume. Pipet 50 ml of 30 percent  $H_2O_2$  into a 500-ml volumetric flask, and dilute to exactly 500 ml with water.

7.2.8 Stock Arsenic Standard, 1 mg As/ml. Dissolve 1.3203 g of primary grade  $As_2O_3$  in 20 ml of 0.1 N NaOH. Slowly add 30 ml of concentrated  $HNO_3$ , and heat in an oven at 105 °C (221 °F) for 2 hours. Allow to cool, and dilute to 1 liter with deionized distilled water.

7.2.9 Nitrous Oxide. Suitable quality for AAS analysis.

7.2.10 Acetylene. Suitable quality for AAS analysis.

7.2.11 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

**Note:** The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

#### *8.0 Sample Collection, Preservation, Transport, and Storage*

8.1 Sample Collection. A sample that is representative of the ore lot to be tested must be taken prior to analysis. (A portion of the samples routinely collected for metals analysis may be used provided the sample is representative of the ore being tested.)

8.2 Sample Preparation. The sample must be ground into a finely pulverized state.

#### *9.0 Quality Control*

Section	Quality control measure	Effect
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminate matrix effects
11.6	Audit sample analysis	Evaluate analyst's technique and standards preparation.

#### *10.0 Calibration and Standardizations*

**Note:** Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Pipet 1, 5, 10, and 25 ml of the stock As solution into separate 100-ml volumetric flasks. Add 10 ml KCl solution and dilute to the mark with 0.5 N  $HNO_3$ . This will give standard concentrations of 10, 50, 100, and 250  $\mu g$  As/ml. For low-level arsenic samples that require the use of a graphite furnace or vapor generator, follow the procedures in Section 11.3:1. Dilute 10 ml of KCl solution to 100 ml with 0.5 N  $HNO_3$  and use as a reagent blank.

10.2 Calibration Curve. Analyze the reagent blank and each standard solution according to the procedures outlined in Section 11.3. Repeat this procedure on each standard solution until two consecutive peaks agree within 3 percent of their average value. Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of each standard solution. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of As from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding final total As weight in the solution.

10.3 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations must be less than 7 percent for all standards.

**Note:** For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary. In all cases, follow calibration and operational procedures in the manufacturer's instruction manual.

#### *11.0 Analytical Procedure*

11.1 Sample Preparation. Weigh 50 to 500 mg of finely pulverized sample to the nearest 0.1 mg. Transfer the sample into the Teflon cup of the digestion bomb, and add 2 ml each of concentrated  $\text{HNO}_3$  and  $\text{HF}$ . Seal the bomb immediately to prevent the loss of any volatile arsenic compounds that may form. Heat in an oven at  $105^\circ\text{C}$  ( $221^\circ\text{F}$ ) for 2 hours. Remove the bomb from the oven and allow to cool. Using a Teflon filter, quantitatively filter the digested sample into a 50-ml polypropylene volumetric flask. Rinse the bomb three times with small portions of 0.5 N  $\text{HNO}_3$ , and filter the rinses into the flask. Add 5 ml of KCl solution to the flask, and dilute to 50 ml with 0.5 N  $\text{HNO}_3$ .

#### 11.2 Spectrophotometer Preparation.

11.2.1 Turn on the power; set the wavelength, slit width, and lamp current. Adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.2.2 Develop a spectrophotometer calibration curve as outlined in Sections 10.2 and 10.3.

11.3 Arsenic Determination. Analyze an appropriately sized aliquot of each diluted sample (from Section 11.1) until two consecutive peak heights agree within 3 percent of their average value. If applicable, follow the procedures outlined in Section 11.3.1. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.5 N  $\text{HNO}_3$  so that the final concentration falls within the range of the curve. Using the calibration curve, determine the As concentration in each sample.

**Note:** Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

11.3.1 Arsenic Determination at Low Concentration. The lower limit of flame AAS is  $10\text{ }\mu\text{g As/ml}$ . If the arsenic concentration of any sample is at a lower level, use the vapor generator or graphite furnace which is available as an accessory component. Flame, graphite furnace, or vapor generators may be used for samples whose concentrations are between 10 and  $30\text{ }\mu\text{g/ml}$ . Follow the manufacturer's instructions in the use of such equipment.

11.3.1.1 Vapor Generator Procedure. Place a sample containing between 0 and  $5\text{ }\mu\text{g}$  of arsenic in the reaction tube, and dilute to 15 ml with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional AAS until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 ml of concentrated  $\text{HCl}$  into each tube. Add 1 ml of 30 percent  $\text{KI}$  solution. Place the reaction tube into a  $50^\circ\text{C}$  ( $120^\circ\text{F}$ ) water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 ml of 5 percent  $\text{NaBH}_4$  and integrate the resulting spectrophotometer signal over a 30-second time period.

11.3.1.2 Graphite Furnace Procedure. Pipet 5 ml of the digested solution into a 10-ml volumetric flask. Add 1 ml of the 1 percent nickel nitrate solution, 0.5 ml of 50 percent  $\text{HNO}_3$ , and 1 ml of the 3 percent  $\text{H}_2\text{O}_2$ , and dilute to 10 ml with water. The sample is now ready to inject in the furnace for analysis.



11.4 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5 Mandatory Check for Matrix Effects on the Arsenic Results. Same as Method 12, Section 11.5.

11.6 Audit Sample Analysis.

11.6.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of EPA audit samples must be analyzed, subject to availability.

11.6.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

**Note:** It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.7 Audit Sample Results.

11.7.1 Calculate the audit sample concentrations in  $\text{g/m}^3$  and submit results using the instructions provided with the audit samples.

11.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.7.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.7.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

## 12.0 Data Analysis and Calculations

12.1 Calculate the percent arsenic in the ore sample as follows:

$$\% \text{ As} = \frac{5C_a F_d}{W} \quad \text{Eq. 108A-1}$$

Where:

$C_a$  = Concentration of As as read from the standard curve,  $\mu\text{g/ml}$ .

$F_d$  = Dilution factor (equals to 1 if the sample has not been diluted).

W = Weight of ore sample analyzed, mg.

5 = (50 ml sample \* 100)/(10<sup>3</sup> µg/mg).

### 13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS is 10 µg As/ml. The analytical procedure includes provisions for the use of a graphite furnace or vapor generator for samples with a lower arsenic concentration.

### 14.0 Pollution Prevention.[Reserved]

### 15.0 Waste Management.[Reserved]

### 16.0 References

Same as References 1 through 9 of Section 17.0 of Method 5, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods of Atomic Absorption Spectrophotometry. 303–0152. Norwalk, Connecticut. September 1976. pp 5–6.
2. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980. 35 pp.
3. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

### 17.0 Tables, Diagrams, Flowcharts, and Validation Data.[Reserved]

### Method 108B—Determination of Arsenic Content in Ore Samples From Nonferrous Smelters

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this appendix and in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 12 and Method 108A.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440–38–2	Lower limit 10 µg/ml.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations. Samples resulting in an analytical concentration greater than 10 µg As/ml may be analyzed by this method. For lower level arsenic samples, Method 108C should be used.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by flame atomic absorption spectrophotometry (AAS).

### 3.0 Definitions[Reserved]

### 4.0 Interferences

Analysis for As by flame AAS is sensitive to the chemical composition and to the physical properties ( e.g., viscosity, pH) of the sample. The analytical procedure includes a check for matrix effects (Section 11.4).

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO<sub>4</sub>). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO<sub>4</sub> only in hoods specifically designed for HClO<sub>4</sub>.

### 6.0 Equipment and Supplies

6.1 Sample Preparation. The following items are required for sample preparation:

6.1.1 Teflon Beakers. 150-ml.

6.1.2 Graduated Pipets. 5-ml disposable.

6.1.3 Graduated Cylinder. 50-ml.

6.1.4 Volumetric Flask. 100-ml.

6.1.5 Analytical Balance. To measure within 0.1 mg.

6.1.6 Hot Plate.

6.1.7 Perchloric Acid Fume Hood.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm.

6.2.2 Beaker and Watch Glass. 400-ml.

6.2.3 Volumetric Flask. 1-liter.

6.2.4 Volumetric Pipets. 1-, 5-, 10-, and 25-ml.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Preparation. The following reagents are required for sample preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193-77 or 91 Type 3 (incorporated by reference—see §61.18).

7.1.2 Nitric Acid, Concentrated.

7.1.3 Hydrofluoric Acid, Concentrated.

7.1.4 Perchloric Acid, 70 Percent.

7.1.5 Hydrochloric Acid, Concentrated.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Stock Arsenic Standard, 1.0 mg As/ml. Dissolve 1.3203 g of primary grade  $\text{As}_2\text{O}_3$  [dried at 105 °C (221 °F)] in a 400-ml beaker with 10 ml of  $\text{HNO}_3$  and 5 ml of  $\text{HCl}$ . Cover with a watch glass, and heat gently until dissolution is complete. Add 10 ml of  $\text{HNO}_3$  and 25 ml of  $\text{HClO}_4$ , evaporate to strong fumes of  $\text{HClO}_4$ , and reduce to about 20 ml volume. Cool, add 100 ml of water and 100 ml of  $\text{HCl}$ , and transfer quantitatively to a 1-liter volumetric flask. Dilute to volume with water and mix.

7.2.3 Acetylene. Suitable quality for AAS analysis.

7.2.4 Air. Suitable quality for AAS analysis.

7.2.5 Quality Assurance Audit Samples. Same as in Method 108A, Section 7.2.11.

## 8.0 Sample Collection, Preservation, Transport, and Storage

Same as in Method 108A, Sections 8.1 and 8.2.

## 9.0 Quality Control

Section	Quality control measure	Effect
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.4	Check for matrix effects	Eliminate matrix effects.
11.5	Audit sample analysis	Evaluate analyst's technique and standards preparation.

## 10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Pipet 1, 5, 10, and 25 ml of the stock As solution into separate 100-ml volumetric flasks. Add 2 ml of  $\text{HClO}_4$ , 10 ml of  $\text{HCl}$ , and dilute to the mark with water. This will provide standard concentrations of 10, 50, 100, and 250  $\mu\text{g As/ml}$ .

10.2 Calibration Curve and Spectrophotometer Calibration Quality Control. Same as Method 108A, Sections 10.2 and 10.3

#### 11.0 Analytical Procedure

11.1 Sample Preparation. Weigh 100 to 1000 mg of finely pulverized sample to the nearest 0.1 mg. Transfer the sample to a 150-ml Teflon beaker. Dissolve the sample by adding 15 ml of  $\text{HNO}_3$ , 10 ml of  $\text{HCl}$ , 10 ml of  $\text{HF}$ , and 10 ml of  $\text{HClO}_4$  in the exact order as described, and let stand for 10 minutes. In a  $\text{HClO}_4$  fume hood, heat on a hot plate until 2–3 ml of  $\text{HClO}_4$  remain, then cool. Add 20 ml of water and 10 ml of  $\text{HCl}$ . Cover and warm until the soluble salts are in solution. Cool, and transfer quantitatively to a 100-ml volumetric flask. Dilute to the mark with water.

11.2 Spectrophotometer Preparation. Same as in Method 108A, Section 11.2.

11.3 Arsenic Determination. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 2 percent  $\text{HClO}_4$ /10 percent  $\text{HCl}$  (prepared by diluting 2 ml concentrated  $\text{HClO}_4$  and 10 ml concentrated  $\text{HCl}$  to 100 ml with water) so that the final concentration falls within the range of the curve. Using the calibration curve, determine the As concentration in each sample.

Note: Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instrument manufacturer's detailed operating instructions should be followed.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected average peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.4 Mandatory Check for Matrix Effects on the Arsenic Results. Same as Method 12, Section 11.5.

11.5 Audit Sample Analysis. Same as in Method 108A, Section 11.6.

#### 12.0 Data Analysis and Calculations

Same as in Method 108A, Section 12.0.

#### 13.0 Method Performance

13.1 Sensitivity. The lower limit of flame AAS is 10  $\mu\text{g As/ml}$ .

#### 14.0 Pollution Prevention[Reserved]

#### 15.0 Waste Management[Reserved]

#### 16.0 References

Same as in Method 108A, Section 16.0.

#### 17.0 Tables, Diagrams, Flowcharts, and Validation Data[Reserved]

Method 108C—Determination of Arsenic Content in Ore Samples From Nonferrous Smelters (Molybdenum Blue Photometric Procedure)

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 108A.

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Arsenic compounds as arsenic (As)	7440–38–2	Lower limit 0.0002 percent As by weight.

1.2 Applicability. This method applies to the determination of inorganic As content of process ore and reverberatory matte samples from nonferrous smelters and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

Arsenic bound in ore samples is liberated by acid digestion and analyzed by the molybdenum blue photometric procedure.

#### 3.0 Definitions.[Reserved]

#### 4.0 Interferences.[Reserved]

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures that prevent chemical splashes are recommended. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors are highly toxic and can cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO<sub>4</sub>). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO<sub>4</sub> only in hoods specifically designed for HClO<sub>4</sub>.

5.2.5 Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

## 6.0 Equipment and Supplies

6.1 Sample Preparation. The following items are required for sample preparation:

6.1.1 Analytical Balance. To measure to within 0.1 mg.

6.1.2 Erlenmeyer Flask, 300-ml.

6.1.3 Hot Plate.

6.1.4 Distillation Apparatus. No. 6, in ASTM E 50–82, 86, or 90 (Reapproved 1995)(incorporated by reference—see §61.18); detailed in Figure 108C–1.

6.1.5 Graduated Cylinder. 50-ml.

6.1.6 Perchloric Acid Fume Hood.

6.2 Analysis. The following items are required for analysis:

6.2.1 Spectrophotometer. Capable of measuring at 660 nm.

6.2.2 Volumetric Flasks. 50- and 100-ml.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Preparation. The following reagents are required for sample preparation:

7.1.1 Water. Deionized distilled to meet ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §61.18). When high concentrations of organic matter are not expected to be present, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted. Use in all dilutions requiring water.

7.1.2 Nitric Acid, Concentrated.

7.1.3 Hydrofluoric Acid, Concentrated.

7.1.4 Sulfuric Acid, Concentrated.

7.1.5 Perchloric Acid, 70 Percent.

7.1.6 Hydrochloric Acid, Concentrated.

7.1.7 Dilute Hydrochloric Acid. Add one part concentrated HCl to nine parts water.

7.1.8 Hydrazine Sulfate  $((\text{NH}_2)_2\text{H}_2\text{SO}_4)$ .

7.1.9 Potassium Bromide (KBr).

7.1.10 Bromine Water, Saturated.

7.2 Analysis. The following reagents and standards are required for analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Methyl Orange Solution, 1 g/liter.

7.2.3 Ammonium Molybdate Solution, 5 g/liter. Dissolve 0.5 g  $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in water in a 100-ml volumetric flask, and dilute to the mark. This solution must be freshly prepared.

7.2.4 Standard Arsenic Solution, 10  $\mu\text{g}$  As/ml. Dissolve 0.13203 g of  $\text{As}_2\text{O}_3$  in 100 ml HCl in a 1-liter volumetric flask. Add 200 ml of water, cool, dilute to the mark with water, and mix. Transfer 100 ml of this solution to a 1-liter volumetric flask, add 40 ml HCl, cool, dilute to the mark, and mix.

7.2.5 Hydrazine Sulfate Solution, 1 g/liter. Dissolve 0.1 g of  $[(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4]$  in water, and dilute to 100 ml in a volumetric flask. This solution must be freshly prepared.

7.2.6 Potassium Bromate ( $\text{KBrO}_3$ ) Solution, 0.03 Percent Weight by Volume (W/V). Dissolve 0.3 g  $\text{KBrO}_3$  in water, and dilute to 1 liter with water.

7.2.7 Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ), Concentrated.

7.2.8 Boiling Granules.

7.2.9 Hydrochloric Acid, 50 percent by volume. Dilute equal parts concentrated HCl with water.

7.2.10 Quality Assurance Audit Samples. Same as in Method 108A, Section 7.2.11.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

Same as in Method 108A, Sections 8.1 and 8.2.

#### 9.0 Quality Control

Section	Quality control measure	Effect
10.2	Calibration curve preparation	Ensure linearity of spectrophotometric analysis of standards.
11.3	Audit sample analysis	Evaluate analyst's technique and standards preparation.

#### 10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Preparation of Standard Solutions. Transfer 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, and 20.0 ml of standard arsenic solution (10  $\mu\text{g}/\text{ml}$ ) to each of seven 50-ml volumetric flasks. Dilute to 20 ml with dilute HCl. Add one drop of methyl orange solution and neutralize to the yellow color with dropwise addition of  $\text{NH}_4\text{OH}$ . Just bring back to the red color by dropwise addition of dilute HCl, and add 10 ml in excess. Proceed with the color development as described in Section 11.2.

10.2 Calibration Curve. Plot the spectrophotometric readings of the calibration solutions against  $\mu\text{g}$  As per 50 ml of solution. Use this curve to determine the As concentration of each sample.

10.3 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than  $\pm 2$  percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations must be less than 7 percent for all standards.

#### 11.0 Analytical Procedure



### 11.1 Sample Preparation.

11.1.1 Weigh 1.0 g of finely pulverized sample to the nearest 0.1 mg. Transfer the sample to a 300 ml Erlenmeyer flask and add 15 ml of  $\text{HNO}_3$ , 4 ml  $\text{HCl}$ , 2 ml  $\text{HF}$ , 3 ml  $\text{HClO}_4$ , and 15 ml  $\text{H}_2\text{SO}_4$ , in the order listed. In a  $\text{HClO}_4$  fume hood, heat on a hot plate to decompose the sample. Then heat while swirling over an open flame until dense white fumes evolve. Cool, add 15 ml of water, swirl to hydrate the  $\text{H}_2\text{SO}_4$  completely, and add several boiling granules. Cool to room temperature.

11.1.2 Add 1 g of  $\text{KBr}$ , 1 g hydrazine sulfate, and 50 ml  $\text{HCl}$ . Immediately attach the distillation head with thermometer and dip the side arm into a 50-ml graduated cylinder containing 25 ml of water and 2 ml of bromine water. Keep the graduated cylinder immersed in a beaker of cold water during distillation. Distill until the temperature of the vapor in the flask reaches  $107^\circ\text{C}$  ( $225^\circ\text{F}$ ). When distillation is complete, remove the flask from the hot plate, and simultaneously wash down the side arm with water as it is removed from the cylinder.

11.1.3 If the expected arsenic content is in the range of 0.0020 to 0.10 percent, dilute the distillate to the 50-ml mark of the cylinder with water, stopper, and mix. Transfer a 5.0-ml aliquot to a 50-ml volumetric flask. Add 10 ml of water and a boiling granule. Place the flask on a hot plate, and heat gently until the bromine is expelled and the color of methyl orange indicator persists upon the addition of 1 to 2 drops. Cool the flask to room temperature. Neutralize just to the yellow color of the indicator with dropwise additions of  $\text{NH}_4\text{OH}$ . Bring back to the red color by dropwise addition of dilute  $\text{HCl}$ , and add 10 ml excess. Proceed with the molybdenum blue color development as described in Section 11.2.

11.1.4 If the expected arsenic content is in the range of 0.0002 to 0.0010 percent  $\text{As}$ , transfer either the entire initial distillate or the measured remaining distillate from Section 11.1.2 to a 250-ml beaker. Wash the cylinder with two successive portions of concentrated  $\text{HNO}_3$ , adding each portion to the distillate in the beaker. Add 4 ml of concentrated  $\text{HClO}_4$ , a boiling granule, and cover with a flat watch glass placed slightly to one side. Boil gently on a hot plate until the volume is reduced to approximately 10 ml. Add 3 ml of  $\text{HNO}_3$ , and continue the evaporation until  $\text{HClO}_4$  is refluxing on the beaker cover. Cool briefly, rinse the underside of the watch glass and the inside of the beaker with about 3–5 ml of water, cover, and continue the evaporation to expel all but 2 ml of the  $\text{HClO}_4$ .

Note: If the solution appears cloudy due to a small amount of antimony distilling over, add 4 ml of 50 percent  $\text{HCl}$  and 5 ml of water, cover, and warm gently until clear. If cloudiness persists, add 5 ml of  $\text{HNO}_3$  and 2 ml  $\text{H}_2\text{SO}_4$ . Continue the evaporation of volatile acids to solubilize the antimony until dense white fumes of  $\text{H}_2\text{SO}_4$  appear. Retain at least 1 ml of the  $\text{H}_2\text{SO}_4$ .

11.1.5 To the 2 ml of  $\text{HClO}_4$  solution or 1 ml of  $\text{H}_2\text{SO}_4$  solution, add 15 ml of water, boil gently for 2 minutes, and then cool. Proceed with the molybdenum blue color development by neutralizing the solution directly in the beaker just to the yellow indicator color by dropwise addition of  $\text{NH}_4\text{OH}$ . Obtain the red color by dropwise addition of dilute  $\text{HCl}$ . Transfer the solution to a 50-ml volumetric flask. Rinse the beaker successively with 10 ml of dilute  $\text{HCl}$ , followed by several small portions of water. At this point the volume of solution in the flask should be no more than 40 ml. Continue with the color development as described in Section 11.2.

### 11.2 Analysis.

11.2.1 Add 1 ml of  $\text{KBrO}_3$  solution to the flask and heat on a low-temperature hot plate to about  $50^\circ\text{C}$  ( $122^\circ\text{F}$ ) to oxidize the arsenic and methyl orange. Add 5.0 ml of ammonium molybdate solution to the warm solution and mix. Add 2.0 ml of hydrazine sulfate solution, dilute until the solution comes within the neck of the flask, and mix. Place the flask in a 400 ml beaker, 80 percent full of boiling water, for 10 minutes. Enough heat must be supplied to prevent the water bath from cooling much below the boiling point upon inserting the volumetric flask. Remove the flask, cool to room temperature, dilute to the mark, and mix.

11.2.2 Transfer a suitable portion of the reference solution to an absorption cell, and adjust the spectrophotometer to the initial setting using a light band centered at 660 nm. While maintaining this spectrophotometer adjustment, take the readings of the calibration solutions followed by the samples.

11.3 Audit Sample Analysis. Same as in Method 108A, Section 11.6.

### 12.0 Data Analysis and Calculations

Same as in Method 108A, Section 12.0.

### 13.0 Method Performance.[Reserved]

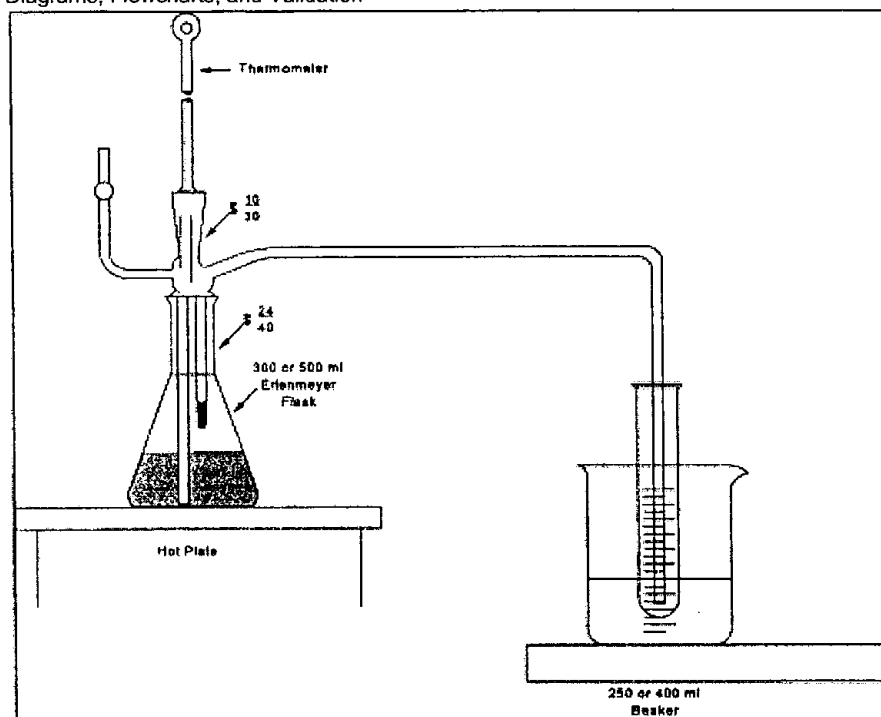
14.0 Pollution Prevention.[Reserved]

15.0 Waste Management.[Reserved]

## 16.0 References

1. Ringwald, D. Arsenic Determination on Process Materials from ASARCO's Copper Smelter in Tacoma, Washington. Unpublished Report. Prepared for the Emission Measurement Branch, Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980. 35 pp.

## 17.0 Tables, Diagrams, Flowcharts, and Validation



Data **Figure 108C-1. Distillation Apparatus.**

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### Method 111—Determination of Polonium-210 Emissions From Stationary Sources

Note: This method does not include all of the specifications ( e.g., equipment and supplies) and procedures ( e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

#### 1.0 Scope and Application

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Polonium	7440-08-6	Not specified.

1.2 Applicability. This method is applicable for the determination of the polonium-210 content of particulate matter samples collected from stationary source exhaust stacks, and for the use of these data to calculate polonium-210 emissions from individual sources and from all affected sources at a facility.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

A particulate matter sample, collected according to Method 5, is analyzed for polonium-210 content: the polonium-210 in the sample is put in solution, deposited on a metal disc, and the radioactive disintegration rate measured. Polonium in acid solution spontaneously deposits on surfaces of metals that are more electropositive than polonium. This principle is routinely used in the radiochemical analysis of polonium-210. Data reduction procedures are provided, allowing the calculation of polonium-210 emissions from individual sources and from all affected sources at a facility, using data obtained from Methods 2 and 5 and from the analytical procedures herein.

## 3.0 Definitions[Reserved]

## 4.0 Interferences[Reserved]

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.3 Nitric Acid (HNO<sub>3</sub>). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Perchloric Acid (HClO<sub>4</sub>). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO<sub>4</sub> only in hoods specifically designed for HClO<sub>4</sub>.

## 6.0 Equipment and Supplies

6.1 Alpha Spectrometry System. Consisting of a multichannel analyzer, biasing electronics, silicon surface barrier detector, vacuum pump and chamber.

6.2 Constant Temperature Bath at 85 °C (185 °F).

6.3 Polished Silver Discs. 3.8 cm diameter, 0.4 mm thick with a small hole near the edge.

6.4 Glass Beakers. 400 ml, 150 ml.

6.5 Hot Plate, Electric.

6.6 Fume Hood.

6.7 Teflon Beakers, 150 ml.

6.8 Magnetic Stirrer.

6.9 Stirring Bar.

6.10 Hooks. Plastic or glass, to suspend plating discs.

6.11 Internal Proportional Counter. For measuring alpha particles.

6.12 Nucleopore Filter Membranes. 25 mm diameter, 0.2 micrometer pore size or equivalent.

6.13 Planchets. Stainless steel, 32 mm diameter with 1.5 mm lip.

6.14 Transparent Plastic Tape. 2.5 cm wide with adhesive on both sides.

6.15 Epoxy Spray Enamel.

6.16 Suction Filter Apparatus. For 25 mm diameter filter.

6.17 Wash Bottles, 250 ml capacity.

6.18 Graduated Cylinder, plastic, 25 ml capacity.

6.19 Volumetric Flasks, 100 ml, 250 ml.

#### *7.0 Reagents and Standards*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Ascorbic Acid.

7.2 Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ), 15 M.

7.3 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 (incorporated by reference—see §61.18), Type 3. Use in all dilutions requiring water.

7.4 Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 95 percent.

7.5 Hydrochloric Acid, 12 M.

7.6 Hydrochloric Acid, 1 M. Dilute 83 ml of the 12 M HCl to 1 liter with distilled water.

7.7 Hydrofluoric Acid, 29 M.

7.8 Hydrofluoric Acid, 3 M. Dilute 52 ml of the 29 M HF to 500 ml with distilled water. Use a plastic graduated cylinder and storage bottle.

7.9 Lanthanum Carrier, 0.1 mg La<sup>3+</sup>/ml. Dissolve 0.078 gram lanthanum nitrate,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 250 ml of 1 M HCl.

7.10 Nitric Acid, 16 M.

7.11 Perchloric Acid, 12 M.

7.12 Polonium-209 Solution.

7.13 Silver Cleaner. Any mild abrasive commercial silver cleaner.

7.14 Degreaser.

7.15 Standard Solution. Standardized solution of an alpha-emitting actinide element, such as plutonium-239 or americium-241.

## 8.0 Sample Collection, Preservation, Transport, and Storage.[Reserved]

## 9.0 Quality Control

### 9.1 General Requirement.

9.1.1 All analysts using this method are required to demonstrate their ability to use the method and to define their respective accuracy and precision criteria.

### 9.2 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.1	Standardization of alpha spectrometry system	Ensure precision of sample analyses.
10.3	Standardization of internal proportional counter	Ensure precise sizing of sample aliquot.
11.1, 11.2	Determination of procedure background and instrument background	Minimize background effects.
11.3	Audit sample analysis	Evaluate analyst's technique.

## 10.0 Calibration and Standardization

### 10.1 Standardization of Alpha Spectrometry System.

10.1.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final concentration when diluted to a volume of 100 ml will be approximately 1<sub>p</sub>Ci/ml.

10.1.2 Add 10 ml of 16 M HNO<sub>3</sub> and dilute to 100 ml with water.

10.1.3 Add 20 ml of 1 M HCl to each of six 150 ml beakers. Add 1.0 ml of lanthanum carrier, 0.1 mg lanthanum per ml, to the acid solution in each beaker.

10.1.4 Add 1.0 ml of the 1 pCi/ml working solution (from Section 10.1.1) to each beaker. Add 5.0 ml of 3 M HF to each beaker.

10.1.5 Cover beakers and allow solutions to stand for a minimum of 30 minutes. Filter the contents of each beaker through a separate filter membrane using the suction filter apparatus. After each filtration, wash the filter membrane with 10 ml of distilled water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

10.1.6 Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place planchet in an alpha spectrometry system and count each planchet for 1000 minutes.

10.1.7 Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111–1 in Section 12.2.

10.1.8 Determine the average counting efficiency of the detector,  $E_c$ , by calculating the average of the six determinations.

## 10.2 Preparation of Standardized Solution of Polonium-209.

10.2.1 Add a quantity of the Po-209 solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 1 pCi/ml.

10.2.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute 1.0 ml of polonium-209 tracer solution (Section 10.2.1) and 3.0 ml of 15 M ammonium hydroxide for the 1 pCi/ml actinide working solution and the 3 M HF, respectively.

10.2.3 Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111–2 in Section 12.3.

10.2.4 Determine the average activity of the polonium-209 tracer solution,  $F$ , by averaging the results of the six determinations.

## 10.3 Standardization of Internal Proportional Counter

10.3.1 Add a quantity of the actinide standard solution to a 100 ml volumetric flask so that the final concentration when diluted to a 100 ml volume will be approximately 100 pCi/ml.

10.3.2 Follow the procedures outlined in Sections 10.1.2 through 10.1.6, except substitute the 100 pCi/ml actinide working solution for the 1 pCi/ml solution, place the planchet in an internal proportional counter (instead of an alpha spectrometry system), and count for 100 minutes (instead of 1000 minutes).

10.3.3 Calculate the counting efficiency of the internal proportional counter for each aliquot of the 100 pCi/ml actinide working solution using Eq. 111–3 in 12.4.

10.3.4 Determine the average counting efficiency of the internal proportional counter,  $E_i$ , by averaging the results of the six determinations.

## 11.0 Analytical Procedure

**Note:** Perform duplicate analyses of all samples, including background counts, quality assurance audit samples, and Method 5 samples. Duplicate measurements are considered acceptable when the difference between them is less than two standard deviations as described in EPA 600/4–77–001 or subsequent revisions.

11.1 Determination of Procedure Background. Background counts used in all equations are determined by performing the specific analysis required using the analytical reagents only. All procedure background counts and sample counts for the internal proportional counter should utilize a counting time of 100 minutes; for the alpha spectrometry system, 1000 minutes. These background counts should be performed no less frequently than once per 10 sample analyses.

11.2 Determination of Instrument Background. Instrument backgrounds of the internal proportional counter and the alpha spectrometry system should be determined on a weekly basis. Instrument background should not exceed procedure background. If this occurs, it may be due to a malfunction or contamination, and should be corrected before use.

11.3 Quality Assurance Audit Samples. An externally prepared performance evaluation sample shall be analyzed no less frequently than once per 10 sample analyses, and the results reported with the test results.

11.4 Sample Preparation. Treat the Method 5 samples [i.e., the glass fiber filter (Container No. 1) and the acetone rinse (Container No. 2)] as follows:

11.4.1 Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a 150-ml Teflon beaker.

11.4.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the contents to a 400-ml glass beaker. Add polonium-209 tracer solution to the glass beaker in an amount approximately equal to the amount of polonium-210 expected in the total particulate sample. Record the activity of the tracer solution added. Add 16 M nitric acid to the beaker to digest and loosen the residue.

11.4.3 Transfer the contents of the glass beaker to the Teflon beaker containing the glass fiber filter. Rinse the glass beaker with 16 M  $\text{HNO}_3$ . If necessary, reduce the volume in the beaker by evaporation until all of the nitric acid  $\text{HNO}_3$  from the glass beaker has been transferred to the Teflon beaker.

11.4.4 Add 30 ml of 29 M HF to the Teflon beaker and evaporate to near dryness on a hot plate in a properly operating hood.

**Note:** Do not allow the residue to go to dryness and overheat; this will result in loss of polonium.

11.4.5 Repeat step 11.4.4 until the filter is dissolved.

11.4.6 Add 100 ml of 16 M  $\text{HNO}_3$  to the residue in the Teflon beaker and evaporate to near dryness.

**Note:** Do not allow the residue to go to dryness.

11.4.7 Add 50 ml of 16 M  $\text{HNO}_3$  and 10 ml of 12 M perchloric acid to the Teflon beaker and heat until dense fumes of perchloric acid are evolved.

11.4.8 Repeat steps 11.4.4 to 11.4.7 as necessary until sample is completely dissolved.

11.4.9 Add 10 ml of 12 M HCl to the Teflon beaker and evaporate to dryness. Repeat additions and evaporations several times.

11.4.10 Transfer the sample to a 250-ml volumetric flask and dilute to volume with 3 M HCl.

11.5 Sample Screening. To avoid contamination of the alpha spectrometry system, check each sample as follows:

11.5.1 Add 20 ml of 1 M HCl, 1 ml of the lanthanum carrier solution (0.1 mg La/ml), a 1 ml aliquot of the sample solution from Section 11.4.10, and 3 ml of 15 M ammonium hydroxide to a 250-ml beaker in the order listed. Allow this solution to stand for a minimum of 30 minutes.

11.5.2 Filter the solution through a filter membrane using the suction filter apparatus. Wash the filter membrane with 10 ml of water and 5 ml of ethanol, and allow the filter membrane to air dry on the filter apparatus.

11.5.3 Carefully remove the filter membrane and mount it, filtration side up, with double-side tape on the inner surface of a planchet. Place the planchet in an internal proportional counter, and count for 100 minutes.

11.5.4 Calculate the activity of the sample using Eq. 111–4 in Section 12.5.

11.5.5 Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210, such that the aliquot contains an activity between 1 and 4 picocuries. Use Eq. 111–5 in Section 12.6.

11.6 Preparation of Silver Disc for Spontaneous Electrodeposition.

11.6.1 Clean both sides of the polished silver disc with silver cleaner and with degreaser.

11.6.2 Place disc on absorbent paper and spray one side with epoxy spray enamel. This should be carried out in a well-ventilated area, with the disc lying flat to keep paint on one side only. Allow paint to dry for 24 hours before using disc for deposition.

11.7 Sample Analysis.

11.7.1 Add the aliquot of sample solution from Section 11.4.10 to be analyzed for polonium-210, the volume of which was determined in Section 11.5.5, to a suitable 200-ml container to be placed in a constant temperature bath.

**Note:** Aliquot volume may require a larger container.

11.7.2 If necessary, bring the volume to 100 ml with 1 M HCl. If the aliquot volume exceeds 100 ml, use total aliquot.

11.7.3 Add 200 mg of ascorbic acid and heat solution to 85 °C (185 °F) in a constant temperature bath.

11.7.4 Suspend a silver disc in the heated solution using a glass or plastic rod with a hook inserted through the hole in the disc. The disc should be totally immersed in the solution, and the solution must be stirred constantly, at all times during the plating operation. Maintain the disc in solution for 3 hours.

11.7.5 Remove the silver disc, rinse with deionized distilled water, and allow to air dry at room temperature.

11.7.6 Place the disc, with deposition side (unpainted side) up, on a planchet and secure with double-side plastic tape. Place the planchet with disc in alpha spectrometry system and count for 1000 minutes.

## 12.0 Data Analysis and Calculations.

### 12.1 Nomenclature.

A = Picocuries of polonium-210 in the Method 5 sample (from Section 12.8).

A<sub>A</sub> = Picocuries of actinide added.

A<sub>L</sub> = Volume of sample aliquot used, in ml (specified in Section 11.5.1 as 1 ml).

A<sub>S</sub> = Aliquot to be analyzed, in ml.

B<sub>B</sub> = Procedure background counts measured in polonium-209 spectral region.

B<sub>T</sub> = Polonium-209 tracer counts in sample.

C<sub>T</sub> = Total counts in polonium-210 spectral region.

D = Decay correction for time "t" (in days) from sample collection to sample counting, given by:  $D = e^{-0.0051t}$

E<sub>C</sub> = Average counting efficiency of detector (from Section 10.1.8), as counts per disintegration.

E<sub>CI</sub> = Counting efficiency of the detector for aliquot i of the actinide working solution, counts per disintegration.

E<sub>I</sub> = Average counting efficiency of the internal proportional counter, as determined in Section 10.3.4, counts per disintegration.

E<sub>II</sub> = Counting efficiency of the internal proportional counter for aliquot i of the 100 pCi/ml actinide working solution, counts per disintegration.

E<sub>Y</sub> = The fraction of polonium-209 recovered on the planchet (from Section 12.7).

F = Average activity of polonium-209 in sample (from Section 10.2.4), in pCi.

F<sub>i</sub> = activity of aliquot i of the polonium-209 tracer solution, in pCi.

L = Dilution factor (unitless). This is the volume of sample solution prepared (specified as 250 ml in Section 11.1.10) divided by the volume of the aliquot of sample solution analyzed for polonium-210 (from Section 11.7.1).



$M_i$  = Phosphorous rock processing rate of the source being tested, during run i, Mg/hr.

$M_k$  = Phosphate rock processed annually by source k, in Mg/yr.

n = Number of calciners at the elemental phosphorus plant.

P = Total activity of sample solution from Section 11.4.10, in pCi (see Eq. 111-4).

$Q_{sd}$  = Volumetric flow rate of effluent stream, as determined by Method 2, in dscm/hr.

S = Annual polonium-210 emissions from the entire facility, in curies/yr.

$V_m(\text{std})$  = Volume of air sample, as determined by Method 5, in dscm.

$X_k$  = Emission rate from source k, from Section 12.10, in curies/Mg.

$10^{-12}$  = Curies per picocurie.

2.22 = Disintegrations per minute per picocurie.

250 = Volume of solution from Section 11.4.10, in ml.

12.2 Counting Efficiency. Calculate the counting efficiency of the detector for each aliquot of the 1 pCi/ml actinide working solution using Eq. 111-1.

$$E_{\alpha} = \frac{C_s - C_B}{2.22 A_A T} \quad \text{Eq. 111-1}$$

Where:

$C_B$  = Background counts in same peak area as  $C_s$ .

$C_s$  = Gross counts in actinide peak.

T = Counting time in minutes, specified in Section 10.1.6 as 1000 minutes.

12.3 Polonium-209 Tracer Solution Activity. Calculate the activity of each aliquot of the polonium-209 tracer solution using Eq. 111-2.

$$F_i = \frac{C_s - C_B}{2.22 E_{ci} T} \quad \text{Eq. 111-2}$$

Where:

$C_B$  = Background counts in the 4.88 MeV region of spectrum the in the counting time T.

$C_s$  = Gross counts of polonium-209 in the 4.88 MeV region of the spectrum in the counting time T.

T = Counting time, specified in Section 10.1.6 as 1000 minutes.

12.4 Control Efficiency of Internal Proportional Counter. Calculate the counting efficiency of the internal proportional counter for each aliquot of the 100 pCi/ml actinide working solution using Eq. 111-3.

$$E_R = \frac{C_S - C_B}{2.22 A_A T} \quad \text{Eq. 111-3}$$

Where:

C<sub>B</sub>= Gross counts of procedure background.

C<sub>S</sub>= Gross counts of standard.

T = Counting time in minutes, specified in Section 10.3.2 as 100 minutes.

12.5 Calculate the activity of the sample using Eq. 111-4.

$$P = \frac{250 (C_S - C_B)}{2.22 \bar{E}_I A_I T} \quad \text{Eq. 111-4}$$

Where:

C<sub>B</sub>= Total counts of procedure background. (See Section 11.1).

C<sub>S</sub>= Total counts of screening sample.

T = Counting time for sample and background (which must be equal), in minutes (specified in Section 11.5.3 as 100 minutes).

12.6 Aliquot Volume. Determine the aliquot volume of the sample solution from Section 11.4.10 to be analyzed for polonium-210, such that the aliquot contains an activity between 1 and 4 picocuries using Eq. 111-5.

$$A_j = \frac{250 (\text{desired picocuries in aliquot})}{P} \quad \text{Eq. 111-5}$$

12.7 Polonium-209 Recovery. Calculate the fraction of polonium-209 recovered on the planchet, E<sub>V</sub>, using Eq. 111-6.

$$E_V = \frac{B_T - B_B}{2.22 \bar{F} \bar{E}_C T} \quad \text{Eq. 111-6}$$

Where:

T = Counting time, specified in Section 11.1 as 1000 minutes.

12.8 Polonium-210 Activity. Calculate the activity of polonium-210 in the Method 5 sample (including glass fiber filter and acetone rinse) using Eq. 111-7.

$$A = \frac{(C_T - C_B) L}{2.22 E_y \bar{E}_C T D} \quad \text{Eq. 111-7}$$

Where:

C<sub>B</sub>= Procedure background counts in polonium-210 spectral region.

T = Counting time, specified in Section 11.1 as 1000 minutes for all alpha spectrometry sample and background counts.

## 12.9 Emission Rate from Each Stack.

12.9.1 For each test run, i, on a stack, calculate the measured polonium-210 emission rate,  $R_{Si}$ , using Eq. 111-8.

$$R_{Si} = \frac{(10^{-12}) A Q_{sd}}{V_{std} M_i} \quad \text{Eq. 111-8}$$

12.9.2 Determine the average polonium-210 emission rate from the stack,  $R_s$ , by taking the sum of the measured emission rates for all runs, and dividing by the number of runs performed.

12.9.3 Repeat steps 12.9.1 and 12.9.2 for each stack of each calciner.

12.10 Emission Rate from Each Source. Determine the total polonium-210 emission rate,  $X_k$ , from each source, k, by taking the sum of the average emission rates from all stacks to which the source exhausts.

12.11 Annual Polonium-210 Emission Rate from Entire Facility. Determine the annual elemental phosphorus plant emissions of polonium-210, S, using Eq. 111-9.

$$S = \frac{\sum_{k=1}^n (X_k M_k)}{n} \quad \text{Eq. 111-9}$$

## 13.0 Method Performance.[Reserved]

## 14.0 Pollution Prevention.[Reserved]

## 15.0 Waste Management.[Reserved]

## 16.0 References

1. Blanchard, R.L. "Rapid Determination of Lead-210 and Polonium-210 in Environmental Samples by Deposition on Nickel." Anal. Chem., 38:189, pp. 189-192. February 1966.

## 17.0 Tables, Diagrams, Flowcharts, and Validation Data[Reserved]

# Method 114—Test Methods for Measuring Radionuclide Emissions from Stationary Sources

## 1. Purpose and Background

This method provides the requirements for: (1) Stack monitoring and sample collection methods appropriate for radionuclides; (2) radiochemical methods which are used in determining the amounts of radionuclides collected by the stack sampling and; (3) quality assurance methods which are conducted in conjunction with these measurements. These methods are appropriate for emissions for stationary sources. A list of references is provided.

Many different types of facilities release radionuclides into air. These radionuclides differ in the chemical and physical forms, half-lives and type of radiation emitted. The appropriate combination of sample extraction, collection and analysis for an individual radionuclide is dependent upon many interrelated factors including the mixture of other radionuclides present. Because of this wide range of conditions, no single method for monitoring or sample collection and analysis of a radionuclide is applicable to all types of facilities. Therefore, a series of methods based on "principles of measurement" are described for monitoring and sample collection and analysis which are applicable to the measurement of radionuclides found in effluent streams at stationary sources. This approach provides the user with the flexibility to choose the most appropriate combination of monitoring and sample collection and analysis methods which are applicable to the effluent stream to be measured.

## 2. Stack Monitoring and Sample Collection Methods

Monitoring and sample collection methods are described based on "principles of monitoring and sample collection" which are applicable to the measurement of radionuclides from effluent streams at stationary sources. Radionuclides of most elements will be in the particulate form in these effluent streams and can be readily collected using a suitable filter media. Radionuclides of hydrogen, oxygen, carbon, nitrogen, the noble gases and in some circumstances iodine will be in the gaseous form. Radionuclides of these elements will require either the use of an in-line or off-line monitor to directly measure the radionuclides, or suitable sorbers, condensers or bubblers to collect the radionuclides.

2.1 Radionuclides as Particulates. The extracted effluent stream is passed through a filter media to remove the particulates. The filter must have a high efficiency for removal of sub-micron particles. The guidance in ANSI/HPS N13.1-1999 (section 6.6.2 Filter media) shall be followed in using filter media to collect particulates (incorporated by reference—see §61.18 of this part).

2.2 Radionuclides as Gases.

2.2.1 The Radionuclide Tritium (H-3). Tritium in the form of water vapor is collected from the extracted effluent sample by sorption, condensation or dissolution techniques. Appropriate collectors may include silica gel, molecular sieves, and ethylene glycol or water bubblers.

Tritium in the gaseous form may be measured directly in the sample stream using Method B-1, collected as a gas sample or may be oxidized using a metal catalyst to tritiated water and collected as described above.

2.2.2 Radionuclides of Iodine. Iodine is collected from an extracted sample by sorption or dissolution techniques. Appropriate collectors may include charcoal, impregnated charcoal, metal zeolite and caustic solutions.

2.2.3 Radionuclides of Argon, Krypton and Xenon. Radionuclides of these elements are either measured directly by an in-line or off-line monitor, or are collected from the extracted sample by low temperature sorption techniques. Appropriate sorbers may include charcoal or metal zeolite.

2.2.4 Radionuclides of Oxygen, Carbon, Nitrogen and Radon. Radionuclides of these elements are measured directly using an in-line or off-line monitor. Radionuclides of carbon in the form of carbon dioxide may be collected by dissolution in caustic solutions.

## 2.3 Definition of Terms

*In-line monitor* means a continuous measurement system in which the detector is placed directly in or adjacent to the effluent stream. This may involve either gross radioactivity measurements or specific radionuclide measurements. Gross measurements shall be made in conformance with the conditions specified in Methods A-4, B-2 and G-4.

*Off-line monitor* means a measurement system in which the detector is used to continuously measure an extracted sample of the effluent stream. This may involve either gross radioactivity measurements or specific radionuclide measurements. Gross measurements shall be made in conformance with the conditions specified in Methods A-4, B-2 and G-4.

*Sample collection* means a procedure in which the radionuclides are removed from an extracted sample of the effluent using a collection media. These collection media include filters, absorbers, bubblers and condensers. The collected sample is analyzed using the methods described in Section 3.

## 3. Radionuclide Analysis Methods

A series of methods based on "principles of measurement" are described which are applicable to the analysis of radionuclides collected from airborne effluent streams at stationary sources. These methods are applicable only under the conditions stated and within the limitations described. Some methods specify that only a single radionuclide be present in the sample or the chemically separated sample. This condition should be interpreted to mean that no other radionuclides are present in quantities which would interfere with the measurement.

Also identified (Table 1) are methods for a selected list of radionuclides. The listed radionuclides are those which are most commonly used and which have the greatest potential for causing dose to members of the public. Use of methods based on principles of measurement other than those described in this section must be approved in advance of use by the Administrator. For radionuclides not listed in Table 1, any of the described methods may be used provided the user can demonstrate that the applicability conditions of the method have been met.

The type of method applicable to the analysis of a radionuclide is dependent upon the type of radiation emitted, i.e., alpha, beta or gamma. Therefore, the methods described below are grouped according to principles of measurements for the analysis of alpha, beta and gamma emitting radionuclides.

### 3.1 Methods for Alpha Emitting Radionuclides

#### 3.1.1 Method A-1, Radiochemistry-Alpha Spectrometry.

*Principle:* The element of interest is separated from other elements, and from the sample matrix using radiochemical techniques. The procedure may involve precipitation, ion exchange, or solvent extraction. Carriers (elements chemically similar to the element of interest) may be used. The element is deposited on a planchet in a very thin film by electrodeposition or by coprecipitation on a very small amount of carrier, such as lanthanum fluoride. The deposited element is then counted with an alpha spectrometer. The activity of the nuclide of interest is measured by the number of alpha counts in the appropriate energy region. A correction for chemical yield and counting efficiency is made using a standardized radioactive nuclide (tracer) of the same element. If a radioactive tracer is not available for the element of interest, a predetermined chemical yield factor may be used.

*Applicability:* This method is applicable for determining the activity of any alpha-emitting radionuclide, regardless of what other radionuclides are present in the sample provided the chemical separation step produces a very thin sample and removes all other radionuclides which could interfere in the spectral region of interest. APHA-605(2), ASTM-D-3972(13).

#### 3.1.2 Method A-2, Radiochemistry-Alpha Counting.

*Principle:* The element of interest is separated from other elements, and from the sample matrix using radiochemistry. The procedure may involve precipitation, ion exchange, or solvent extraction. Carriers (elements chemically similar to the element of interest) may be used. The element is deposited on a planchet in a thin film and counted with an alpha counter. A correction for chemical yield (if necessary) is made. The alpha count rate measures the total activity of all emitting radionuclides of the separated element.

*Applicability:* This method is applicable for the measurement of any alpha-emitting radionuclide, provided no other alpha emitting radionuclide is present in the separated sample. It may also be applicable for determining compliance, when other radionuclides of the separated element are present, provided that the calculated emission rate is assigned to the radionuclide which could be present in the sample that has the highest dose conversion factor. IDO-12096(18).

#### 3.1.3 Method A-3, Direct Alpha Spectrometry.

*Principle:* The sample, collected on a suitable filter, is counted directly on an alpha spectrometer. The sample must be thin enough and collected on the surface of the filter so that any absorption of alpha particle energy in the sample or the filter, which would degrade the spectrum, is minimal.

*Applicability:* This method is applicable to simple mixtures of alpha emitting radionuclides and only when the amount of particulates collected on the filter paper are relatively small and the alpha spectra is adequately resolved. Resolutions should be 50 keV (FWHM) or better, ASTM-D-3084(16).

#### 3.1.4 Method A-4, Direct Alpha Counting (Gross alpha determination).

*Principle:* The sample, collected on a suitable filter, is counted with an alpha counter. The sample must be thin enough so that self-absorption is not significant and the filter must be of such a nature that the particles are retained on the surface.

*Applicability:* Gross alpha determinations may be used to measure emissions of specific radionuclides only (1) when it is known that the sample contains only a single radionuclide, or the identity and isotopic ratio of the radionuclides in the sample are well-known, and (2) measurements using either Method A-1, A-2 or A-5 have shown that this method provides a reasonably accurate measurement of the emission rate. Gross alpha measurements are applicable to unidentified mixtures of radionuclides only for the purposes and under the conditions described in section 3.7. APHA-601(3), ASTM-D-1943(10).

#### 3.1.5 Method A-5, Chemical Determination of Uranium.

*Principle:* Uranium may be measured chemically by either colorimetry or fluorometry. In both procedures, the sample is dissolved, the uranium is oxidized to the hexavalent form and extracted into a suitable solvent. Impurities are removed from the solvent layer. For colorimetry, dibenzoylmethane is added, and the uranium is measured by the absorbance in a

colorimeter. For fluorometry, a portion of the solution is fused with a sodium fluoride-lithium fluoride flux and the uranium is determined by the ultraviolet activated fluorescence of the fused disk in a fluorometer.

*Applicability:* This method is applicable to the measurements of emission rates of uranium when the isotopic ratio of the uranium radionuclides is well known. ASTM-E-318(15), ASTM-D-2907(14).

### 3.1.6 Method A-6, Radon-222—Continuous Gas Monitor.

*Principle:* Radon-222 is measured directly in a continuously extracted sample stream by passing the air stream through a calibrated scintillation cell. Prior to the scintillation cell, the air stream is treated to remove particulates and excess moisture. The alpha particles from radon-222 and its decay products strike a zinc sulfide coating on the inside of the scintillation cell producing light pulses. The light pulses are detected by a photomultiplier tube which generates electrical pulses. These pulses are processed by the system electronics and the read out is in pCi/l of radon-222.

*Applicability:* This method is applicable to the measurement of radon-222 in effluent streams which do not contain significant quantities of radon-220. Users of this method should calibrate the monitor in a radon calibration chamber at least twice per year. The background of the monitor should also be checked periodically by operating the instrument in a low radon environment. EPA 520/1-89-009(24).

### 3.1.7 Method A-7, Radon-222-Alpha Track Detectors

*Principle:* Radon-222 is measured directly in the effluent stream using alpha track detectors (ATD). The alpha particles emitted by radon-222 and its decay products strike a small plastic strip and produce submicron damage tracks. The plastic strip is placed in a caustic solution that accentuates the damage tracks which are counted using a microscope or automatic counting system. The number of tracks per unit area is correlated to the radon concentration in air using a conversion factor derived from data generated in a radon calibration facility.

*Applicability:* Prior approval from EPA is required for use of this method. This method is only applicable to effluent streams which do not contain significant quantities of radon-220, unless special detectors are used to discriminate against radon-220. This method may be used only when ATDs have been demonstrated to produce data comparable to data obtained with Method A-6. Such data should be submitted to EPA when requesting approval for the use of this method. EPA 520/1-89-009(24).

## 3.2 Methods for Gaseous Beta Emitting Radionuclides.

### 3.2.1 Method B-1, Direct Counting in Flow-Through Ionization Chambers.

*Principle:* An ionization chamber containing a specific volume of gas which flows at a given flow rate through the chamber is used. The sample (effluent stream sample) acts as the counting gas for the chamber. The activity of the radionuclide is determined from the current measured in the ionization chamber.

*Applicability:* This method is applicable for measuring the activity of a gaseous beta-emitting radionuclide in an effluent stream that is suitable as a counting gas, when no other beta-emitting nuclides are present. DOE/EP-0096(17), NCRP-58(23).

### 3.2.2 Method B-2, Direct Counting With In-line or Off-line Beta Detectors.

*Principle:* The beta detector is placed directly in the effluent stream (in-line) or an extracted sample of the effluent stream is passed through a chamber containing a beta detector (off-line). The activities of the radionuclides present in the effluent stream are determined from the beta count rate, and a knowledge of the radionuclides present and the relationship of the gross beta count rate and the specific radionuclide concentration.

*Applicability:* This method is applicable only to radionuclides with maximum beta particle energies greater than 0.2 MeV. This method may be used to measure emissions of specific radionuclides only when it is known that the sample contains only a single radionuclide or the identity and isotopic ratio of the radionuclides in the effluent stream are well known. Specific radionuclide analysis of periodic grab samples may be used to identify the types and quantities of radionuclides present and to establish the relationship between specific radionuclide analyses and gross beta count rates.

This method is applicable to unidentified mixtures of gaseous radionuclides only for the purposes and under the conditions described in section 3.7.

## 3.3 Methods for Non-Gaseous Beta Emitting Radionuclides.

### 3.3.1 Method B-3, Radiochemistry-Beta Counting.

*Principle:* The element of interest is separated from other elements, and from the sample matrix by radiochemistry. This may involve precipitation, distillation, ion exchange, or solvent extraction. Carriers (elements chemically similar to the element of interest) may be used. The element is deposited on a planchet, and counted with a beta counter. Corrections for chemical yield, and decay (if necessary) are made. The beta count rate determines the total activity of all radionuclides of the separated element. This method may also involve the radiochemical separation and counting of a daughter element, after a suitable period of ingrowth, in which case it is specific for the parent nuclide.

*Applicability:* This method is applicable for measuring the activity of any beta-emitting radionuclide, with a maximum energy greater than 0.2 MeV, provided no other radionuclide is present in the separated sample. APHA-608(5).

### 3.3.2 Method B-4, Direct Beta Counting (Gross beta determination).

*Principle:* The sample, collected on a suitable filter, is counted with a beta counter. The sample must be thin enough so that self-absorption corrections can be made.

*Applicability:* Gross beta measurements are applicable only to radionuclides with maximum beta particle energies greater than 0.2 MeV. Gross beta measurements may be used to measure emissions of specific radionuclides only (1) when it is known that the sample contains only a single radionuclide, and (2) measurements made using Method B-3 show reasonable agreement with the gross beta measurement. Gross beta measurements are applicable to mixtures of radionuclides only for the purposes and under the conditions described in section 3.7. APHA-602(4), ASTM-D-1890(11).

### 3.3.3 Method B-5, Liquid Scintillation Spectrometry.

*Principle:* An aliquot of a collected sample or the result of some other chemical separation or processing technique is added to a liquid scintillation "cocktail" which is viewed by photomultiplier tubes in a liquid scintillation spectrometer. The spectrometer is adjusted to establish a channel or "window" for the pulse energy appropriate to the nuclide of interest. The activity of the nuclide of interest is measured by the counting rate in the appropriate energy channel. Corrections are made for chemical yield where separations are made.

*Applicability:* This method is applicable to any beta-emitting nuclide when no other radionuclide is present in the sample or the separated sample provided that it can be incorporated in the scintillation cocktail. This method is also applicable for samples which contain more than one radionuclide but only when the energies of the beta particles are sufficiently separated so that they can be resolved by the spectrometer. This method is most applicable to the measurement of low-energy beta emitters such as tritium and carbon-14. APHA-609(6), EML-LV-539-17(19).

## 3.4 Gamma Emitting Radionuclides

### 3.4.1 Method G-1, High Resolution Gamma Spectrometry.

*Principle:* The sample is counted with a high resolution gamma detector, usually either a Ge(Li) or a high purity Ge detector, connected to a multichannel analyzer or computer. The gamma emitting radionuclides in the sample are measured from the gamma count rates in the energy regions characteristic of the individual radionuclide. Corrections are made for counts contributed by other radionuclides to the spectral regions of the radionuclides of interest. Radiochemical separations may be made prior to counting but are usually not necessary.

*Applicability:* This method is applicable to the measurement of any gamma emitting radionuclide with gamma energies greater than 20 keV. It can be applied to complex mixtures of radionuclides. The samples counted may be in the form of particulate filters, absorbers, liquids or gases. The method may also be applied to the analysis of gaseous gamma emitting radionuclides directly in an effluent stream by passing the stream through a chamber or cell containing the detector. ASTM-3649(9), IDO-12096(18).

### 3.4.2 Method G-2, Low Resolution Gamma Spectrometry.

*Principle:* The sample is counted with a low resolution gamma detector, a thallium activated sodium iodide crystal. The detector is coupled to a photomultiplier tube and connected to a multichannel analyzer. The gamma emitting radionuclides in the sample are measured from the gamma count rates in the energy regions characteristic of the individual radionuclides. Corrections are made for counts contributed by other radionuclides to the spectral regions of the radionuclides of interest. Radiochemical separation may be used prior to counting to obtain less complex gamma spectra if needed.

*Applicability:* This method is applicable to the measurement of gamma emitting radionuclides with energies greater than 100 keV. It can be applied only to relatively simple mixtures of gamma emitting radionuclides. The samples counted may be in the form of particulate filters, absorbers, liquids or gas. The method can be applied to the analysis of gaseous radionuclides directly in an effluent stream by passing the gas stream through a chamber or cell containing the detector. ASTM-D-2459(12), EMSL-LV-0539-17(19).

#### 3.4.3 Method G-3, Single Channel Gamma Spectrometry.

*Principle:* The sample is counted with a thallium activated sodium iodide crystal. The detector is coupled to a photomultiplier tube connected to a single channel analyzer. The activity of a gamma emitting radionuclide is determined from the gamma counts in the energy range for which the counter is set.

*Applicability:* This method is applicable to the measurement of a single gamma emitting radionuclide. It is not applicable to mixtures of radionuclides. The samples counted may be in the form of particulate filters, absorbers, liquids or gas. The method can be applied to the analysis of gaseous radionuclides directly in an effluent stream by passing the gas stream through a chamber or cell containing the detector.

#### 3.4.4 Method G-4, Gross Gamma Counting.

*Principle:* The sample is counted with a gamma detector usually a thallium activated sodium iodine crystal. The detector is coupled to a photomultiplier tube and gamma rays above a specific threshold energy level are counted.

*Applicability:* Gross gamma measurements may be used to measure emissions of specific radionuclides only when it is known that the sample contains a single radionuclide or the identity and isotopic ratio of the radionuclides in the effluent stream are well known. When gross gamma measurements are used to determine emissions of specific radionuclides periodic measurements using Methods G-1 or G-2 should be made to demonstrate that the gross gamma measurements provide reliable emission data. This method may be applied to analysis of gaseous radionuclides directly in an effluent stream by placing the detector directly in or adjacent to the effluent stream or passing an extracted sample of the effluent stream through a chamber or cell containing the detector.

3.5 Counting Methods. All of the above methods with the exception of Method A-5 involve counting the radiation emitted by the radionuclide. Counting methods applicable to the measurement of alpha, beta and gamma radiations are listed below. The equipment needed and the counting principles involved are described in detail in ASTM-3648(8).

##### 3.5.1 Alpha Counting:

- *Gas Flow Proportional Counters.* The alpha particles cause ionization in the counting gas and the resulting electrical pulses are counted. These counters may be windowless or have very thin windows.
- *Scintillation Counters.* The alpha particles transfer energy to a scintillator resulting in a production of light photons which strike a photomultiplier tube converting the light photons to electrical pulses which are counted. The counters may involve the use of solid scintillation materials such as zinc sulfide or liquid scintillation solutions.
- *Solid-State Counters.* Semiconductor materials, such as silicon surface-barrier p-n junctions, act as solid ionization chambers. The alpha particles interact which the detector producing electron hole pairs. The charged pair is collected by an applied electrical field and the resulting electrical pulses are counted.
- *Alpha Spectrometers.* Semiconductor detectors used in conjunction with multichannel analyzers for energy discrimination.

##### 3.5.2 Beta Counting:

- *Ionization Chambers.* These chambers contain the beta-emitting nuclide in gaseous form. The ionization current produced is measured.
- *Geiger-Muller (GM) Counters-or Gas Flow Proportional Counters.* The beta particles cause ionization in the counting gas and the resulting electrical pulses are counted. Proportional gas flow counters which are heavily shielded by lead or other metal, and provided with an anti-coincidence shield to reject cosmic rays, are called low background beta counters.
- *Scintillation Counters.* The beta particles transfer energy to a scintillator resulting in a production of light photons, which strike a photomultiplier tube converting the light photon to electrical pulses which are counted. This may involve the use of anthracene crystals, plastic scintillator, or liquid scintillation solutions with organic phosphors.



- *Liquid Scintillation Spectrometers.* Liquid scintillation counters which use two photomultiplier tubes in coincidence to reduce background counts. This counter may also electronically discriminate among pulses of a given range of energy.

### 3.5.3 Gamma Counting:

- *Low-Resolution Gamma Spectrometers.* The gamma rays interact with thallium activated sodium iodide or cesium iodide crystal resulting in the release of light photons which strike a photomultiplier tube converting the light pulses to electrical pulses proportional to the energy of the gamma ray. Multi-channel analyzers are used to separate and store the pulses according to the energy absorbed in the crystal.

- *High-Resolution gamma Spectrometers.* Gamma rays interact with a lithium-drifted (Ge(Li)) or high-purity germanium (HPGe) semiconductor detectors resulting in a production of electron-hole pairs. The charged pair is collected by an applied electrical field. A very stable low noise preamplifier amplifies the pulses of electrical charge resulting from the gamma photon interactions. Multichannel analyzers or computers are used to separate and store the pulses according to the energy absorbed in the crystal.

- *Single Channel Analyzers.* Thallium activated sodium iodide crystals used with a single window analyzer. Pulses from the photomultiplier tubes are separated in a single predetermined energy range.

3.5.4 Calibration of Counters. Counters are calibrated for specific radionuclide measurements using a standard of the radionuclide under either identical or very similar conditions as the sample to be counted. For gamma spectrometers a series of standards covering the energy range of interest may be used to construct a calibration curve relating gamma energy to counting efficiency.

In those cases where a standard is not available for a radionuclide, counters may be calibrated using a standard with energy characteristics as similar as possible to the radionuclide to be measured. For gross alpha and beta measurements of the unidentified mixtures of radionuclides, alpha counters are calibrated with a natural uranium standard and beta counters with a cesium-137 standard. The standard must contain the same weight and distribution of solids as the samples, and be mounted in an identical manner. If the samples contain variable amounts of solids, calibration curves relating weight of solids present to counting efficiency are prepared. Standards other than those prescribed may be used provided it can be shown that such standards are more applicable to the radionuclide mixture measured.

3.6 Radiochemical Methods for Selected Radionuclides. Methods for a selected list of radionuclides are listed in Table 1. The radionuclides listed are those which are most commonly used and which have the greatest potential for causing doses to members of the public. For radionuclides not listed in Table 1, methods based on any of the applicable "principles of measurement" described in section 3.1 through 3.4 may be used.

3.7 Applicability of Gross Alpha and Beta Measurements to Unidentified Mixtures of Radionuclides. Gross alpha and beta measurements may be used as a screening measurement as a part of an emission measurement program to identify the need to do specific radionuclide analyses or to confirm or verify that unexpected radionuclides are not being released in significant quantities.

Gross alpha (Method A-4) or gross beta (Methods B-2 or B-4) measurements may also be used for the purpose of comparing the measured concentrations in the effluent stream with the limiting "Concentration Levels for Environmental Compliance" in table 2 of appendix E. For unidentified mixtures, the measured concentration value shall be compared with the lowest environmental concentration limit for any radionuclide which is not known to be absent from the effluent stream.

**Table 1—List of Approved Methods for Specific Radionuclides**

Radionuclide	Approved methods of analysis
Am-241	A-1, A-2, A-3, A-4
Ar-41	B-1, B-2, G-1, G-2, G-3, G-4
Ba-140	G-1, G-2, G-3, G-4
Br-82	G-1, G-2, G-3, G-4
C-11	B-1, B-2, G-1, G-2, G-3, G-4

C-14	B-5
Ca-45	B-3, B-4, B-5
Ce-144	G-1, G-2, G-3, G-4
Cm-244	A-1, A-2, A-3, A-4
Co-60	G-1, G-2, G-3, G-4
Cr-51	G-1, G-2, G-3, G-4
Cs-134	G-1, G-2, G-3, G-4
Cs-137	G-1, G-2, G-3, G-4
Fe-55	B-5, G-1
Fe-59	G-1, G-2, G-3, G-4
Ga-67	G-1, G-2, G-3, G-4
H-3 (H <sub>2</sub> O)	B-5
H-3 (gas)	B-1
I-123	G-1, G-2, G-3, G-4
I-125	G-1
I-131	G-1, G-2, G-3, G-4
In-113m	G-1, G-2, G-3, G-4
Ir-192	G-1, G-2, G-3, G-4
Kr-85	B-1, B-2, B-5, G-1, G-2, G-3, G-4
Kr-87	B-1, B-2, G-1, G-2, G-3, G-4
Kr-88	B-1, B-2, G-1, G-2, G-3, G-4
Mn-54	G-1, G-2, G-3, G-4
Mo-99	G-1, G-2, G-3, G-4
N-13	B-1, B-2, G-1, G-2, G-3, G-4
O-15	B-1, B-2, G-1, G-2, G-3, G-4
P-32	B-3, B-4, B-5
Pm-147	B-3, B-4, B-5
Po-210	A-1, A-2, A-3, A-4
Pu-238	A-1, A-2, A-3, A-4
Pu-239	A-1, A-2, A-3, A-4

Pu-240	A-1, A-2, A-3, A-4
Ra-226	A-1, A-2, G-1, G-2
S-35	B-5
Se-75	G-1, G-2, G-3, G-4
Sr-90	B-3, B-4, B-5
Tc-99	B-3, B-4, B-5
Te-201	G-1, G-2, G-3, G-4
Uranium (total alpha)	A-1, A-2, A-3, A-4
Uranium (Isotopic)	A-1, A-3
Uranium (Natural)	A-5
Xe-133	G-1
Yb-169	G-1, G-2, G-3, G-4
Zn-65	G-1, G-2, G-3, G-4

#### 4. Quality Assurance Methods

Each facility required to measure their radionuclide emissions shall conduct a quality assurance program in conjunction with the radionuclide emission measurements. This program shall assure that the emission measurements are representative, and are of known precision and accuracy and shall include administrative controls to assure prompt response when emission measurements indicate unexpectedly large emissions. The program shall consist of a system of policies, organizational responsibilities, written procedures, data quality specifications, audits, corrective actions and reports. This quality assurance program shall include the following program elements:

4.1 The organizational structure, functional responsibilities, levels of authority and lines of communications for all activities related to the emissions measurement program shall be identified and documented.

4.2 Administrative controls shall be prescribed to ensure prompt response in the event that emission levels increase due to unplanned operations.

4.3 The sample collection and analysis procedures used in measuring the emissions shall be described including where applicable:

4.3.1 Identification of sampling sites and number of sampling points, including the rationale for site selections.

4.3.2 A description of sampling probes and representativeness of the samples.

4.3.3 A description of any continuous monitoring system used to measure emissions, including the sensitivity of the system, calibration procedures and frequency of calibration.

4.3.4 A description of the sample collection systems for each radionuclide measured, including frequency of collection, calibration procedures and frequency of calibration.

4.3.5 A description of the laboratory analysis procedures used for each radionuclide measured, including frequency of analysis, calibration procedures and frequency of calibration.

4.3.6 A description of the sample flow rate measurement systems or procedures, including calibration procedures and frequency of calibration.

4.3.7 A description of the effluent flow rate measurement procedures, including frequency of measurements, calibration procedures and frequency of calibration.

4.4 The objectives of the quality assurance program shall be documented and shall state the required precision, accuracy and completeness of the emission measurement data including a description of the procedures used to assess these parameters. Accuracy is the degree of agreement of a measurement with a true or known value. Precision is a measure of the agreement among individual measurements of the same parameters under similar conditions. Completeness is a measure of the amount of valid data obtained compared to the amount expected under normal conditions.

4.5 A quality control program shall be established to evaluate and track the quality of the emissions measurement data against preset criteria. The program should include where applicable a system of replicates, spiked samples, split samples, blanks and control charts. The number and frequency of such quality control checks shall be identified.

4.6 A sample tracking system shall be established to provide for positive identification of samples and data through all phases of the sample collection, analysis and reporting system. Sample handling and preservation procedures shall be established to maintain the integrity of samples during collection, storage and analysis.

4.7 Regular maintenance, calibration and field checks shall be performed for each sampling system in use by satisfying the requirements found in Table 2: Maintenance, Calibration and Field Check Requirements.

**Table 2—Maintenance, Calibration and Field Check Requirements**

<b>Sampling system components</b>	<b>Frequency of activity</b>
Cleaning of thermal anemometer elements	As required by application.
Inspect pitot tubes for contaminant deposits	At least annually.
Inspect pitot tube systems for leaks	At least annually.
Inspect sharp-edged nozzles for damage	At least annually or after maintenance that could cause damage.
Check nozzles for alignment, presence of deposits, or other potentially degrading factors	Annually.
Check transport lines of HEPA-filtered applications to determine if cleaning is required	Annually.
Clean transport lines	Visible deposits for HEPA-filtered applications. Mean mass of deposited material exceeds 1 g/m <sup>2</sup> for other applications.
Inspect or test the sample transport system for leaks	At least annually.
Check mass flow meters of sampling systems with a secondary or transfer standard	At least quarterly.
Inspect rotameters of sampling systems	At the start of each sampling period.

for presence of foreign matter	
Check response of stack flow rate systems	At least quarterly.
Calibration of flow meters of sampling systems	At least annually.
Calibration of effluent flow measurement devices	At least annually.
Calibration of timing devices	At least annually.

4.8 Periodic internal and external audits shall be performed to monitor compliance with the quality assurance program. These audits shall be performed in accordance with written procedures and conducted by personnel who do not have responsibility for performing any of the operations being audited.

4.9 A corrective action program shall be established including criteria for when corrective action is needed, what corrective actions will be taken and who is responsible for taking the corrective action.

4.10 Periodic reports to responsible management shall be prepared on the performance of the emissions measurements program. These reports should include assessment of the quality of the data, results of audits and description of corrective actions.

4.11 The quality assurance program should be documented in a quality assurance project plan that should address each of the above requirements.

## 5. References

(1) American National Standards Institute "Guide to Sampling Airborne Radioactive Materials in Nuclear Facilities", ANSI-N13.1-1969, American National Standards Institute, New York, New York (1969).

(2) American Public Health Association, "Methods of Air Sampling", 2nd Edition, Method 605, "Tentative Method of Analysis for Plutonium Content of Atmospheric Particulate Matter". American Public Health Association, New York, NY (1977).

(3) Ibid, Method 601, "Tentative Method of Analysis for Gross Alpha Radioactivity Content of the Atmosphere".

(4) Ibid, Method 602, "Tentative Method of the Analysis for Gross Beta Radioactivity Content of the Atmosphere".

(5) Ibid, Method 608, "Tentative Method of Analysis for Strontium-90 Content of Atmospheric Particulate Matter".

(6) Ibid, Method 609, "Tentative Method of Analysis for Tritium Content of the Atmosphere".

(7) Ibid, Method 603, "Tentative Method of Analysis for Iodine-131 Content of the Atmosphere".

(8) American Society for Testing and Materials, 1986 Annual Book ASTM Standards, Designation D-3648-78, "Standard Practices for the Measurement of Radioactivity". American Society for Testing and Materials, Philadelphia, PA (1986).

(9) Ibid, Designation D-3649-85, "Standard Practice for High Resolution Gamma Spectrometry".

(10) Ibid, Designation D-1943-81, "Standard Test Method for Alpha Particle Radioactivity of Water".

(11) Ibid, Designation D-1890-81, "Standard Test Method for Beta Particle Radioactivity of Water".

(12) Ibid, Designation D-2459-72, "Standard Test Method for Gamma Spectrometry of Water".

- (13) Ibid, Designation D-3972-82, "Standard Test Method for Isotopic Uranium in Water by Radiochemistry".
- (14) Ibid, Designation D-2907-83, "Standard Test Methods for Microquantities of Uranium in Water by Fluorometry".
- (15) Ibid, Designation E-318, "Standard Test Method for Uranium in Aqueous Solutions by Colorimetry".
- (16) Ibid, Designation D-3084-75, "Standard Practice for Alpha Spectrometry of Water".
- (17) Corley, J.P. and C.D. Corbit, "A Guide for Effluent Radiological Measurements at DOE Installations", DOE/EP-0096, Pacific Northwest Laboratories, Richland, Washington (1983).
- (18) Department of Energy, "RESL Analytical Chemistry Branch Procedures Manual", IDO-12096, U.S. Department of Energy, Idaho Falls, Idaho (1982).
- (19) Environmental Protection Agency, "Radiochemical Analytical Procedures for Analysis of Environmental Samples", EMSL-LV-0539-17, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, Nevada (1979).
- (20) Environmental Protection Agency, "Radiochemistry Procedures Manual", EPA 520/5-84-006, Eastern Environmental Radiation Facility, Montgomery, Alabama (1984).
- (21) National Council on Radiation Protection and Measurements, NCRP Report No. 50, "Environmental Radiation Measurements", National Council on Radiation Protection and Measurement, Bethesda, Maryland (1976).
- (22) Ibid, Report No. 47, "Tritium Measurement Techniques". (1976).
- (23) Ibid, Report No. 58 "A Handbook of Radioactivity Measurement Procedures" (1985).
- (24) Environmental Protection Agency, "Indoor Radon and Radon Decay Product Measurement Protocols", EPA 520/1-89-009, U.S. Environmental Protection Agency, Washington, DC (1989).

#### Method 115—Monitoring for Radon-222 Emissions

This appendix describes the monitoring methods which must be used in determining the radon-222 emissions from underground uranium mines, uranium mill tailings piles, phosphogypsum stacks, and other piles of waste material emitting radon.

##### 1. Radon-222 Emissions from Underground Uranium Mine Vents

1.1 Sampling Frequency and Calculation of Emissions. Radon-222 emissions from underground uranium mine vents shall be determined using one of the following methods:

1.1.1 Continuous Measurement. These measurements shall be made and the emissions calculated as follows:

(a) The radon-222 concentration shall be continuously measured at each mine vent whenever the mine ventilation system is operational.

(b) Each mine vent exhaust flow rate shall be measured at least 4 times per year.

(c) A weekly radon-222 emission rate for the mine shall be calculated and recorded weekly as follows:

$$A_w = C_1 Q_1 T_1 + C_2 Q_2 T_2 + \dots C_i Q_i T_i$$

Where:

$A_w$  = Total radon-222 emitted from the mine during week (Ci)

$C_i$  = Average radon-222 concentration in mine vent  $i$  (Ci/m<sup>3</sup>)

$Q_i$ =Volumetric flow rate from mine vent i( $m^3$  /hr)

$T_i$ =Hours of mine ventilation system operation during week for mine vent i(hr)

(d) The annual radon-222 emission rate is the sum of the weekly emission rates during a calendar year.

1.1.2 Periodic Measurement. This method is applicable only to mines that continuously operate their ventilation system except for extended shutdowns. Mines which start up and shut down their ventilation system frequently must use the continuous measurement method describe in Section 1.1.1 above. Emission rates determined using periodic measurements shall be measured and calculated as follows:

(a) The radon-222 shall be continuously measured at each mine vent for at least one week every three months.

(b) Each mine vent exhaust flow rate shall be measured at least once during each of the radon-222 measurement periods.

(c) A weekly radon-222 emission rate shall be calculated for each weekly period according to the method described in Section 1.1.1. In this calculation  $T=168$  hr.

(d) The annual radon-222 emission rate from the mine should be calculated as follows:

$$A_y = \frac{52 - W_s}{n} (A_{w1} + A_{w2} + \cdots A_{wi})$$

Where:

$A_y$ =Annual radon-222 emission rate from the mine(Ci)

$A_{wi}$ =Weekly radon-222 emission rate during the measurement period i (Ci)

$n$ =Number of weekly measurement periods per year

$W_s$ =Number of weeks during the year that the mine ventilation system is shut down in excess of 7 consecutive days, i.e. the sum of the number of weeks each shut down exceeds 7 days

## 1.2 Test Methods and Procedures

Each underground mine required to test its emissions, unless an equivalent or alternative method has been approved by the Administrator, shall use the following test methods:

1.2.1 Test Method 1 of appendix A to part 60 shall be used to determine velocity traverses. The sampling point in the duct shall be either the centroid of the cross section or the point of average velocity.

1.2.2 Test Method 2 of appendix A to part 60 shall be used to determine velocity and volumetric flow rates.

1.2.3 Test Methods A-6 or A-7 of appendix B, Method 114 to part 61 shall be used for the analysis of radon-222. Use of Method A-7 requires prior approval of EPA based on conditions described in appendix B.

1.2.4 A quality assurance program shall be conducted in conformance with the programs described for Continuous Radon Monitors and Alpha Track Detectors in EPA 520/1-89-009. (2)

## 2. Radon-222 Emissions from Uranium Mill Tailings Piles

### 2.1 Measurement and Calculation of Radon Flux from Uranium Mill Tailings Piles.

2.1.1 Frequency of Flux Measurement. A single set of radon flux measurements may be made, or if the owner or operator chooses, more frequent measurements may be made over a one year period. These measurements may involve quarterly, monthly or weekly intervals. All radon measurements shall be made as described in paragraphs 2.1.2 through

2.1.6 except that for measurements made over a one year period, the requirement of paragraph 2.1.4(c) shall not apply. The mean radon flux from the pile shall be the arithmetic mean of the mean radon flux for each measurement period. The weather conditions, moisture content of the tailings and area of the pile covered by water existing at the time of the measurement shall be chosen so as to provide measurements representative of the long term radon flux from the pile and shall be subject to EPA review and approval.

2.1.2 Distribution of Flux Measurements. The distribution and number of radon flux measurements required on a pile will depend on clearly defined areas of the pile (called regions) that can have significantly different radon fluxes due to surface conditions. The mean radon flux shall be determined for each individual region of the pile. Regions that shall be considered for operating mill tailings piles are:

- (a) Water covered areas,
- (b) Water saturated areas (beaches),
- (c) Dry top surface areas, and
- (d) Sides, except where earthen material is used in dam construction.

For mill tailings after disposal the pile shall be considered to consist of only one region.

2.1.3 Number of Flux Measurements. Radon flux measurements shall be made within each region on the pile, except for those areas covered with water. Measurements shall be made at regularly spaced locations across the surface of the region, realizing that surface roughness will prohibit measurements in some areas of a region. The minimum number of flux measurements considered necessary to determine a representative mean radon flux value for each type of region on an operating pile is:

- (a) Water covered area—no measurements required as radon flux is assumed to be zero,
- (b) Water saturated beaches—100 radon flux measurements,
- (c) Loose and dry top surface—100 radon flux measurements,
- (d) Sides—100 radon flux measurements, except where earthen material is used in dam construction.

For a mill tailings pile after disposal which consists of only one region a minimum of 100 measurements are required.

2.1.4 Restrictions to Radon Flux Measurements. The following restrictions are placed on making radon flux measurements:

- (a) Measurements shall not be initiated within 24 hours of a rainfall.
- (b) If a rainfall occurs during the 24 hour measurements period, the measurement is invalid if the seal around the lip of the collector has washed away or if the collector is surrounded by water.
- (c) Measurements shall not be performed if the ambient temperature is below 35 °F or if the ground is frozen.

2.1.5 Areas of Pile Regions. The approximate area of each region of the pile shall be determined in units of square meters.

2.1.6 Radon Flux Measurement. Measuring radon flux involves the adsorption of radon on activated charcoal in a large-area collector. The radon collector is placed on the surface of the pile area to be measured and allowed to collect radon for a time period of 24 hours. The radon collected on the charcoal is measured by gamma-ray spectroscopy. The detailed measurement procedure provided in appendix A of EPA 520/5-85-0029(1) shall be used to measure the radon flux on uranium mill tailings, except the surface of the tailings shall not be penetrated by the lip of the radon collector as directed in the procedure, rather the collector shall be carefully positioned on a flat surface with soil or tailings used to seal the edge.

2.1.7 Calculations. The mean radon flux for each region of the pile and for the total pile shall be calculated and reported as follows:



(a) The individual radon flux calculations shall be made as provided in appendix A EPA 86 (1). The mean radon flux for each region of the pile shall be calculated by summing all individual flux measurements for the region and dividing by the total number of flux measurements for the region.

(b) The mean radon flux for the total uranium mill tailings pile shall be calculated as follows.

$$J_s = \frac{J_1 A_1 + \cdots J_2 A_2 \cdots J_i A_i}{A_t}$$

Where:

$J_s$ =Mean flux for the total pile (pCi/m<sup>2</sup> -s)

$J_i$ =Mean flux measured in region i (pCi/m<sup>2</sup> -s)

$A_i$ =Area of region i (m<sup>2</sup> )

$A_t$ =Total area of the pile (m<sup>2</sup> )

2.1.8 Reporting. The results of individual flux measurements, the approximate locations on the pile, and the mean radon flux for each region and the mean radon flux for the total stack shall be included in the emission test report. Any condition or unusual event that occurred during the measurements that could significantly affect the results should be reported.

### 3.0 Radon-222 Emissions from Phosphogypsum Stacks.

3.1 Measurement and Calculation of the Mean Radon Flux. Radon flux measurements shall be made on phosphogypsum stacks as described below:

3.1.1 Frequency of Measurements. A single set of radon flux measurements may be made after the phosphogypsum stack becomes inactive, or if the owner or operator chooses, more frequent measurements may be made over a one year period. These measurements may involve quarterly, monthly or weekly intervals. All radon measurements shall be made as described in paragraphs 3.1.2 through 3.1.6 except that for measurements made over a one year period, the requirement of paragraph 3.1.4(c) shall not apply. For measurements made over a one year period, the radon flux shall be the arithmetic mean of the mean radon flux for each measurement period.

3.1.2 Distribution and Number of Flux Measurements. The distribution and number of radon flux measurements required on a stack will depend on clearly defined areas of the stack (called regions) that can have significantly different radon fluxes due to surface conditions. The mean radon flux shall be determined for each individual region of the stack. Regions that shall be considered are:

- (a) Water covered areas,
- (b) Water saturated areas (beaches),
- (c) Loose and dry top surface areas,
- (d) Hard-packed roadways, and
- (e) Sides.

3.1.3 Number of Flux Measurements. Radon flux measurements shall be made within each region on the phosphogypsum stack, except for those areas covered with water. Measurements shall be made at regularly spaced locations across the surface of the region, realizing that surface roughness will prohibit measurements in some areas of a region. The minimum number of flux measurements considered necessary to determine a representative mean radon flux value for each type of region is:

- (a) Water covered area—no measurements required as radon flux is assumed to be zero,

- (b) Water saturated beaches—50 radon flux measurements,
- (c) Loose and dry top surface—100 radon flux measurements,
- (d) Hard-packed roadways—50 radon flux measurements, and
- (e) Sides—100 radon flux measurements.

A minimum of 300 measurements are required. A stack that has no water cover can be considered to consist of two regions, top and sides, and will require a minimum of only 200 measurements.

3.1.4 Restrictions to Radon Flux Measurements. The following restrictions are placed on making radon flux measurements:

- (a) Measurements shall not be initiated within 24 hours of a rainfall.
- (b) If a rainfall occurs during the 24 hour measurement period, the measurement is invalid if the seal around the lip of the collector has washed away or if the collector is surrounded by water.
- (c) Measurements shall not be performed if the ambient temperature is below 35 °F or if the ground is frozen.

3.1.5 Areas of Stack Regions. The approximate area of each region of the stack shall be determined in units of square meters.

3.1.6 Radon Flux Measurements. Measuring radon flux involves the adsorption of radon on activated charcoal in a large-area collector. The radon collector is placed on the surface of the stack area to be measured and allowed to collect radon for a time period of 24 hours. The radon collected on the charcoal is measured by gamma-ray spectroscopy. The detailed measurement procedure provided in appendix A of EPA 520/5-85-0029(1) shall be used to measure the radon flux on phosphogypsum stacks, except the surface of the phosphogypsum shall not be penetrated by the lip of the radon collector as directed in the procedure, rather the collector shall be carefully positioned on a flat surface with soil or phosphogypsum used to seal the edge.

3.1.7 Calculations. The mean radon flux for each region of the phosphogypsum stack and for the total stack shall be calculated and reported as follows:

(a) The individual radon flux calculations shall be made as provided in appendix A EPA 86 (1). The mean radon flux for each region of the stack shall be calculated by summing all individual flux measurements for the region and dividing by the total number of flux measurements for the region.

(b) The mean radon flux for the total phosphogypsum stack shall be calculated as follows.

$$J_s = \frac{J_1 A_1 + J_2 A_2 + \cdots J_i A_i}{A_t}$$

Where:

$J_s$ =Mean flux for the total stack (pCi/m<sup>2</sup> -s)

$J_i$ =Mean flux measured in region i (pCi/m<sup>2</sup> -s)

$A_i$ =Area of region i (m<sup>2</sup> )

$A_t$ =Total area of the stack

3.1.8 Reporting. The results of individual flux measurements, the approximate locations on the stack, and the mean radon flux for each region and the mean radon flux for the total stack shall be included in the emission test report. Any condition or unusual event that occurred during the measurements that could significantly affect the results should be reported.

#### 4.0 Quality Assurance Procedures for Measuring Rn-222 Flux

##### A. Sampling Procedures

Records of field activities and laboratory measurements shall be maintained. The following information shall be recorded for each charcoal canister measurement:

- (a) Site
- (b) Name of pile
- (c) Sample location
- (d) Sample ID number
- (e) Date and time on
- (f) Date and time off
- (g) Observations of meteorological conditions and comments

Records shall include all applicable information associated with determining the sample measurement, calculations, observations, and comments.

##### B. Sample Custody

Custodial control of all charcoal samples exposed in the field shall be maintained in accordance with EPA chain-of-custody field procedures. A control record shall document all custody changes that occur between the field and laboratory personnel.

##### C. Calibration Procedures and Frequency

The radioactivity of two standard charcoal sources, each containing a carefully determined quantity of radium-226 uniformly distributed through 180g of activated charcoal, shall be measured. An efficiency factor is computed by dividing the average measured radioactivity of the two standard charcoal sources, minus the background, in cpm by the known radioactivity of the charcoal sources in dpm. The same two standard charcoal sources shall be counted at the beginning and at the end of each day's counting as a check of the radioactivity counting equipment. A background count using unexposed charcoal should also be made at the beginning and at the end of each counting day to check for inadvertent contamination of the detector or other changes affecting the background. The unexposed charcoal comprising the blank is changed with each new batch of charcoal used.

##### D. Internal Quality Control Checks and Frequency

The charcoal from every tenth exposed canister shall be recounted. Five percent of the samples analyzed shall be either blanks (charcoal having no radioactivity added) or samples spiked with known quantities of radium-226.

##### E. Data Precision, Accuracy, and Completeness

The precision, accuracy, and completeness of measurements and analyses shall be within the following limits for samples measuring greater than  $1.0 \text{ pCi/m}^2 \text{ -s}$ .

- (a) Precision: 10%
- (b) Accuracy:  $\pm 10\%$
- (c) Completeness: at least 85% of the measurements must yield useable results.

#### 5.0 References

(1) Hartley, J.N. and Freeman, H.D., "Radon Flux Measurements on Gardiner and Royster phosphogypsum Piles Near Tampa and Mulberry, Florida," U.S. Environmental Protection Agency Report, EPA 520/5-85-029, January 1986.

(2) Environmental Protection Agency, "Indoor Radon and Radon Decay Product Measurement Protocols", EPA 520/1-89-009, U.S. Environmental Protection Agency, Washington, DC. (1989).

[38 FR 8826, Apr. 6, 1973]

**Editorial Notes:** 1. For Federal Register citations to appendix B see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

2. At 65 FR 62161, Oct. 17, 2000, appendix B to part 61 was amended by revising Methods 101, 101A, 102, 103, 104, 105, 106, 107, 107A, 108, 108A, 108B, 108C, and 111. However, because the amendment contains no revised text for Method 107A, this part of the revision could not be incorporated.

## **Appendix C to Part 61—Quality Assurance Procedures**

### *Procedure 1—Determination of Adequate Chromatographic Peak Resolution*

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from  $-2\sigma$  to  $+2\sigma$ . This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance,  $b$ , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits  $b-2\sigma_s$  to  $b+2\sigma_s$ , where  $\sigma_s$  is the standard deviation of the sample curve.

This calculation can be simplified in several ways. Overlap can be determined for curves of unit area; then actual areas can be introduced. Desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments, Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_c}^{b+2\sigma_c} e^{-\frac{(x-b)^2}{2\sigma_c^2}} dx = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_c}{\sigma_c}}^{\frac{b+2\sigma_c}{\sigma_c}} e^{-\frac{x^2}{2}} dx = \frac{1}{\sqrt{2\pi}} \int_{-\frac{2}{\sigma_c}}^{\frac{2}{\sigma_c}} e^{-\frac{x^2}{2}} dx$$

The following calculation steps are required:<sup>a</sup>

$$1. \quad 2\sigma_c = t_w / \sqrt{2 \ln 2}$$

$$2. \quad \sigma_c = t_w / (2 \sqrt{2 \ln 2})$$

$$3. \quad x_1 = (b - 2\sigma_c) / \sigma_c$$

$$4. \quad x_2 = (b + 2\sigma_c) / \sigma_c$$

$$5. \quad Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{-\frac{x^2}{2}} dx$$

$$6. \quad Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{-\frac{x^2}{2}} dx$$

$$7. \quad I_o = Q(x_1) - Q(x_2)$$

$$8. \quad A_o = I_o A_s / A_c$$

$$9. \quad \text{Percentage overlap} = A_o \times 100$$

where:

$A_s$  = Area of the sample peak of interest determined by electronic integration or by the formula  $A_s = t_w h_s$

$A_c$  = Area of the contaminant peak, determined in the same manner as  $A_s$

$b$  = Distance on the chromatographic chart that separates the maxima of the two peaks.

$h_s$  = Peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

$t_w$  = width of sample peak of interest at 1/2 peak height.

$t_w$  = width of the contaminant peak at 1/2 or base height

$\sigma_s$  = Standard deviation of the sample compound of interest elution curve.

$\sigma_c$  = Standard deviation of the contaminant elution curve.

$Q(x_1)$  = Integral of the normal distribution function from  $x_1$  to infinity.

$Q(x_2)$  = Integral of the normal distribution function from  $x_2$  to infinity.

$I_o$  = Overlap integral

$A_o$  = Area overlap fraction.

<sup>a</sup>In most instances,  $Q(x_2)$  is very small and may be neglected.

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In judging the suitability of alternate GC columns or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for  $t_w$  as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

## Procedure 2—Procedure for Field Auditing GC Analysis

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. The audit supervisor verifies that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism.

B. At the beginning and conclusion of the audit, the analyst records each cylinder number and pressure. An audit cylinder is never analyzed when the pressure drops below 200 psi.

C. During the audit, the analyst performs a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples, normally immediately after GC calibration and prior to sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within  $\pm 10$  percent, he directs the analyst to begin analyzing source samples. Audit supervisor judgment and/or supervisory policy determine action when agreement is not within  $\pm 10$  percent. When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor records each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told actual audit concentrations until calculated concentrations have been submitted to the audit supervisor.

#### Field Audit Report

*Part A*—To be filled out by organization supplying audit cylinders.

1. Organization supplying audit sample(s) and shipping address

\_\_\_\_\_

2. Audit supervisor, organization, and phone number

\_\_\_\_\_

\_\_\_\_\_

3. Shipping instructions: Name, Address, Attention

\_\_\_\_\_

\_\_\_\_\_

4. Guaranteed arrival date for cylinders \_\_\_\_\_

5. Planned shipping date for cylinders \_\_\_\_\_

6. Details on audit cylinders from last analysis

	Low conc.	High conc.
a. Date of last analysis		
b. Cylinder number		
c. Cylinder pressure, psi		
d. Audit gas(es)/balance gas		
e. Audit gas(es), ppm		
f. Cylinder construction		

*Part B*—To be filled out by audit supervisor.

1. Process sampled \_\_\_\_\_

2. Audit location \_\_\_\_\_

3. Name of individual audit \_\_\_\_\_

4. Audit date \_\_\_\_\_

5. Audit results:

	Low conc. cylinder	High conc. cylinder
a. Cylinder number		
b. Cylinder pressure before audit, psi		
c. Cylinder pressure after audit, psi		
d. Measured concentration, ppm Injection #1* Injection #2* Average		
e. Actual audit concentration, ppm (Part A, 6e)		
f. Audit accuracy: <sup>1</sup>		
Low Conc. Cylinder		
High Conc. Cylinder		
Percent <sup>1</sup> accuracy=		
Measured Conc. – Actual Conc.		
<u>                    </u> × 100		
Actual Conc.		
g. Problems detected (if any)		

<sup>1</sup>Results of two consecutive injections that meet the sample analysis criteria of the test method.

[47 FR 39178, Sept. 7, 1982]

## Appendix D to Part 61—Methods for Estimating Radionuclide Emissions

## 1. Purpose and Background

Facility owners or operators may estimate radionuclide emissions to the atmosphere for dose calculations instead of measuring emissions. Particulate emissions from mill tailings piles should be estimated using the procedures listed in reference re #2. All other emissions may be estimated by using the "Procedures" listed below, or using the method described in reference #1.

## 2. Procedure

To estimate emissions to the atmosphere:

(a) Determine the amount (in curies) used at facilities for the period under consideration. Radioactive materials in sealed packages that remain unopened, and have not leaked during the assessment period should not be included in the calculation.

(b) Multiply the amount used by the following factors which depend on the physical state of the radionuclide. They are:

(i) 1 for gases;

(ii)  $10^{-3}$  for liquids or particulate solids; and

(iii)  $10^{-6}$  for solids.

If any nuclide is heated to a temperature of 100 degrees Celsius or more, boils at a temperature of 100 degrees Celsius or less, or is intentionally dispersed into the environment, it must be considered to be a gas.

(c) If a control device is installed between the place of use and the point of release, multiply emissions from (b) by an adjustment factor. These are presented in Table 1.

**Table 1—Adjustment to Emission Factors for Effluent Controls**

<b>Controls</b>	<b>Types of radionuclides controlled</b>	<b>Adjustment factor to emissions</b>	<b>Comments and conditions</b>
HEPA filters	Particulates	0.01	Not applicable to gaseous radionuclides; periodic testing is prudent to ensure high removal efficiency.
Fabric filter	Particulates	0.1	Monitoring would be prudent to guard against tears in filter.
Sintered metal	Particulates	1	Insufficient data to make recommendation.
Activated carbon filters	Iodine gas	0.1	Efficiency is time dependent; monitoring is necessary to ensure effectiveness.
Douglas bags: Held one week or longer for decay	Xenon	0.5/wk	Based on xenon half-life of 5.3 days;
Douglas bags: Released within one week	Xenon	1	Provides no reduction of exposure to general public.
Venturi scrubbers	Particulates Gases	0.05 1	Although venturis may remove gases, variability in gaseous removal efficiency dictates adjustment factor for particulates only.
Packed bed scrubbers	Gases	0.1	Not applicable to particulates.
Electrostatic precipitators	Particulates	0.05	Not applicable for gaseous radionuclides
Xenon traps	Xenon	0.1	Efficiency is time dependent; monitoring is necessary to ensure



			effectiveness.
Fume hoods	All	1	Provides no reduction to general public exposures.
Vent stacks	All	1	Generally provides no reduction of exposure to general public.

#### References

(1) Environmental Protection Agency, "A Guide for Determining Compliance with the Clean Air Act Standards for Radionuclides Emissions from NRC-Licensed and Non-DOE Federal Facilities", EPA 520/1-89-002, January 1989.

(2) Nuclear Regulatory Commission, "Methods for Estimating Radioactive and Toxic Airborne Source Terms for Uranium Milling Operations", U.S. Nuclear Regulatory Commission Regulatory Guide 3.59, March 1987.

[54 FR 51711, Dec. 15, 1989]

### Appendix E to Part 61—Compliance Procedures Methods for Determining Compliance With Subpart I

#### 1. Purpose and Background

This Appendix provides simplified procedures to reduce the burden on Nuclear Regulatory Commission (NRC) licensees, and non-Department of Energy Federal facilities in determining compliance with 40 CFR part 61, subpart I. The procedures consist of a series of increasingly more stringent steps, depending on the facility's potential to exceed the standard.

First, a facility can be found in compliance if the quantity of radioactive material possessed during the year is less than that listed in a table of annual possession quantities. A facility will also be in compliance if the average annual radionuclide emission concentration is less than that listed in a table of air concentration levels. If the facility is not in compliance by these tables, it can establish compliance by estimating a dose using screening procedure developed by the National Council on Radiation Protection and Measurements with a radiological source term derived using EPA approved emission factors. These procedures are described in a "Guide for Determining Compliance with the Clean Air Act Standards for Radionuclide Emissions From NRC-Licensed and Non-DOE Federal Facilities."

A user-friendly computer program called COMPLY has been developed to reduce the burden on the regulated community. The Agency has also prepared a "User's Guide for the COMPLY Code" to assist the regulated community in using the code, and in handling more complex situations such as multiple release points. The basis for these compliance procedures are provided in "Background Information Document: Procedures Approved for Demonstrating Compliance with 40 CFR Part 61, Subpart I". The compliance model is the highest level in the COMPLY computer code and provides for the most realistic assessment of dose by allowing the use of site-specific information.

#### 2. Table of Annual Possession Quantity

(a) Table 1 may be used for determining if facilities are in compliance with the standard. The possession table can only be used if the following conditions are met:

- (i) No person lives within 10 meters of any release point; and
- (ii) No milk, meat, or vegetables are produced within 100 meters of any release point.

(b) Procedures described in Reference (1) shall be used to determine compliance or exemption from reporting by use of Table 2.

**Table 1—Annual Possession Quantities for Environmental Compliance**

[Annual Possession Quantities (Ci/yr)]

<b>Radionuclide</b>	<b>Gaseous form*</b>	<b>Liquid/powder forms</b>	<b>Solid form*</b>
Ac-225	9.6E-05	9.6E-02	9.6E+01
Ac-227	1.6E-07	1.6E-04	1.6E-01
Ac-228	3.4E-03	3.4E+00	3.4E+03
Ag-106	1.6E+00	1.6E+03	1.6E+06
Ag-106m	2.6E-03	2.6E+00	2.6E+03
Ag-108m	6.5E-06	6.5E-03	6.5E+00
Ag-110m	9.4E-05	9.4E-02	9.4E+01
Ag-111	6.7E-02	6.7E+01	6.7E+04
Al-26	4.0E-06	4.0E-03	4.0E+00
Am-241	2.3E-06	2.3E-03	2.3E+00
Am-242	1.8E-02	1.8E+01	1.8E+04
Am-242m	2.5E-06	2.5E-03	2.5E+00
Am-243	2.3E-06	2.3E-03	2.3E+00
Am-244	4.6E-02	4.6E+01	4.6E+04
Am-245	7.0E+00	7.0E+03	7.0E+06
Am-246	9.8E-01	9.8E+02	9.8E+05
Ar-37	1.4E+06		
Ar-41	1.4E+00		
As-72	2.9E-02	2.9E+01	2.9E+04
As-73	6.0E-02	6.0E+01	6.0E+04
As-74	4.3E-03	4.3E+00	4.3E+03
As-76	8.8E-02	8.8E+01	8.8E+04
As-77	7.9E-01	7.9E+02	7.9E+05
At-211	1.0E-02	1.0E+01	1.0E+04
Au-193	4.2E-01	4.2E+02	4.2E+05
Au-194	3.5E-02	3.5E+01	3.5E+04
Au-195	3.3E-03	3.3E+00	3.3E+03
Au-198	4.6E-02	4.6E+01	4.6E+04

Au-199	1.5E-01	1.5E+02	1.5E+05
Ba-131	1.0E-02	1.0E+01	1.0E+04
Ba-133	4.9E-05	4.9E-02	4.9E+01
Ba-133m	9.3E-02	9.3E+01	9.3E+04
Ba-135m	5.8E-01	5.8E+02	5.8E+05
Ba-139	4.7E+00	4.7E+03	4.7E+06
Ba-140	2.1E-03	2.1E+00	2.1E+03
Ba-141	1.3E+00	1.3E+03	1.3E+06
Ba-142	1.1E+00	1.1E+03	1.1E+06
Be-7	2.3E-02	2.3E+01	2.3E+04
Be-10	3.0E-03	3.0E+00	3.0E+03
Bi-206	3.1E-03	3.1E+00	3.1E+03
Bi-207	8.4E-06	8.4E-03	8.4E+00
Bi-210	4.2E-03	4.2E+00	4.2E+03
Bi-212	4.7E-02	4.7E+01	4.7E+04
Bi-213	6.0E-02	6.0E+01	6.0E+04
Bi-214	1.4E-01	1.4E+02	1.4E+05
Bk-249	7.0E-04	7.0E-01	7.0E+02
Bk-250	1.0E-01	1.0E+02	1.0E+05
Br-77	7.5E-02	7.5E+01	7.5E+04
Br-80	1.2E+01	1.2E+04	1.2E+07
Br-80m	1.5E+00	1.5E+03	1.5E+06
Br-82	1.6E-02	1.6E+01	1.6E+04
Br-83	9.9E+00	9.9E+03	9.9E+06
Br-84	5.6E-01	5.6E+02	5.6E+05
C-11	1.3E+00	1.3E+03	1.3E+06
C-14	2.9E-01	2.9E+02	2.9E+05
Ca-41	2.7E-02	2.7E+01	2.7E+04
Ca-45	5.8E-02	5.8E+01	5.8E+04

Ca-47	1.1E-02	1.1E+01	1.1E+04
Cd-109	5.0E-03	5.0E+00	5.0E+03
Cd-113	3.3E-04	3.3E-01	3.3E+02
Cd-113m	4.4E-04	4.4E-01	4.4E+02
Cd-115	5.4E-02	5.4E+01	5.4E+04
Cd-115m	1.0E-02	1.0E+01	1.0E+04
Cd-117	5.6E-02	5.6E+01	5.6E+04
Cd-117m	1.3E-01	1.3E+02	1.3E+05
Ce-139	2.6E-03	2.6E+00	2.6E+03
Ce-141	1.8E-02	1.8E+01	1.8E+04
Ce-143	1.0E-01	1.0E+02	1.0E+05
Ce-144	1.7E-03	1.7E+00	1.7E+03
Cf-248	2.0E-05	2.0E-02	2.0E+01
Cf-249	1.7E-06	1.7E-03	1.7E+00
Cf-250	4.0E-06	4.0E-03	4.0E+00
Cf-251	1.7E-06	1.7E-03	1.7E+00
Cf-252	6.4E-06	6.4E-03	6.4E+00
Cf-253	3.3E-04	3.3E-01	3.3E+02
Cf-254	3.6E-06	3.6E-03	3.6E+00
Cl-36	1.9E-04	1.9E-01	1.9E+02
Cl-38	6.5E-01	6.5E+02	6.5E+05
Cm-242	6.0E-05	6.0E-02	6.0E+01
Cm-243	3.3E-06	3.3E-03	3.3E+00
Cm-244	4.2E-06	4.2E-03	4.2E+00
Cm-245	2.3E-06	2.3E-03	2.3E+00
Cm-246	2.3E-06	2.3E-03	2.3E+00
Cm-247	2.3E-06	2.3E-03	2.3E+00
Cm-248	6.4E-07	6.4E-04	6.4E-01
Cm-249	4.6E+00	4.6E+03	4.6E+06

Cm-250	1.1E-07	1.1E-04	1.1E-01
Co-56	2.4E-04	2.4E-01	2.4E+02
Co-57	1.6E-03	1.6E+00	1.6E+03
Co-58	9.0E-04	9.0E-01	9.0E+02
Co-58m	1.7E-01	1.7E+02	1.7E+05
Co-60	1.6E-05	1.6E-02	1.6E+01
Co-60m	4.0E+00	4.0E+03	4.0E+06
Co-61	3.8E+00	3.8E+03	3.8E+06
Cr-49	9.0E-01	9.0E+02	9.0E+05
Cr-51	6.3E-02	6.3E+01	6.3E+04
Cs-129	1.5E-01	1.5E+02	1.5E+05
Cs-131	2.8E-01	2.8E+02	2.8E+05
Cs-132	1.3E-02	1.3E+01	1.3E+04
Cs-134	5.2E-05	5.2E-02	5.2E+01
Cs-134m	3.2E-01	3.2E+02	3.2E+05
Cs-135	2.4E-02	2.4E+01	2.4E+04
Cs-136	2.1E-03	2.1E+00	2.1E+03
Cs-137	2.3E-05	2.3E-02	2.3E+01
Cs-138	4.4E-01	4.4E+02	4.4E+05
Cu-61	4.0E-01	4.0E+02	4.0E+05
Cu-64	5.2E-01	5.2E+02	5.2E+05
Cu-67	1.5E-01	1.5E+02	1.5E+05
Dy-157	4.4E-01	4.4E+02	4.4E+05
Dy-165	5.6E+00	5.6E+03	5.6E+06
Dy-166	8.1E-02	8.1E+01	8.1E+04
Er-169	4.0E-01	4.0E+02	4.0E+05
Er-171	3.6E-01	3.6E+02	3.6E+05
Es-253	2.6E-04	2.6E-01	2.6E+02
Es-254	2.3E-05	2.3E-02	2.3E+01

Es-254m	1.8E-03	1.8E+00	1.8E+03
Eu-152	1.6E-05	1.6E-02	1.6E+01
Eu-152m	3.5E-01	3.5E+02	3.5E+05
Eu-154	2.0E-05	2.0E-02	2.0E+01
Eu-155	5.2E-04	5.2E-01	5.2E+02
Eu-156	3.2E-03	3.2E+00	3.2E+03
F-18	5.6E-01	5.6E+02	5.6E+05
Fe-52	4.9E-02	4.9E+01	4.9E+04
Fe-55	1.4E-01	1.4E+02	1.4E+05
Fe-59	1.3E-03	1.3E+00	1.3E+03
Fm-254	1.8E-02	1.8E+01	1.8E+04
Fm-255	4.0E-03	4.0E+00	4.0E+03
Fr-223	1.4E-01	1.4E+02	1.4E+05
Ga-66	5.6E-02	5.6E+01	5.6E+04
Ga-67	1.1E-01	1.1E+02	1.1E+05
Ga-68	7.6E-01	7.6E+02	7.6E+05
Ga-72	3.6E-02	3.6E+01	3.6E+04
Gd-152	4.4E-06	4.4E-03	4.4E+00
Gd-153	2.0E-03	2.0E+00	2.0E+03
Gd-159	6.8E-01	6.8E+02	6.8E+05
Ge-68	2.3E-04	2.3E-01	2.3E+02
Ge-71	2.6E+00	2.6E+03	2.6E+06
Ge-77	1.0E-01	1.0E+02	1.0E+05
H-3	1.5E+01	1.5E+04	1.5E+07
Hf-181	2.5E-03	2.5E+00	2.5E+03
Hg-193m	9.5E-02	9.5E+01	9.5E+04
Hg-197	2.4E-01	2.4E+02	2.4E+05
Hg-197m	2.5E-01	2.5E+02	2.5E+05
Hg-203	5.2E-03	5.2E+00	5.2E+03

Ho-166	2.8E-01	2.8E+02	2.8E+05
Ho-166m	6.0E-06	6.0E-03	6.0E+00
I-123	4.9E-01	4.9E+02	4.9E+05
I-124	9.3E-03	9.3E+00	9.3E+03
I-125	6.2E-03	6.2E+00	6.2E+03
I-126	3.7E-03	3.7E+00	3.7E+03
I-128	9.3E+00	9.3E+03	9.3E+06
I-129	2.6E-04	2.6E-01	2.6E+02
I-130	4.6E-02	4.6E+01	4.6E+04
I-131	6.7E-03	6.7E+00	6.7E+03
I-132	2.0E-01	2.0E+02	2.0E+05
I-133	6.7E-02	6.7E+01	6.7E+04
I-134	3.2E-01	3.2E+02	3.2E+05
I-135	1.2E-01	1.2E+02	1.2E+05
In-111	4.9E-02	4.9E+01	4.9E+04
In-113m	2.1E+00	2.1E+03	2.1E+06
In-114m	4.9E-03	4.9E+00	4.9E+03
In-115	2.7E-04	2.7E-01	2.7E+02
In-115m	1.4E+00	1.4E+03	1.4E+06
In-116m	3.5E-01	3.5E+02	3.5E+05
In-117	1.3E+00	1.3E+03	1.3E+06
In-117m	7.6E-02	7.6E+01	7.6E+04
Ir-190	3.5E-03	3.5E+00	3.5E+03
Ir-192	9.7E-04	9.7E-01	9.7E+02
Ir-194	2.5E-01	2.5E+02	2.5E+05
Ir-194m	1.5E-04	1.5E-01	1.5E+02
K-40	6.8E-05	6.8E-02	6.8E+01
K-42	2.9E-01	2.9E+02	2.9E+05
K-43	6.0E-02	6.0E+01	6.0E+04

K-44	4.9E-01	4.9E+02	4.9E+05
Kr-79	7.0E+00		
Kr-81	1.8E+02		
Kr-83m	2.0E+04		
Kr-85	8.4E+02		
Kr-85m	1.1E+01		
Kr-87	2.0E+00		
Kr-88	4.2E-01		
La-140	1.6E-02	1.6E+01	1.6E+04
La-141	1.1E+00	1.1E+03	1.1E+06
La-142	2.3E-01	2.3E+02	2.3E+05
Lu-177	1.4E-01	1.4E+02	1.4E+05
Lu-177m	3.5E-04	3.5E-01	3.5E+02
Mg-28	2.1E-02	2.1E+01	2.1E+04
Mn-52	3.5E-03	3.5E+00	3.5E+03
Mn-52m	5.2E-01	5.2E+02	5.2E+05
Mn-53	5.7E-02	5.7E+01	5.7E+04
Mn-54	2.5E-04	2.5E-01	2.5E+02
Mn-56	2.5E-01	2.5E+02	2.5E+05
Mo-93	1.5E-03	1.5E+00	1.5E+03
Mo-99**	5.7E-02	5.7E+01	5.7E+04
Mo-101	8.4E-01	8.4E+02	8.4E+05
Na-22	3.2E-05	3.2E-02	3.2E+01
Na-24	2.6E-02	2.6E+01	2.6E+04
Nb-90	2.5E-02	2.5E+01	2.5E+04
Nb-93m	1.2E-02	1.2E+01	1.2E+04
Nb-94	6.0E-06	6.0E-03	6.0E+00
Nb-95	2.3E-03	2.3E+00	2.3E+03
Nb-95m	2.0E-02	2.0E+01	2.0E+04



Nb-96	2.5E-02	2.5E+01	2.5E+04
Nb-97	1.0E+00	1.0E+03	1.0E+06
Nd-147	3.0E-02	3.0E+01	3.0E+04
Nd-149	1.1E+00	1.1E+03	1.1E+06
Ni-56	2.0E-03	2.0E+00	2.0E+03
Ni-57	2.1E-02	2.1E+01	2.1E+04
Ni-59	2.2E-02	2.2E+01	2.2E+04
Ni-63	1.4E-01	1.4E+02	1.4E+05
Ni-65	7.0E-01	7.0E+02	7.0E+05
Np-235	3.0E-02	3.0E+01	3.0E+04
Np-237	1.8E-06	1.8E-03	1.8E+00
Np-238	1.9E-02	1.9E+01	1.9E+04
Np-239	1.0E-01	1.0E+02	1.0E+05
Np-240	6.5E-01	6.5E+02	6.5E+05
Np-240m	4.7E+00	4.7E+03	4.7E+06
Os-185	9.2E-04	9.2E-01	9.2E+02
Os-191m	9.0E-01	9.0E+02	9.0E+05
Os-191	3.8E-02	3.8E+01	3.8E+04
Os-193	2.9E-01	2.9E+02	2.9E+05
P-32	1.7E-02	1.7E+01	1.7E+04
P-33	1.2E-01	1.2E+02	1.2E+05
Pa-230	6.3E-04	6.3E-01	6.3E+02
Pa-231	8.3E-07	8.3E-04	8.3E-01
Pa-233	9.3E-03	9.3E+00	9.3E+03
Pa-234	9.3E-02	9.3E+01	9.3E+04
Pb-203	8.3E-02	8.3E+01	8.3E+04
Pb-205	1.2E-02	1.2E+01	1.2E+04
Pb-209	1.1E+01	1.1E+04	1.1E+07
Pb-210	5.5E-05	5.5E-02	5.5E+01

Pb-211	1.2E-01	1.2E+02	1.2E+05
Pb-212	6.0E-03	6.0E+00	6.0E+03
Pb-214	1.2E-01	1.2E+02	1.2E+05
Pd-103	2.1E-01	2.1E+02	2.1E+05
Pd-107	8.2E-02	8.2E+01	8.2E+04
Pd-109	9.4E-01	9.4E+02	9.4E+05
Pm-143	7.6E-04	7.6E-01	7.6E+02
Pm-144	1.1E-04	1.1E-01	1.1E+02
Pm-145	5.2E-04	5.2E-01	5.2E+02
Pm-146	4.4E-05	4.4E-02	4.4E+01
Pm-147	2.6E-02	2.6E+01	2.6E+04
Pm-148	1.7E-02	1.7E+01	1.7E+04
Pm-148m	7.6E-04	7.6E-01	7.6E+02
Pm-149	2.8E-01	2.8E+02	2.8E+05
Pm-151	1.2E-01	1.2E+02	1.2E+05
Po-210	9.3E-05	9.3E-02	9.3E+01
Pr-142	2.8E-01	2.8E+02	2.8E+05
Pr-143	1.0E-01	1.0E+02	1.0E+05
Pr-144	1.5E+01	1.5E+04	1.5E+07
Pt-191	6.4E-02	6.4E+01	6.4E+04
Pt-193	2.1E-02	2.1E+01	2.1E+04
Pt-193m	4.8E-01	4.8E+02	4.8E+05
Pt-195m	1.4E-01	1.4E+02	1.4E+05
Pt-197	1.1E+00	1.1E+03	1.1E+06
Pt-197m	3.6E+00	3.6E+03	3.6E+06
Pu-236	7.0E-06	7.0E-03	7.0E+00
Pu-237	2.3E-02	2.3E+01	2.3E+04
Pu-238	2.7E-06	2.7E-03	2.7E+00
Pu-239	2.5E-06	2.5E-03	2.5E+00

Pu-240	2.5E-06	2.5E-03	2.5E+00
Pu-241	1.3E-04	1.3E-01	1.3E+02
Pu-242	2.5E-06	2.5E-03	2.5E+00
Pu-243	3.8E+00	3.8E+03	3.8E+06
Pu-244	2.4E-06	2.4E-03	2.4E+00
Pu-245	2.1E-01	2.1E+02	2.1E+05
Pu-246	4.8E-03	4.8E+00	4.8E+03
Ra-223	1.3E-04	1.3E-01	1.3E+02
Ra-224	3.2E-04	3.2E-01	3.2E+02
Ra-225	1.3E-04	1.3E-01	1.3E+02
Ra-226	5.5E-06	5.5E-03	5.5E+00
Ra-228	1.3E-05	1.3E-02	1.3E+01
Rb-81	4.2E-01	4.2E+02	4.2E+05
Rb-83	1.4E-03	1.4E+00	1.4E+03
Rb-84	2.0E-03	2.0E+00	2.0E+03
Rb-86	1.7E-02	1.7E+01	1.7E+04
Rb-87	1.0E-02	1.0E+01	1.0E+04
Rb-88	1.7E+00	1.7E+03	1.7E+06
Rb-89	6.4E-01	6.4E+02	6.4E+05
Re-184	1.8E-03	1.8E+00	1.8E+03
Re-184m	3.6E-04	3.6E-01	3.6E+02
Re-186	1.9E-01	1.9E+02	1.9E+05
Re-187	9.3E+00	9.3E+03	9.3E+06
Re-188	3.7E-01	3.7E+02	3.7E+05
Rh-103m	1.7E+02	1.7E+05	1.7E+08
Rh-105	3.4E-01	3.4E+02	3.4E+05
Ru-97	8.3E-02	8.3E+01	8.3E+04
Ru-103	3.1E-03	3.1E+00	3.1E+03
Ru-105	2.9E-01	2.9E+02	2.9E+05

Ru-106	5.9E-04	5.9E-01	5.9E+02
S-35	7.5E-02	7.5E+01	7.5E+04
Sb-117	2.0E+00	2.0E+03	2.0E+06
Sb-122	3.9E-02	3.9E+01	3.9E+04
Sb-124	6.0E-04	6.0E-01	6.0E+02
Sb-125	1.4E-04	1.4E-01	1.4E+02
Sb-126	1.8E-03	1.8E+00	1.8E+03
Sb-126m	7.6E-01	7.6E+02	7.6E+05
Sb-127	2.0E-02	2.0E+01	2.0E+04
Sb-129	1.8E-01	1.8E+02	1.8E+05
Sc-44	1.4E-01	1.4E+02	1.4E+05
Sc-46	4.0E-04	4.0E-01	4.0E+02
Sc-47	1.1E-01	1.1E+02	1.1E+05
Sc-48	1.1E-02	1.1E+01	1.1E+04
Sc-49	1.0E+01	1.0E+04	1.0E+07
Se-73	1.6E-01	1.6E+02	1.6E+05
Se-75	1.1E-03	1.1E+00	1.1E+03
Se-79	6.9E-03	6.9E+00	6.9E+03
Si-31	4.7E+00	4.7E+03	4.7E+06
Si-32	7.2E-04	7.2E-01	7.2E+02
Sm-147	1.4E-05	1.4E-02	1.4E+01
Sm-151	3.5E-02	3.5E+01	3.5E+04
Sm-153	2.4E-01	2.4E+02	2.4E+05
Sn-113	1.9E-03	1.9E+00	1.9E+03
Sn-117m	2.3E-02	2.3E+01	2.3E+04
Sn-119m	2.8E-02	2.8E+01	2.8E+04
Sn-123	1.8E-02	1.8E+01	1.8E+04
Sn-125	7.2E-03	7.2E+00	7.2E+03
Sn-126	4.7E-06	4.7E-03	4.7E+00

Sr-82	1.9E-03	1.9E+00	1.9E+03
Sr-85	1.9E-03	1.9E+00	1.9E+03
Sr-85m	1.5E+00	1.5E+03	1.5E+06
Sr-87m	1.2E+00	1.2E+03	1.2E+06
Sr-89	2.1E-02	2.1E+01	2.1E+04
Sr-90	5.2E-04	5.2E-01	5.2E+02
Sr-91	1.2E-01	1.2E+02	1.2E+05
Sr-92	2.5E-01	2.5E+02	2.5E+05
Ta-182	4.4E-04	4.4E-01	4.4E+02
Tb-157	2.2E-03	2.2E+00	2.2E+03
Tb-160	8.4E-04	8.4E-01	8.4E+02
Tc-95	9.0E-02	9.0E+01	9.0E+04
Tc-95m	1.4E-03	1.4E+00	1.4E+03
Tc-96	5.6E-03	5.6E+00	5.6E+03
Tc-96m	7.0E-01	7.0E+02	7.0E+05
Tc-97	1.5E-03	1.5E+00	1.5E+03
Tc-97m	7.2E-02	7.2E+01	7.2E+04
Tc-98	6.4E-06	6.4E-03	6.4E+00
Tc-99	9.0E-03	9.0E+00	9.0E+03
Tc-99m	1.4E+00	1.4E+03	1.4E+06
Tc-101	3.8E+00	3.8E+03	3.8E+06
Te-121	6.0E-03	6.0E+00	6.0E+03
Te-121m	5.3E-04	5.3E-01	5.3E+02
Te-123	1.2E-03	1.2E+00	1.2E+03
Te-123m	2.7E-03	2.7E+00	2.7E+03
Te-125m	1.5E-02	1.5E+01	1.5E+04
Te-127	2.9E+00	2.9E+03	2.9E+06
Te-127m	7.3E-03	7.3E+00	7.3E+03
Te-129	6.5E+00	6.5E+03	6.5E+06

Te-129m	6.1E-03	6.1E+00	6.1E+03
Te-131	9.4E-01	9.4E+02	9.4E+05
Te-131m	1.8E-02	1.8E+01	1.8E+04
Te-132	6.2E-03	6.2E+00	6.2E+03
Te-133	1.2E+00	1.2E+03	1.2E+06
Te-133m	2.9E-01	2.9E+02	2.9E+05
Te-134	4.4E-01	4.4E+02	4.4E+05
Th-226	3.0E-02	3.0E+01	3.0E+04
Th-227	6.4E-05	6.4E-02	6.4E+01
Th-228	2.9E-06	2.9E-03	2.9E+00
Th-229	4.9E-07	4.9E-04	4.9E-01
Th-230	3.2E-06	3.2E-03	3.2E+00
Th-231	8.4E-01	8.4E+02	8.4E+05
Th-232	6.0E-07	6.0E-04	6.0E-01
Th-234	2.0E-02	2.0E+01	2.0E+04
Ti-44	5.2E-06	5.2E-03	5.2E+00
Ti-45	4.0E-01	4.0E+02	4.0E+05
Tl-200	4.4E-02	4.4E+01	4.4E+04
Tl-201	1.8E-01	1.8E+02	1.8E+05
Tl-202	1.0E-02	1.0E+01	1.0E+04
Tl-204	2.5E-02	2.5E+01	2.5E+04
Tm-170	2.4E-02	2.4E+01	2.4E+04
Tm-171	5.9E-02	5.9E+01	5.9E+04
U-230	5.0E-05	5.0E-02	5.0E+01
U-231	1.4E-01	1.4E+02	1.4E+05
U-232	1.3E-06	1.3E-03	1.3E+00
U-233	7.6E-06	7.6E-03	7.6E+00
U-234	7.6E-06	7.6E-03	7.6E+00
U-235	7.0E-06	7.0E-03	7.0E+00

U-236	8.4E-06	8.4E-03	8.4E+00
U-237	4.7E-02	4.7E+01	4.7E+04
U-238	8.6E-06	8.6E-03	8.6E+00
U-239	8.3E+00	8.3E+03	8.3E+06
U-240	1.8E-01	1.8E+02	1.8E+05
V-48	1.4E-03	1.4E+00	1.4E+03
V-49	1.3E+00	1.3E+03	1.3E+06
W-181	1.1E-02	1.1E+01	1.1E+04
W-185	1.6E-01	1.6E+02	1.6E+05
W-187	1.1E-01	1.1E+02	1.1E+05
W-188	1.0E-02	1.0E+01	1.0E+04
Xe-122	7.6E-02	7.6E+01	7.6E+04
Xe-123	1.6E+00	1.6E+03	1.6E+06
Xe-125	6.0E-01		
Xe-127	7.0E+00		
Xe-129m	7.6E+01		
Xe-131m	2.2E+02		
Xe-133	5.2E+01		
Xe-133m	6.0E+01		
Xe-135	7.6E+00		
Xe-135m	4.2E+00		
Xe-138	9.9E-01		
Y-86	2.8E-02	2.8E+01	2.8E+04
Y-87	2.3E-02	2.3E+01	2.3E+04
Y-88	2.5E-04	2.5E-01	2.5E+02
Y-90	1.1E-01	1.1E+02	1.1E+05
Y-90m	4.3E-01	4.3E+02	4.3E+05
Y-91	1.8E-02	1.8E+01	1.8E+04
Y-91m	1.6E+00	1.6E+03	1.6E+06

Y-92	7.0E-01	7.0E+02	7.0E+05
Y-93	3.8E-01	3.8E+02	3.8E+05
Yb-169	5.5E-03	5.5E+00	5.5E+03
Yb-175	2.1E-01	2.1E+02	2.1E+05
Zn-62	8.6E-02	8.6E+01	8.6E+04
Zn-65	4.4E-04	4.4E-01	4.4E+02
Zn-69	2.7E+01	2.7E+04	2.7E+07
Zn-69m	2.0E-01	2.0E+02	2.0E+05
Zr-86	2.4E-02	2.4E+01	2.4E+04
Zr-88	2.7E-04	2.7E-01	2.7E+02
Zr-89	1.6E-02	1.6E+01	1.6E+04
Zr-93	2.8E-03	2.8E+00	2.8E+03
Zr-95	6.4E-04	6.4E-01	6.4E+02
Zr-97	4.6E-02	4.6E+01	4.6E+04

\*Radionuclides boiling at 100°C or less, or exposed to a temperature of 100°C, must be considered a gas. Capsules containing radionuclides in liquid or powder form can be considered to be solids.

\*\*Mo-99 contained in a generator to produce Technetium-99 can be assumed to be a solid.

### 3. Table of Concentration Levels

(a) Table 2 may be used for determining if facilities are in compliance with the standard.

1. The concentration table as applied to emission estimates can only be used if all releases are from point sources and concentrations have been measured at the stack or vent using EPA-approved methods, and the distance between each stack or vent and the nearest resident is greater than 3 times the diameter of the stack or vent. Procedures provided in Ref. (1) shall be used to determine compliance or exemption from reporting by use of Table 2.

2. The concentration table may be used to determine compliance with the standard based on environmental measurements provided these measurements are made in conformance with the requirements of §61.107(b)(5).

### 4. NCRP Screening Model

The procedures described in Reference (4) may be used to determine doses to members of the general public from emissions of radionuclides to the atmosphere. Both the total dose from all radionuclides emitted, and the dose caused by radioactive iodine must be considered in accordance with the procedures in Ref. (1).

### 5. The COMPLY Computer Code

The COMPLY computer code may be used to determine compliance with subpart I. The compliance model in the COMPLY computer code may be used to determine the dose to members of the general public from emissions of radionuclides to the atmosphere. The EPA may add radionuclides to all or any part of COMPLY to cover radionuclides that may be used by the regulated community.



Table 2—Concentration Levels for Environmental Compliance

Radionuclide	Concentration (Ci/m <sup>3</sup> )	Radionuclide	Concentration (Ci/m <sup>3</sup> )
Ac-225	9.1E-14	Bi-207	1.0E-14
Ac-227	1.6E-16	Bi-210	2.9E-13
Ac-228	3.7E-12	Bi-212	5.6E-11
Ag-106	1.9E-09	Bi-213	7.1E-11
Ag-106m	1.2E-12	Bi-214	1.4E-10
Ag-108m	7.1E-15	Bk-249	5.6E-13
Ag-110m	9.1E-14	Bk-250	9.1E-11
Ag-111	2.5E-12	Br-77	4.2E-11
Al-26	4.8E-15	Br-80	1.4E-08
Am-241	1.9E-15	Br-80m	1.8E-09
Am-242	1.5E-11	Br-82	1.2E-11
Am-242m	2.0E-15	Br-83	1.2E-08
Am-243	1.8E-15	Br-84	6.7E-10
Am-244	4.0E-11	C-11	1.5E-09
Am-245	8.3E-09	C-14	1.0E-11
Am-246	1.2E-09	Ca-41	4.2E-13
Ar-37	1.6E-03	Ca-45	1.3E-12
Ar-41	1.7E-09	Ca-47	2.4E-12
As-72	2.4E-11	Cd-109	5.9E-13
As-73	1.1E-11	Cd-113	9.1E-15
As-74	2.2E-12	Cd-113m	1.7E-14
As-76	5.0E-11	Cd-115	1.6E-11
As-77	1.6E-10	Cd-115m	8.3E-13
At-211	1.1E-11	Cd-117	6.7E-11
Au-193	3.8E-10	Cd-117m	1.6E-10
Au-194	3.2E-11	Ce-139	2.6E-12
Au-195	3.1E-12	Ce-141	6.3E-12
Au-198	2.1E-11	Ce-143	3.0E-11

Au-199	4.8E-11	Ce-144	6.2E-13
Ba-131	7.1E-12	Cf-248	1.8E-14
Ba-133	5.9E-14	Cf-249	1.4E-15
Ba-133m	5.9E-11	Cf-250	3.2E-15
Ba-135m	1.8E-10	Cf-251	1.4E-15
Ba-139	5.6E-09	Cf-252	5.6E-15
Ba-140	1.3E-12	Cf-253	3.1E-13
Ba-141	1.4E-09	Cf-254	3.0E-15
Ba-142	1.3E-09	Cl-36	2.7E-15
Be-7	2.3E-11	Cl-38	7.7E-10
Be-10	1.6E-12	Cm-242	5.3E-14
Bi-206	2.3E-12	Cm-243	2.6E-15
Cm-244	3.3E-15	Eu-156	1.9E-12
Cm-245	1.8E-15	F-18	6.7E-10
Cm-246	1.9E-15	Fe-52	5.6E-11
Cm-247	1.9E-15	Fe-55	9.1E-12
Cm-248	5.0E-16	Fe-59	6.7E-13
Cm-249	3.7E-09	Fm-254	2.0E-11
Cm-250	9.1E-17	Fm-255	4.3E-12
Co-56	1.8E-13	Fr-223	3.3E-11
Co-57	1.3E-12	Ga-66	6.2E-11
Co-58	6.7E-13	Ga-67	7.1E-11
Co-58m	1.2E-10	Ga-68	9.1E-10
Co-60	1.7E-14	Ga-72	3.8E-11
Co-60m	4.3E-09	Gd-152	5.0E-15
Co-61	4.5E-09	Gd-153	2.1E-12
Cr-49	1.1E-09	Gd-159	2.9E-10
Cr-51	3.1E-11	Ge-68	2.0E-13
Cs-129	1.4E-10	Ge-71	2.4E-10
Cs-131	3.3E-11	Ge-77	1.0E-10

Cs-132	4.8E-12	H-3	1.5E-09
Cs-134	2.7E-14	Hf-181	1.9E-12
Cs-134m	1.7E-10	Hg-193m	1.0E-10
Cs-135	4.0E-13	Hg-197	8.3E-11
Cs-136	5.3E-13	Hg-197m	1.1E-10
Cs-137	1.9E-14	Hg-203	1.0E-12
Cs-138	5.3E-10	Ho-166	7.1E-11
Cu-61	4.8E-10	Ho-166m	7.1E-15
Cu-64	5.3E-10	I-123	4.3E-10
Cu-67	5.0E-11	I-124	6.2E-13
Dy-157	5.0E-10	I-125	1.2E-13
Dy-165	6.7E-09	I-126	1.1E-13
Dy-166	1.1E-11	I-128	1.1E-08
Er-169	2.9E-11	I-129	9.1E-15
Er-171	4.0E-10	I-130	4.5E-11
Es-253	2.4E-13	I-131	2.1E-13
Es-254	2.0E-14	I-132	2.3E-10
Es-254m	1.8E-12	I-133	2.0E-11
Eu-152	2.0E-14	I-134	3.8E-10
Eu-152m	3.6E-10	I-135	1.2E-10
Eu-154	2.3E-14	In-111	3.6E-11
Eu-155	5.9E-13	In-113m	2.5E-09
In-114m	9.1E-13	Nb-95	2.2E-12
In-115	7.1E-14	Nb-95m	1.4E-11
In-115m	1.6E-09	Nb-96	2.4E-11
In-116m	4.2E-10	Nb-97	1.2E-09
In-117	1.6E-09	Nd-147	7.7E-12
In-117m	9.1E-11	Nd-149	7.1E-10
Ir-190	2.6E-12	Ni-56	1.7E-12
Ir-192	9.1E-13	Ni-57	1.8E-11

Ir-194	1.1E-10	Ni-59	1.5E-11
Ir-194m	1.7E-13	Ni-63	1.4E-11
K-40	2.7E-14	Ni-65	8.3E-10
K-42	2.6E-10	Np-235	2.5E-11
K-43	6.2E-11	Np-237	1.2E-15
K-44	5.9E-10	Np-238	1.4E-11
Kr-79	8.3E-09	Np-239	3.8E-11
Kr-81	2.1E-07	Np-240	7.7E-10
Kr-83m	2.3E-05	Np-240m	5.6E-09
Kr-85	1.0E-06	Os-185	1.0E-12
Kr-85m	1.3E-08	Os-191m	2.9E-10
Kr-87	2.4E-09	Os-191	1.1E-11
Kr-88	5.0E-10	Os-193	9.1E-11
La-140	1.2E-11	P-32	3.3E-13
La-141	7.7E-10	P-33	2.4E-12
La-142	2.7E-10	Pa-230	3.2E-13
Lu-177	2.4E-11	Pa-231	5.9E-16
Lu-177m	3.6E-13	Pa-233	4.8E-12
Mg-28	1.5E-11	Pa-234	1.1E-10
Mn-52	2.8E-12	Pb-203	6.2E-11
Mn-52m	6.2E-10	Pb-205	5.6E-12
Mn-53	1.5E-11	Pb-209	1.3E-08
Mn-54	2.8E-13	Pb-210	2.8E-15
Mn-56	2.9E-10	Pb-211	1.4E-10
Mo-93	1.1E-12	Pb-212	6.3E-12
Mo-99	1.4E-11	Pb-214	1.2E-10
Mo-101	1.0E-09	Pd-103	3.8E-11
Na-22	2.6E-14	Pd-107	3.1E-11
Na-24	2.6E-11	Pd-109	4.8E-10
Nb-90	2.6E-11	Pm-143	9.1E-13

Nb-93m	1.0E-11	Pm-144	1.3E-13
Nb-94	7.1E-15	Pm-145	6.2E-13
Pm-146	5.3E-14	Re-184m	3.7E-13
Pm-147	1.1E-11	Re-186	1.8E-11
Pm-148	5.0E-12	Re-187	2.6E-10
Pm-148m	6.7E-13	Re-188	1.7E-10
Pm-149	4.2E-11	Rh-103m	2.1E-07
Pm-151	7.1E-11	Rh-105	1.3E-10
Po-210	7.1E-15	Ru-97	6.7E-11
Pr-142	1.1E-10	Ru-103	2.6E-12
Pr-143	7.1E-12	Ru-105	2.8E-10
Pr-144	1.8E-08	Ru-106	3.4E-13
Pt-191	4.3E-11	S-35	1.3E-12
Pt-193	1.8E-11	Sb-117	2.4E-09
Pt-193m	4.8E-11	Sb-122	1.4E-11
Pt-195m	3.2E-11	Sb-124	5.3E-13
Pt-197	4.0E-10	Sb-125	1.6E-13
Pt-197m	2.6E-09	Sb-126	1.4E-12
Pu-236	5.9E-15	Sb-126m	9.1E-10
Pu-237	1.9E-11	Sb-127	7.1E-12
Pu-238	2.1E-15	Sb-129	7.7E-11
Pu-239	2.0E-15	Sc-44	1.7E-10
Pu-240	2.0E-15	Sc-46	4.2E-13
Pu-241	1.0E-13	Sc-47	3.8E-11
Pu-242	2.0E-15	Sc-48	9.1E-12
Pu-243	4.2E-09	Sc-49	1.2E-08
Pu-244	2.0E-15	Se-73	1.7E-10
Pu-245	2.1E-10	Se-75	1.7E-13
Pu-246	2.2E-12	Se-79	1.1E-13
Ra-223	4.2E-14	Si-31	5.6E-09

Ra-224	1.5E-13	Si-32	3.4E-14
Ra-225	5.0E-14	Sm-147	1.4E-14
Ra-226	3.3E-15	Sm-151	2.1E-11
Ra-228	5.9E-15	Sm-153	5.9E-11
Rb-81	5.0E-10	Sn-113	1.4E-12
Rb-83	3.4E-13	Sn-117m	5.6E-12
Rb-84	3.6E-13	Sn-119m	5.3E-12
Rb-86	5.6E-13	Sn-123	1.1E-12
Rb-87	1.6E-13	Sn-125	1.7E-12
Rb-88	2.1E-09	Sn-126	5.3E-15
Rb-89	7.1E-10	Sr-82	6.2E-13
Re-184	1.5E-12	Sr-85	1.8E-12
Sr-85m	1.6E-09	Th-232	6.2E-16
Sr-87m	1.4E-09	Th-234	2.2E-12
Sr-89	1.8E-12	Ti-44	6.2E-15
Sr-90	1.9E-14	Ti-45	4.8E-10
Sr-91	9.1E-11	Tl-200	4.5E-11
Sr-92	2.9E-10	Tl-201	1.0E-10
Ta-182	4.5E-13	Tl-202	5.0E-12
Tb-157	2.5E-12	Tl-204	1.2E-12
Tb-160	7.7E-13	Tm-170	3.3E-12
Tc-95	1.0E-10	Tm-171	2.6E-11
Tc-95m	1.4E-12	U-230	1.5E-14
Tc-96	5.6E-12	U-231	4.2E-11
Tc-96m	6.7E-10	U-232	1.3E-15
Tc-97	7.1E-13	U-233	7.1E-15
Tc-97m	7.1E-12	U-234	7.7E-15
Tc-98	6.7E-15	U-235	7.1E-15
Tc-99	1.4E-13	U-236	7.7E-15
Tc-99m	1.7E-09	U-237	1.0E-11

Tc-101	4.5E-09	U-238	8.3E-15
Te-121	1.0E-12	U-239	4.3E-09
Te-121m	1.2E-13	U-240	1.3E-10
Te-123	1.4E-13	V-48	1.0E-12
Te-123m	2.0E-13	V-49	1.6E-10
Te-125m	3.6E-13	W-181	6.7E-12
Te-127	1.0E-09	W-185	2.6E-12
Te-127m	1.5E-13	W-187	7.7E-11
Te-129	7.7E-09	W-188	5.3E-13
Te-129m	1.4E-13	Xe-122	9.1E-11
Te-131	9.1E-11	Xe-123	1.6E-09
Te-131m	1.0E-12	Xe-125	1.1E-11
Te-132	7.1E-13	Xe-127	8.3E-09
Te-133	9.1E-10	Xe-129m	9.1E-08
Te-133m	2.2E-10	Xe-131m	2.6E-07
Te-134	5.3E-10	Xe-133	6.2E-08
Th-226	3.4E-11	Xe-133m	7.1E-08
Th-227	3.8E-14	Xe-135	9.1E-09
Th-228	3.1E-15	Xe-135m	5.0E-09
Th-229	5.3E-16	Xe-138	1.2E-09
Th-230	3.4E-15	Y-86	3.0E-11
Th-231	2.9E-10	Y-87	1.7E-11
Y-88	2.7E-13	Zn-65	9.1E-14
Y-90	1.3E-11	Zn-69	3.2E-08
Y-90m	1.9E-10	Zn-69m	1.7E-10
Y-91	2.1E-12	Zr-86	2.4E-11
Y-91m	1.3E-09	Zr-88	3.1E-13
Y-92	8.3E-10	Zr-89	1.3E-11
Y-93	2.9E-10	Zr-93	2.6E-12
Yb-169	3.7E-12	Zr-95	6.7E-13

Yb-175	4.3E-11	Zr-97	3.8E-11
Zn-62	9.1E-11		

#### 6. References

(1) Environmental Protection Agency, "A Guide for Determining Compliance with the Clean Air Act Standards for Radionuclides Emissions from NRC-Licensed and Non-DOE Federal Facilities", EPA 520/1-89-002, October 1989.

(2) Environmental Protection Agency, "User's Guide for the COMPLY Code", EPA 520/1-89-003, October 1989.

(3) Environmental Protection Agency, "Background Information Document: Procedures Approved for Demonstrating Compliance with 40 CFR Part 61, Subpart I", EPA 520/1-89-001, January 1989.

(4) National Council on Radiation Protection and Measurement, "Screening Techniques for Determining Compliance with Environmental Standards" NCRP Commentary No. 3, Revision of January 1989 with addendum of October, 1989.

[54 FR 51711, Dec. 15, 1989]

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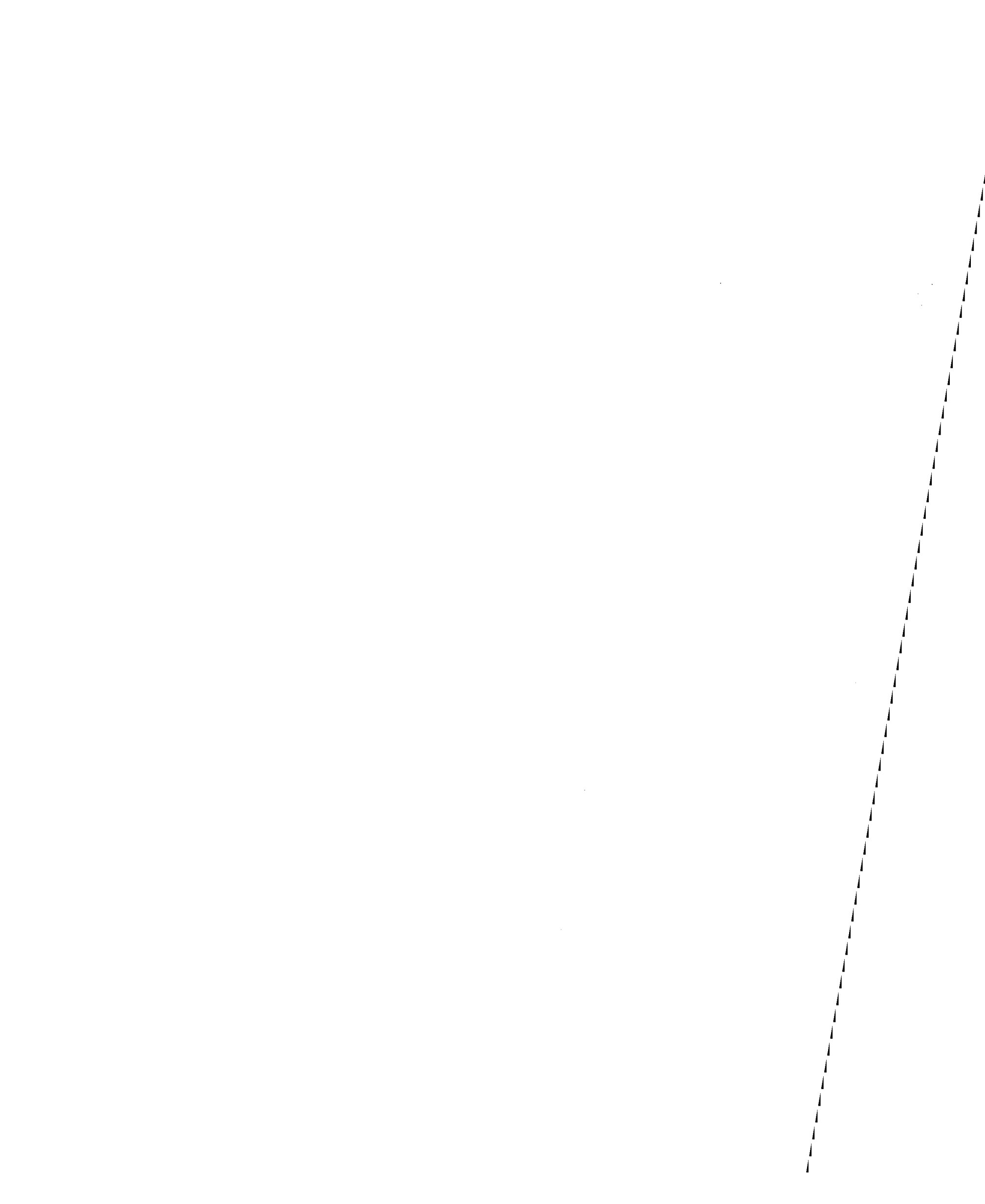
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## **APPENDIX D**

40 CFR Part 60, Subpart Kb

*Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984*



## e-CFR Data is current as of October 28, 2008

### Title 40: Protection of Environment

#### PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

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### Subpart Kb—Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984

**Source:** 52 FR 11429, Apr. 8, 1987, unless otherwise noted.

#### § 60.110b Applicability and designation of affected facility.

(a) Except as provided in paragraph (b) of this section, the affected facility to which this subpart applies is each storage vessel with a capacity greater than or equal to 75 cubic meters ( $\text{m}^3$ ) that is used to store volatile organic liquids (VOL) for which construction, reconstruction, or modification is commenced after July 23, 1984.

(b) This subpart does not apply to storage vessels with a capacity greater than or equal to 151  $\text{m}^3$  storing a liquid with a maximum true vapor pressure less than 3.5 kilopascals (kPa) or with a capacity greater than or equal to 75  $\text{m}^3$  but less than 151  $\text{m}^3$  storing a liquid with a maximum true vapor pressure less than 15.0 kPa.

(c) [Reserved]

(d) This subpart does not apply to the following:

- (1) Vessels at coke oven by-product plants.
- (2) Pressure vessels designed to operate in excess of 204.9 kPa and without emissions to the atmosphere.
- (3) Vessels permanently attached to mobile vehicles such as trucks, railcars, barges, or ships.
- (4) Vessels with a design capacity less than or equal to 1,589.874  $\text{m}^3$  used for petroleum or condensate stored, processed, or treated prior to custody transfer.
- (5) Vessels located at bulk gasoline plants.
- (6) Storage vessels located at gasoline service stations.
- (7) Vessels used to store beverage alcohol.
- (8) Vessels subject to subpart GGGG of 40 CFR part 63.

(e) *Alternative means of compliance* —(1) *Option to comply with part 65.* Owners or operators may choose to comply with 40 CFR part 65, subpart C, to satisfy the requirements of §§60.112b through 60.117b for storage vessels that are subject to this subpart that meet the specifications in paragraphs (e)(1)(i) and (ii) of this section. When choosing to comply with 40 CFR part 65, subpart C, the monitoring requirements of §60.116b(c), (e), (f)(1), and (g) still apply. Other provisions applying to owners or operators who choose to comply with 40 CFR part 65 are provided in 40 CFR 65.1.

(i) A storage vessel with a design capacity greater than or equal to 151  $\text{m}^3$  containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 5.2 kPa; or

(ii) A storage vessel with a design capacity greater than 75  $\text{m}^3$  but less than 151  $\text{m}^3$  containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 27.6 kPa.

(2) *Part 60, subpart A.* Owners or operators who choose to comply with 40 CFR part 65, subpart C, must also comply with §§60.1, 60.2, 60.5, 60.6, 60.7(a)(1) and (4), 60.14, 60.15, and 60.16 for those storage vessels. All sections and

paragraphs of subpart A of this part that are not mentioned in this paragraph (e)(2) do not apply to owners or operators of storage vessels complying with 40 CFR part 65, subpart C, except that provisions required to be met prior to implementing 40 CFR part 65 still apply. Owners and operators who choose to comply with 40 CFR part 65, subpart C, must comply with 40 CFR part 65, subpart A.

(3) *Internal floating roof report.* If an owner or operator installs an internal floating roof and, at initial startup, chooses to comply with 40 CFR part 65, subpart C, a report shall be furnished to the Administrator stating that the control equipment meets the specifications of 40 CFR 65.43. This report shall be an attachment to the notification required by 40 CFR 65.5(b).

(4) *External floating roof report.* If an owner or operator installs an external floating roof and, at initial startup, chooses to comply with 40 CFR part 65, subpart C, a report shall be furnished to the Administrator stating that the control equipment meets the specifications of 40 CFR 65.44. This report shall be an attachment to the notification required by 40 CFR 65.5(b).

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989; 65 FR 78275, Dec. 14, 2000; 68 FR 59332, Oct. 15, 2003]

## **§ 60.111b Definitions.**

Terms used in this subpart are defined in the Act, in subpart A of this part, or in this subpart as follows:

*Bulk gasoline plant* means any gasoline distribution facility that has a gasoline throughput less than or equal to 75,700 liters per day. Gasoline throughput shall be the maximum calculated design throughput as may be limited by compliance with an enforceable condition under Federal requirement or Federal, State or local law, and discoverable by the Administrator and any other person.

*Condensate* means hydrocarbon liquid separated from natural gas that condenses due to changes in the temperature or pressure, or both, and remains liquid at standard conditions.

*Custody transfer* means the transfer of produced petroleum and/or condensate, after processing and/or treatment in the producing operations, from storage vessels or automatic transfer facilities to pipelines or any other forms of transportation.

*Fill* means the introduction of VOL into a storage vessel but not necessarily to complete capacity.

*Gasoline service station* means any site where gasoline is dispensed to motor vehicle fuel tanks from stationary storage tanks.

*Maximum true vapor pressure* means the equilibrium partial pressure exerted by the volatile organic compounds (as defined in 40 CFR 51.100) in the stored VOL at the temperature equal to the highest calendar-month average of the VOL storage temperature for VOL's stored above or below the ambient temperature or at the local maximum monthly average temperature as reported by the National Weather Service for VOL's stored at the ambient temperature, as determined:

(1) In accordance with methods described in American Petroleum Institute Bulletin 2517, Evaporation Loss From External Floating Roof Tanks, (incorporated by reference—see §60.17); or

(2) As obtained from standard reference texts; or

(3) As determined by ASTM D2879–83, 96, or 97 (incorporated by reference—see §60.17);

(4) Any other method approved by the Administrator.

*Petroleum* means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

*Petroleum liquids* means petroleum, condensate, and any finished or intermediate products manufactured in a petroleum refinery.

*Process tank* means a tank that is used within a process (including a solvent or raw material recovery process) to collect material discharged from a feedstock storage vessel or equipment within the process before the material is transferred to other equipment within the process, to a product or by-product storage vessel, or to a vessel used to store recovered solvent or raw material. In many process tanks, unit operations such as reactions and blending are conducted. Other process tanks, such as surge control vessels and bottoms receivers, however, may not involve unit operations.

*Reid vapor pressure* means the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids except liquified petroleum gases, as determined by ASTM D323–82 or 94 (incorporated by reference—see §60.17).

*Storage vessel* means each tank, reservoir, or container used for the storage of volatile organic liquids but does not include:

- (1) Frames, housing, auxiliary supports, or other components that are not directly involved in the containment of liquids or vapors;
- (2) Subsurface caverns or porous rock reservoirs; or
- (3) Process tanks.

*Volatile organic liquid (VOL)* means any organic liquid which can emit volatile organic compounds (as defined in 40 CFR 51.100) into the atmosphere.

*Waste* means any liquid resulting from industrial, commercial, mining or agricultural operations, or from community activities that is discarded or is being accumulated, stored, or physically, chemically, or biologically treated prior to being discarded or recycled.

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989; 65 FR 61756, Oct. 17, 2000; 68 FR 59333, Oct. 15, 2003]

#### **§ 60.112b Standard for volatile organic compounds (VOC).**

(a) The owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m<sup>3</sup> containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 5.2 kPa but less than 76.6 kPa or with a design capacity greater than or equal to 75 m<sup>3</sup> but less than 151 m<sup>3</sup> containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 27.6 kPa but less than 76.6 kPa, shall equip each storage vessel with one of the following:

(1) A fixed roof in combination with an internal floating roof meeting the following specifications:

(i) The internal floating roof shall rest or float on the liquid surface (but not necessarily in complete contact with it) inside a storage vessel that has a fixed roof. The internal floating roof shall be floating on the liquid surface at all times, except during initial fill and during those intervals when the storage vessel is completely emptied or subsequently emptied and refilled. When the roof is resting on the leg supports, the process of filling, emptying, or refilling shall be continuous and shall be accomplished as rapidly as possible.

(ii) Each internal floating roof shall be equipped with one of the following closure devices between the wall of the storage vessel and the edge of the internal floating roof:

(A) A foam- or liquid-filled seal mounted in contact with the liquid (liquid-mounted seal). A liquid-mounted seal means a foam- or liquid-filled seal mounted in contact with the liquid between the wall of the storage vessel and the floating roof continuously around the circumference of the tank.

(B) Two seals mounted one above the other so that each forms a continuous closure that completely covers the space between the wall of the storage vessel and the edge of the internal floating roof. The lower seal may be vapor-mounted, but both must be continuous.

(C) A mechanical shoe seal. A mechanical shoe seal is a metal sheet held vertically against the wall of the storage vessel by springs or weighted levers and is connected by braces to the floating roof. A flexible coated fabric (envelope) spans the annular space between the metal sheet and the floating roof.

(iii) Each opening in a noncontact internal floating roof except for automatic bleeder vents (vacuum breaker vents) and the rim space vents is to provide a projection below the liquid surface.

(iv) Each opening in the internal floating roof except for leg sleeves, automatic bleeder vents, rim space vents, column wells, ladder wells, sample wells, and stub drains is to be equipped with a cover or lid which is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use. The cover or lid shall be equipped with a gasket. Covers on each access hatch and automatic gauge float well shall be bolted except when they are in use.

- (v) Automatic bleeder vents shall be equipped with a gasket and are to be closed at all times when the roof is floating except when the roof is being floated off or is being landed on the roof leg supports.
  - (vi) Rim space vents shall be equipped with a gasket and are to be set to open only when the internal floating roof is not floating or at the manufacturer's recommended setting.
  - (vii) Each penetration of the internal floating roof for the purpose of sampling shall be a sample well. The sample well shall have a slit fabric cover that covers at least 90 percent of the opening.
  - (viii) Each penetration of the internal floating roof that allows for passage of a column supporting the fixed roof shall have a flexible fabric sleeve seal or a gasketed sliding cover.
  - (ix) Each penetration of the internal floating roof that allows for passage of a ladder shall have a gasketed sliding cover.
- (2) An external floating roof. An external floating roof means a pontoon-type or double-deck type cover that rests on the liquid surface in a vessel with no fixed roof. Each external floating roof must meet the following specifications:
- (i) Each external floating roof shall be equipped with a closure device between the wall of the storage vessel and the roof edge. The closure device is to consist of two seals, one above the other. The lower seal is referred to as the primary seal, and the upper seal is referred to as the secondary seal.
    - (A) The primary seal shall be either a mechanical shoe seal or a liquid-mounted seal. Except as provided in §60.113b(b)(4), the seal shall completely cover the annular space between the edge of the floating roof and tank wall.
    - (B) The secondary seal shall completely cover the annular space between the external floating roof and the wall of the storage vessel in a continuous fashion except as allowed in §60.113b(b)(4).
  - (ii) Except for automatic bleeder vents and rim space vents, each opening in a noncontact external floating roof shall provide a projection below the liquid surface. Except for automatic bleeder vents, rim space vents, roof drains, and leg sleeves, each opening in the roof is to be equipped with a gasketed cover, seal, or lid that is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use. Automatic bleeder vents are to be closed at all times when the roof is floating except when the roof is being floated off or is being landed on the roof leg supports. Rim vents are to be set to open when the roof is being floated off the roof legs supports or at the manufacturer's recommended setting. Automatic bleeder vents and rim space vents are to be gasketed. Each emergency roof drain is to be provided with a slotted membrane fabric cover that covers at least 90 percent of the area of the opening.
  - (iii) The roof shall be floating on the liquid at all times (i.e., off the roof leg supports) except during initial fill until the roof is lifted off leg supports and when the tank is completely emptied and subsequently refilled. The process of filling, emptying, or refilling when the roof is resting on the leg supports shall be continuous and shall be accomplished as rapidly as possible.
- (3) A closed vent system and control device meeting the following specifications:
- (i) The closed vent system shall be designed to collect all VOC vapors and gases discharged from the storage vessel and operated with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background and visual inspections, as determined in part 60, subpart VV, §60.485(b).
  - (ii) The control device shall be designed and operated to reduce inlet VOC emissions by 95 percent or greater. If a flare is used as the control device, it shall meet the specifications described in the general control device requirements (§60.18) of the General Provisions.
- (4) A system equivalent to those described in paragraphs (a)(1), (a)(2), or (a)(3) of this section as provided in §60.114b of this subpart.
- (b) The owner or operator of each storage vessel with a design capacity greater than or equal to 75 m<sup>3</sup> which contains a VOL that, as stored, has a maximum true vapor pressure greater than or equal to 76.6 kPa shall equip each storage vessel with one of the following:
- (1) A closed vent system and control device as specified in §60.112b(a)(3).
  - (2) A system equivalent to that described in paragraph (b)(1) as provided in §60.114b of this subpart.

(c) *Site-specific standard for Merck & Co., Inc.'s Stonewall Plant in Elkton, Virginia.* This paragraph applies only to the pharmaceutical manufacturing facility, commonly referred to as the Stonewall Plant, located at Route 340 South, in Elkton, Virginia ("site").

(1) For any storage vessel that otherwise would be subject to the control technology requirements of paragraphs (a) or (b) of this section, the site shall have the option of either complying directly with the requirements of this subpart, or reducing the site-wide total criteria pollutant emissions cap (total emissions cap) in accordance with the procedures set forth in a permit issued pursuant to 40 CFR 52.2454. If the site chooses the option of reducing the total emissions cap in accordance with the procedures set forth in such permit, the requirements of such permit shall apply in lieu of the otherwise applicable requirements of this subpart for such storage vessel.

(2) For any storage vessel at the site not subject to the requirements of 40 CFR 60.112b (a) or (b), the requirements of 40 CFR 60.116b (b) and (c) and the General Provisions (subpart A of this part) shall not apply.

[52 FR 11429, Apr. 8, 1987, as amended at 62 FR 52641, Oct. 8, 1997]

### **§ 60.113b Testing and procedures.**

The owner or operator of each storage vessel as specified in §60.112b(a) shall meet the requirements of paragraph (a), (b), or (c) of this section. The applicable paragraph for a particular storage vessel depends on the control equipment installed to meet the requirements of §60.112b.

(a) After installing the control equipment required to meet §60.112b(a)(1) (permanently affixed roof and internal floating roof), each owner or operator shall:

(1) Visually inspect the internal floating roof, the primary seal, and the secondary seal (if one is in service), prior to filling the storage vessel with VOL. If there are holes, tears, or other openings in the primary seal, the secondary seal, or the seal fabric or defects in the internal floating roof, or both, the owner or operator shall repair the items before filling the storage vessel.

(2) For Vessels equipped with a liquid-mounted or mechanical shoe primary seal, visually inspect the internal floating roof and the primary seal or the secondary seal (if one is in service) through manholes and roof hatches on the fixed roof at least once every 12 months after initial fill. If the internal floating roof is not resting on the surface of the VOL inside the storage vessel, or there is liquid accumulated on the roof, or the seal is detached, or there are holes or tears in the seal fabric, the owner or operator shall repair the items or empty and remove the storage vessel from service within 45 days. If a failure that is detected during inspections required in this paragraph cannot be repaired within 45 days and if the vessel cannot be emptied within 45 days, a 30-day extension may be requested from the Administrator in the inspection report required in §60.115b(a)(3). Such a request for an extension must document that alternate storage capacity is unavailable and specify a schedule of actions the company will take that will assure that the control equipment will be repaired or the vessel will be emptied as soon as possible.

(3) For vessels equipped with a double-seal system as specified in §60.112b(a)(1)(ii)(B):

(i) Visually inspect the vessel as specified in paragraph (a)(4) of this section at least every 5 years; or

(ii) Visually inspect the vessel as specified in paragraph (a)(2) of this section.

(4) Visually inspect the internal floating roof, the primary seal, the secondary seal (if one is in service), gaskets, slotted membranes and sleeve seals (if any) each time the storage vessel is emptied and degassed. If the internal floating roof has defects, the primary seal has holes, tears, or other openings in the seal or the seal fabric, or the secondary seal has holes, tears, or other openings in the seal or the seal fabric, or the gaskets no longer close off the liquid surfaces from the atmosphere, or the slotted membrane has more than 10 percent open area, the owner or operator shall repair the items as necessary so that none of the conditions specified in this paragraph exist before refilling the storage vessel with VOL. In no event shall inspections conducted in accordance with this provision occur at intervals greater than 10 years in the case of vessels conducting the annual visual inspection as specified in paragraphs (a)(2) and (a)(3)(ii) of this section and at intervals no greater than 5 years in the case of vessels specified in paragraph (a)(3)(i) of this section.

(5) Notify the Administrator in writing at least 30 days prior to the filling or refilling of each storage vessel for which an inspection is required by paragraphs (a)(1) and (a)(4) of this section to afford the Administrator the opportunity to have an observer present. If the inspection required by paragraph (a)(4) of this section is not planned and the owner or operator could not have known about the inspection 30 days in advance or refilling the tank, the owner or operator shall notify the Administrator at least 7 days prior to the refilling of the storage vessel. Notification shall be made by telephone immediately followed by written documentation demonstrating why the inspection was unplanned. Alternatively, this notification including the written documentation may be made in writing and sent by express mail so that it is received by the Administrator at least 7 days prior to the refilling.

(b) After installing the control equipment required to meet §60.112b(a)(2) (external floating roof), the owner or operator shall:

(1) Determine the gap areas and maximum gap widths, between the primary seal and the wall of the storage vessel and between the secondary seal and the wall of the storage vessel according to the following frequency.

(i) Measurements of gaps between the tank wall and the primary seal (seal gaps) shall be performed during the hydrostatic testing of the vessel or within 60 days of the initial fill with VOL and at least once every 5 years thereafter.

(ii) Measurements of gaps between the tank wall and the secondary seal shall be performed within 60 days of the initial fill with VOL and at least once per year thereafter.

(iii) If any source ceases to store VOL for a period of 1 year or more, subsequent introduction of VOL into the vessel shall be considered an initial fill for the purposes of paragraphs (b)(1)(i) and (b)(1)(ii) of this section.

(2) Determine gap widths and areas in the primary and secondary seals individually by the following procedures:

(i) Measure seal gaps, if any, at one or more floating roof levels when the roof is floating off the roof leg supports.

(ii) Measure seal gaps around the entire circumference of the tank in each place where a 0.32-cm diameter uniform probe passes freely (without forcing or binding against seal) between the seal and the wall of the storage vessel and measure the circumferential distance of each such location.

(iii) The total surface area of each gap described in paragraph (b)(2)(ii) of this section shall be determined by using probes of various widths to measure accurately the actual distance from the tank wall to the seal and multiplying each such width by its respective circumferential distance.

(3) Add the gap surface area of each gap location for the primary seal and the secondary seal individually and divide the sum for each seal by the nominal diameter of the tank and compare each ratio to the respective standards in paragraph (b)(4) of this section.

(4) Make necessary repairs or empty the storage vessel within 45 days of identification in any inspection for seals not meeting the requirements listed in (b)(4) (i) and (ii) of this section:

(i) The accumulated area of gaps between the tank wall and the mechanical shoe or liquid-mounted primary seal shall not exceed 212 Cm<sup>2</sup> per meter of tank diameter, and the width of any portion of any gap shall not exceed 3.81 cm.

(A) One end of the mechanical shoe is to extend into the stored liquid, and the other end is to extend a minimum vertical distance of 61 cm above the stored liquid surface.

(B) There are to be no holes, tears, or other openings in the shoe, seal fabric, or seal envelope.

(ii) The secondary seal is to meet the following requirements:

(A) The secondary seal is to be installed above the primary seal so that it completely covers the space between the roof edge and the tank wall except as provided in paragraph (b)(2)(iii) of this section.

(B) The accumulated area of gaps between the tank wall and the secondary seal shall not exceed 21.2 cm<sup>2</sup> per meter of tank diameter, and the width of any portion of any gap shall not exceed 1.27 cm.

(C) There are to be no holes, tears, or other openings in the seal or seal fabric.

(iii) If a failure that is detected during inspections required in paragraph (b)(1) of §60.113b(b) cannot be repaired within 45 days and if the vessel cannot be emptied within 45 days, a 30-day extension may be requested from the Administrator in the inspection report required in §60.115b(b)(4). Such extension request must include a demonstration of unavailability of alternate storage capacity and a specification of a schedule that will assure that the control equipment will be repaired or the vessel will be emptied as soon as possible.

(5) Notify the Administrator 30 days in advance of any gap measurements required by paragraph (b)(1) of this section to afford the Administrator the opportunity to have an observer present.



(6) Visually inspect the external floating roof, the primary seal, secondary seal, and fittings each time the vessel is emptied and degassed.

(i) If the external floating roof has defects, the primary seal has holes, tears, or other openings in the seal or the seal fabric, or the secondary seal has holes, tears, or other openings in the seal or the seal fabric, the owner or operator shall repair the items as necessary so that none of the conditions specified in this paragraph exist before filling or refilling the storage vessel with VOL.

(ii) For all the inspections required by paragraph (b)(6) of this section, the owner or operator shall notify the Administrator in writing at least 30 days prior to the filling or refilling of each storage vessel to afford the Administrator the opportunity to inspect the storage vessel prior to refilling. If the inspection required by paragraph (b)(6) of this section is not planned and the owner or operator could not have known about the inspection 30 days in advance of refilling the tank, the owner or operator shall notify the Administrator at least 7 days prior to the refilling of the storage vessel. Notification shall be made by telephone immediately followed by written documentation demonstrating why the inspection was unplanned. Alternatively, this notification including the written documentation may be made in writing and sent by express mail so that it is received by the Administrator at least 7 days prior to the refilling.

(c) The owner or operator of each source that is equipped with a closed vent system and control device as required in §60.112b (a)(3) or (b)(2) (other than a flare) is exempt from §60.8 of the General Provisions and shall meet the following requirements.

(1) Submit for approval by the Administrator as an attachment to the notification required by §60.7(a)(1) or, if the facility is exempt from §60.7(a)(1), as an attachment to the notification required by §60.7(a)(2), an operating plan containing the information listed below.

(i) Documentation demonstrating that the control device will achieve the required control efficiency during maximum loading conditions. This documentation is to include a description of the gas stream which enters the control device, including flow and VOC content under varying liquid level conditions (dynamic and static) and manufacturer's design specifications for the control device. If the control device or the closed vent capture system receives vapors, gases, or liquids other than fuels from sources that are not designated sources under this subpart, the efficiency demonstration is to include consideration of all vapors, gases, and liquids received by the closed vent capture system and control device. If an enclosed combustion device with a minimum residence time of 0.75 seconds and a minimum temperature of 816 °C is used to meet the 95 percent requirement, documentation that those conditions will exist is sufficient to meet the requirements of this paragraph.

(ii) A description of the parameter or parameters to be monitored to ensure that the control device will be operated in conformance with its design and an explanation of the criteria used for selection of that parameter (or parameters).

(2) Operate the closed vent system and control device and monitor the parameters of the closed vent system and control device in accordance with the operating plan submitted to the Administrator in accordance with paragraph (c)(1) of this section, unless the plan was modified by the Administrator during the review process. In this case, the modified plan applies.

(d) The owner or operator of each source that is equipped with a closed vent system and a flare to meet the requirements in §60.112b (a)(3) or (b)(2) shall meet the requirements as specified in the general control device requirements, §60.18 (e) and (f).

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989]

#### **§ 60.114b Alternative means of emission limitation.**

(a) If, in the Administrator's judgment, an alternative means of emission limitation will achieve a reduction in emissions at least equivalent to the reduction in emissions achieved by any requirement in §60.112b, the Administrator will publish in the Federal Register a notice permitting the use of the alternative means for purposes of compliance with that requirement.

(b) Any notice under paragraph (a) of this section will be published only after notice and an opportunity for a hearing.

(c) Any person seeking permission under this section shall submit to the Administrator a written application including:

(1) An actual emissions test that uses a full-sized or scale-model storage vessel that accurately collects and measures all VOC emissions from a given control device and that accurately simulates wind and accounts for other emission variables such as temperature and barometric pressure.

(2) An engineering evaluation that the Administrator determines is an accurate method of determining equivalence.

(d) The Administrator may condition the permission on requirements that may be necessary to ensure operation and maintenance to achieve the same emissions reduction as specified in §60.112b.

### **§ 60.115b Reporting and recordkeeping requirements.**

The owner or operator of each storage vessel as specified in §60.112b(a) shall keep records and furnish reports as required by paragraphs (a), (b), or (c) of this section depending upon the control equipment installed to meet the requirements of §60.112b. The owner or operator shall keep copies of all reports and records required by this section, except for the record required by (c)(1), for at least 2 years. The record required by (c)(1) will be kept for the life of the control equipment.

(a) After installing control equipment in accordance with §60.112b(a)(1) (fixed roof and internal floating roof), the owner or operator shall meet the following requirements.

(1) Furnish the Administrator with a report that describes the control equipment and certifies that the control equipment meets the specifications of §60.112b(a)(1) and §60.113b(a)(1). This report shall be an attachment to the notification required by §60.7(a)(3).

(2) Keep a record of each inspection performed as required by §60.113b (a)(1), (a)(2), (a)(3), and (a)(4). Each record shall identify the storage vessel on which the inspection was performed and shall contain the date the vessel was inspected and the observed condition of each component of the control equipment (seals, internal floating roof, and fittings).

(3) If any of the conditions described in §60.113b(a)(2) are detected during the annual visual inspection required by §60.113b(a)(2), a report shall be furnished to the Administrator within 30 days of the inspection. Each report shall identify the storage vessel, the nature of the defects, and the date the storage vessel was emptied or the nature of and date the repair was made.

(4) After each inspection required by §60.113b(a)(3) that finds holes or tears in the seal or seal fabric, or defects in the internal floating roof, or other control equipment defects listed in §60.113b(a)(3)(ii), a report shall be furnished to the Administrator within 30 days of the inspection. The report shall identify the storage vessel and the reason it did not meet the specifications of §60.112b(a)(1) or §60.113b(a)(3) and list each repair made.

(b) After installing control equipment in accordance with §60.112b(a)(2) (external floating roof), the owner or operator shall meet the following requirements.

(1) Furnish the Administrator with a report that describes the control equipment and certifies that the control equipment meets the specifications of §60.112b(a)(2) and §60.113b(b)(2), (b)(3), and (b)(4). This report shall be an attachment to the notification required by §60.7(a)(3).

(2) Within 60 days of performing the seal gap measurements required by §60.113b(b)(1), furnish the Administrator with a report that contains:

(i) The date of measurement.

(ii) The raw data obtained in the measurement.

(iii) The calculations described in §60.113b (b)(2) and (b)(3).

(3) Keep a record of each gap measurement performed as required by §60.113b(b). Each record shall identify the storage vessel in which the measurement was performed and shall contain:

(i) The date of measurement.

(ii) The raw data obtained in the measurement.

(iii) The calculations described in §60.113b (b)(2) and (b)(3).

(4) After each seal gap measurement that detects gaps exceeding the limitations specified by §60.113b(b)(4), submit a report to the Administrator within 30 days of the inspection. The report will identify the vessel and contain the information specified in paragraph (b)(2) of this section and the date the vessel was emptied or the repairs made and date of repair.

(c) After installing control equipment in accordance with §60.112b (a)(3) or (b)(1) (closed vent system and control device other than a flare), the owner or operator shall keep the following records.

(1) A copy of the operating plan.

(2) A record of the measured values of the parameters monitored in accordance with §60.113b(c)(2).

(d) After installing a closed vent system and flare to comply with §60.112b, the owner or operator shall meet the following requirements.

(1) A report containing the measurements required by §60.18(f) (1), (2), (3), (4), (5), and (6) shall be furnished to the Administrator as required by §60.8 of the General Provisions. This report shall be submitted within 6 months of the initial start-up date.

(2) Records shall be kept of all periods of operation during which the flare pilot flame is absent.

(3) Semiannual reports of all periods recorded under §60.115b(d)(2) in which the pilot flame was absent shall be furnished to the Administrator.

### **§ 60.116b Monitoring of operations.**

(a) The owner or operator shall keep copies of all records required by this section, except for the record required by paragraph (b) of this section, for at least 2 years. The record required by paragraph (b) of this section will be kept for the life of the source.

(b) The owner or operator of each storage vessel as specified in §60.110b(a) shall keep readily accessible records showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel.

(c) Except as provided in paragraphs (f) and (g) of this section, the owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure greater than or equal to 3.5 kPa or with a design capacity greater than or equal to 75 m<sup>3</sup> but less than 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure greater than or equal to 15.0 kPa shall maintain a record of the VOL stored, the period of storage, and the maximum true vapor pressure of that VOL during the respective storage period.

(d) Except as provided in paragraph (g) of this section, the owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure that is normally less than 5.2 kPa or with a design capacity greater than or equal to 75 m<sup>3</sup> but less than 151 m<sup>3</sup> storing a liquid with a maximum true vapor pressure that is normally less than 27.6 kPa shall notify the Administrator within 30 days when the maximum true vapor pressure of the liquid exceeds the respective maximum true vapor pressure values for each volume range.

(e) Available data on the storage temperature may be used to determine the maximum true vapor pressure as determined below.

(1) For vessels operated above or below ambient temperatures, the maximum true vapor pressure is calculated based upon the highest expected calendar-month average of the storage temperature. For vessels operated at ambient temperatures, the maximum true vapor pressure is calculated based upon the maximum local monthly average ambient temperature as reported by the National Weather Service.

(2) For crude oil or refined petroleum products the vapor pressure may be obtained by the following:

(i) Available data on the Reid vapor pressure and the maximum expected storage temperature based on the highest expected calendar-month average temperature of the stored product may be used to determine the maximum true vapor pressure from nomographs contained in API Bulletin 2517 (incorporated by reference—see §60.17), unless the Administrator specifically requests that the liquid be sampled, the actual storage temperature determined, and the Reid vapor pressure determined from the sample(s).

(ii) The true vapor pressure of each type of crude oil with a Reid vapor pressure less than 13.8 kPa or with physical properties that preclude determination by the recommended method is to be determined from available data and recorded if the estimated maximum true vapor pressure is greater than 3.5 kPa.

(3) For other liquids, the vapor pressure:

- (i) May be obtained from standard reference texts, or
  - (ii) Determined by ASTM D2879–83, 96, or 97 (incorporated by reference—see §60.17); or
  - (iii) Measured by an appropriate method approved by the Administrator; or
  - (iv) Calculated by an appropriate method approved by the Administrator.
- (f) The owner or operator of each vessel storing a waste mixture of indeterminate or variable composition shall be subject to the following requirements.
- (1) Prior to the initial filling of the vessel, the highest maximum true vapor pressure for the range of anticipated liquid compositions to be stored will be determined using the methods described in paragraph (e) of this section.
- (2) For vessels in which the vapor pressure of the anticipated liquid composition is above the cutoff for monitoring but below the cutoff for controls as defined in §60.112b(a), an initial physical test of the vapor pressure is required; and a physical test at least once every 6 months thereafter is required as determined by the following methods:
- (i) ASTM D2879–83, 96, or 97 (incorporated by reference—see §60.17); or
  - (ii) ASTM D323–82 or 94 (incorporated by reference—see §60.17); or
  - (iii) As measured by an appropriate method as approved by the Administrator.
- (g) The owner or operator of each vessel equipped with a closed vent system and control device meeting the specification of §60.112b or with emissions reductions equipment as specified in 40 CFR 65.42(b)(4), (b)(5), (b)(6), or (c) is exempt from the requirements of paragraphs (c) and (d) of this section.

[52 FR 11429, Apr. 8, 1987, as amended at 65 FR 61756, Oct. 17, 2000; 65 FR 78276, Dec. 14, 2000; 68 FR 59333, Oct. 15, 2003]

#### **§ 60.117b Delegation of authority.**

- (a) In delegating implementation and enforcement authority to a State under section 111(c) of the Act, the authorities contained in paragraph (b) of this section shall be retained by the Administrator and not transferred to a State.
- (b) Authorities which will not be delegated to States: §§60.111b(f)(4), 60.114b, 60.116b(e)(3)(iii), 60.116b(e)(3)(iv), and 60.116b(f)(2)(iii).

[52 FR 11429, Apr. 8, 1987, as amended at 52 FR 22780, June 16, 1987]

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## **APPENDIX E**

### **Example of Loading Rack Emission Calculation**



**Appendix E**  
**Example of Loading Rack Emission Calculations Format for Loading Racks**

**VOC Emission Calculation:**

Equation  $LL = 12.46 * S * P * M / T$

where

LL = loading loss, pounds per 1000 gallons of liquid loaded  
S = saturation factor from AP-42 Table 5.2-1  
P = true vapor pressure of liquid loaded, psia  
M = molecular weight of vapors, pounds per pound-mole (see AP-42 Table 7.1-2)  
T = temperature of bulk liquid loaded, R (F + 460)

**SN-14 Diesel, Naptha, Kerosene Loading Rack**

Product	S	P	M	T	LL
Diesel	0.5	0.0074	130	520	0.012
Naptha	0.5	1.3	80	520	1.246
Kerosene	0.5	0.0085	130	520	0.013

**VOC Emissions**

Product	Hourly Production Rate (gallons)	Yearly Throughput (gallons)	VOC Emission Rate (lb/hr)	VOC Emission Rate (tpy)
Diesel	0	21,949,306	0.000	0.126
Naptha	0	3,010,224	0.000	1.875
Kerosene	0	300,048	0.000	0.002
		Maximum	0.000	2.004

**HAP Emissions**

Pollutant	Diesel			Kerosene			Naphtha			Total	
	HAP Wt%	lb/hr	tpy	HAP Wt%	lb/hr	tpy	HAP Wt%	lb/hr	tpy	lb/hr	ton/yr
2,2,4-Trimethylpentane	0.284	0.000	0.006	0.327	0.000	0.007	0.355	0.000	0.007	0.000	0.019
Benzene	12.383	0.000	0.248	2.149	0.000	0.043	1.063	0.000	0.021	0.000	0.312
Cumene	0.375	0.000	0.008	0.194	0.000	0.004	0.037	0.000	0.001	0.000	0.012
Ethylbenzene	0.876	0.000	0.018	0.892	0.000	0.018	0.118	0.000	0.002	0.000	0.038
Hexane	24.761	0.000	0.496	22.823	0.000	0.457	10.266	0.000	0.206	0.000	1.159
Naphthalene	0.089	0.000	0.002	0.080	0.000	0.002	0.001	0.000	0.000	0.000	0.003
Phenol	0.013	0.000	0.000	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Styrene	0.079	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Toluene	4.357	0.000	0.087	6.003	0.000	0.120	1.295	0.000	0.026	0.000	0.234
Xylene	2.453	0.000	0.049	2.910	0.000	0.058	0.395	0.000	0.008	0.000	0.115
Total HAP										0.00	1.90

**SN-15/SN-16/SN-32 Asphalt Loading**

Product	S	P	M	T	LL
Asphalt	1.45	0.002	165	960	0.006

**VOC Emissions**

Product	Hourly Production Rate (gallons)	Yearly Throughput (gallons)	Emission Rate (lb/hr)	Emission Rate (tpy)
Asphalt	0	14,930,110	0.000	0.046

**SN-17/SN-18/SN-21 Lube Oil Loading**

Product	S	P	M	T	LL
Lube Oil	1.45	0.0003	150	520	0.002

**VOC Emissions**

Product	Hourly Production Rate (gallons)	Yearly Throughput (gallons)	Emission Rate (lb/hr)	Emission Rate (tpy)
Lube Oil	0	62,595,370	0.000	0.049

**HAP Emissions:**

Pollutant	HAP Wt %	HAP Emissions (lb/hr)	HAP Emissions (tpy)
Benzene	22.755	0.00	0.01
Hexane	28.608	0.00	0.01
Toluene	7.031	0.00	0.00
Total HAP		0.00	0.03





**CERTIFICATE OF SERVICE**

I, Pam Owen, hereby certify that a copy of this permit has been mailed by first class mail to  
Cross Oil Refining & Marketing, Inc., 484 East 6th Street, Smackover, AR, 71762, on this  
27<sup>th</sup> day of march 2009.

Pam Owen  
Pam Owen, AAIL, Air Division

