Attachment B

Selenium QAPP

Lion Oil Company

Quality Assurance Project Plan for Use Attainability Analysis of Loutre Creek

FINAL DRAFT

March 25, 2009

Quality Assurance Project Plan for Use Attainability Analysis of Loutre Creek

Prepared for:

Lion Oil Company
1000 McHenry Ave
El Dorado, AR 71730

Prepared by:

GBM^{c} & Associates
219 Brown Lane
Bryant, AR 72022

FINAL DRAFT
March 25, 2009

I. PROJECT MANAGEMENT (GROUP A)

A1 Title and Approval Sheet

Title: Use Attainability Analysis of Loutre Creek

Completed By: GBMc & Associates for Lion Oil, El Dorado, Arkansas

QAPP Approved by:

Russell Nelson Water Quality Coordinator EPA Region VI	_____ Signature _____ Date
Sarah Clem Branch manager, Water Division ADEQ	_____ Signature _____ Date
Chuck Hammock Coordinator Lion Oil	_____ Signature _____ Date
Roland McDaniel Project manager GBMc and Associates	_____ Signature _____ Date
Greg Phillips. Quality Assurance Officer GBMc and Associates	_____ Signature _____ Date

Effective Date:_____

A2 Table of Contents

FIGURES

TABLES

A3 Distribution List

The following list of individuals and their respective organizations will receive a finalized, signed, USEPA Region VI approved QAPP, and copies of subsequent revisions GBMc & Associates:

Individual	Associated Agency
Russell Nelson	U. S. Environmental Protection Agency
Sarah Clem	ADEQ
Mitch Colvin	Lion Oil Company
Roland McDaniel	GBM^c and Associates
Greg Phillips	GBM^c and Associates
Kyle Hathcote	GBM^c and Associates
Dennis McIntyre	Great Lakes Environmental Center
Bill Perry	Ana-Lab Corporation

A4 Project/Task Organization

Russell Nelson USEPA Region VI USEPA Project Officer	Responsible for QAPP review & approval, and final report approval.
Sarah Clem Water Division ADEQ	Responsible for QAPP review & approval, and final report approval.
Mitch Colvin Lion Oil Project Coordinator	Responsible for project coordination
Roland McDaniel GBMc and Associates Project Manager	Responsible for project management
Greg Phillips GBMc and Associates Quality Assurance Officer	Responsible for adherence to QAPP
Kyle Hathcote GBMc and Associates Field Study Coordinator	Responsible for field studies and data collected from field studies
Dennis McIntyre Great Lakes Environmental Center Research Scientist	Responsible for selenium uptake and sub-lethal effects testing
Bill Perry Ana-Lab Corporation Lab Manager	Responsible for analytical lab analysis

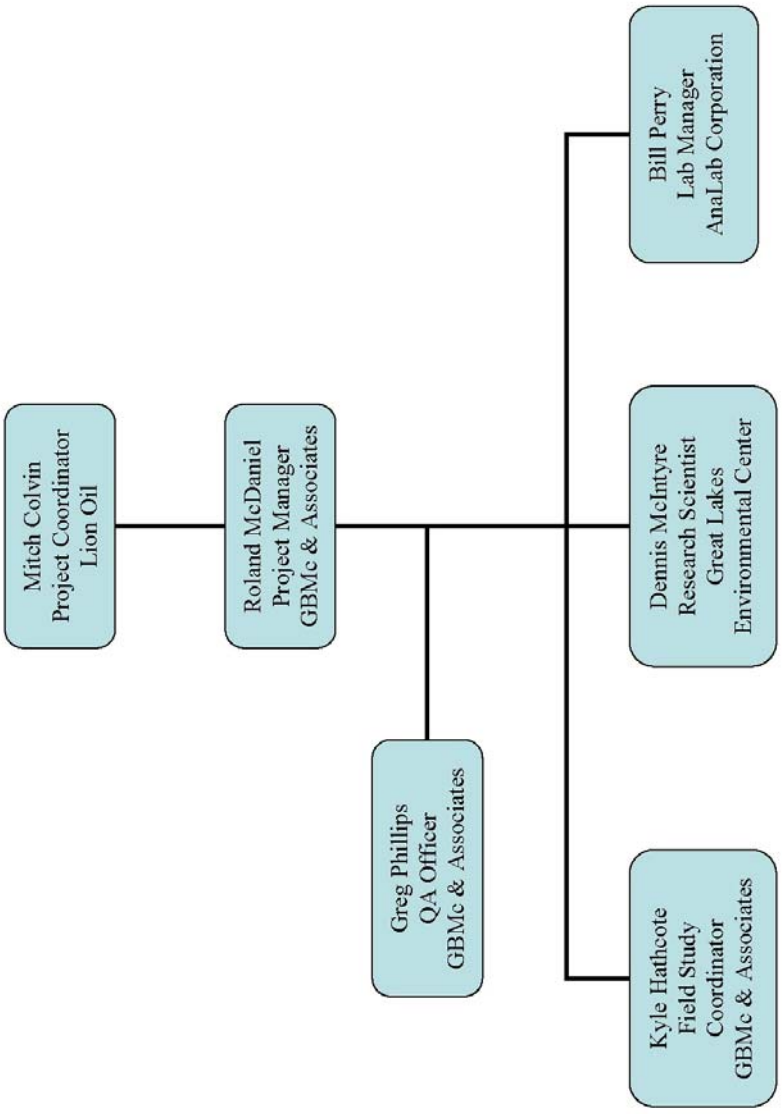

Figure 1. Organizational chart.

A5 Problem Definition/Background

Study Objective - The objective of the study is to complete a Use Attainability Analysis (UAA) of Loutre Creek to determine if the system is fully supporting its fisheries use, and if not, to develop a sub-category of the fisheries use that characterizes the existing use and is consistent with the long term historical land uses of the watershed. The sub-category fisheries use designation will then allow a site specific water quality criterion to be developed for selenium through the 3rd party rule making process reflection of the long term historical selenium concentrations of the receiving stream.

Background – Loutre Creek is a small sub-watershed (less the 4 mi^2) to Bayou de Loutre (less than 5 mi^2 at the mouth of Loutre Creek) in Union county Arkansas that drains the southern portion of the City of El Dorado (Figure 2.) The Loutre Creek watershed is largely represented by oil field and industrial land-uses that have existed for over 80 years. Lion Oil Company operates a refinery in the watershed and discharges treated wastewater to Loutre Creek through NPDES Outfall 001 (NPDES No. AR000647). Lion Oil is the only permitted discharger in the Loutre Creek Watershed.

During the most recent NPDES permit renewal, final permit limits for total selenium at Outfall 001 was established as 5.8 micrograms per liter (µg/L) monthly average and 11.65µg/L daily maximum. The sampling during the interim period of the new permit indicated the discharge from Outfall 001 would on occasion exceed the monthly maximum concentration (Appendix A). This condition, in addition to other permit issues (e.g. final zinc limitations, dissolved minerals rulemaking and storm water segregation project) led to the development of the consent administrative order (CAO LIS No. 08-104). In accordance with Item 3 of the CAO, Lion Oil developed a Compliance Action Plan that outlined a plan of action to remedy the selenium compliance issue. One of the major components of the CAP was to complete a UAA and develop site specific criteria (SSC) for selenium in Loutre Creek and potentially in Bayou De Loutre.

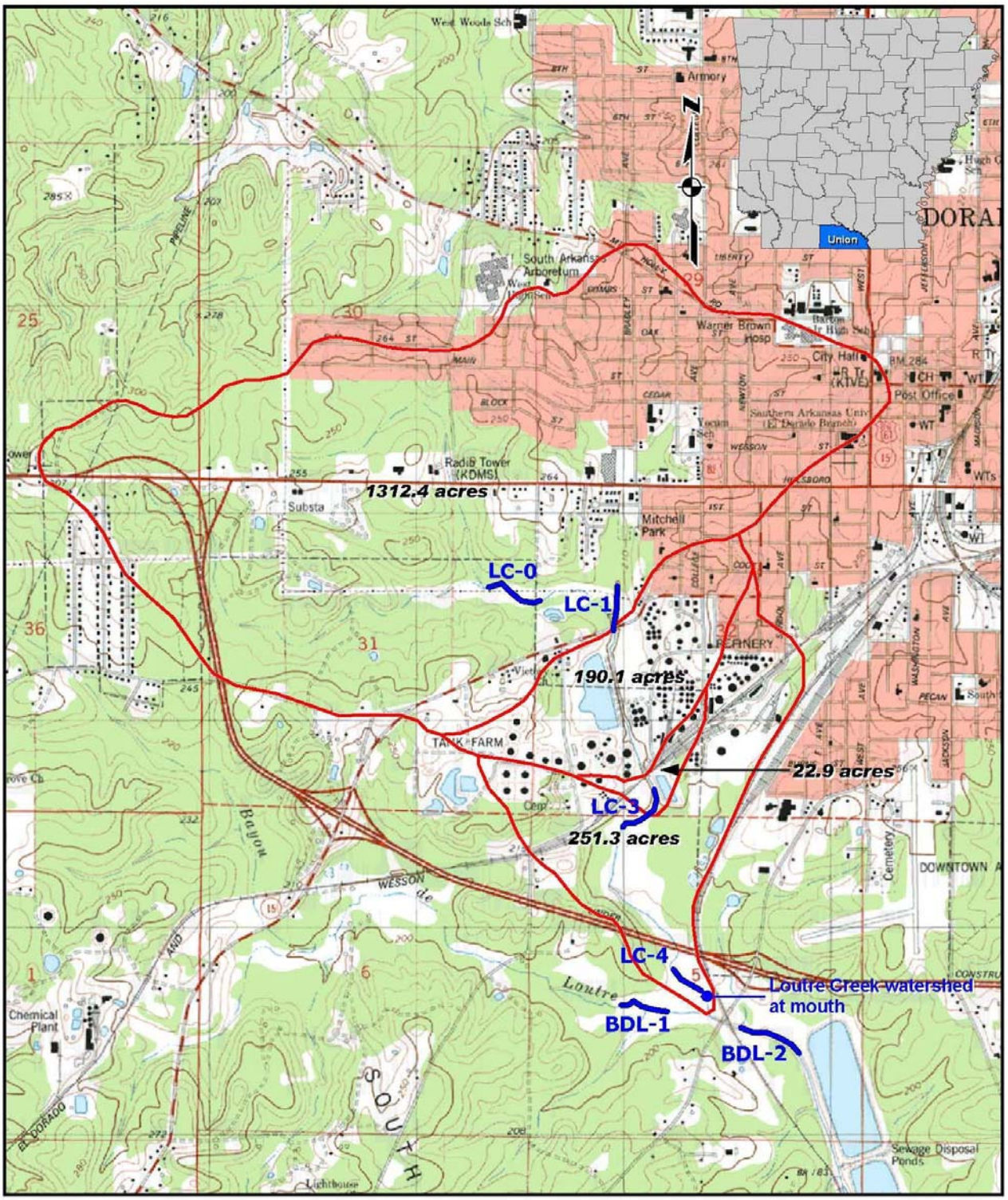

Figure 2. Sample Stations/Reaches for the UAA.

A6 Project/Task Description

The following tasks support the UAA and associated SSC development.

Task 1 - Biological Assessment

An biological assessment (bioassessment) will be completed to document the existing conditions of the streams aquatic communities and physical habitat. Fish and macroinvertebrate collections will be completed once during the spring season and once during the summer season to assess the health of the biota and maintenance of biological integrity. Detailed habitat assessment will be completed to document the available habitat, the existing condition of the channel and the condition of the riparian corridor. Fish will be collected using electro fishing techniques supplemented with seine hauls where appropriate. Macroinvertebrates will be collected with kick nets using multi-habitat protocols. All specimens will be identified to the lowest taxonomic level practicable. Collections will be analyzed with several biometrics to determine community status. Data generated during this Project will be compared to available historical data to evaluate long-term trends in biological communities.

Task 2 - Toxicity Assessment

An evaluation of selenium toxicity will be completed to determine the effect of selenium on resident biota from Loutre Creek. The assessment will focus on reproductive and embryological effects to fishes in the Centrachidae (sunfish) family. Selenium levels from the water column, sediment and within primary producer and primary consumer trophic levels will be measured to develop a relationship between water column levels and those affecting the test sunfish species.

Additionally, the historical Whole Effluent Toxicity (WET) test results completed as a requirement of the NPDES permit will be reviewed and summarized to document that the effluent from Outfall 001 has consistently PASSED biomonitoring at high critical dilution requirements and the potential effects of selenium in those test results.

Task 3 - Chemical and In-Situ Analysis

Various chemical parameters will be monitored during the study. During each of the two bioassessments and on four additional sample trips in-situ parameters will be analyzed and samples collected for laboratory analysis. In-situ parameters shall consist of pH, temperature, dissolved oxygen, specific conductance and turbidity. Samples delivered to the laboratory will be analyzed for total selenium, dissolved selenium, total hardness, total suspended solids, total dissolved solids and volatile suspended solids.

Task 4 - Fate and Transport Modeling

A water quality model will be utilized to support the field data and further assess the fate of selenium in the aquatic environment. The focus of the modeling will be to determine the transport and deposition of selenium in the aquatic environment and to assess where in the trophic structure the selenium is being taken up, how much bioaccumulation can be projected over time and at what concentrations impacts would be projected to occur to the resident biota. Should the analytical and toxicity results from the study indicate no impact from selenium to the biota then the modeling effort will be adjusted to focus on uptake and effect. However, if the results indicate an impact to biota then the effort will be focused on transport and threshold dynamics.

Task 5 - Use Determination

Maintenance of the fisheries use will be evaluated. Feasibility of designating Loutre Creek with a fisheries sub-category consistent with the historical land uses will be explored. If feasible, a new use sub-category will be assigned to Loutre Creek and characterized using resident data.

Task 6 - Alternatives Analysis

Alternatives solutions to the selenium SSC will be investigated. Alternatives explored will include wastewater treatment, manufacturing changes and housekeeping improvements. Each alternative will be evaluated to determine if it would reduce selenium levels in the discharge sufficiently and if the alternative is economically feasible.

Task 7 - SSC Development

Upon assignment of the fisheries use sub-category to Loutre Creek a site SSC for selenium will be developed for Loutre Creek. The SSC will be based on historical selenium data from the stream and from Lion Oil Outfall 001.

Task 8 – Project Schedule

A project schedule was developed for and adopted from the COA Lis No.08-10. However, due to the protracted period required to finalize the CAO; the complex nature of UAA documentation; field conditions; unforeseen natural occurrences, and extended regulatory reviews, the ultimate project completion date may be modified. Any additional modifications to the project schedule will be communicated as early in the process or practicable.

Schedule:

Task No.	Task Description	Start Date	Completion Date
1	Biological Assessment	February 1, 2009	October 30, 2009
2	Toxicity Assessment	April 1, 2009	November 30, 2009
3	Chemical and in-Situ Analysis	February 1, 2009	November 30, 2009
4	Fate and Transport Modeling	May 1, 2009	November 30, 2009
5	Use Determination	July 1, 2009	November 30, 2009
6	Alternative Analysis	January 1, 2009	August 30, 2009
7	SSC Development	November 30, 2009	May 2010
8	Deliverable - Draft Report	---	June 2010
9	Deliverable - Final Report	---	July 2010

A7 Data Quality Objectives for Measurement Data

Task 1 – Biological Assessment

Field teams collecting biota are led by experienced aquatic biologists and ecologists. Field forms designed specifically for collection studies and set up to include all pertinent field data are completed for each sample site. All field forms are reviewed at the end of the study for completeness and accuracy. Identification of fish and macroinvertebrates is verified in the laboratory by an experienced invertebrate biologist. Periodic spot checks to verify laboratory identifications are made by a qualified biologist on the team. Collection techniques are largely based on EPA bioassessment methodologies (Barbour, 1999) and are considered comparable to results attained by other regional agencies, including the ADEQ.

Representativeness and precision are measured for macroinvertebrate assessment through collection of duplicate samples. Duplicate samples are collected at one of ten study sites. One duplicate sample will be collected during each season (spring and summer). A similarity index is calculated for the duplicate and base samples. Index results indicating similarity less than 65% are suspect and require investigation.

Fish sampling equipment is routinely inspected to maintain and ensure proper working order prior to a sampling trip. Electro shocking equipment is adjusted in the field to ensure the most productive collection at each station. All available habitats are shocked to ensure a representative sample is collected. Consistent level of effort (pedal down time) is exerted at all stations to ensure results are comparable.

Task 2 – Toxicity Assessment

Routine WET testing has been completed following the EPA specific guidance for WET testing (EPA-821-R-02-012 and EPA-821-R-02-013). Use of Quality Assurance consistent with those guidelines and sufficient to meet DMR reporting requirements provides an adequate level of data quality for this study and ensures data comparability. Toxicity testing repeatability and precision is monitored through routine reference toxicity testing. Reference toxicant endpoints should fall within the laboratory defined control limits to ensure the test results are precise and repeatable. The completeness criteria for

the toxicity portion of the project is that 90% of the historical, testing results in data meeting the data quality objectives.

Selenium reproductive and embryological effects testing will be completed consistent with general EPA toxicity testing guidelines to ensure data is accurate and repeatable. That is, test subjects (eggs and embryo-larval fish) will be tested in replicate, include controls, utilize a reference condition, and test conditions will be monitored and controlled according to specific guidelines. Toxicity endpoints (measures of toxic effects) will be defined (see Section B4) specifically in this QAPP and strictly adhered to, to ensure repeatability and limit bias.

Task 3 – Chemical and In-Situ Analysis

Sample collection techniques are based on those recommended by EPA for specific media types in various guidance documents. Use of accepted methodology ensures that the results are comparable. The completeness criteria for this project are that 90% of the samples from each media provide usable results. That is, through the collection, handling and analysis process there is an allowance that 10% of the samples (maximum) could be lost, contaminated or rendered unusable due to field technician or laboratory error.

Representativeness of samples collected is assured by collecting a field duplicate sample at a rate of 10% of samples collected, one per day of sampling, minimum. Duplicates within +/- 20% of each other, are considered to prove the representativeness of collection techniques.

The bias of sample handling will be assessed using field blanks for selenium. The data quality objectives for sample handling are as follows:

QC test	Frequency	Results	Objective
Field blanks	Once per sample event	Accuracy bias	< 120% MDL

An overview of data quality objectives for the laboratory are provided in the table below. EPA approved methods will be utilized and the laboratory will be certified in the State of Arkansas and/or hold a NELAC/NELAR accreditation. Specific laboratory quality assurance and quality control requirements are provided in detail in Section B5.

Sample Analysis

Parameter	Source/Method	Units	MDL	Duplicate RPD
Total Selenium	EPA200.8	ug/l	1.0	±20%*
Dissolved Selenium	EPA200.8	ug/l	1.0	±20%*
Fish Tissue Selenium	EPA6020	mg/kg	0.1	±20%*
Total Alkalinity	SM2320B	mg/l	2.0	±20%
TDS	SM2540C	mg/l	1.0	±20%
TSS	SM2540D	mg/l	1.0	±20%
VSS	EPA160.4 / SM2540E	mg/l	1.0	±20%
Total Solids (Fish Tissue)	Sm2540G	%	0.1	±20%
Chlorophyll a	SM10200H	ug/l	2.0	±15%

*In the case of selenium the duplicates are matrix spike duplicates

A8 Special Training Requirements/Certification

All personnel participating in studies have been trained by experienced scientists/engineers to complete the necessary tasks or are in the process of being trained with appropriate oversight. Personnel participating in scientific studies shall be familiar with the SOPs appropriate to that particular study and the QAP. Personnel participating in scientific studies conducted pursuant to specific procedures specified by a regulatory authority (e.g., a state or federal environmental agency) shall be familiar with those specific procedures.

GBMc & Associates will oversee all sample collections, including collection of aquatic biota. All field technicians will be trained for proper sample handling, preventative maintenance, calibration and sample custody procedures. GBMc & Associates is responsible for assuring that all field technicians are properly trained.

Great Lakes Environmental Center is responsible for toxicity testing and related laboratory testing. All technicians are trained in the appropriate techniques and familiar with the appropriate GLEC SOP's. An SOP specific to the reproduction and embryo-laurel terratogenicity test will be developed prior to initiation of the spring bioassessment. This SOP will be site specific to the species of sunfish identified during early spring reconnaissance.

AnaLab is responsible for chemical analysis of water, sediment and tissue samples. All technicians are trained in the appropriate techniques and familiar with Analab SOP's.

A9 Documentation and Records

A bound field logbook will be maintained documenting field activities during the study. Log book entries shall include, dates of field activities, type of activities completed, list of samples collected, and general observations pertinent to the study. Field data, including sample collection and collection of aquatic biota will be recorded in a field log book or on a field data sheet designed specifically for the field activity. Entries will include: date and time of sample collection, name of person collecting samples, problems encountered, and date and time of sample delivery. Logbooks and field data sheets will be kept at the GBMc & Associates office except when in the field. Copies will be made of all entries once per quarter.

All data collected during scientific studies should be checked by the team leader for completeness and accuracy. Field data forms should be complete and initialed by the completing scientist and the reviewing scientist.

Data entry to spreadsheets and databases along with spreadsheet calculations shall be checked for accuracy at a rate of 10% (minimum) of the entries and calculation cells. Copies of the checked data and spreadsheets should be initialed by the reviewer and retained in the records.

All calculations should be detailed in the body of written reports, or shown on GBMc & Associates Calculation Pages. Good notes regarding calculations should be kept and filed in the project notebook.

All scientific reports shall be peer reviewed and/or reviewed by the Project Manager prior to approval by a GBMc & Associates Principal.

Quality Assurance Assessment Reports will be prepared and submitted electronically to the Project Manager at the mid point of the study and upon study completion. These reports will document all QA problems and corrective actions, if any.

All laboratory data (from both toxicity testing and analytical analyses) shall be reported quarterly, at a minimum, to GBMc & Associates in both hard copy and electronic format. Data will be stored at GBMc & Associates for a minimum of 3 years.

The QAPP will be updated as necessary following an adaptive management protocol. The Project Manager is responsible for providing updates to all of the parties listed in element A3.

II. DATA GENERATION AND ACQUISITION (GROUP B)

B1 Sampling Process Design

The objective of the study is to complete a UAA of Loutre Creek and to develop a SSC for Selenium based on the determined designated use and the historical water quality. Figure 1 provides the locations of the sampling sites that will be utilized during the study and Table B1.1 describes the stations. Field assessments and all sample collection will be completed by GBMc & Associates field teams.

Table B1.1. Description of and Rationale for Project Sample Stations.

Station I.D.	Station Description
LC-0	Secondary background station on Loutre Creek, upstream of Outfall 001 and direct storm water influences from developed urban watershed.
LC-1	Background station on Loutre Creek, upstream of Outfall 001 and direct storm water influences from Lion Oil.
LC-3	Loutre Creek downstream of Outfall 001 in area of greatest effluent concentrations.
LC-4	Loutre Creek downstream of Outfall 001 and immediately upstream of confluence with Bayou De Loutre.
BDL-1	Background station on Bayou De Loutre, upstream of confluence with Loutre Creek but in potential land-use area affected by historical oil field uses.
BDL-2	Bayou De Loutre downstream of confluence with Loutre Creek.

Task 1 – Biological Assessment

A biological assessment (bioassessment) will be completed by GBMc & Associates at each of the four sample stations to document the existing conditions of the streams aquatic communities and physical habitat. Fish and macroinvertebrate collections will be completed once during the spring season and once during the summer season to assess the health of the aquatic community, maintenance of biological integrity and maintenance of fishery uses. Detailed habitat assessment will be completed during each assessment to document the available habitat, the existing condition of the channel and the condition of the riparian corridor. Habitat data will be used to help discern if the aquatic community

is being impacted by habitat alone or also by water quality or combination thereof. Fish will be collected using electro fishing techniques supplemented with seine hauls where appropriate. Macroinvertebrates will be collected with kick nets using multi-habitat protocols. All specimens will be identified to the lowest taxonomic level practicable. Collections will be analyzed with several biometrics to determine community status. Results of the assessment will be used to determine if Loutre Creek is maintaining an perennial or seasonal fishery and if the biological integrity is impacted in such a way from historical land uses that these uses are unattainable an warrant development of a sub-category use. A summary of the experimental design is included in Table B1.2.

Task 2 – Toxicity Assessment

An evaluation of selenium toxicity will be completed to determine the effect of selenium on resident biota from Loutre Creek. The assessment will focus on reproductive and embryological effects to fishes in the Centrachidae (sunfish) family. During the spring/summer sampling season fertile females will be stripped and the eggs field fertilized. Eggs will be sent to Great Lakes Environmental Centers laboratory for hatching and development to a 96-hour stage. Eggs will be evaluated for fecundity and embryo-larval stage fish will be evaluated for deformity to ascertain the potential impact of selenium. Section B4 provides details of the testing protocol and the deformity assessment. Selenium levels from the water column, eggs, fish tissue, sediment and within primary producer (periphyton, phytoplankton, etc.) and primary consumer (macroinvertebrates, fish, etc.) trophic levels will be measured at this time to develop a relationship between water column levels and those affecting the test sunfish species. That is, this relationship will be used to link total selenium levels in the water to levels that cause impacts to fish reproduction in Loutre Creek. Samples from each media will be collected at each sample station during the spring biological assessment event. Samples of fish tissue, sediment and within primary producer and primary consumer trophic levels will also be collected during the summer event. Sample size for fish tissue analysis will be a minimum of four fish per station. A summary of the experimental design is included in Table B1.2.

Task 3 – Chemical and In-Situ Analysis

Various chemical parameters will be monitored during the study. During each of two bioassessments and on four additional sample trips in-situ parameters will be analyzed and samples collected for laboratory analysis from each sample station and from Outfall 001. In-situ parameters shall consist of pH, temperature, dissolved oxygen, specific conductance and turbidity. Water samples delivered to the laboratory will be analyzed for total selenium, dissolved selenium, total alkalinity, total suspended solids, total dissolved solids and volatile suspended solids. Samples from other media, if collected, will be analyzed for total selenium. Additional parameters may be added as necessary. In-Situ parameters will be measured by GBMc & Associates. Samples from other media will be analyzed by AnaLab. Data from the chemical analysis will be utilized to set-up and calibrate the fate and transport model. A summary of the experimental design is included in Table B1.2.

Task 4 – Fate and Transport Modeling

A water quality model will be utilized to support the field data and further assess the fate of selenium in the aquatic environment. The focus of the modeling will be to determine the transport and deposition of selenium in the aquatic environment and to assess where in the trophic structure the selenium is being deposited and/or taken up, and how much bioaccumulation might be anticipated over time. Data for model initial conditions and calibration will originate from the field data collected during this study. That is, upstream measured water quality will serve as the background condition (or boundary condition) in the modeling. The water quality inputs from Outfall 001 will serve as inputs to the system and the downstream water quality will serve as targets for the calibration via coefficients adjustments. In the case of the food chain model (trophic structure), data from each tier in the food chain (producers, consumers, etc.) at each station, will serve as inputs and a calibration guide for the modeling. Constants, coefficients and rates may be determined from the field data collected, originate from the body of literature or be set by the calibration process (but staying within the range of literature values).

Table B1.2. Summary of Sample Design

Parameter	Bioassessment	Chemical and In-Situ (Water)	Toxicity (Eggs)	Toxicity (Fish tissue, sediment, etc.)
Station I.D.	Parameters Being Analyzed			
LC-1	Fish, Macroinvertebrates, Habitat	pH, temperature, dissolved oxygen, specific conductance, turbidity, total selenium, dissolved selenium, total alkalinity, total suspended solids, total dissolved solids, volatile suspended solids	Total Selenium, fecundity, deformity	Total Selenium Total Solids
LC-3	Same as above	Same as above	Same as above	Same as above
LC-4	Same as above	Same as above	Same as above	Same as above
BDL-1	Same as above	Same as above	Same as above	Same as above
BDL-2	Same as above	Same as above	Same as above	Same as above
Outfall 001	n/a	Same as above	n/a	n/a
Number Sample Events/Station	2	6	1	2
Samples/Station	1	1	1	2/4*

*Fish tissue sample includes analysis from four fish minimum.

B2 Sampling Methods Requirements

The following section provides details of the sampling methodology and procedures that will be utilized during the Loutre Creek UAA. Table B2.1 provides a summary of sampling methodologies to be used during the study. GBMc & Associates maintains a Quality Assurance Plan (QAP) for field data collection and data handling (GBMc & Associates, 2008). Standard operating procedures (SOP's) from the QAP referenced in this section are provided in Appendix B.

Trained scientists will conduct the field sampling and other associated activities at each sample location. Notes will be kept in field notebooks and/or specific field data forms that record information collected during the study, unusual observations, and a log of each day's activities. All data forms, calibration logs, field notes, and other study documentation will be reviewed by the Project Manager or Senior Scientist for completeness and accuracy. Concerns over field data collection success or required deviations to SOP will be reported to the project Quality Assurance Officer for review. Any deviations to the methodologies described in this QAPP will be recorded and presented, in detail (including an assessment of potential effect on data), in the final project report.

Task 1 – Biological Assessment

Bioassessments will be completed at each sample station to document the existing conditions of the streams aquatic communities and physical habitat. Fish and macroinvertebrate collections will be completed once during the spring season and once during the summer season and detailed habitat assessment will be completed during each bioassessment. Habitat assessment protocols will follow the SOP for Semi-Quantitative Habitat Assessment as described in the GBMc & Associates Quality Assurance Plan (QAP). The habitat assessment will cover an area of stream (the reach) equal to a distance of at least 20X the average bankfull width. A two man field team will complete the assessment. Data collected during the habitat assessment includes qualitative (dominant substrate, bank stability, canopy density, etc) and quantitative (thalwag depth, bankful depth and width, velocity, flow, etc) measures. Flow

measurements will be made at each station as part of the habitat assessment. Flow will be measured using a velocity meter and wading rod and following GBMc SOP. Flow will be calculated according to the velocity area method. Habitat data will be used to help discern if the aquatic community is being impacted by habitat alone or also by water quality.

Fish will be collected within the defined habitat reach using electro fishing techniques supplemented with seine hauls where appropriate. Fish collection procedures will follow the GBMc SOP as found in their QAP (GBMc & Associates, 2008). Collected fish will be placed in a 5-gallon style bucket prior to analysis. After cursory field identification and enumeration large healthy specimens are returned to the stream and recorded as "released" in the log book and on the field record sheet. The remainder of the collection is preserved in formalin for transport to GBMc & Associates. Fish will be positively identified by trained taxonomists at GBMc & Associates. Each assemblage collected will be evaluated with several biometrics to determine health of the community and maintenance of biological integrity. Comparisons will be made between stations to determine the maintenance of the fishery use downstream of Outfall001.

Macroinvertebtrate collections will be completed within the defined habitat reach using a kick net in multiple habitats (multi-habitat consisting of rootwads, emergent vegetation, undercut banks, deposition, etc.) found in the pool dominated stream system. The method utilized is generally based on the Rapid Bioassessment (RBA) Protocols of the USEPA (Barbour, 1999) where a dip net is utilized to sample a defined area of aquatic habitat (typically $3m^2$) or for a defined time period (typically 3 minutes) in each sample reach. Material from each bucket is condensed and field sorted or, preserved and transported to the lab for sorting and enumeration. A grid and sorting tray (Caton style) is used to randomly select sub-samples of the collected material for picking (organism removal). Each randomly selected grid was picked until all organisms were removed. Following protocol, when the number of picked organisms exceeds 90 (100 ± 10%) the sub-sample is considered complete. If the number of organisms is less than 90, another grid is randomly selected and all organisms are removed. This process continues until the number of organisms exceeds 90. All organisms are preserved in 70% ethanol and identified to the lowest practicable taxonomic level, generally to genus. Further detail on

these protocols can be found in the GBMc QAP. Collections will be analyzed with several biometrics to determine community status.

Task 2 – Toxicity Assessment

An evaluation of selenium toxicity will be completed to determine the effect of selenium on resident biota from Loutre Creek. Samples from each media (water column, eggs, fish tissue, sediment and within primary producer (periphyton, phytoplankton, etc.) and primary consumer (macroinvertebrates, fish, etc.) trophic levels) will be collected at each sample station during the spring biological assessment event and analyzed for selenium and other constituents (see Task 3 below). Samples of fish tissue, sediment and primary producer and primary consumer trophic levels will also be collected during the summer event. Sample size for fish tissue analysis will be a minimum of four fish per station. The assessment will focus on reproductive and embryological effects to fishes in the Centrachidae (sunfish) family. During the spring sampling season fertile females will be captured, striped and the eggs field fertilized. Eggs will be assessed and hatched by Great Lakes Environmental Centers laboratory. Eggs will be incubated, monitored individually and fecundity recorded. Once hatched the fish will be raised to an age of 5-days and evaluated for deformity using a deformity index (GSI, etc.) Details on the deformity index are provided in Section B4. This process will be completed for each of the sample stations, including the LC-1 station which will serve as a baseline for fecundity and deformity. Specific details of the sampling for the toxicity assessment are provided below.

A. *Source of test organisms* - Eggs from a sunfish species will be collected from each monitoring station. Eggs will be collected from 5 to 10 fish from each site (same species for all sites).
B. *Collection of eggs* - Eggs will be fertilized in the field using milt from males collected from the same site. Eggs will be hand-expressed from the females. Milt will be hand expressed or gonads will be simply removed from 2 to 3 ripe males and then composited. Each batch of eggs will be fertilized with one to two ml of sperm and gently mixed. Dead and/or broken eggs will be removed. Fertilized eggs will be water-harden for 1 to 2 hours. The water-hardened eggs will be

transported to an on-site or local laboratory in O_2-saturated laboratory or reference water.

C. *Tissue analysis* - After removing the eggs, female lengths and weights will be measured. Selenium will be measured in the each female from which eggs were collected (muscle and whole body) and in a sub-sample of each batch of eggs. Tissue samples will be kept frozen prior to analysis.

Task 3 – Chemical and In-Situ Analysis

Various chemical parameters will be monitored during the study. During each of six sample events in-situ parameters will be analyzed and samples collected for laboratory analysis from each sample station and from Outfall 001. In-situ parameters shall consist of pH, temperature, dissolved oxygen, specific conductance and turbidity. In-Situ parameters will be measured at the time of sample collection using a portable field meter(s). Field meters will be calibrated following the SOP from the GBMc & Associates QAP which generally adheres to manufacturer's recommendations.

Water samples will be collected as grab samples from the main flow area in the channel. Water samples delivered to the laboratory will be analyzed for total selenium, dissolved selenium, total alkalinity, total suspended solids, total dissolved solids and volatile suspended solids. Sediment samples will be collected with clean stainless steel sample apparatus (spoons, corers, etc.) and placed in clean containers for shipment to the laboratory. Samples from other media will be collected following similar protocols using clean containers. Samples from all media will be analyzed for total selenium. Additional parameters may be added as necessary. In-Situ parameters will be measured by GBMc & Associates. Samples from other media will be analyzed by AnaLab. Data from the chemical analysis will be utilized to set-up and calibrate the fate and transport model.

Samples will be analyzed in the laboratory according to the procedures outlined in the most current release of *Standard Methods for the Examination of Water and Wastewater*. Where specific EPA approved analysis methods exist the laboratory shall use them. Table B2.2 summarizes the samples taken, the analytical method, the preservative, and the holding time. A laboratory certified in the state of Arkansas shall

conduct all chemical analyses. AnaLab will serve as the laboratory of record for the analytical analyses.

Table B2.1. Summary of Sampling Methods

Sample Type	GBMc QAP SOP Number	Sampling Equipment	Field Processing Protocol	Storage Vessel	Preservative	Designated Record Sheet (Y / N)
Fish	SOP 10.0	Electro Shocker, Seines	Sort, Cursry ID and Tally, Preserve, Label, Store	Large PE Bottles/Buckets	Formalin	Y
Macroinvertebrates	SOP 9.0	Aquatic Dip Net	Condense, Qualitative Tallies, Preserve, Store	Large PE Bottles/Buckets	70% Ethanol or Kaylee's	Y
Habitat	SOP 7.0, 5.0	Wading Rod, Tape Measure, Flow Meter	n/a	n/a	n/a	Y
Water	SOP 12.0	Sample Bottles	Label and Store in Ice Chest	Various Bottles (see Table ##)	Various (see Table ##)	Y
In-Situ	SOP 1.0, 2.0, 3.0, 4.0, 14.0	Field Meters	Calibrate, Measure in Main Channel	n/a	n/a	Y
Sediment	n/a	Stainless Steel Spoons, Corer	Label and Store in Ice Chest	Wide Mouth Glass Jars	4° C	Y
Eggs	n/a	Gloves, Glass Containers, Mixing Containers	Label and Store in Ice Chest	Plastic Widemouth Bottles	None	Y
Fish Tissue	SOP 17.0	Knives, Calibrated Scales, process Composite	Label and Store in Ice Chest	Decon. Aluminum Foil, Foil/Brown Pot Plastic Bags	4° C	Y
Biomass (whole body/cell)	SOP 15.0, 16.0	Periphytometer, Dip Nets, Sample Bottles	Label and Store in Ice Chest	PE Bottles or Whirl Paks	4° C	N

Table B2.2. Summary of water samples taken for analytical analysis for each monitoring event.

Parameter	Number Samples/Event	Analytical Method	Preservative	Holding Time
Total Selenium	6	EPA200.8	HNO3, 4° C	180 Days
Dissolved Selenium	6	EPA200.8	HNO3, 4° C	180 Days
Total Alkalinity	6	SM2320B	4° C	14 Days
TDS	6	SM2540C	4° C	4 Days
TSS	6	SM2540D	4° C	7 Days
VSS	6	EPA160.4 / SM2540E	4° C	7 Days
Chlorophyll a	6	SM10200H	Frozen	21 Days[1]

SM = Standard Methods for the Examination of Water and Wastewater.

[1] Filtered and frozen in field prior to shipment to extend holding time.

B3 Sample Handling and Custody Requirements

All samples will be placed in the appropriate clean containers supplied by the laboratory. Each sample container will be labeled with the sample I.D., date, time, and initials of collector(s). Samples will be placed in ice chests and maintained at 4º C for delivery to the laboratory in a timely manner conducive to maintenance of regulatory holding times. Samples collected for chlorophyll-a analysis will be filtered and frozen prior to shipping to prolong the holding time to 21 days. Chain of Custody (COC) forms that include information on each sample delivered to the laboratory for analysis will be completed. Each COC form will be signed by each person handling the samples from collection in the field to receipt in the laboratory. The COC form will include all required information and will be checked for completeness prior to submission of samples to the laboratory.

.

B4 Analytical Methods Requirements

Chemical Analysis

All procedures used for analyzing chemical parameters of water quality for reporting purposes will follow USEPA approved methods and/or Standard Methods for the Examination of Water and Wastewater (latest edition).

Analytical methods are listed below, along with specific performance requirements. All analytical analyses will be completed by a laboratory certified in the State of Arkansas. All analytical methods will be conducted under the AnaLab Quality Assurance Plan in which there is a specific SOP for each method (Appendix C). All methods fall under the specific quality control requirements outlined in the Quality Assurance Plan. Any failure in the analytical systems will be the responsibility of AnaLab to apply necessary corrective action.

Failures in the QA system encountered by AnaLab shall be reported to the project Quality Assurance Officer (QAO) as soon as reasonably possible.

Table B4.1. Summary of analytical methods.

Parameter	Source/Method	Units	MDL
Total Selenium	EPA200.8	ug/l	1.0
Dissolved Selenium	EPA200.8	ug/l	1.0
Fish Tissue	EPA6020	Mg/kg	0.1
Total Alkalinity	SM2320B	mg/l	2.0
TDS	SM2540C	mg/l	1.0
TSS	SM2540D	mg/l	1.0
VSS	EPA160.4 / SM2540E	mg/l	1.0
Total Solids	SM2540G	%	0.1
Chlorophyll a	SM10200H	ug/l	2.0

Toxicity Assessment

The toxicity assessment task is focused on the reproductive and embryo-larval effect. A description is provided below.

Reproductive and embryo-larval effect assessment

Fertilized eggs will be monitored in a Great Lakes Environmental Center laboratory or on-site laboratory for:

- Percent hatch
- Larval survival (to swim-up stage, 5 days post hatch)
- Embryo-larval malformations, including
    - Edema
    - Skeletal deformities (lordosis, kephosis, and scoliosis)
    - Craniofacial deformities (head, eyes, or jaw)
    - Fin deformities
    - Embryo-larval malformations will be graded using a scoring system termed graduated severity index (GSI)

A detailed description for the toxicity assessment is provided below. Table B4.2 provides a summary of the test conditions.

A. *Egg and Larvae Rearing for Effects Assessment* – Sub-samples from each batch of eggs will be assessed for percent hatch/larval survival and malformations.

B. Percent hatch and larval survival - From a given batch of eggs, 200 fertilized eggs will be divided into 4 replicate hatching jars (50 eggs/jar). Hatching jars will have a screen (e.g., 35 mesh) on the bottom. Hatching jars will be submerged in a temperature controlled aquaria containing reference water. A rocker arm will continuously move the jars up and down in the aquaria to maintain movement of fresh water across the eggs. The reference water in the aquaria will be aerated and replaced at a rate of at least 4 tank turnovers per day via a flow through system. The number of hatched larvae will be monitored daily.

From each hatching jar, 25 newly hatched larvae will be transferred to a separate beaker with a screen on the bottom for the 5-day larval survival assessment; i.e., for each batch of eggs there will be 4 replicate larval survival beakers containing 25 larvae each. Each survival beaker will be suspended in a temperature controlled

flow-through aquarium containing well aerated reference (synthetic) water. Survival will be monitored daily through the swim-up stage, 5 days post hatch.

C. *Malformations (deformity) assessment* - From a give batch of eggs, 500 fertilized eggs will be placed into a hatching jar for the assessment of embryo-larval malformations. The bottom of each hatching jar will be a screen (35 mesh). The hatching jar will submerged in an aquarium and fitted to a rocker arm similar to that described above. At the completion of yolk sac absorption, larvae will be sacrificed with MS-222 (0.8 g/L) and preserved in Davidson's solution.

All hatched larvae after yolk absorption will be assessed for the frequency and severity of skeletal (lordosis, kephosis, and scoliosis), craniofacial (head, eyes, or jaw) and fin deformities as well as edema. For each deformity type, the number of deformed progeny from a single adult will be summed and divided by the total number of larvae assessed from that adult (×100) to obtain a mean percentage of deformities. Each fish will be scored on the basis of the severity of each type of deformity on a scale from 0 (normal) to 3 (severely deformed). Photographs of the deformities and associated scores will be taken and used in the grading of the graduated severity index (GSI). In general, scoring of the deformities will be: 0 = normal, 1 = slight defect of size or structure, 2 = moderate defect of size or structure, and 3 = severe defect of size or structure. The sum of the individual scores for each larva will be calculated for each of the four malformations (edema, skeletal, craniofacial and fin deformities) and a GSI score will be determined for female/batch of eggs. At least 10% of the scores made by the primary analyst will be confirmed by a separate analyst to confirm consistency in scoring. If there is greater than a 20% difference in scoring, samples will be reanalyzed after consultation with the analysts and review of the criteria for scoring provided with the photographs.

A statistical procedure consistent with those used for routine toxicity testing (ANOVA, Bonferroni test, Kruskal-Wallis test, etc.) will be used to determine if a

significant difference exists between the control conditions and the test conditions. The statistical tests will be completed at an alpha level of 0.05. Alternatively, a tolerance or predictive interval approach may be used based on the distribution of control (background) data and establishment of an effect threshold.

Table B4.2. Summary of test conditions for Reproductive Toxicity Testing.

Parameter	**Test condition (Eggs)**	**Test Condition (Embryo-Larval)**
Test Type	Flow Through Hatching Chamber	Flow Through Rearing Chamber
Temperature	25°C	25°C
Light Quality	Ambient Laboratory	Ambient Laboratory
Light Intensity	50-100 ft-c	50-100 ft-c
Photoperiod	16h light, 8h dark	16h light, 8h dark
Test Chamber Type	Flow through chambers (special built)	Flow through chambers (special built)
Test Solution Volume	1-5 L	1-5 L
Solution Renewal	4 chamber volumes/day	4 chamber volumes/day
Age of Test Organisms	Eggs	Hatch to 5 days
No. Organisms/Chamber	50	25
No. of Replicate Chambers	4	4
Feeding Regime	None	None
Aeration	Continuous	Continuous

B5 Quality Control Requirements

Field Sampling

Duplicate samples for key constituents (Total Selenium, TSS, and VSS) shall be collected at a minimum frequency of 10% of the samples collected for the entire study. At least one duplicate sample will be collected for each day of sampling. Duplicate samples shall vary by no more than 20% relative percent difference (RPD) or the sample results will be considered suspect. In the event an RPD exceeds 20%, the Project QAO will investigate the incident to determine the cause of the exceedance and what action, if any, is necessary.

One field blank will be collected during each sample event for analysis of total selenium. Field blanks will consist of a sample of ultra pure laboratory water poured into the appropriate sample container in the field to simulate all possible contaminant exposures. Sampling methodology and equipment must be the same for field blanks as for routine sampling in the study. If a field blank is found to be contaminated, by a chemical of concern, an analysis will be conducted to determine the potential impact of the contamination on the results of the associated batch of samples. The Project QAO will determine the appropriate course of action from the results of the analysis.

Analytical Laboratory

The laboratory will validate analytical data by use of blanks, laboratory controls, spikes, and spike duplicates. Laboratory blanks measure the amount of each respective analyte contributed from the analytical procedure. A laboratory blank is considered out of control for a specific analyte if the value exceeds the higher of either the minimum detection limit (MDL) or 5% of the measured concentration in the sample. A laboratory control measures the ability of the laboratory to recover an analyte from a blank matrix. The laboratory spike sample is used to evaluate the laboratory's ability to recover an analyte in the sample matrix. The QC exceedence criteria for laboratory controls and spikes is based on upper and lower control limits derived from the laboratory's method specialized limits. The laboratory spike duplicate is used to evaluate the laboratory's precision (ability to attain similar analytical results from duplicate samples). A RPD is

calculated for the spike and spike duplicate. The RPD is compared to method specialized limits to determine QC exceedance. Any significant excursion from one of the QC parameters will result in a repeat of the analysis in question following an investigation by the laboratory as to the cause of the QC excursion and a report of the corrective actions taken to the project QAO.

Specific laboratory quality control requirements for each analytical method is listed for each parameter in the table below.

Table B5.1. Summary of laboratory QA requirements.

Parameter	Source/Method	Duplicate RPD (%)	LCS Recovery (%)	LCS RPD (%)	Matrix Spike Recovery (%)	Matrix Spike RPD (%)
Total Selenium	EPA200.8	n/a	85-115	20	70-130	20
Dissolved Selenium	EPA200.8	n/a	n/a	n/a	70-130	20
Fish Tissue Selenium	EPA6020	n/a	85-115	20	70-113	20
Total Alkalinity	SM2320B	20	n/a	n/a	10	n/a
TDS	SM2540C	20	15	n/a	n/a	n/a
TSS	SM2540D	20	10	n/a	n/a	n/a
VSS	EPA160.4/SM2540E	20	n/a	n/a	n/a	n/a
Total Solids (fish tissue)	SM2540G	20	n/a	n/a	n/a	n/a
Chlorophyll a	SM10200H	15	15	n/a	n/a	n/a

Toxicological Laboratory

Great Lakes Environmental Center will validate toxicity data through use of a reference site condition and laboratory controls. Eggs from fish collected from a reference site will be carried through the testing process to serve as a baseline for selenium effects. Laboratory controls demonstrate that the test organisms used are healthy and able to produce reasonable results. Potential variability in the malformation assessment phase will be controlled by regular audits of the scores and by duplication of scoring on selected batches at a rate of 10%.

B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Equipment cleaning and maintenance procedures will follow manufacturer recommendations. Records of maintenance of field sampling equipment will be kept in a record book listing name of technician, date and type of maintenance. Portable field meters should be calibrated in the lab at least twice/month (every other week) to monitor readiness and ensure proper functionality. Each day during a field trip equipment should be inspected before use (during calibration, etc.) to ensure functionality. All equipment will be inspected and cleaned immediately following a field trip and stored in a safe place to allow its future readiness.

Where appropriate, calibration and performance tests are described in the SOP of the respective application. Generally, all equipment will be utilized per the manufacturer's directions. If during the course of the field activities equipment fails to conform to known QA/QC requirements, the equipment will be repaired or replaced with similar equipment that will meet QA/QC requirements.

B7 Instrument Calibration and Frequency

Field meters will be calibrated prior to each sampling event. DO Probes will be corrected for barometric pressure and calibrated to 100% saturation. Ph probes will be calibrated using a pH 4 and a pH 7 calibration solution. Turbidity meter readings will be checked against standards, if more than 20% off the known value the meter will be calibrated following the SOP. Specific conductance will be checked against known standards, if more than 20% off the known value the meter will be calibrated following the SOP. All meter calibrations will be completed following GBMc SOP's which are provided in Appendix B of this document.

.

B8 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables used for this project will include sample bottles, preservative, toxicity sample materials, laboratory reagents necessary for the tests performed and calibration standards. All sample bottles will be new clean bottles of a style and material consistent with analytical requirements. All consumables will be purchased new. All lab supplies and consumables will be approved by the Project Manager or the Lab Manager (in the case of analytical or toxicity testing). All chemicals and reagents will be dated and inspected for proper expiration date when purchased and prior to use. All supplies will be inspected when purchased and any damaged or open containers or packaging will be refused.

B9 Non-Direct Measurements

Existing data from past studies and from the existing literature will be used in portions of this study. The table below outlines the data that will be used, where it will be used in the study and the acceptance criteria for its use.

Table B9.1. Summary of use of non-direct data (existing) data in the study.

Data Description	Use in Study	Acceptance Criteria
Selenium data from recent studies. Media include water, sediment and fish tissue.	Support for toxicity testing, modeling and SSC development.	Meets same rigors as that outlined in this QAPP.
Routine WET Test as required by the NPDES permit.	Support for toxicity testing and SSC development.	Meets NPDES program requirements for reporting on DMR's.
Scientific studies from the body of literature dealing with Selenium toxicity and bioaccumulation	Support in toxicity testing and SSC development.	Only peer reviewed scientific literature or published test books will be considered.
Scientific literature for modeling rates, constants and coefficients.	Aid in development of modeling rates, constants and coefficients for prediction of selenium fate and transport in the aquatic environment.	Only peer reviewed scientific literature or published test books will be considered. Focus will be given to EPA guidance documents.
Scientific literature concerning selenium treatability.	Support alternatives analysis.	Only peer reviewed scientific literature or published test books will be considered.

B10 Data Management

Upon conclusion of all activities at a given study location, the QAPP/study plan should be reviewed to ensure all necessary data was collected. The field team should review all completed data forms and sample labels for accuracy, completeness, and legibility, and make a final inspection of samples. If information is missing from the forms or labels, the team leader should fill in the missing information prior to proceeding to the next study location. Any missing and/or compromised samples should be collected immediately. A field notebook should be maintained by the field team leader (at a minimum) to document field activities, data collected, deviations from method, and general observations and information related to the study. Every person should maintain individual field logs to document activities and observations during daily activities.

All data collected during scientific studies should be checked by the team leader for completeness and accuracy. Field data forms should be complete and initialed by the completing scientist and the reviewing scientist. All field data sheets and log books will be kept at GBMc and maintained for a period of 5 years.

All field data will be entered to spreadsheets (or databases) or scanned into pdf files for electronic storage. Data will be stored electronically in project files on a secure network. The network is backed up weekly onto magnetic tape media. Data entry to spreadsheets and databases along with spreadsheet calculations shall be checked for accuracy at a rate of 10% (minimum) of the entries and calculation cells. Copies of the checked data and spreadsheets should be initialed by the reviewer and retained in the records. All calculations should be detailed in the body of written reports, or shown on GBMc & Associates Calculation Pages. Good notes regarding calculations will be kept and filed in the project notebook.

GBMc & Associates is responsible for the compilation of all data (in-situ, bioassessment, analytical, toxicity, etc.) collected during the study. Analytical and toxicity results as well as QA/QC results will be reported in electronic format to the Project Manager once per quarter, at a minimum. This data will be stored on the GBMc & Associates network for a minimum of fine years after the end of the project.

All deliverables (scientific reports, QA/QC reports, etc.) developed as part of this study shall be peer reviewed and/or reviewed by the Project Manager prior to being sent to Lion Oil, ADEQ or EPA.

III. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

Data will be reviewed by the GBMc QA Officer to evaluate the QAPP and its implementation. The review will include the following objectives:

a) collection of samples

b) corrective actions

Laboratory performance may be checked using external audit samples. GBMc QA Officer will be the internal individual responsible for detecting any errors or malfunctions and performing corrective actions. If errors are detected or anomalous data is suspected, the data will be traced back through the acquisition process until the error is found. In the advent that no error is found the data will be considered appropriate for reporting. If an error is found and cannot be resolved, then the effected data will be discarded.

Regulatory reviews by ADEQ and EPA of the draft and final documents will facilitate adherence to the QAPP.

C2 Reports to Management

Quarterly progress reports will be made to the Project Manager by Great Lakes Environmental Center (GLEC) and Ana-Lab detailing significant occurrences related to the project including number of samples taken, surveys completed operational problems and corrective actions. Quarterly Quality Assurance reports will be made to the QAO and the Project Manager by the Field Coordinator, GLEC and Ana-Lab detailing all QA problems and corrective actions. Copies of all reports will be maintained at the GBMc & Associates office for a period of five years.

As required by the CAO Lis No 08-104, quarterly reports relating schedule compliance will be submitted to ADEQ NPDES Enforcement Section.

IV. DATA VALIDATION AND USABILITY

D1 Data Review, Validation, and Verification Requirements

Chemical results will be rejected if they fall outside of the standard deviation for the respective parameter as outlined in Section A7. The review, validation and verification of the analytical data are the responsibility of Ana-Lab. The review, validation and verification of the toxicological data are the responsibility of GLEC.

The review, validation and verification of field data and lab results for reporting are the responsibility of GBMc & Associates.

D2 Validation and Verification Methods

The field and lab data will be combined in the spreadsheets and reported to the Project Manager once per quarter at a minimum. GBMc & Associates will validate and verify the data in the reports to be correct by checking all entries against lab results and field notebook entries.

D3 Reconciliation with Data Quality Objectives

Laboratory data quality objectives and their fulfillment will be assessed immediately after the analyses are performed. Data found to be outside objectives will be reanalyzed immediately if possible and discarded if not. Laboratory objectives and assessment in element B5.

Sample handling data quality objectives will be assessed by analysis of field blanks. Sample handling quality objectives will be assessed quarterly, at a minimum once per year and reported in the final report.

Sampling data quality objectives will be met by designing the sampling protocol so that the error involved in sampling is equal to or less than the prescribed objective. They will be assessed by analysis of field duplicates. They should agree with each other within 20 percent.

Any deviations from the objectives will be reported to the GBMc QAO quarterly and attempts will be made to determine and fix the causes of the data not meeting objectives.

Appendix A
Selenium Data from Lion Oil Company Outfall 001

Lion Oil
Outfall 001 Selenium Data Summary POR 1/4/2005 torough 10/6/2008
POR January 2005 - January 2007

DATE		selenium
		mg/L*
1/4/2005		0.012
2/1/2005		0.0125
3/1/2005		0.00999
3/28/2005		0.0124
4/5/2005		0.0251
5/3/2005		0.0153
6/6/2005		0.0235
7/4/2005		0.0371
8/1/2005		0.0213
9/5/2005		0.0182
10/3/2005		0.0155
11/7/2005		0.0109
12/5/2005		0.0112
1/2/2006		0.00951
2/6/2006		0.00955
3/6/2006		0.0152
4/3/2006		0.0148
5/1/2006		0.017
6/5/2006		0.0392
7/10/2005		0.0202
8/7/2006		0.0286
9/4/2006		0.0341
10/2/2006		0.0277
11/6/2006		0.0208
12/4/2006		0.0224
12/18/2006		---
12/26/2006		---
1/1/2007		0.0188
1/8/2007		
2/5/2007		0.0214
3/5/2007		0.0325
3/12/2007		0.0389
3/19/2007		0.0297
3/26/2007		0.0364
4/2/2007		0.0331
4/9/2007		0.0302
4/16/2007		0.0254
4/23/2007		0.0283
4/29/2007		0.0282
5/7/2007		0.0283
6/4/2007		0.0234
7/2/2007		0.0265
8/6/2007		0.0126
9/3/2007		0.0209
10/1/2007		0.0174
11/5/2007		0.0242
12/3/2007		0.0209
1/1/2008		0.0207
2/4/2008		0
3/3/2008		0.0223
4/7/2008		0.0125
5/5/2008		0.0206
6/2/2008		0.0128
7/7/2008		0.0246
8/4/2008		0.0176
9/1/2008		0.0097
10/6/2008		0.0165
	Count	54
	min	0
	max	0.0392
	Mean	0.0211
	SD	0.009338255
	99%	0.039041
	95%	0.036645
	90%	0.03292

Appendix B
GBMc SOP

1.0 pH Meter Calibration SOP

Purpose

This SOP describes the methods for calibration and use of portable pH meters (capable of 2-point calibration) such as the Orion® Star Series pH meter and YSI Multi Probe System (MPS). Field forms used for meter calibration and measurement recording are attached to this SOP.

Procedure

Orion® Star Series (or similar pH meter)

Calibration

1. Be sure that the electrode (probe) is properly attached and that a good battery is installed.

2. Turn the meter on and check the read-out for any warning messages ("Low Bat.", etc.) If problems occur refer to the owners manual for help.

3. Record the proper information (date, time, etc.) on the Calibration Field Form (attached) or in a field logbook.

4. Remove the probe protection cap, rinse and place the probe in pH buffer solution 7.00 (yellow in color) submerging the end to ***at least 1 inch***. Allow the meter to adjust to the buffers pH for approximately 1 minute.

5. Press the Calibration button on the meter to begin the calibration process. The display should read "CAL.1" along with the pH reading.

6. When the meter has accepted the buffer the **pH** will stop flashing. Press the Calibration button to accept the value and proceed to the next calibration point "CAL.2"

7. Remove the probe from the 7.00 buffer and rinse with distilled water to remove any excess buffer solution.

8. Place the probe in the second buffer solution, 4.01 (pink) or 10.01 (blue), whichever best brackets the expected pH range to be measured, and stir it gently.

9. When the meter has accepted the value the **pH** will stop flashing as in step 6 above. Press “Save” to accept this value. Record this number on the pH Calibration Record sheet.

10. The display will immediately show the slope, a number that should be between 92% and 102%. Record this number on the pH Calibration Record sheet. If the slope is larger or smaller than this range the meter should be recalibrated.

11. A calibration check should be done once the meter is calibrated. This is done by rinsing the probe with distilled water and then placing it in the pH 7.00 buffer solution and taking a reading. Make sure the measure symbol is lit, if not press the “Measure” button to return to measurement mode. When the **pH** stops flashing record this reading on the pH Calibration Record form. If the reading is between 6.90 and 7.10 then the original calibration remains valid. If the measurement falls outside this range then the meter should be recalibrated.

12. Gently shake or rinse off excess liquid from the probe. The meter is now ready for use.

13. The pH meter should be calibrated once per day on days that it is used. The pH meter should have its calibration checked once for each sampling trip or once every 10 samples whichever is greater. This is done simply by placing the probe in the pH 7.00 buffer solution and taking a reading. Record this reading on the pH Calibration Record form. If the reading is between 6.90 and 7.10 then the original calibration remains valid. If the measurement falls outside this range then the meter should be recalibrated. Furthermore, if the battery or probe is ever disconnected from the meter during use, a new calibration would be required.

YSI MPS

1. Be sure that the pH electrode (probe) is properly attached and that a good battery is installed.

2. Turn the meter on and check the read-out for any warning messages (“Low Bat.”, etc.) If problems occur refer to the owners manual for help.

3. Record the proper information (date, time, etc.) on the Calibration Field Form (attached) or in a field logbook.

4. Press the On/off key to display the run screen then press the Escape key to display the Main Menu screen.

5. Use the arrow key to highlight the Calibrate selection and press Enter.

6. Use the arrow keys to highlight the pH selection and press Enter to display the pH calibration screen.

7. Select the 2-point option to calibrate the pH sensor using two calibration standards then press Enter. The pH Entry Screen is displayed.

8. Remove the transport/calibration cup from the end of the probe and place the probe in pH buffer solution 7.00 (yellow in color) so that the sensor is completely immersed, ***approximately 30 mL.***

9. Screw the transport/calibration cup on the threaded end until securely tightened. Gently rotate and/or move probe module up and down to remove any bubbles from the pH sensor.

10. Use the keypad to enter the calibration value of the buffer being used and press Enter. The pH calibration screen is displayed. Allow at least one minute for temperature equilibration before proceeding.

11. Observe the reading under pH, when the reading shows no significant change for approximately 30 seconds, press Enter. The screen will indicate that the calibration has been accepted and prompt you to press Enter to Continue.

12. Press Enter. This returns you to the Specified pH Entry Screen. Rinse the probe module, transport/calibration cup and sensors in distilled water.

13. Repeat steps 8 through 11 using the second pH buffer solution, 4.01 (pink) or 10.01 (blue), whichever best brackets the expected pH range to be measured.

14. Press Escape to return to Main Menu. Use the keypad and select Run.

15. A calibration check should be done once the meter is calibrated. This is done simply by placing the probe in the pH 7.00 buffer solution and taking a reading. Record this reading on the pH Calibration Record form. If the reading is between 6.90 and 7.10 then the original calibration remains valid. If the measurement falls outside this range then the meter should be recalibrated.

16. Gently shake or rinse off excess liquid from the probe. The meter is now ready for use.

17. The pH meter should be calibrated once per day on days that it is used. The pH meter should have its calibration checked once for each sampling trip or once every 10 samples whichever is greater. This is done simply by placing the probe in the pH 7.00 buffer solution and taking a reading. Record this reading on the pH Calibration Record form. If the reading is between 6.90 and 7.10 then the original calibration remains valid. If the measurement falls outside this range then the

meter should be recalibrated. Furthermore, if the battery or probe is ever disconnected from the meter during use, a new calibration would be required.

pH Measurements

Orion® Star Series (or similar pH meter)

1. Place the probe in the liquid to be analyzed and stir it gently. The probe should be submerged so that the sensor is ***at least 1 inch*** into the liquid.

2. Press the "Measure" button to begin. The measure symbol will flash until the reading is stable. When the **pH** stops flashing record the reading to the nearest tenth of a unit.

3. Be sure to turn off the meter when the final pH measurement has been taken and recorded.

YSI MPS

1. Select Run from the main menu to display run screen.

2. With probe sensor guard installed, completely immerse all sensors into sample.

3. Allow the meter to stabilize and record the pH reading to the nearest tenth of a unit.

Meter Maintenance/Storage

Orion® Star Series (or similar pH meter)

1. Store the meter in a safe dry place.

2. Keep the probe cover on the probe when not in use and between measurements.

3. A small piece of sponge or paper towel soaked in pH buffer 7.00 should be placed in the bottom of the probe cover to keep the probe surface wetted with the buffer. The probe should **never** be allowed to dry out.

4. Use only "Low Maintenance Triode" ATC probes with the Star series pH meters (model # 9107BNMD or equivalent.)

YSI MPS

1. Store the meter in a safe dry place.

2. Keep a moist sponge in the transport/calibration cup and keep sealed when not in use and between measurements. The probes should **never** be allowed to dry out.

Quality Assurance/Quality Control

1. Meters are calibrated biweekly (at a minimum) to ensure proper function and accuracy.

2. Values measured during biweekly calibrations are compared between meters to verify accuracy.

3. Duplicate measurements should be taken at a rate of 10% (minimum) of samples analyzed.

2.0 Dissolved Oxygen (D.O.) Meter Calibration SOP

Purpose

This SOP describes the methods for calibration and use of the portable YSI Model 58 and Model 85 D.O. meters as well as the YSI MPS. Field forms used for meter calibration and measurement recording are attached to this SOP.

Procedure

Calibration

Model 58

1. Be sure that the oxygen probe is properly attached to the meter and that the end of the probe is affixed in storage bottle containing a piece of wet sponge or towel to keep the probe moist, and to provide a water-saturated air environment.

2. Turn the meter on and check the read-out for the "LOBAT" warning, and for the normally observed display readings. If problems occur refer to the owners manual for help.

3. Record the proper information (date, time, etc.) on the Dissolved Oxygen Calibration Record sheet or in a field logbook.

4. Set the D.O. meter to "ZERO" and use the "O2 ZERO" knob to adjust the display to 0.0. If the meter will not adjust to zero refer to the owners manual for guidance.

5. Perform a Calibration according to one of the following procedures:

   Winkler Titration (verification calibration)

   a) Fill a container with at least 500 mL distilled water (or tap water if distilled not available) and allow it to acclimate. It can be aerated overnight to achieve 100% oxygen saturation if desired.
   b) Fill each of two BOD bottles with the water from the container by gently submerging them into the container.
   c) Add one each of the HACH manganous sulfate and alkaline iodide-azide powder pillows to each bottle. Cap the bottles and invert them 15-20 times to mix the solution thoroughly.
   d) Allow the bottles to settle until a precipitate appears in the bottom half of the bottle. This will usually take 3-5 minutes.
   e) Add one HACH sulfamic acid powder pillow to each BOD bottle. Invert the bottles until all the precipitate has been dissolved.

f) Using a graduated cylinder measure and place 200 mL of the solution into a flask.
g) Add 1 mL of HACH starch indicator to the flask. The solution should turn black.
h) Using a burette filled with sodium thiosulfate (at room temperature) titrate the solution in the flask drop-wise until the solution turns clear.
i) Record the starting and ending volumes from the burette.
j) Repeat this titration (steps f-I) for a second flask filled with fresh solution.
k) Subtract ending volumes from starting volumes to arrive at the volume used for each titration. The volume used is equivalent to the dissolved oxygen content of the water in mg/L.
l) If the D.O. values from the two titrations differ by more than 5%RPD then the titrations should be repeated.
m) Remove the D.O probe from the storage bottle and place it in the container holding the water. It must be submerged at least 1 inch below the waters surface. Set the meter to the "0.1 mg/l" measurement mode. Swirl the probe gently and slowly in the water.
n) Calibrate the meter to the average of the two dissolved oxygen measurements by turning the "O2 CALIB" knob until the display reads the corresponding D.O. concentration. Record the final calibrated value.

Air Calibration (Standard Calibration)

a) Set the meter to the temperature measurement mode ("TEMP…").
b) Record the temperature of the probe in the storage bottle on the record form or in a field logbook.
c) Refer to the attached table presenting Solubility of Oxygen in Water values (also on back of meter) and find the solubility of oxygen at the corresponding temperature.
d) Record the appropriate barometric pressure or altitude (use pressure when available).
e) Refer to the attached table presenting Calibration Values at Various Pressures and Altitudes (also on back of meter) and record the "CALIB VALUE" in % saturation at the corresponding pressure or altitude.
f) Using the solubility of oxygen value and the % saturation value as a decimal calculate the calibration value by multiplication (i.e. at an altitude Of 1413 ft. and a temperature of 20°C the calibration value would be 8.64 mg/L or 8.6 mg/L).
g) Set the meter to the D.O. measurement mode ("0.1 mg/l") and adjust the display using the "O2 CALIB" knob to read the calibration value as calculated.
h) Record the final calibrated value on the record form or in a field logbook.

Model 85

1. Turn on the meter and make sure the meter is in the D.O. mode (will display mg/L).

2. Wet the sponge in the calibration/storage chamber and insert the probe into the chamber.

3. Allow the D.O. and Temperature readings to stabilize (up to 15 minutes).

4. Press the up arrow and down arrow buttons simultaneously.

5. When prompted to do so, enter the local altitude in hundreds of feet by scrolling up or down with the up or down arrow buttons.

6. Press enter when the correct altitude is displayed. Base altitude on barometric pressure when possible, as it will have an affect on the calibration. See "Air Calibration" above for details.

7. When the percent reading is stable, press enter. Save will be displayed on the screen for a few seconds, then the meter will return to the normal operation mode.

NOTE: Each time either of the meters is turned off they should be recalibrated.

YSI MPS

Air Calibration (Standard Calibration)

1. Be sure that the D.O. electrode (probe) is properly attached and that a good battery is installed.

2. Turn the meter on and check the read-out for any warning messages ("Low Bat.", etc.) If problems occur refer to the owners manual for help.

3. Record the proper information (date, time, etc.) on the Calibration Field Form (attached) or in a field logbook.

4. Press the On/off key to display the run screen then press the Escape key to display the Main Menu screen.

5. Use the arrow key to highlight the Calibrate selection and press Enter.

6. Use the arrow keys to highlight the Dissolved Oxygen selection and press Enter to display the DO calibration screen.

7. Highlight the DO % selection and press Enter. The DO Barometric Pressure Entry Screen is displayed.

8. Place approximately 3 mm (1/8 inch) of water in the bottom of the transport/calibration cup or ensure the sponge is “dripping” wet and engage only 1 or 2 threads of the transport/calibration cup to the probe module to ensure the DO sensor is vented to the atmosphere. Make sure the DO and temperature sensors are **not** in an upright position and immersed in the water.

9. Use the keypad to enter the current local barometric pressure either measured by the YSI556 or from the NWS/NOAA for your area. Barometer readings from the NWS/NOAA are generally corrected to sea level and must be uncorrected before use. For field DO calibrations, use the following equation to correct National Weather Service & NOAA sea level corrected barometric pressure to absolute barometric pressure:

   BP ~ SLBP – 2.5(A/100)

   SLBP = sea level BP
   A = altitude in feet above sea level

10. Press Enter. The DO % saturation calibration screen is displayed. Allow approximately ten minutes for the air in the transport/calibration cup to become saturated and for temperature to equilibrate before proceeding.

11. Observe reading under DO %. When the reading shows no significant change for approximately 30 seconds, press Enter. The screen will indicate that the calibration has been accepted and prompt you to press Enter to Continue. Record the resulting % saturation value, which should be between 95% and 105%.

12. Press Enter to return to the DO calibration screen then press Escape to return to the calibrate menu.

13. Gently shake or rinse off excess liquid from the probe. The meter is now ready for use.

Winkler Titration (verification calibration)

1. DO calibration in mg/L may also be carried out using a known concentration of dissolved oxygen.

2. Go to the DO calibrate screen and highlight the DO mg/L selection. Press Enter.

3. Repeat the calibration steps (a. through m.) under Model 58 Winkler Titration.

4. Observe the DO mg/L reading after the reading has stabilized for approximately 30 seconds. Record calibration reading then press Enter. The screen will indicate that the calibration has been accepted and prompt you to press Enter to Continue.

5. Press Enter to return to the DO calibration screen and press Escape to return to the calibrate menu. Rinse probe and sensors in distilled water.

D.O. Measurements

Model 58 and 85

1. Set the meter to the D.O. measurement mode. Place the probe in the liquid to be analyzed and stir it gently and slowly to keep water passing over the probe membrane. The probe should be submerged ***at least 1 inch*** into the liquid.

2. Allow the meter to stabilize on a reading (should take less than one minute). Once the meter has stabilized record the reading.

3. If the meter will not stabilize check the probe for air bubbles. If bubbles are found shake the probe firmly but not violently a couple of times and re-measure. If problems still occur, probe maintenance is necessary.

4. The meter should be placed in the "ZERO" mode between measurements to conserve battery life. Be sure to turn off the meter when the final D.O. measurement has been taken and recorded.

YSI MPS

1. Select Run from the main menu to display run screen.

2. With probe sensor guard installed, completely immerse all sensors into sample.

3. Allow the meter to stabilize and record the DO reading to the nearest tenth a mg/L.

Meter Maintenance/Storage

1. Store the meter in a safe dry place.

2. Keep the probe cover on the probe when not in use and between measurements.

3. A small piece of sponge or paper towel soaked in clean water should be place in the bottom of the probe cover to keep the probe surface moist. The probe should **never** be allowed to dry out.

4. The probe membrane should be replaced at a minimum every 6 months or whenever the meter fails to perform to standard.

5. Use only YSI replacement parts and probes with the meter.

Quality Assurance/Quality Control

1. Meters are calibrated biweekly (at a minimum) to ensure proper function and accuracy.

2. Values measured during biweekly calibrations are compared between meters to verify accuracy.

3. Duplicate measurements should be taken at a rate of 10% (minimum) of samples analyzed.

3.0 Conductivity Meter Calibration and Measurement SOP

Purpose

This SOP describes the methods for calibration and use of portable YSI Model 30 meter, the Model 85 conductivity meter, and the YSI MPS meter. Field forms used for meter calibration and measurement recording are attached to this SOP.

Procedure

Calibration and Bi-Weekly Accuracy Checks

Model 30, Model 58 and YSI MPS

Calibration of YSI Model 58 and Model 85 conductivity meters is performed by the manufacturer and is rarely needed. However, the accuracy of the meter should be monitored bi-weekly and before each use. The bi-weekly monitoring of accuracy should be recorded in the calibration log book, along with date/time performed and name of person performing task.

Accuracy Check

1. Turn the instrument on and allow it to complete its self test procedure.

2. Bi-weekly the instrument should be checked for accuracy using a standard of 200 uS/cm (±10%). The meter should be set to measure specific conductance. The steps listed below under "Conductivity Measurements" should be followed for checking conductivity accuracy. This standard check should be recorded in the calibration log book.

3. YSI conductivity meters are calibrated a minimum of once a year or when there is reason to believe the instrument is reading incorrectly (outside the range of the standard ±10% in uS/cm during the accuracy check).

Calibration Model 30 & 85

1. To calibrate, select a calibration solution, which is most similar to the sample you will be measuring. The following should serve as a guideline:

   for sea water choose a 50 mS/cm conductivity standard,
   for fresh water choose a 1 mS/cm or 500 mS/cm conductivity standard, and
   for brackish water choose a 10 mS/cm conductivity standard.

2. Place at least 3 inches of solution in a clean glass beaker.

3. Insert the probe into the beaker deep enough to completely cover the oval shaped hole on the side of the probe. Do not rest the probe on the bottom of the container -- suspend it above the bottom at least 1/4 inch.

4. Allow at least 60 seconds for the temperature reading to become stable.

5. Move the probe vigorously from side to side to dislodge any air bubbles from the electrodes.

6. Press and release the up and down keys ($\wedge$,$\vee$) at the same time. The CAL symbol will appear at the bottom left of the display to indicate that the instrument is now in Calibration Mode.

7. Use the up or down arrow key to adjust the reading on the display until it matches the value of the calibration solution you are using.

8. Once the display reads the exact value of the calibration solution being used press the ENTER key once. The word "SAVE" will flash across the display for a second indicating that the calibration has been accepted.

YSI MPS Calibration

1. Select Calibrate from the main menu and use the arrow keys to highlight the Conductivity selection.

2. Press Enter and then highlight the Specific Conductance selection, press Enter.

3. The Conductivity Calibration Entry Screen is displayed. Place approximately 55 mL of conductivity standard into dry or pre-rinsed transport/calibration cup.
   Note: It is ideal to pre-rinse with a small amount of standard that can be discarded.

4. When calibrating, select a calibration solution, which is most similar to the sample you will be measuring. The following should serve as a guideline:

   for sea water choose a 50 mS/cm conductivity standard,
   for fresh water choose a 1 mS/cm or 500 mS/cm conductivity standard, and
   for brackish water choose a 10 mS/cm conductivity standard.

5. Carefully immerse the sensor into the solution and gently rotate to remove any bubbles from the conductivity cell. Screw the transport/calibration and securely tighten.

6. Use the keypad to enter the calibration value of the standard being used. Be sure to enter the value in **mS/cm at 25ºC**, press Enter.

7. The Conductivity Calibration Screen is displayed. Allow at least one minute for temperature equilibration before proceeding.

8. Observe the reading under Specific Conductance until no significant change or for approximately 30 seconds, press Enter. After calibration has been accepted, press Enter to continue.

9. Press Enter and then press Escape to return to calibrate menu. Rinse probe and sensors with distilled water. Gently shake or rinse off excess liquid from the probe. The meter is now ready for use.

Conductivity Measurements

Model 58 and Model 85

1. Press the "ON/OFF" button to turn the meter on. The meter will go through a self-test procedure, which will last for several seconds. The cell constant will be displayed when the self-test is finished. Consult the Operations Manual if an error is displayed during the self-test.

2. Select the mode of measurement on the meter by pressing and releasing the "MODE" button on the meter. GBM^C generally measures specific conductance in its field studies. The following are the modes of measurement capable of the YSI 30 meter:

   Conductivity - measurement of the conductive material in the liquid sample without regard to temperature. Displayed when the large numbers on the display will be followed by the respective units, and the temperature units will not be flashing.

   Specific Conductance - temperature compensated conductivity which automatically adjusts the reading to a calculated value which would have been read if the sample had been at 25°C. Displayed when the large numbers on the display will be followed by the respective units, and the temperature units will be flashing.

   Salinity - A calculation done by the instrument electronics, based upon the conductivity and temperature readings. Displayed when large numbers on the display will be followed by ppt.

3. Insert the probe into the solution being measured for conductivity, making sure that the probe is inserted deep enough to cover the hole located on its side. If possible, refrain from touching any solid located in the solution, and hold the probe at least 1/4

inch from the bottom and sides of any container used to hold the sample. The probe should also be vigorously shaken in the solution to dislodge any air bubbles, which may be adhered.

NOTE: The YSI meters are factory calibrated, and retain the last calibration conducted. This means that once batteries are installed, or when the meter is turned on, you are ready to begin taking measurements.

YSI MPS

1. Select Run from the main menu to display run screen.

2. With probe sensor guard installed, completely immerse all sensors into sample.

3. Allow the meter to stabilize and record the Conductivity reading.

Meter Maintenance/Storage

Always rinse the conductivity cell with clean water after each use.

Cleaning the conductivity cell

1. Dip the cell in cleaning solution of 1:1 isopropyl alcohol and 10N HCl, and agitate for two to three minutes.

2. Remove the cell from the cleaning solution.

3. Use a nylon brush to dislodge any contaminants from inside the electrode chamber.

4. Repeat steps one and two until the cell is completely clean. Rinse the cell thoroughly in deionized water.

5. Store the conductivity cell in the meter storage chamber.

Quality Assurance/Quality Control

1. Meters are calibrated biweekly (at a minimum) to ensure proper function and accuracy.
2. Values measured during biweekly calibrations are compared between meters to verify accuracy.
3. Duplicate measurements should be taken at a rate of 10% (minimum) of samples analyzed.

4.0 Temperature Measurement/Check SOP

Purpose

This SOP describes the methods for the measurement of temperature using various instruments including the Orion Star Series pH meter, YSI MODEL 58 DO meter, YSI MODEL 30 conductivity meter, YSI MODEL 85 combination meter and YSI MPS as well as other meters with temperature capability. Field forms used for meter calibration and measurement recording are attached to this SOP.

Procedure

Accuracy Check for all Instruments

1. Insert the probe for the corresponding instrument into a container holding water, and allow the temperature reading to stabilize.
2. Record the temperature displayed on each respective instrument in the calibration log book along with date/time and individual performing the task.
3. Compare the actual temperature of the water measured with a certified calibrated thermometer to the temperature measured by the respective instruments.
4. If the temperature relative percent difference exceeds 20%, then do not use that particular meter for temperature analysis.

Temperature Measurement

Orion Star Series pH meter

1. Connect the combination pH/temperature electrode to the meter.
2. Turn the meter on, and allow it to go through its self-test.
3. Insert the probe into the solution to be measured.
4. The temperature read out is located in the upper left of the LCD on the meter.

HACH EC10 pH/mV/temperature meter

1. Connect the combination pH/temperature electrode to the meter.
2. Turn the meter on, and allow it to go through its self-test.
3. Insert the probe into the solution to be measured.
4. The temperature read out is located in the prompt line followed by ATC.

YSI Model 30 Conductivity meter and YSI Model 85 Combination meter

1. Turn the meter on.
2. Insert the probe into the solution to be measured.
3. The temperature read out is located in the lower right of the LCD on the meter.

YSI Model 58 Dissolved Oxygen meter

1. Turn the meter to temperature mode.
2. Insert the probe into the solution to be measured.
3. The temperature read out is located on the screen.

YSI MPS

1. Select Run from the main menu to display run screen.
2. With probe sensor guard installed, completely immerse all sensors into sample.
3. Allow the meter to stabilize and record the Temperature reading.

Quality Assurance/Quality Control

1. Meters are calibrated biweekly (at a minimum) to ensure proper function and accuracy.
2. Values measured during biweekly calibrations are compared between meters to verify accuracy.
3. Duplicate measurements should be taken at a rate of 10% (minimum) of samples analyzed.

5.0 Flow Measurements SOP

Purpose

This SOP describes the procedure used in the determination of water flow, which is necessary for the calculation of water volume passing through a given water body.

No single method for measuring discharge is applicable to all types of stream channels. The preferred procedure for obtaining discharge data is based on "velocity-area" methods (e.g., Rantz and others, 1982; Linsley et al., 1982). For streams that are too small or too shallow to use the equipment required for the velocity-area procedure, two alternative procedures are presented.

Stream discharge is equal to the product of the mean current velocity and vertical cross sectional area of flowing water. Discharge measurements are critical for assessing pollutant loading and reaeration rates used for dissolved oxygen modeling, as well as, other characteristics that are very sensitive to stream flow differences. Discharge will be measured at a suitable location within the sample reach that is as close as possible to the location where chemical samples are collected so that these data correspond. Field data forms for recording measurements are attached to this SOP.

Procedure

Velocity Area Procedure

Because velocity and depth typically vary greatly across a stream, accuracy in field measurements is achieved by measuring the mean velocity and flow cross-sectional area of many increments across a channel. Each increment gives a subtotal of the stream discharge, and the whole is calculated as the sum of these parts.

A Marsh McBirney Model 201 Portable Water Current Meter will be used whenever conditions allow. The site selected for flow measurements will be chosen on the basis of the most uniform streambed cross-section. This facilitates the best measurements since non-uniform streambeds may cause errors in velocity and depth. Manmade structures (bridges and culverts) may be used as flow measurement sites, but are not ideal.

Discharge measurements are generally made at only one carefully chosen channel cross section within the sampling reach. It is important to choose a channel cross section that is as much like a canal as possible, void of obstructions, as this provides the best conditions for measuring discharge by the velocity-area method. Rocks and other obstructions may be removed to improve the cross-section before any measurements are made. However, because removing obstacles from one part of a

cross-section affects adjacent water velocities, you must not change the cross-section once you commence collecting the set of velocity and depth measurements.

The procedure for obtaining depth and velocity measurements is outlined below:

1) Locate a cross-section of the stream channel for discharge determination that exhibits as many of these qualities as possible: Segment of stream above and below cross-section is straight, depths mostly greater than .5 feet, and velocities mostly greater than 0.5 feet/second. Do not measure discharge in a pool, when possible. Flow should be relatively uniform, with no eddies, backwaters, or excessive turbulence.

2) Stretch a tape measure across the stream perpendicular to its flow, with the "zero" end of the rod or tape on the left bank, as viewed when looking downstream. Tightly suspend the measuring tape across the stream, approximately one-foot above water level and secure at both ends.

3) Record the total wetted distance indicated by the tape from the left descending bank (LDB) to the right descending bank (RDB).

4) Attach the velocity meter probe to the calibrated wading rod that indicates depth and holds the flow probe at 60% depth. Check to ensure the meter is functioning properly and the correct calibration value is displayed. If necessary the meter and probe can be calibrated according to the instructions in the QA/QC section of this SOP (which is based on manufacturer's recommendations).

5) Divide the total wetted stream width into equally sized intervals, generally one foot wide (minimum of ten measurement locations, but never less than 1/2 foot increments).

6) Stand downstream of the tape and to the side of the midpoint of the first interval (closest to the LDB).

7) Place the wading rod in the stream at the midpoint of the interval. Record the distance from the left bank (in feet) and the depth indicated on the wading rod (in tenths of a foot) on the Flow Measurement Form.

8) Stand downstream of the probe to avoid disrupting the stream flow. If the water depth is less than or equal to 2.5 ft., adjust the position of the probe on the wading rod so it is at 60% of the measured depth below the surface of the water (Meador et al., 1993). The probe is set at the 60% depth by adjusting the foot scale on the sliding rod with the tenth scale on the depth gauge rod. If the water depth is greater than 2.5 ft., take measurements at 20% and 80% of the depth from the water surface. The average of these two readings is considered the water velocity for the respective measurement point. To set the probe at the 20% depth, first multiply the water depth by two, and then use the calculated number to line up the

foot scale as with the 60% depth. The same method is used for the 80% depth, except the calculated value is the water depth divided by two.

9) Face the probe upstream at a right angle to the cross-section. Do not adjust the angle of the probe, even if local flow eddies hit at oblique angles to the cross-section.

10) Wait 20 seconds to allow the meter to equilibrate then measure the velocity. Record the value on the Flow Measurement Form. For the electromagnetic current meter (e.g., Marsh-McBirney), use the lowest time constant scale setting on the meter that provides stable readings.

11) Move to the midpoint of the next interval and repeat Steps 6 through 8. Continue until depth and velocity measurements have been recorded for all intervals.

12) Record the data from each measurement on the Discharge Flow Recording form.

Timed Filling Procedure

In channels too "small" for the velocity-area method, discharge can be determined directly by measuring the time it takes to fill a container of known volume. "Small" is defined as a channel so shallow that the current velocity probe cannot be placed in the water, or where the channel is broken up and irregular due to rocks and debris, and suitable cross-section for using the velocity area procedure is not available. This can be an extremely precise and accurate method, but requires a natural or constructed spillway of free-falling water. If obtaining data by this procedure will result in a lot of channel disturbance or stir up a lot of sediment, wait until after all biological and chemical measurements and sampling activities have been completed.

Choose a cross-section of the stream that contains one or more natural spillways or plunges that collectively include the entire stream flow. A temporary spillway can also be constructed using a portable V-notch weir, plastic sheeting, or other materials that are available onsite. Choose a location within the sampling reach that is narrow and easy to block when using a portable weir. Position the weir in the channel so that the entire flow of the stream is completely rerouted through its notch. Impound the flow with the weir, making sure that water is not flowing beneath or around the side of the weir. Use mud or stones and plastic sheeting to get a good waterproof seal. The notch must be high enough to create a small spillway as water flows over its sharp crest.

Make sure that the entire flow of the spillway is going into the bucket. Record the time it takes to fill a measured volume on the Field Measurement Form. Repeat the procedure five times. If the cross-section contains multiple spillways, you will need to do separate determinations for each spillway. If so, clearly indicate which time and volume data replicates should be averaged together for each spillway; use additional field measurement forms if necessary.

Neutrally-Buoyant Object Procedure

In streams too shallow to use the velocity-area method the neutrally-buoyant object method may be employed. This procedure involves measuring the time it takes a floating object to pass a known stream distance. This is done using buoyant objects that float low in the water such as key limes, sticks, or small rubber balls. The following steps should always be followed to ensure accurate results.

1. Mark off on the stream bank the starting and ending points. These should be far enough apart to allow at least 10 seconds of drift time between them. Record the distance between the two points in feet to the nearest 0.1 foot.

2. Place the buoyant object in the water upstream of the starting point and begin timing on a stopwatch when the object reaches the start line.

3. Record the elapsed time till the object crosses the end line, in seconds to the nearest 0.1 seconds.

4. Repeat steps two and three at least three times to develop an average time of passage in seconds.

5. Average velocity is equal to distance divided by average elapsed time.

6. Measure cross sectional depths and width in the middle of the flow path to acquire a cross sectional wetted area. This can be used along with the average velocity to determine flow in cubic feet per second.

Observations and Calculations

Discharge is usually determined after collecting water chemistry samples. Although discharge is part of the physical habitat indicator, it is presented as a separate section.

Flow data will be recorded on the Discharge Flow Recording forms or on a field computer. Any additional observations will be recorded in field notebooks. Calculations will be performed using hand held calculators to determine flow volume in CFS. The calculated volume will be evaluated for reasonableness and may be repeated if there are questions regarding the flow accuracy. A sketch of the stream cross section can be added to the flow form, especially if there were critical conditions that may have impacted the flow measurement.

The following calculations are used to calculate flow/discharge:

a. Calculate Area (A) by multiplying Width (W) X Depth (D).
b. Calculate discharge (Q) by multiplying Velocity (V) by Area (A).
c. Calculate total Area (A) and Discharge (Q) in each respective column.

d. Calculate average Velocity (V) by dividing summed Discharge (Q) by summed area or by taking an average of each velocity measurement.

QA/QC Stream flow Current Velocity Meters

Field teams will be using an electromagnetic type meter (e.g., Marsh McBirney Model 201 D). General guidelines regarding performance checks and inspection of current meters are presented below. If required the operating manual for the specific meter will be referenced for information as necessary.

Periodically or prior to field studies, the meter is calibrated to a zero value using a bucket of quiescent water and the following routine. The probe is placed in the bucket and allowed to sit for 30 minutes with no disturbance. The velocity value obtained should be 0.0 $\pm$ 0.1. The meter is adjusted to zero if the value is outside this range.

Duplicate flow measurements are taken for at least one in ten sites where flow is measured. Duplicates do not have to be taken at the same exact location but should be in the same reach to avoid potential water gains or losses. A relative percent difference (RPD) is calculated, and must be less than 20% to be within control parameters. Any values exceeding 20% are investigated to determine the cause and the need for corrective action. When possible flow measurement values are compared to gauging station data or data from fixed flow meters as a QA check

7.0 Semi-Quantitative Habitat Assessment SOP

Purpose

Physical habitat in streams includes all those physical attributes that influence or provide sustenance to biological attributes, both botanical and zoological, within the stream. Stream physical habitat varies naturally, as do biological characteristics; thus, habitat conditions differ even in the absence of point and anthropogenic non-point disturbance. Within a given ecoregion, stream drainage area, stream gradient and the geology are likely to be strong natural determinants of many aspects of stream habitat, because of their influence on discharge, flood stage, and stream energy (both static and kinetic). Kaufmann (1993) identified seven general physical habitat attributes important in influencing stream ecology and the maintenance of biological integrity:

1) channel dimensions,
2) channel gradient,
3) channel substrate size and type,
4) habitat complexity and cover,
5) riparian vegetation cover and structure,
6) anthropogenic alterations, and
7) channel-riparian interaction.

Land use activities can directly or indirectly alter any and/or all of these attributes. Nevertheless, the trends for each attribute will naturally vary with stream size (drainage area) and overall gradient. The relationships of specific physical habitat measurements described in this section to these seven attributes are discussed by Kaufmann (1993). Although they are actually biological measures, aquatic macrophytes, riparian vegetation, in-stream habitat and canopy cover are included in this and other physical habitat assessments because of their role in habitat structure and light inputs.

The objectives of a habitat characterization are to:

1) assess the availability and quality of habitat for the development and maintenance of benthic invertebrate and fish communities, and
2) evaluate the role of habitat quality in relation to the attainment of designated uses and biological integrity.

There are three main headings for the components of the physical habitat characterization each with several categories. Measurements for each of the components (14 categories total) are recorded on copies of a two-page field form entitled Stream Habitat Assessment (Semi-Quantitative), and include:

1) Channel Morphology
   a) Reach Length Determination
   b) Riffle-Pool Sequence
   c) Depth and Width Regime

2) In-Stream Structure
   a) Epifaunal substrate
   b) In-Stream Habitat
   c) Substrate Characterization
   d) Embeddedness
   e) Sediment Deposition
   f) Aquatic Macrophytes and Periphyton
3) Riparian Characteristics
   a) Canopy Cover
   b) Bank Stability and slope
   c) Vegetative Protection
   d) Riparian Vegetative Zone Width
   e) Land-use Stream Impacts

Field physical habitat measurements from a field habitat characterization are used in conjunction with water chemistry, temperature, macroinvertebrate and vertebrate (typically fish) community analyses, and other data sources to assess attainment of designated uses, potential aquatic life impacts from stressors or maintenance of an expected level of biological integrity.

These procedures are intended for evaluating physical habitat in wadeable streams, but may be adapted for use in larger streams as necessary. The field procedures applied to this characterization are most efficiently applied during low flow conditions and during times when terrestrial vegetation is active, but can also be applied during spring seasonal conditions when higher base flows are present; or during fall or winter low flow conditions. This collection of procedures is designed for monitoring applications where robust, quantitative or semi-quantitative descriptions of habitat are desired. This semi-quantitative habitat procedure is usually used in conjunction with the *General Physical Habitat Characterization* and the *Qualitative Habitat Assessment* to provide a detailed view of the streams habitat condition.

The habitat characterization protocol provided herein differs from other rapid habitat assessment approaches (e.g., Plafkin et al., 1989, Rankin, 1995) by employing a, systematic spatial sampling that minimizes bias in the placement and positioning of measurements. Measures are taken over defined channel areas and these sampling areas are placed systematically at spacing that is proportional to the length of the entire study reach. This systematic sampling design provides resolution appropriate to the length of the study reach. The habitat assessment protocol summarized in this SOP is based on those of USEPA in their EMAP and RBP procedures (Lazorchak, 1998 and Barbour, 1999), USGS NAWQA program (Fitzpatrick, 1998) and Missouri Department of Natural Resources ESP (Sarver, 2000).

We strive to make the protocol objective and repeatable by using previously developed methods to produce repeatable measures of physical habitat in place of estimation techniques wherever possible.

Two people typically complete the specified assessment, including stream flow measurements, in about two hours of field time. However, the time required can vary considerably with channel characteristics.

The procedures are employed on a sampling reach of length equal to 20 times the bankfull width, or at least 100 yards of in-stream distance. The semi-quantitative habitat sampling reach length should coincide as much as possible with that of the fish and macroinvertebrate

collection reaches. Measurements are taken in each of 10 sub-reaches, which are systematically placed, at intervals equal to approximately one tenth (1/10) the length of the represented study reach. Measurements and observations for each habitat characteristic are made in each of the sub-reaches as the assessment team moves along the stream channel. An average or total of the scores for each of the 10 sub-reaches is then calculated resulting in a mean value for each characteristic for the entire reach.

Procedure

The habitat assessment will be conducted within (or to the extent possible) the stream reach from which the benthic and fish communities are to be characterized. The physical habitat will be characterized from measurements and observations of stream attributes made within 10 sub-reaches. The team assessing habitat should move along the stream channel (near the thalwag) observing habitat characteristics within each sub-reach. A description of and the rational for measuring each of the attributes is provided below. The details of how these attributes are recorded/evaluated are also described below in the following sections.

Channel Morphology

Channel morphology (or geomorphology) is a characterization of the shape of the stream channel including measurements and/or visual estimates of channel dimensions and riffle-pool sequences. i.e. a measure of the amount of riffles, runs and pools that occur in a given reach.

The channel observed includes that portion of the stream between the base flow wetted area and the top of the normal high water channel often referred to as the bankfull stage (Figure 1.) The "bankfull" or "active" channel is defined as the channel that is filled by moderate-sized flood events that typically occur every one or two years. Such flow levels are on the verge of entering the flood plain and are believed to control channel dimensions in most streams.

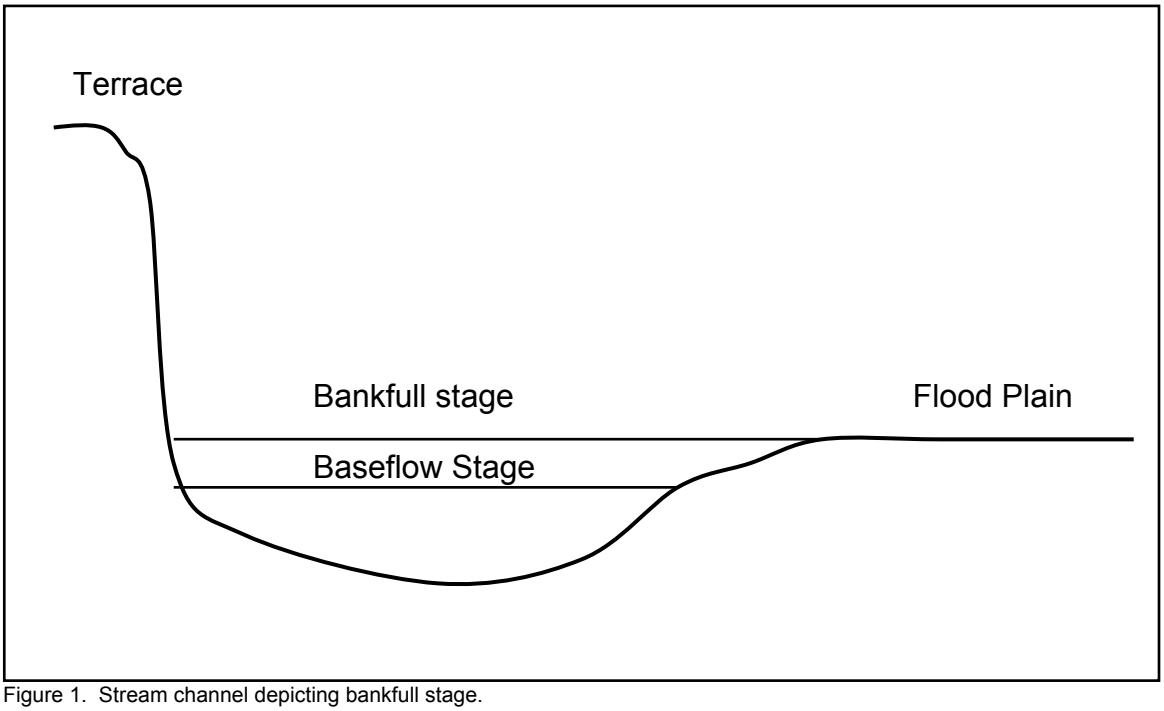

Figure 1. Stream channel depicting bankfull stage.

1) Reach and Sub Reach Length Determination

Reach length is determined by measuring bankfull width at five locations, deriving an average bankfull width and multiplying that average by 20. First, bankfull stage or normal high water is identified at 5 transects within the study area. At least two separate riffles (or alternatively runs in streams not exhibiting riffle morphology) must be included among the 5 transects. Then bankfull width and depth (bankfull depth can only be determined from the riffle/run morphology) is determined from the 5 streams transects and recorded on the record sheet. Transect locations should be selected to include each prominent morphology type represented in the stream. Bankfull widths are measured to the nearest foot and bankfull depths are measured to the nearest 1/10 foot using a wading rod and tape measure/range finder, respectively. This total reach length (average width x 20) is then divided by ten to determine the length of each of ten sub-reaches for analysis. Analysis of the first sub-reach should begin at the head of a given stream morphology type (i.e. riffle, run or pool).

2) Riffle-Pool Sequence

Stream morphology refers to the abundance and placement (sequencing) of riffles, runs, and pools in a stream system. This sequencing is an indicator of a streams hydrological regime and stability as well as a determinant of its potential to sustain diverse aquatic communities. Within the overall reach and beginning at the head of a morphological type (riffle, run or pool) the length of each morphological type in the sub-reach should be measured using a tape measure range finder or and recorded on the record sheet. The sequence of each morphological type should be depicted for that sub-reach on the record sheet using the provided notations so as to create a map or drawing to the location of each riffle, run or pool. The resulting measurements should provide a quantitative measure of the percent of the overall study reach representing each stream morphological type (i.e. 40% riffle, 30% run, 30% pool, etc).

3) Depth and Width Regime

Average stream depth and width will be calculated in riffles (or runs in the absence of riffles) and pools in each sub-reach as follows. Depths will be measured across the stream, similar to that depicted in Figure 2, in a representative section of each riffle, run, and pool within the sub-reach. Depths are generally taken in the thalwag (deepest area in stream channel) and approximately half way between the thalwag and the left and right banks. An estimated average depth for riffles, runs, and pools occurring in a sub-reach is derived from the cross-sectional depth measurements and recorded on the record sheet to the nearest 1/10 foot.

An average thalwag depth is also recorded on the record sheet to the nearest 1/10 foot. Once completed for all 10 sub-reaches this should provide accurate semi-quantitative measurements of riffle, run and pool average depth and depth variability across the entire stream reach.

Stream wetted widths will be measured along a transect in a representative section of each riffle, run and pool in the sub-reach. An estimated average width for each morphological type in a sub-reach should be recorded on the record sheet to the nearest foot. Once completed for all 10 sub-reaches this should provide accurate semi-quantitative measurements of riffle, run and pool widths across the entire stream reach.

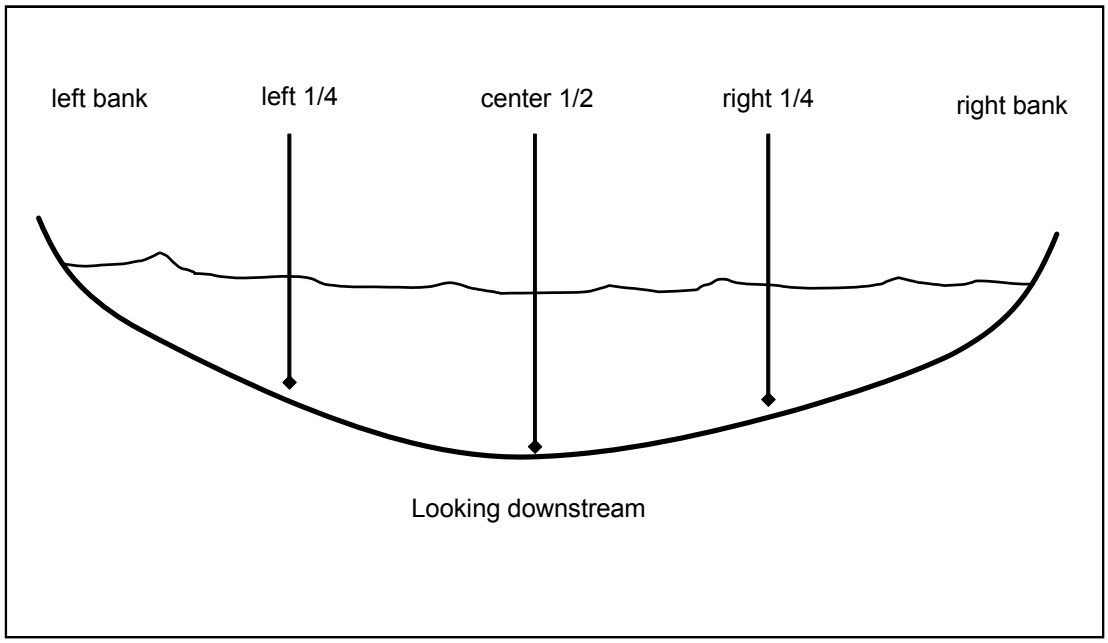

Figure 2. Approximate position of measurements across transect.

In-Stream Structure

In-stream structure describes the characteristics of the stream within the wetted perimeter that makes up the habitat suitable for colonization of aquatic biota. This includes information about natural substrates (gravel, boulders, etc), aquatic plants and algae, and debris that has been washed into or fallen into the stream, such as logs, leaves, etc. A stream capable of sustaining diverse aquatic communities will contain a variety of in-stream structure including some that is permanent and some that is mobile during high flow events.

4) Epifaunal Substrate (Macroinvertebrates)

   Epifaunal substrate refers to the area on the bottom of the stream (entire wetted bottom) where macroinvertebrates inhabit. This attribute is scored as a percentage of the stream bottom in a sub-reach which contains substrates suitable for macroinvertebrate colonization. Scoring for this attribute should rely heavily on the stability of the substrate, the size of the interstitial spaces, and the cleanliness (not covered in thick algae or sediment deposits) of the substrate. Cobbles and coarse gravel will score higher percentages as they contain larger interstitial spaces for colonization, while sand and silt would score lower since they provide little spaces. In addition, root wads along the bank would score higher as they are more stable features than are depositional areas or small woody debris. Epifaunal substrate is scored on a “percent stable habitat coverage” within the sub-reach.

5) In-Stream Habitat (Fish)

   In-stream habitat refers to the habitat features within the wetted area of the stream sub-reach which are available for fish colonization. This attribute is scored as the percentage of the wetted stream bottom in a sub-reach which is covered with fish

habitat. Similar to the epifaunal substrate attribute, substrates composed of cobbles and boulders score higher for fish cover as they provide better spaces for colonization. Other habitats that score high are large woody debris (individual logs with diameter >4 inches or complex woody structures composed of rootwads, logs, or limbs with diameter of 1.5 ft. or greater)and undercut banks. While habitats that score lower are those such as depositional areas, leaf packs, and fine sediments or sand. In-stream habitat is scored on a “percent stable habitat coverage” within the sub-reach.

6) Substrate Characterization

The dominant stream substrate size classification for riffles and pools within each sub-reach will be recorded on the record sheet. Only substrates within the wetted perimeter are evaluated. This information will be used to characterize the similarities and or differences in substrate structure and complexity in the riffles, runs and pools of the study reach as it relates to the development and maintenance of the systems biological integrity.

Classify the particle into one of the size classes listed on the Semi-Quantitative Habitat Assessment Field Form based on the size of the intermediate axis (median dimension) of its length, width, and depth. This "median" dimension is the sieve size through which the particle can pass.

Bedrock	smooth or rough
Boulder	>25 cm (>10 in.)
Cobble	6-25 cm (3 – 10 in.)
Coarse Gravel	1.6 – 6 cm (<3 in.)
Fine Gravel	0.2 – 1.6 cm
Sand	<0.2 cm
Silt/Mud/Clay	fine, not gritty

Always make notations for unusual substrates such as concrete or asphalt and denote these artificial substrates as "other" and describe them in the comments section of the field data form. Code and describe other artificial (such as large appliances, tires, car bodies, etc.) substrates in the same manner.

7) Embeddedness

Embeddedness is the fraction of a particle's surface that is surrounded by (embedded in) sand or finer sediments on the stream bottom. By definition, the embeddedness of sand, silt, clay, and muck is 100 percent and the embeddedness of hardpan and bedrock is 0 percent.

For this attribute estimations are not made per sub-reach but for the entire stream reach as a whole. An estimation of the "percent embedded" is recorded for coarse riffle substrates in the study reach. This is accomplished by removing 12 pieces of cobble, gravel, or small boulders in at least two different riffles (three maximum) and recording the percent embedded for each. Percent embedded can be visually observed as the darkened portion of the coarse substrate that was buried in the streams fine bed material. If the darkened area covers half the coarse substrates height than the percent embedded is 50%, etc (Figure 3.)

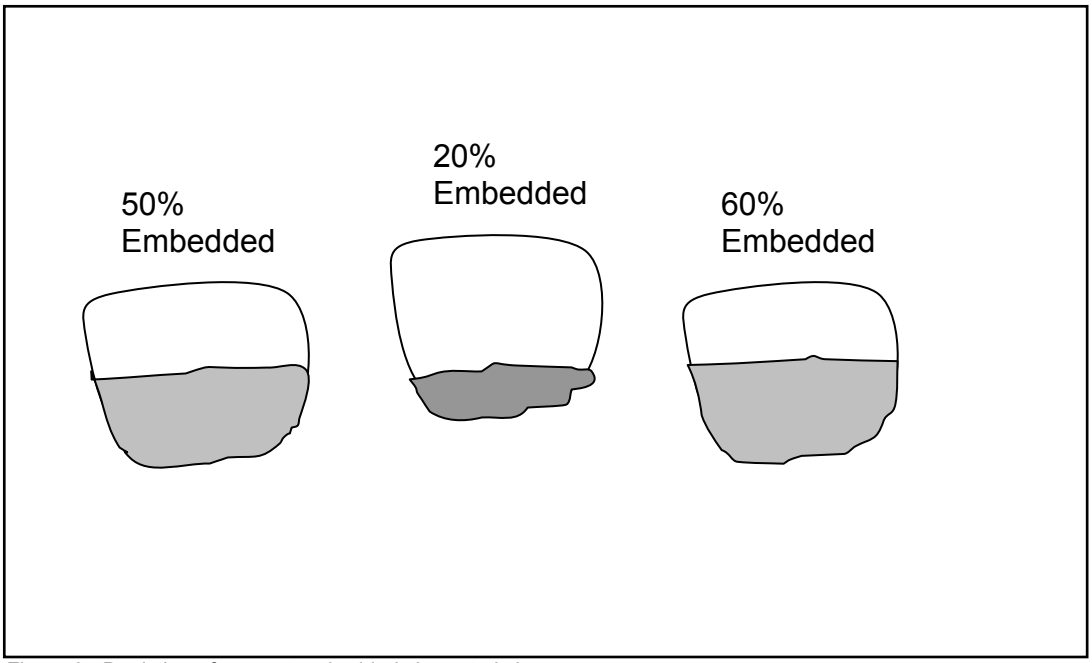

Figure 3. Depiction of percent embedded characteristics.

8) Sediment Deposition

   The sediment deposition attribute refers to the amount of stream bottom (in the wetted perimeter) that is covered by fine sediments and/or particulate organic matter. This attribute is scored as a percentage of the wetted portion of the stream bottom in each sub-reach which is covered by such loose materials.

9) Aquatic Macrophytes and Periphyton Coverage

   An estimate of the percentage of area covered by macrophytes and periphyton in a sub-reach is made and recorded for riffles, runs and pools. Macrophytes refers to aquatic plants that grow in the stream (both emergent and submerged), and periphyton refers to algae that grows on fixed surfaces. This attribute helps biologists determine stream productivity from a nutrient enrichment perspective and also for the availability of food sources for aquatic biota.

Riparian Characteristics

The riparian area includes the area from the stream bank in a direction away from the stream into the upland areas. It is these stream-side riparian zones that ultimately help shape the stream and provide organic material as nutrients to the aquatic system. A well developed riparian area protects stream banks form erosion, provides shading, inputs nutrients, provides materials as habitat (in-stream structure) and filters run-off entering the stream. In the absence of well developed riparian zones the stream is more impacted by encroaching land-uses.

10) Canopy Cover

Canopy cover (percent stream shading) over the stream is determined for each of the sub-reaches. Estimates of cover are made by looking into the canopy over the stream channel. Estimates are made from mid-channel and each quarter channel to determine the average percent canopy cover for the width of the stream in the sub-reach. Percent stream shading at each measurement point can be estimated visually or by use of a spherial densiometer.

11) Bank Stability, Height, and Slope

Bank stability is an important attribute that is an indication of a stream reaches overall hydrologic equilibrium. A bank's stability also determines its ability to provide stable habitat for biota and its propensity to release large sediment yields to the stream, which ultimately cause high turbidity and deposition in downstream reaches. The right and left banks are classified separately according to the following categories:

Score 9-10 = Stable, little evidence of erosion, < 5% bank eroding
Score 6-8 = Moderately stable, some evidence of new erosion, 5-29% bank eroding
Score 3-5 = Moderately unstable, obvious new erosion, 30-59% bank eroding
Score 1-2 = Unstable, most of bank actively eroding, 60-100% bank eroding

Banks composed of sands and gravels are much less stable than banks composed of silt/mud/clay or cobbles. The density of well rooted (more permanent) vegetation and root structure also help to improve a banks stability. Stability is determined by visual observation.

Average bank height (in feet) in each sub-reach is recorded for each bank (left & right). Bank height affects stability of a bank and is an indicator of erosion potential. Bank height can also be an indicator of vertical movement within the stream (i.e. down-cutting). Bank height is estimated by visual observations.

Average bank slope (in degrees) in a sub-reach, is recorded for each bank (left and right). Bank slope affects the stability of a bank and is an indicator of past erosion. A gentle slope may average 30º while a steep or undercut bank may average 90º or 100º, respectively. Bank slope is estimated by visual observation.

12) Vegetative Protection

Bank vegetative protection is evaluated as a percent of the bank surface area which is covered by stable riparian vegetation and their associated roots in a sub-reach. The percent protected is that portion that is stable and not prone to erode by high flows. Each bank (right and left) is assessed separately and the value recorded on the record sheet. Banks are assessed by visual observation from the edge of the water to the top of the first terrace or normal top of bank.

13) Riparian Vegetative Zone Width

Riparian zone width encompasses the area from the top of the normal stream bank outwards into the upland area. The broader the riparian vegetative zone width the more protected the stream banks are from alteration, the fewer pollutants will enter the stream

from run-off, and the more available food sources there are to be deposited into the stream from the surrounding forest. Riparian zone width is scored for each bank in a sub-reach according to the following scale:

Score 9-10 = Riparian Zone Width > 18 meters
Score 6-8 = Riparian Zone Width 18 - 12 meters
Score 3-5 = Riparian Zone Width 11 - 6 meters
Score 1-2 = Riparian Zone Width < 6 meters

The width of the riparian zone is estimated by visual observation. Typically, particularly if stream banks are tall, the observation is from the top of the stream bank looking outward. It is often not possible to determine riparian width from the stream.

14) Land-Use Stream Impacts

Significant Alteration of the land-uses in the immediate riparian area can have detrimental affects on the stream habitat and biota. Urban and agricultural activities are often considered the more prominent of those land-uses that may impact a stream. These impacts are assessed by indicting a specific land-use impact associated with a sub-reach (on either bank) on the record sheet and assigning a degree of impact score to the land-use. Land use assessments should be made while arriving or leaving the site by observation of land uses in the general area of the stream. The following land-use categories and impact scoring system are provided:

Land-uses:
C = Cattle,
R = Row Crops,
U = Urban encroachment,
I = Industrial Encroachment, and
O = Other (noted on field form)

Scoring:
0 = no land-use impacts,
1 = minor impacts,
2 = moderate impacts, and
3 = major impacts

Scoring and Analysis of Habitat Assessment Data

Scores from the Semi-Quantitative Habitat Assessment can be utilized in two different ways. First, data collected for each attribute (assessment category) can be used independently to describe the study reach collectively. This method results in information such as: average riffle depth, average pool width, %riffle in entire reach, average bank stability, average (median) substrate size class in pools and riffles, mean %canopy cover, etc. Second, the data collected during the assessment can be used in conjunction with the Qualitative Habitat Assessment procedure to score each of the ten “qualitative” indices with near quantitative accuracy (semi-quantitative). A combination of the two methodologies should be incorporated into all intensive aquatic biota field studies where habitat assessment accuracy and repeatability is critical. The following sections outline the scoring of the qualitative habitat indices using the semi-quantitative data.

High Gradient (riffle-pool stream complexes)

1) Epifaunal Substrate / Available Fish Cover

Average values from semi-quantitative categories 4 (Epifaunal Substrate) and 5 (In-Stream habitat) are combined into an overall average percent coverage and used to score this metric.

The following table presents the scoring criteria:

Rank	Optimal	Sub-Optimal	Marginal	Poor
% Coverage	>70%	40%-70%	20%-39%	<20%
Score	20 -16	15 -11	10 - 6	5 - 1

2) Embeddedness

Reach average percent embedded (from category 7) is used directly to score this metric.

Rank	Optimal	Sub-Optimal	Marginal	Poor
% Embedded	<25%	25%-50%	49%-75%	>75%
Score	20 -16	15 -11	10 - 6	5 - 1

3) Velocity / Depth Regime

Semi-Quantitative categories 2 (Riffle-Pool Sequence) and 3 (Depth and Width regime) along with flow and velocity data collected in the reach is used to score this metric. Use the following table to determine which regimes are present:

Rank	Slow-deep	Slow-shallow	Fast deep	Fast shallow
Velocity	<1 fps	<1 fps	>1 fps	>1 fps
Depth Regime	>1.6 feet	<1.6 feet	>1.6 feet	<1.6 feet
Typical Morphology	Deep pool	Shallow pool	run	riffle

If a reach has deep and shallow pools, and distinctive run and riffle morphology, then you have at least three regimes and possible all four regimes. Score each rank lower if shallow regimes are the missing regimes. Scoring is applied as per the following table.

Rank	Optimal	Sub-Optimal	Marginal	Poor
No. Regimes	Four regimes present	Three regimes present	Two regimes present	One regime present
Score	20 -16	15 -11	10 - 6	5 - 1

4) Channel Alteration

Scored from visual assessment of entire reach. Not aided by semi-quantitative attributes.

5) Sediment Deposition

Reach average percent bottom affected by deposition (from category 8) is used directly to score this metric.

Rank	Optimal	Sub-Optimal	Marginal	Poor
% Bottom Affected	<5%	5%-30%	31%-50%	>50%
Score	20 -16	15 -11	10 - 6	5 - 1

Utilize the lower end of each scale to represent reaches where recent sediment bar formation is evident.

6) Frequency of Riffles

Using semi-quantitative category 3 (Depth and Width Regime) the average width of the stream is determined as the average of riffle and pool widths combined. Using category 2 (Riffle-Pool Sequence) the distance between riffles can be calculated using the sequencing notations and the morphological lengths. The table presented below should be used to develop scores for this metric.

Example: a reach with an average width of 18 feet, with 4 riffles separated by a 50 foot pool, a 20 foot run, and a 100 foot pool would result in an average distance between riffles of 57 feet. Therefore, the ratio = 57/18 = 3.2 and would rank as Optimal (score @ 18).

Rank	Optimal	Sub-Optimal	Marginal	Poor
Ratio (distance between riffles : stream width)	<7 : 1	7 – 15 : 1	16 -25 : 1	>25 : 1
Score	20 -16	15 -11	10 - 6	5 - 1

In continuous riffle streams the consistent placement of boulders and logs provides scores in the highest range of the optimal category.

7) Channel Flow Status

Scored from visual assessment of entire reach. Not aided by semi-quantitative attributes.

8) Bank Stability

The average bank stability score for each represented bank from the semi-quantitative assessment (category 11) is directly applied to the qualitative assessment scoring for this metric (i.e. an average reach score of 8 for the right bank and 7 for the left bank gets transferred directly to the qualitative score sheet as such.)

9) Vegetative Protection

Reach average percent bank protected (from category 12 of the semi-quantitative record sheet) is used directly to score this metric for the right and left bank.

Rank	Optimal	Sub-Optimal	Marginal	Poor
% Protected	>90%	70% - 90%	50% - 69%	<50%
Score	10-9	8-6	5-3	2-1

10) Riparian Vegetative Zone Width

The average riparian zone width score for each represented bank from the semi-quantitative assessment (category 13) is directly applied to the qualitative assessment scoring for this metric (i.e. an average reach score of 8 for the right bank and 7 for the left bank gets transferred directly to the qualitative score sheet as such.)

Alternative Metrics for Low Gradient Streams (pool dominated complexes)

1) Pool Substrate Characterization (replacement for Embeddedness)

Using the Substrate Characterization data from the semi-quantitative assessment (category 6) and the aquatic vegetation assessment (category 9) the following table may be used to score this metric.

Rank	Optimal		Sub-Optimal	Marginal	Poor
Substrate	Cobble or Gravel		Sand/Silt/Clay	Sand/Silt/Clay	Bedrock or Clay Only
Macrophytes Present	Yes	No	Yes	No	No
Score	20 - 18	17 - 16	15 - 11	10 - 6	5 - 1

2) Pool Variability (replacement for Velocity/Depth Regime)

Semi-Quantitative categories 2 (Riffle-Pool Sequence) and 3 (Depth and Width regime) are used to help score this metric. Use the following table to determine pool variability.

Pool Characteristic	Large-Deep	Large-Shallow	Small-Deep	Small-Shallow
Size	Length ≥ Width	Length ≥ Width	Length < Width	Length < Width
Depth	≥3.2 feet	< 3.2 feet	≥3.2 feet	< 3.2 feet

An equal balance of all four pool types achieves higher scores. A prevalence of shallow pools scores lower.

3) Channel Sinuosity (replacement for Frequency of Riffles)

This metric is assessed separately from the semi-quantitative data. It can be estimated in the field, measured during a longitudinal survey or calculated from current aerial photographs.

9.0 Benthic Macroinvertebrate Protocol SOP

Purpose

Benthic invertebrates inhabit the sediment or live on the bottom substrates of streams. The diversity and the presence of an expected level of benthic community reflect the maintenance of a systems biological integrity. Monitoring these assemblages is useful in assessing the status of the water body and detecting trends in ecological condition. Benthic communities respond to a wide array of stressors in different ways so that it is often possible to determine the type of stress that has affected a macroinvertebrate community (e.g., Klemm et al., 1990). Because many macroinvertebrates have relatively long life cycles of a year or more and are relatively immobile, macroinvertebrate community structure can be a function of present or past conditions. The benthic invertebrate community also reflects the effects of habitat availability, and the long-term exposure to physical and chemical properties of the water in which they develop and live.

The benthic macroinvertebrate protocol is intended to evaluate the biological integrity of wadeable streams for the purpose of detecting stresses on community structure, assessing the relative severity of these stresses, and determine the maintenance of the designated uses. The approach is based on the *Rapid Bioassessment Protocols for Wadeable Streams and Rivers* published by the U.S. Environmental Protection Agency (Barbour, 1999). Variations of the approach are utilized by the U.S. Geological Survey for their National Water-Quality Assessment Program (NAWQA; Cuffney et al., 1993) and by the EPA in their Environmental Monitoring and Assessment Program (EMAP, Lazorchak, 1998). The protocol requires only one person and is the preferred macroinvertebrate collecting method where habitat is variable (a second person can be used for water safety and to keep time and record information on the field forms). The methodology used by GBMc & Associates is a modification of the EPA "Multi-habitat Approach" (Barbour, 1999) designed to better assess pool dominated streams and riffle dominated streams using similar but different collection techniques. The approach can be generally considered a semi-quantitative methodology, in that there is some measure of abundance on a per sample basis and data is comparable to other collections. This protocol typifies the methodology used in GBMc & Associates aquatic biologists. However, variations on this approach is commonly utilized to fit specific state monitoring program methodology, such that direct collection comparisons can be made.

Procedure

Pool Dominated Stream/Multihabitat Approach (Timed Method)

An aquatic dip net is used to sample all available microhabitats present within the stream reach. Sampling is conducted using kicking, jabbing, and sweeping techniques. Kicking involves placing the net on the substrate and kicking the substrate upstream of the net allowing the dislodged invertebrates and debris to float into the net. Jabbing involves quick jabs of the net into submerged or exposed habitat types (macrophytes, root wads, branches, etc.) in an effort to dislodge invertebrates for capture. Sweeping entails sweeping the net through or above a habitat type to dislodge and capture invertebrates. Sweeping is often done above sandy and silty areas and root wads so as to capture as little debris as possible but still dislodge organisms. Sampling effort is timed on a stopwatch for a total of three minutes. Only time

actually spent kicking, jabbing, or sweeping is allowed to accrue on the timer. The number of kicks, jabs or sweeps may be tallied to provide a measure of area sampled. That is, for every kick, jab or sweep approximately 0.25m^2 is sampled, dependent on the size of the net and the approach utilized by the collector. The net is periodically emptied into a bucket for transport of the sample up and down the stream reach.

Riffle Dominated Stream Approach (Timed Method)

An aquatic dip net (generally the rectangular sort at least 16" wide) is used to sample the riffle habitat in a stream. The net is placed on the stream bottom and the substrate upstream of the net is vigorously kicked or raked by the sampler to dislodge invertebrates allowing them to drift into the net. Sampling is conducted in this manner at different riffle locations throughout the study reach for a total kick time of 5 minutes. It may be useful to sweep the net through the dislodged and drifting debris in an effort to pick up as many invertebrates as possible. Kick time is monitored with a stop watch allowing time to accrue only during kicking and subsequent drift time. The net contents are placed in a bucket for holding after each riffle sample is collected. An area of approximately 1m^2 should be kicked at each location sampled, and the total number of locations sampled should be tallied to provide an estimate of total sampled area.

Riffle Focused Multi-habitat Approach (Area Method)

An alternate sampling protocol for collection of macroinvertebrates in riffle dominated streams involves the collection of all dominant habitats with an emphasis in the riffles. In this protocol 5m^2 of riffle habitat are sampled as described above and 5m^2 of non-riffle, pool and run habitat (root wads, deposition, vegetation, etc.) are sampled as described in the pool dominated stream protocol. The two samples (riffle and non-riffle) are kept in separate buckets and processed separately so that analysis in the lab will provide a riffle collection and a run/pool collection.

Sample Processing

After collection, samples are initially sorted and concentrated using a series of U.S. standard sieves the smallest of which has a #35 mesh with an opening size of 500μm.

One of two processing methods may be utilized. Either method can be completed in the field.

1. Random Pick Method - Random sub-samples of the concentrated sample will be placed on a white sorting tray from which the macroinvertebrates will be removed. A 100 organism sub-sample will be randomly picked from the tray and field identified to the lowest possible taxon. A representative amount of the concentrated sample is picked to be sure that each type of debris (i.e. leafs, algal mats, sediment, etc.) have been checked for macroinvertebrates.
2. Random sub-sampling – The sample collected is condensed and spread evenly in a sorting tray (caton style or similar). The tray is composed of several equal sized grids and random numbers are drawn (or rolled on dice) to determine which grid(s) is picked. The debris from selected grids is removed and placed in a tray. All organisms from the debris, from a single grid, are removed This process is continued until the appropriate sample size (100, 200 etc.) within ±10% is achieved. It may take on e grid or several grids, dependent on organism abundance, top attain the

required sample size. Once picking of a grid begins all organisms must be removed regardless of surpassing the target sample size. As an alternative to the grided sorting tray a 4" ring (crochet style) may be tossed at random into a tray debris spread evenly. All the debris within the ring is removed and processed in the same manner as for a grid. This process is also repeated until the required sample size is attained.

The sub-samples will be preserved in Kaylee's Solution (a fixative, 15 pts. ethanol, 6 pts. formalin, 1 pt. glacial acetic acid, 30 pts. deionized water) or 70% ethanol for lab verification of field identifications and as a voucher to be used if more detailed analysis becomes necessary. If the sample is placed in Kaylee's solution it is removed and placed in 70% ethanol within 7-days. Each sample is labeled inside with a waterproof label and outside with laboratory tape containing the following information:

- station I.D.,
- location (waterbody, county, state),
- project number,
- date/time,
- initials of collector, and
- collection method/duration.

After the random sample is collected, labeled and preserved, the larger debris items (e.g. leaves, sticks, rocks etc.) in the collected sample will be examined for clinging benthic macroinvertebrates. Any organisms will be removed prior to the debris being discarded. The remainder of the original sample not utilized in the selection of the sub-sample will be concentrated and retained as a voucher for the sample picking (sub-sampling) techniques used. The voucher samples will be preserved in either Kaylee's Solution (7-day maximum) or 70 % ethanol. Voucher samples will be held at GBM^c for a period of 24 months, from the conclusion of the study at which time the samples may be submitted to an academic zoological collection.

For each study site, a complete tabulation of taxa, numbers of individuals and their percent composition will be included on the Benthic Macroinvertebrates Field Data Form (attached). The first page of the form will include general information identifying the sample reach and investigators as well as site observations to include:

1. time sampled,
2. relative abundance of aquatic trophic level communities (periphyton, macrophytes, etc.),
3. percent of major habitats sampled,
4. percent of specific microhabitats sampled, and
5. relative abundance of the ordinal groups observed during sample collection.

The second page provides for the listing of the taxa comprising the 100 organism sub-sample and the field identifications and the numbers of each. Also included on page 2 are the general reach identifiers and preliminary summary sections to be used in the application of selected biometric scoring criteria.

All macroinvertebrate identifications shall be verified in the laboratory by experienced invertebrate biologists. Laboratory verification will be accomplished using general keys including but not limited to Merritt & Cummings, (1996); and Pennak, (1989). In addition more

taxa specific keys such as Mayflies of North and Central America (Edmunds et, al, 1976), Dragonflies of North America, (Needham & Westfall, 1975) or species specific keys developed for a state or region will be utilized for the laboratory verification of the field identifications.

Community Biometric Analysis

The qualitative samples are used to taxonomically characterize the aquatic community, identify indicator taxa and determine relative abundance of taxa and ecological types. The macroinvertebrate assemblages from each station are analyzed according to several benthic community biometrics. These will include richness (number of different taxa), EPT richness (number of different taxa represented in the orders Ephemeroptera, Plecoptera, and Trichoptera), percent EPT, percentage of dominant ordinal groups, species diversity as determined by the Shannon-Wiener diversity Index, a biotic index (measure of species tolerance to perturbation) such as Hilsenhoff's Biotic Insex (HBI) and and functional feeding group assessment. The analysis may also include the seven biometrics used by the State of Arkansas (ADPC&E, 1988) in their RBA scoring system, as well as other state specific biotic indexes. The biometric scoring activity will indicate the impacts to a benthic community when compared to the benthic community of different reaches, to demonstrate effects of point and or non-point source contributions between reaches.

Alternative Sampling and Processing Methodologies

An alternative processing technique may be used for the macroinvertebrate samples collected using the preceding RBA protocols. This technique involves concentrating the entire sample in the field and preserving it for transport to the laboratory. No on-site picking occurs. Once in the lab the sample is further concentrated and sorted to size using standard sieves. The sample is then placed into white sorting trays. Every macroinvertebrate in the sample is either picked out individually or a grid may be used to random pick a specific amount of debris. Once the entire sample has been picked and all organisms are in a single container the macroinvertebrates are poured onto a gridded and numbered sorting tray and swirled to distribute them randomly and as evenly as possible throughout the tray. Random numbers are then drawn that correspond to a given grid. All of the macroinvertebrates found in that grid are then removed and tallied. This process continues until a sample of sufficient size has been achieved, usually 100, 200, or 300 macroinvertebrates. The final sample size is dependant on the level of random error that is acceptable in the study. The macroinvertebrates are then identified to the lowest taxonomic level possible and the assemblage is analyzed as outlined above.

In addition to the semi-quantitative sampling protocols described in the preceding sections other semi-quantitative and quantitative methodology may be utilized where circumstances require a more detailed and precise assessment of the macroinvertebrate community. Quantitative and semi-quantitative protocols utilize sampling devices where a known area of substrate is sampled (i.e. 1.0 ft^2, 0.1 m^2, etc.) such as with a Surber Sampler or a Hester-Dendy , respectively. Quantitative techniques require processing of the entire sample collected to remove all macroinvertebrates captured. Macroinvertebrates are identified to the lowest possible taxonomic level, enumerated, and calculations of density per unit area are completed at varying taxonomic levels. Biometric analysis can then be completed using the same metrics as in the semi-quantitative assessment.

Quality Control

Field teams collecting macroinvertebrates are led by experienced aquatic biologists or ecologists. Field forms designed specifically for macroinvertebrate collection studies and set up to include all pertinent field data are completed for each sample site. All field forms are reviewed at the end of the study for completeness and accuracy. Identification of macroinvertebrates is verified in the laboratory by an experienced invertebrate biologist. Periodic spot checks to verify laboratory identifications are made by a qualified biologist on the team. Efforts are made to remain abreast of current research in macroinvertebrate biology and identification techniques through scientific journals and conferences. In addition, EPA document updates and new information on macroinvertebrate community assessment is tracked via the internet.

Macroinvertebrate duplicate samples are collected at one of ten study sites. In years where less than ten sites are sampled a minimum of one duplicate sample should be collected at a given site. Duplicate samples are treated the same way as the base sample for processing and identification. A similarity index is calculated for the duplicate and base samples. Index results indicating similarity less than 65% are considered out of control. In the case of an "out of control" condition the organism identifications will be assessed as will the collection techniques. Corrective action will be determined by the project manager and/or the senior biologist and could include adjustments to techniques or a re-sampling of the sites in question.

10.0 Fish Collection Protocol SOP

Purpose/Objective

The fish community supported in a stream is in direct response to available habitat, food sources, and water quality of that particular stream. The presence of a certain level of species richness and diversity along with a community structure similar to that expected in typical streams of a ecoregion are indicators of aquatic ecosystem health.

The objective of the fish community characterization is to collect and identify a representative sample of all except very rare species in the assemblage reflective of the relative abundance within the community. Backpack electrofishing equipment is used as the principal sampling gear supplemented by block netting and seining in habitats where flow, substrate and structure affect the capture of fish species. Other methods of fish sampling may be implemented when conditions are not adequate for backpack eletrofishing or seining; these may include, using boat electrofishing equipment and/or hook and line sampling equipment. Usually 2 – 4 team members will make up the sampling team involved in collecting the aquatic vertebrates.

Major factors that influence collecting include flows, water depth, in-stream obstructions, water turbidity, temperature and conductivity. The primary tool utilized in the fish collections will be a Smith-Root backpack electroshocker. However, seines and block nets may be utilized as necessary to adequately characterize a sampling reach. The shocker is equipped with an automated timing mechanism which records the amount of time that electricity is actually being applied, or “pedal down time” (PDT).

Sampling fish species to determine their proportionate abundance will be conducted after all water quality parameters and/or samples are collected but prior to the collection of the macroinvertebrate sample and habitat data.

Shocked fish will be captured with hand held dip nets and held in buckets while the sampling continued. The entire stream width within the sampling reach will be sampled. PDT time will continue for not less than 30 minutes unless the wetted habitat of any reach limits the PDT or if the principal investigator determines that a representative collection has been obtained. In addition to the PDT, the total collection time will be recorded.

Unless specified in a project specific sampling analysis plan (SAP), there will not be a maximum time limit for the collection period, however the collections may be terminated when the principal investigator determines that a representative collection has been obtained. Sampling information is recorded on the Fish Community Collection Form, general comments (perceived fishing efficiency, missed fish, fish released and gear operation suggestions) will be recorded on the lines provided on this form.

An effort to search for and collect fish will be completed at all targeted reaches, even if the stream is extremely small, and it appears that sampling may not collect any specimens. If no specimens are collected, complete the "NONE COLLECTED" field on the Fish Collection Form. Provide an explanation in the comments section of the form.

Procedure

Electroshocking

The procedure to sample with the backpack electrofisher unit is presented below:

Initially a decision will have to be made on what type of current to be used, alternating current (AC) or direct current (DC). AC flows between the anode and the cathode with an alternating direction of current flow. This alternating flow of current causes the fish to have strong muscle contractions, resulting in immobilization. AC has the highest electrofishing success rate but also poses the highest risk of permanent injury to the fish (particularly to larger specimens). DC is the direct flow of electrical current from the cathode to the anode. DC causes the fishes muscles to contract in such a way that the fish swim towards the anode probe. Muscle contractions occur until the fish is so close to the probe that the higher level of electricity stuns the fish. DC pulse length and duration can be adjusted with the shocking unit mode switches to more efficiently apply electricity that will draw fish to the probe without causing injury.

Make sure that the unit is full of properly mixed gas and oil (100:1), attach cathode (cable tail that drags behind operator, and anode (actual shocking probe with thumb switch to control electricity current)

Select the initial voltage based on the measured conductivity of the stream. For high conductivity water (300 - 1200 μS) use a voltage setting of 100 - 400 volts. For medium conductivity water (100 – 300 μS) use a voltage setting of 500 - 800 volts. For low conductivity water (10 – 100 μS) use a voltage setting of 900 - 1100 volts.

Select the initial frequency and/or wavelength based on the expected size of fish. Find a setting, using the number dial (1 – 16) and the letter dial (A – P), that will allow you to have maximum amperage output without overloading the unit, typically 0.7 – 1.9 amps. Start with a setting of I-6 and adjust letters then numbers to find your setting. A higher mode setting provides more amperage as does a higher voltage setting. Typical setting used by GBMc & Associates are I (5-7) and J (5-7) at a voltage of 100-300 volts.

Record the latitude and longitude of the starting location and the starting time for electrofishing. Start the electrofisher, place the generator on the 300VA position for full generator output, set the timer to zero, and depress the switch to begin fishing. Starting at the bottom of the reach, fish in an upstream direction. **Adjust voltage and waveform output according to sampling effectiveness and incidental mortality to specimens.** The backpack unit is equipped with an audio alarm that sounds when the output voltage exceeds 30 V. It also serves as an input current indicator for pulse

cycles greater than 5Hz. It begins as a strong continuous tone and begins to beep slowly at currents of 1.25 amps. It beeps faster as input current increases. In case of an overload (in excess of 3 amps), the beep becomes very rapid and the overload indicator comes on. Release the anode switch and adjust voltage and waveform and continue fishing.

When fishing, slowly sweep the anode wand from side to side in the water in riffles and pools. Sample available cut-bank and snag habitat areas as well as riffles and pools. Move the wand in and out of large snags or deep cuts or release the electrode switch, move the wand away slightly, depress the switch again and sweep the wand away from the cover to draw fish out into open. In fast, shallow water, it may be more effective to use a seine or a couple of handheld nets as a block net; sweep the anode and fish downstream into the net.

In streams wider than can be effectively sampled during a single pass (generally 5 ft or more), it may be necessary to work from the midline of the stream channel to the banks. Be sure that deep, shallow, fast, slow, complex, and simple habitats are all sampled. In stretches with deep pools, fish the margins of the pool as much as possible, being extremely careful not to step into deep water.

One or two netters follow along beside or slightly behind the person operating the electrofisher (on the anode side). Each netter uses an insulated dip net to retrieve stunned individual fish, which are then deposited into a bucket carried by one of the netters for later processing

At the completion of electrofishing, record the location, note the PDT, total sampling time, the total distance sampled, and information obtained while sampling. Record this information on the Fish Collection Form or in a team member's field notebook.

Electrofishing Precautions

Because fishes and amphibians are collected using portable electrofishing units, safety procedures must be followed meticulously at all times. Primary responsibility for safety while electrofishing rests with the principal investigator. Electrofishing units have a high voltage output and may deliver a dangerous electrical shock. While electrofishing, avoid contact with the water unless sufficiently insulated against electrical shock. Use chest waders and rubber gloves to prevent the chance of electric shock

Avoid contact with the anode and cathode at all times due to the potential shock hazard. While electrofishing avoid reaching into the water. If it is necessary for a team member to reach into the water to pick up a fish or something that has been dropped, do so only after the electrical current has been interrupted and the anode is removed from the water. Do not resume electrofishing until all individuals are clear of the electroshock hazard. The electrofishing equipment is equipped with a 45^{o} tilt switch that interrupts the current and may shut off the unit completely in the event the person carrying the unit

falls. Do not make any modifications to the electrofishing unit that would bypass the unit's automatic shutoff features.

Electrofishing equipment will not be utilized near unprotected people, pets, or livestock. Activity will be discontinued during thunderstorms or heavy rain.

Seining

Seining may be used in conjunction with electrofishing to ensure sampling of those species which may otherwise be under presented by an electrofishing survey alone (e.g., darters, madtoms, and benthic cyprinids). Seining may also be used in sites where the stream is too deep for electrofishing to be conducted safely or in turbid, simple, soft-bottomed streams where it is more effective.

Depending on the particular use (block netting vs. active seining) and the habitat, different sizes of seines are used. In riffle habitats, the seine is held stationary while team members disturb the substrate immediately upstream of the net. In pools, the seine is pulled back and forth across the pool, using the shore and other natural habitat breaks as barriers, or pulled rapidly downstream through the pool and then swept toward the shore. Block nets may be used in very large pools to limit escape or as seines. Large nets are typically deployed parallel to the current and swept to shore.
Proceed upstream through the reach, allocating the seining effort among habitat areas (riffles and pools) so that the entire reach is sampled. Deposit fish collected by seining into a bucket for later processing. It is not necessary to segregate the fish collected via electroshocking or seining. However the number of seine hauls and the time expanded in seining will be recorded on the Fish Field Data Sheet. At the completion of sampling activities (electrofishing and/or seining), record the total fishing time on the Fish Field Data Sheets.

Sample Processing

Sample processing involves tallying and identifying fish, examining individual specimens for external anomalies, preparing voucher specimens for taxonomic confirmation and archival at GBM^c.

Unless otherwise specified in a project specific SAP, at the end of each sampling effort fish from the entire reach are preserved in formalin for identification in the lab. For each study site, a complete tabulation of taxa, numbers of individuals and their percent composition will be included on the 2 page Field Data Sheets – Fish (attached). The first page of the 2-page data form will include general information identifying the sample reach and investigators as well as site observations to include:

time sampled,
pedal down time (PDT),
relative abundance of aquatic trophic level communities,
percent of major habitats sampled,

percent of specific microhabitats sampled, and
relative abundance and scoring of substrate.

The second page provides for the listing of the taxa (field identification) and the numbers of each. Also included on page 2 are the general reach identifiers.
Ultimately, the fish identification will be verified in the lab using keys in the Fishes of Arkansas (Robison, 1988) and the Fishes of Missouri (Pflieger, 1975) to species level where possible.

The fish collections at each reach will be compared according to several biometrics which may include: species richness (number of taxa); sunfish richness; species diversity; abundance; dominant ordinal groups; percent of tolerant species; trophic structure; percent of hybrids; and percent of diseased fish. The analysis may also include the eight biometrics used by the State of Arkansas in their RBA scoring system. This scoring system places a value of 0, 2, or 4 on each of the eight biometrics to achieve a final mean score. The final mean score (0 to 32, 0-8=not supporting, 9-16=impaired, 17-24=generally supporting, 25-32=fully supporting) will indicate the impacts to a fish community when compared to the fish community of different reaches, to demonstrate effects of point and or non-point source contributions between reaches.

Sample Maintenance

At the conclusion of all identifications, all fish collections are placed in 40% - 50% isopropyl alcohol for permanent preservation. The fish collections are maintained at GBM^c & Associates for a period of three years after the completion of the project. An archive list of all fish collections is on file at GBMc & Associates. After the three year time period is up preserved fish may be offered to a scholastic institution or museum, discarded in an appropriate manner, or remain in storage at GBMc & Associates.

Quality Control

Field teams collecting fish are led by experienced aquatic biologists. A team of qualified personnel using proven sampling techniques makes field collections. Sampling equipment is routinely inspected to maintain and ensure proper working order prior to a sampling trip. Adjustment in the field to the equipment and/or techniques can be made in the field by the sampling team to improve the collection results. All aspects of the fish collection are documented in team members' personal field books, as well as specific field forms. The field forms are designed specifically for fish collection studies and are set up to include all pertinent field data. Field forms are completed for each sample site. All field forms are reviewed at the end of the study for completeness and accuracy.

Identification of the collected fish starts in the field and is conducted by one or more experienced aquatic biologists that were involved in the collection effort. Field identifications are later verified in the laboratory by an experienced aquatic biologist. Laboratory identifications are then confirmed by a senior biologist to ensure completeness and accuracy. Efforts are made to remain abreast of current research in

fisheries biology and identification techniques through scientific journals and conferences. In addition, EPA document updates and new information on fish assessment is tracked via the internet.

12.0 Sample Collection and Custody

Purpose

This SOP describes the materials and methods necessary for the routine collection of water and wastewater samples for the analysis of various conventional and unconventional pollutants. It also gives guidance for the completion of the COC forms necessary for each set of samples collected for laboratory analysis. This SOP provides general guidance and should not be substituted for a study specific work plan and/or Sampling and Analysis Plan.

Procedures

Sample Collection

1. Fill out an Equipment Checklist for each sampling trip, checking (✓) all the necessary gear for sample completion.

2. Clean sample bottles should be supplied by the laboratory or a reputable scientific supply company. Be sure to have an extra set of sample bottles on hand on each field trip.

3. Check all bottles prepared by the lab to ensure the proper analyses are covered with the correct type of preservation. (Table 1)

4. A duplicate sample for a given analyte shall be taken, 1 for every 10 samples collected. That is, a duplicate sample will be collected 10% of the time. A duplicate sample is simply a second sample taken from the same location immediately following the original sample. The duplicate sample serves as a quality control check for the sample sources (stream water, etc.) variability, and the sampling methodology repeatability.

5. A field blank shall be collected 10% of the time (1 in 10 samples) when metals or organic chemicals are being analyzed. A field blank is simply a sample bottle filled with deionized water (blank water) on-site at the study location to represent any potential contamination present at the site or in the sampling techniques.

6. A trip blank should be collected at the rate of 1 per 10 samples when metals or organic chemicals are being analyzed. A trip blank is a bottle filled in the lab with deionized water to verify blank water and sample bottle purity.

7. Use appropriate safety precautions while collecting the samples (i.e., wear latex gloves, Tyvek® suits, etc.) as necessary.

8. Place a label on the sample bottle, prior to collecting the samples, and record the following information on the label using a permanent marker (e.g., Sharpie®):

    a. sample identification,
    b. date of collection,
    c. time of collection,
    d. initials of collectors, and
    e. parameters to be analyzed (NH_3-N, Total Cu, etc.)

9. Fill each bottle per site completely, and place the cap securely each bottle.

   When filling sample bottles be sure to choose a representative sample location which is accessible in a manner as to prevent bottom and/or attached solid materials from entering the sample bottle. Samples should be taken in flowing water where possible. Samples should be taken from below the water surface if depth allows.

10. Place the bottle in an ice filled ice chest to keep the sample cool (4°C±2). If the ice chest(s) will be shipped to a laboratory, ice should be placed in a plastic bag(s) to prevent possible sample contamination from melting.

11. Record sample information on the Field Data Form or in a field notebook, along with any pertinent observations. If available, record instantaneous flow at the time of sample collection. This is important if the samples are from an NPDES discharge or other regulatory monitored system.

12. If samples are to be composited according to flow (flow-weighted) the following protocol should be followed:

    a) record a flow for each sample time on the COC form
    b) include compositing instructions on the COC form for laboratory use
    c) or composite on-site prior to delivery to the lab

13. Measure any necessary in-situ parameters (pH, temperature, dissolved oxygen, specific conductivity) and record on the appropriate field form or in a field notebook.

14. When sampling is complete a COC form should be completed.

15. Take note of sample holding times (Table 1) and make an effort to return samples to lab as soon as possible.

Chain of Custody (COC)

1. A COC form (attached) must be filled out for all samples submitted to the laboratory for analysis.

2. The COC form must be filled out with a ballpoint pen, and signed in the appropriate locations by each individual receiving the sample(s).

3. The following information ***must be completed*** on each COC form:

    a. company/facility,
    b. contact name,
    c. address,
    d. phone number,
    e. sample id,
    f. sample description (where taken),
    g. date (from sample bottle),
    h. time (from sample bottle),
    i. number of containers,

j. preservative,
k. parameters to analyze at lab,
l. sampler(s),
m. shipment method,
n. turnaround time required,
o. coc form completed by,
p. coc form checked by, and
q. relinquished by.

4. Each completed COC form shall be photocopied and the copy filed.

5. If shipping ice chests to a laboratory, the original COC form should be placed in a ziplock bag and then taped to the inside top of the ice chest for shipment.

6. At the lab the COC form will be received and signed. A copy of the COC form should be returned by the lab, along with the analysis results, when completed.

14.0 Turbidity Meter Calibration SOP

Purpose

This SOP describes the methods for calibration and use of the portable HACH Model 2100P Turbidimeter.

Calibration

Calibration of the 2100P Turbidimeter should be completed annually or when the Gelex® standards fall outside the acceptable range >± 10%.

Procedure

1. Prepare formazin 20, 100, and 800 NTU calibration dilutions immediately before calibrating. The solutions are made with a well mixed 4000 NTU stock solution and high quality dilution water (<0.5 NTU) as follows:

    - Dilution water--Deionized water. The deionized water should have a turbidity reading <0.5 NTU.
    - 20 NTU--Add 0.5 mL stock solution to a 100 mL volumetric flask and bring to volume.
    - 100 NTU--Add 2.5 mL stock solution to a 100 mL volumetric flask and bring to volume.
    - 800 NTU--Add 20 mL stock solution to a 100mL volumetric flask and bring to volume.
    - (The 4000 NTU solution is stable for up to a year, but dilutions deteriorate more rapidly.)

2. Use the same sample cuvette for each different dilution reading. Rinse the clean cuvette with dilution water three times; then fill to the line with dilution water.

3. Place the instrument on a flat surface. Then insert the sample cuvette into the cuvette compartment with the orientation mark on the cuvette aligned with the mark on the front of the compartment. Close the lid and press I/O.

4. Turn the signal average off by pressing the Signal Average key until off is indicated. Then press calibrate (CAL). CAL and S0 should be displayed on the screen along with the value for the S0 standard for the last calibration.

5. Press READ. After the count down is completed, the blank value will be displayed, then the display will advance to the next standard. Remove the sample cuvette. (In case of error, refer to manual.)

6. S1 and 20 NTU will be displayed on the screen.

7. Rinse the sample cuvette 3 times with the well mixed, 20 NTU standard. Then fill the cuvette to the line with the 20 NTU standard.

8. Clean the outside of the cuvette with a soft, lint-free cloth removing water spots and fingerprints. Then apply a thin film of silicone oil and spread the oil evenly over the outside surface with a soft cloth.

9. Insert the sample cuvette into the cuvette compartment with the orientation mark on the cuvette aligned with the mark on the front of the compartment.

10. Close the lid and press READ. After the count down is completed, the standard value will be displayed, then the display will advance to the next standard. Remove the sample cuvette.

11. Repeat steps 6 through 10 for the S2 and S3 samples (100 and 800 NTU, respectively.)

12. After S3 has been read, the display will show S0. Remove the sample cuvette. Press CAL to accept the calibration.

13. Once the calibration has been accepted, the instrument will automatically proceed to measurement mode.

    (If any errors occur during calibration, revert to manual for explanation.)

Calibration Verification

The 2100P Turbidimeter does not require calibration before every measurement. Gelex® Standards are used for routine calibration checks. Routine calibration checks should be performed bi-monthly. If the Gelex® standards read more than 5% from their recorded value, the meter should be recalibrated.

Procedure

Assigning values to the Gelex® standards

1. Calibrate the meter as described above.

2. Select the automatic range mode using the RANGE key.

3. Turn the signal average off by pressing the SIGNAL AVERAGE key until SIG AVG is not displayed on the screen.

4. Clean the outside of the Gelex® vile with a soft, lint-free cloth removing water spots and fingerprints. Then apply a thin film of silicone oil and spread the oil evenly over the outside surface with a soft cloth.

5. Insert the 0-10 NTU Gelex® standard into the cuvette compartment with the orientation mark on the vile aligned with the mark on the front of the compartment. Close the compartment lid.

6. Press READ and record the displayed value after the lamp signal is no longer displayed on the screen.

7. Remove the vile and mark the value on the band near the top of the vile with a permanent marker.

8. Repeat steps 3 through 6 for the other Gelex® standards.

9. The values for each Gelex® standard should be reassigned each time a new calibration is performed.

Checking meter calibration

1. The Gelex® standards should be used as a routine check for instrument calibration. If the standards do not read within 5% of the assigned value, the instrument should be recalibrated before use, and new values assigned to the Gelex® standards.

2. Place the instrument on a flat surface.

3. After turning the instrument on, select the automatic range mode using the RANGE key.

4. Turn the signal average off by pressing the SIGNAL AVERAGE key until SIG AVG is not displayed on the screen.

5. Clean the outside of the Gelex® vile with a soft, lint-free cloth removing water spots and fingerprints. Then apply a thin film of silicone oil and spread the oil evenly over the outside surface with a soft cloth.

6. Insert the 0-10 NTU Gelex® standard into the cuvette compartment with the orientation mark on the vile aligned with the mark on the front of the compartment. Close the compartment lid.

7. Press READ and record the displayed value after the lamp signal is no longer displayed on the screen.

8. Remove the vile and compare the value on the band near the top of the vile with the recorded value. If the recorded value is within 5% of the value marked on the vile, continue to step 8. Otherwise recalibrate the instrument.

9. Repeat steps 3 through 6 for the other Gelex® standards.

Turbidity Measurements

Procedure

1. Collect a representative sample of the liquid to be analyzed in a clean container. Rinse the clean sample cuvette three times with the sample water and fill to the line with sample, taking care to prevent the formation of air bubbles and not leave fingerprints on the sides of the cuvette.

2. Clean the outside of the cuvette with a soft, lint-free cloth removing water spots and fingerprints. Then apply a thin film of silicone oil and spread the oil evenly over the outside surface with a soft cloth.

3. Place the instrument on a flat surface and turn it on by pressing I/O.

4. Insert the sample cuvette into the cuvette compartment with the orientation mark on the cuvette aligned with the mark on the front of the compartment and close the lid.

5. Select automatic range by pressing the RANGE key until AUTO RNG is displayed.

6. Turn the signal average off by pressing the SIGNAL AVERAGE key until SIG AVG is not displayed on the screen.

7. Press READ and record the turbidity value after the lamp symbol is no longer displayed on the screen.

Meter Maintenance/Storage

1. Store the meter in the designated portable carrying case.

2. The meter should not be stored or left in a "dirty" condition.

3. The sample cuvette, silicone oil, and Gelex® standards should be stored in clean state in the proper boxes in the portable carrying case.

4. The 4000 NTU stock solution should be stored in a refrigerator at 5^0 C.

Quality Assurance/Quality Control

1. Meters are calibrated biweekly (at a minimum) to ensure proper function and accuracy.

2. Duplicate measurements should be taken at a rate of 10% (minimum) of samples analyzed.

15.0 Chlorophyll a Sample Preparation SOP

Purpose

This SOP describes the methods for preparing water samples for chlorophyll a analysis. The preparation technique described below allows holding time to be extended to 21-days. This technique is usable only for water samples with a pH of 7.0 s.u. or higher. The contents of this SOP are based on the procedures in *Standard Methods for the Examination of Water and Wastewater* (20th Ed.)

Procedure

1. Collect water samples for chlorophyll a analysis in amber sample bottles with a volume of at least 500 mL's. Store samples in ice chests at 4ºC±2 following collection.

2. As soon as possible (within 24-h) filter a 500 mL sample (a smaller volume may be used if the water is rich in phytoplankton) through a glass fiber filter or membrane filter (0.45 µm porosity).

    a) Glass fiber filters may be Whatman GF/F (0.7µm), GF/B (1.0 µm), Gelman AE (1.0 µm), or equivalent. (membrane filters should be mixed cellulose/ester type)
    b) Use a solvent-resistant filter assembly.
    c) Various size filters and assemblies can be used but 47 mm versions are preferred.
    d) A syringe style filter assembly or a vacuum assembly may be used.
    e) Carefully rinse the filter and filter assembly with deionized water prior to filtering the water sample.
    f) If filter apparatus are to be re-used for the next sample be sure to clean the apparatus carefully with soap and water and a thorough deionized water rinse. Do not use acids to clean the filter apparatus.

3. Record the volume filtered through each filter disk on a data form or in a field logbook. Also, record the total volume filtered on the Chain of Custody form for each sample I.D.

4. Carefully remove the filter(s) containing the phytoplankton filtrate from the filter apparatus and place it in an airtight plastic bag (Whirl-Pak® or equivalent).

5. Label the outside of the plastic bag with the sample I.D., date, time, initials of sampler, and volume of sample filtered.

6. Wrap the plastic bag in aluminum foil and label the outside of the foil with the same information as in number 5 above.

7. Freeze the wrapped samples immediately.

8. Deliver frozen samples to the laboratory in ice filled coolers (dry ice can be used) as soon as possible, to prevent sample thawing.

16.0 Periphyton Protocol SOP

Purpose

Periphyton (benthic algae) are primary producers and form the base of most aquatic food webs. The abundance and diversity of periphyton may serve as an indication of habitat suitability and water quality, particularly in regards to nutrient enrichment and energy availability. This protocol provides two methods to determine periphyton biomass in a stream system.

Semi-quantitative assessments of benthic algal biomass can be made rapidly with a viewing bucket marked with a grid and a biomass scoring system. This technique enables rapid assessment of algal biomass over large spatial scales. Coarse-level taxonomic characterization of communities is also possible with this technique. This field-based technique, taken from EPA's Rapid Periphyton Survey (Barbour, 1999) protocol, is a simple survey of the existing natural substrate and requires no laboratory processing.

Quantitative assessment of periphyton biomass requires collection of the algae from substrates over known areas. This allows accurate determination of biomass as either chlorophyll-a or dry weight per unit area.

The periphyton protocols are intended to evaluate the biological integrity of wadeable streams for the purpose of detecting stresses on community structure, assessing the relative severity of these stresses, and determine the maintenance of the designated uses. Each approach is based on the *Rapid Bioassessment Protocols for Wadeable Streams and Rivers* published by the U.S. Environmental Protection Agency (Barbour, 1999). The field-based rapid periphyton surveying technique was developed by (Stevenson and Reir, 1998), University of Louisville. The technique requires only one person and is a quick and easy periphyton assessment method where habitat is suitable. This methodology is used by GBMc & Associates to better assess riffle-pool and step-pool dominated stream systems. The approach is considered a semi-quantitative methodology, in that there is some measure of abundance on a per sample basis and data is comparable to other collections.

The periphyton biomass method is a quantitative method which returns biomass of algae as either chlorophyll-a per unit area or grams of algae per unit area. This technique requires removal of all algae cells from a specified area on multiple substrates in the stream. Typically the most suitable substrates are cobbles, large gravel, bedrock and large woody debris. Artificial substrates (periphytometers) may be utilized in streams with little suitable periphyton habitat. Once samples are collected and composited this method also allows for algal sub-samples for taxonomic analysis should detailed assessments be necessary.

Rapid Periphyton Survey (RPS)

Field Equipment

- Viewing bucket with 50-dot grid (made by cutting out the bottom of a large plastic bucket (5 gal), leaving a small ridge around the edge. A piece of clear acrylic sheet, marked with 50 dots in a 7 x 7 grid on the top surface is fitted to the bottom of the plastic bucket with small screws and silicon caulk to water proof. Another dot is added outside the 7 x 7 grid to make the 50-dot grid (7 x 7 + 1).
- Tape Measure
- Pencil
- Rapid Periphyton Survey Field Sheet

Procedure

1. Fill in top of RPS Field Sheet.
2. Establish at least 3 transects across the representative habitat being sampled (preferably riffles or runs within the reach being characterized).
3. Select 3 locations along each transect (e.g. stratified random locations on right, middle, and left bank) in wetted area of stream. If wetted width ≤8 feet then 2 locations is acceptable.
4. Characterize algae in each selected location by immersing the bucket with 50-dot grid in the water as follows:

    - First, characterize macroalgal biomass.

        - Observe the bottom of the stream through the bottom of the viewing bucket and count the number of dots that occur over macroalgae under which substrates cannot be seen. Record the number of dots and type of macroalgae under the dots on the RPS field sheet.
        - Measure and record the maximum length of the macroalgae.
        - If two or more types of macroalgae are present, count the dots, measure and record information for each type separately.

    - Second, characterize microalgal cover (suitable habitat).

        - While viewing the same area, record the number of dots under which substrata occur that are suitable size for microalgal accumulation (gravel > 2 cm in size).
        - Determine the microalgal and estimate the thickness of microalgae under each dot using the following thickness scale:
          0 - substrate rough with no visual evidence of microalgae
          0.5 – substrate slimy, but no visual accumulation of microalgae is evident
          1 – a thin layer of microalgae is visually evident

2 – accumulation of microalgal layer from 0.5-1 mm thick is evident
3 – accumulation of microalgal layer from 1 mm to 5 mm thick is evident
4 - accumulation of microalgal layer from 5 mm to 2 cm thick is evident
5 - accumulation of microalgal layer greater than 2 cm thick is evident

- Record the number of dots that are over each of the specific thickness ranks separately for diatoms, blue-green algae, or other microalgae.

5. Statistically characterize density of algae on substrate by determining:

- Total number of grid points (dots) evaluated at the site (D_t);
- Number of grid points (dots) over macroalgae (D_m)
- Total number of grid points (dots) over suitable substrate for microalgae at the site (d_t);
- Number of grid points over microalga if different thickness ranks for each type of microalgae (d_i);
- Average percent cover of the habitat by each type of macroalgae (i.e. 100X D_m/D_t);
- Maximum length of each type of macroalgae;
- Mean density (i.e., thickness rank) of each type of macroalgae on suitable substrate (i.e., $\Sigma d_i r_i / d_t$); maximum density of each type of macroalgae on suitable substrate.

Periphyton Biomass Analysis

Field Equipment

- Scrapers (small metal scrapers work well)
- Brushes
- Wash bottles
- Sample containers
- Underwater extraction tube (only for immovable substrates)
- Periphytometers (optional)

Substrate Procedure

1. Establish a minimum of three transects in each reach across the representative habitat being sampled (preferably at riffles or shallow runs). Transects should coincide with the RPS if both protocols are being utilized.

2. A minimum of one substrate (2 preferable) is identified at each transect for sampling. Ideal substrates are removable to the bank (cobbles, large gravel, small boulders or pieces of bedrock, large hard woody debris, etc.) to simplify extraction of the periphyton sample.

3. A known area of periphyton (typically about 14 cm^2) is scraped from the substrate and rinsed into a sample bottle. A narrow metal paint scrapper works well. Care is taken to ensure the entire mass of algae is removed. This may require use of brushed and rinsing of brushes into the sample bottle.

4. If substrates are not removable, a 4" (or larger) PVC table with a rubber gasket on one end may be lowered into shallow water and the sample scraped from within the tube. The tube must form a good seal with the substrate to prevent loss of algal cells. All the water in the tube must be siphoned into the sample bottle when this approach is utilized to ensure the entire algal is collected.

5. All periphyton samples from a reach are composited into the same bottle and stored at 4ºC for processing.

6. If chlorophyll-a biomass is to be analyzed the sample should be filtered and frozen within 24-hours of collection and handled according to GBMc SOP #__.

7. Sub-sampling for taxonomic analysis, if necessary, should be completed as soon as possible to provide good cell condition for species identification.

Periphytometer Procedure

1. In water bodies that have insufficient habitat conducive to use of the substrate procedure, periphytometers may be used.

2. A minimum of 4 periphytometer samples (replicates) should be utilized in a given reach.

3. Periphytometers are placed at the appropriate depth, anchored and left for 2-8 weeks.

4. Once retrieved, accumulated sediment is gently removed from the samplers, the algae samples are scraped from the samplers and treated from that point forward in a manner consistent with the Substrate Procedure (starting at No. 5).

Analysis

Periphyton biomass may be analyzed as biomass of chlorophyll-a per unit area (g/m^2) or as dry weight of algal mass in g/m^2. When calculating either indices the area of periphyton in the sample and the volume of the sample must be recorded.

QA/QC

QA/QC includes: training of observers for use of repeatable techniques; allowing one observer to complete all relevant sites that may be compared; comparing coverage results to habitat analysis (GBMc SOP # 7) and quantitative biomass analysis of same stream reach; and comparison of duplicate assessments/analysis.

17.0 Processing of Fish Tissue Samples

Purpose

Fish tissue may accumulate some chemicals (heavy metals, organic chemicals, etc.) in their muscle tissue and/or other body organs. Fish tissue samples are commonly collected and analyzed to determine the bioaccumulation of various toxic chemicals in an effort to protect human health from over consumption of contaminated fish species.

Procedure

The processing of tissue samples for analyses will generally follow procedures outlined by the Mid-America Contaminants Group and the Environmental Protection Agency Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. For routine edible tissue analysis the following procedure is generally followed.

1) Composite samples composed of individual filets from the left side of the carcass will be analyzed, unless tissue mass per individual is not sufficient in which case both left and right filets may be utilized. A minimum of five filets from the targeted species and size range will be composited and analyzed for the chemical of concern (COC). The right filet will be processed and archived (frozen) and available for analysis if required.

2) The processing of each specimen will follow the procedure below.

    a. Fish will be weighed to nearest gram.
    b. Length will be measured in Total Length (TL) to nearest 0.1 inch;
    c. Latex gloves (non-powdered) will be worn by the individuals filleting and processing the fish flesh samples.
    d. Fish will be positioned on a clean cutting board that may be wrapped in decontaminated aluminum foil, if organic chemicals are the COC. The left filet and then right filet is removed and weighed. Each filet will be double wrapped in either decontaminated aluminum foil (for organic COC), shiny side out and over-wrapped in brown paper; or alternatively if metals are the COC, wrapped in clean butcher paper and/or clean high grade plastic bags.
    e. An identification tag will be placed (attached) to each wrapped filet and separate filets will be placed into heavy duty freezer bag with label inserted into each plastic bag.
    f. The filet knife will be decontaminated using ETOH, hexane, and deionized water; the cutting board surface, if covered with aluminum or butcher paper, and disposable gloves will be replaced prior to the next composite being processed.

3) Once processed, the left filets from one species will be placed in a larger freezer bag, labeled appropriately, and frozen. Subsequently, all left side filets collected from all stations will be shipped frozen for analysis to a certified analytical laboratory that has demonstrated the ability to analyze for the COC to a minimum that will be determined by the target analyte. The appropriate chain of custody will be executed for tracking all samples.

4) The right side filets will be placed in a plastic bag and frozen; one right side composite will be selected at random for analysis along with the left filet composite to serve as a measure of analysis variability. The remaining right side filets will be archived for duplicate analysis, if required. All archived samples will be maintained for a minimum of 24 months from collection.

5) In the case where whole body or a particular organ from the fish is desired for analysis, rather than only the filet, the same protocol is followed as for the left side filet according to bullets 1 through 3 in this procedure.

Quality Control

All protocols will be followed and care will be taken to ensure samples are free of contamination from the sample process.

At a minimum, one of the right side composites will be during each study analyzed to provide an evaluation of analytical variability and QA/QC.

In the case of whole body or organ analysis true duplicate samples are not possible. Therefore, variability of COC bioaccumulation in replicate fish specimens will be closely evaluated. Should variability be greater than 40% the results will be examined for possible errors and necessary corrective measures.

Appendix C
Ana Lab SOP

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

METHODS

TSS

Potable Water:..... **SM 2540D, 20th Ed.**
Nonpotable Water:..... **SM 2540D, 20th Ed.**
Solid/Hazardous Waste: ..... **SM 2540D, 20th Ed.**

VSS

Potable Water:..... **SM 2540E, 20th Ed.**/ EPA 160.4
Nonpotable Water:..... **SM 2540E, 20th Ed.**/ EPA 160.4
Solid/Hazardous Waste: ..... **SM 2540E, 20th Ed.**/ EPA 160.4

Mexican Method: NMX-AA-034-SCFI-2001

SCOPE AND APPLICATION

Procedure determines total suspended solids (TSS) and volatile suspended solids (VSS) in unpreserved aqueous samples and other liquids in the range of 1 to 20,000 mg/L. TSS is also referred to by the term "non-filterable residue".

Data objectives for precision, bias, representativeness, comparability and completeness are predetermined. Refer to Quality Control acceptance limits.

***The client's DQOs take precedence if they differ from those stated in this SOP **and apply only to samples governed by the client's DQOs. If client's DQOs are less stringent than the referenced method or NELAC requirements, the analysis is flagged on the analytical report as not meeting NELAC requirements because the client's supplied DQO's govern.**

Procedure is performed by trained personnel with current demonstration of capability and authorization. Refer to Appendix I for training needs.

SUMMARY

A well-mixed sample is filtered through a glass fiber filter. The residue on the filter is dried at

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

103-105°C to a constant weight. TSS is calculated by the difference in weights in relation to the volume of sample filtered and reported in mg/L. The sample size should be adjusted to yield a minimum residue of 1.0 mg and a maximum residue of 200 mg.

If VSS value is required, the TSS residue is ignited at 550°C ± 50 and the loss of weight on ignition is the volatile residue. VSS is calculated based on the original sample volume and reported in mg/L.

DEFINITIONS

1. ALIQUOT – measured, representative portion of a sample used for analysis; subsample.
2. BATCH - 1 to 20 production samples of like matrix plus associated quality control; processed as a unit.
3. DQO (DATA QUALITY OBJECTIVE) - identifies and defines the type, quality, and quantity of data needed to satisfy a specified use.
4. Duplicate - replicate of the sample, quantifies precision.
5. HOLDING TIME B time allowed between sample collection and analysis.
6. LCS (LABORATORY CONTROL SAMPLE) - reagent water or other blank matrices that is spiked with a known quantity of target analyte(s) and carried through preparation and analytical procedures exactly like a sample; typically a mid-range concentration; verifies that bias and precision of the analytical process are within control limits; determines usability of the data
7. LDS (LABORATORY DATA SERVICES) - in-house LIMS; computer software.
8. METHOD BLANK B reagent water or other blank matrices processed simultaneously with and under the same conditions as samples and carried through preparation and analytical procedures exactly like a sample; monitors contamination present in the laboratory environment, equipment or reagents.
9. NEAT MATERIAL - a pure or close to pure manufactured product, 99% pure product, not diluted
10. PRODUCTION SAMPLE - Sample logged-in to LDS with a unique sample number.
11. QC (QUALITY CONTROL) - is the overall system of technical activities that measures the attributes and performance of a process against defined standards to verify that they meet the stated requirements of the client.
12. REPORTING LIMIT - lowest technically valid value; refer to LOQ.

ANA-LAB CORP.® THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

13. LOQ (Limit of Quantitation) - reporting limit; lowest technically valid value; minimum level, concentration, or quantities of a target analyte that can be reported with a specified degree of confidence; lowest concentration that can be reliably achieved with specified limits of precision and accuracy during routine lab operating conditions; typically,10s above the reagent blank signal. Approximate relationships: LOD ≤ LOQ.
14. SET - processed as a unit; an analytical group / analytical batch.
15. TARE - set the balance display to zero; subtracts the weight of what is on the balance, such as a weigh boat.
16. TSS - Total Suspended Solids; non-filterable residue.
17. VSS - Volatile Suspended Solids; the volatile residue portion of TSS.

INTERFERENCES

1. Obtaining a representative aliquot of the sample may be difficult.
   a. Always shake **vigorously** immediately before pouring.
   b. Multi-phase samples may be very difficult. Mix well, keep homogenized if possible.
   c. Large floating particles or submerged masses of nonhomogeneous material should be excluded.
      i. Ex: Insect, stick, rock, leaf, etc.
      ii. **If the material is typical of the sample matrix, do not remove it.**
   d. If a pipette is used to transfer the sample, the pipette tip opening needs to be wide enough not to exclude suspended solids. If the end of a disposable pipette tip is cut to enlarge the opening, it must not be cut in a manner which allows the sample to drip out.
2. Filtration
   a. To prevent a water-entrapping crust, the sample size should be limited to 200 mg of residue on the filter.
   b. A clogged filter may produce a high result because of captured colloidal material.
   c. If the sample is high in dissolved solids, the filter may require additional rinsing thoroughly to remove all of the dissolved material.
   d. If sample is an organic, rinse the filter thoroughly with alcohol. If an organic film remains, contact a supervisor for assistance.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

SAFETY

1. Follow Chemical Hygiene Plan for routine laboratory practices.
2. Follow manufacturer's operating instructions.
3. Follow applicable MSDSs.
4. Wear appropriate personal protective equipment and clothing.

EQUIPMENT AND SUPPLIES

1. Analytical balance.
2. Drying oven, 103-105°C
3. Muffle furnace, 550°C ± 50.
4. Desiccator, with dry desiccant
5. Tongs
6. Glass fiber filter disks without organic binders, appropriate diameter for crucibles.
   a. **Examples of suitable filters:**
      i. **Whatman grade 934AH**
      ii. **Gelman type A/E**
      iii. **Millipore type AP40**
      iv. **E-D Scientific Specialties grade 161**
      v. **Environmental Express Pro Weight.**
7. Vacuum manifold to hold Gooch crucibles
8. Gooch crucibles
9. Tray, appropriate size to hold a set crucibles
10. Vacuum pump
11. Mechanical pipettes with disposable tips, appropriate sizes.
12. Graduated cylinders, appropriate sizes.
13. Paper towels

SUPPLEMENTAL EQUIPMENT AND SUPPLIES

1. Computer with LDS software and printer.
2. Equipment manual(s).
3. Maintenance log(s) or LDS notes.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

4. Test list for applicable test codes.
5. Data sheets.
6. Ballpoint pen, black waterproof ink.
7. Permanent marker, Sharpie or equivalent.
8. Label tape.
9. General office supplies

REAGENTS

GENERAL

1. PURCHASED REAGENTS
   a. Traceable by the Chemical Log number. (C#)
   b. Purchased reference materials and chemicals are traceable to NIST and to CoAs, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in the chemical or the solvent storage room or in the designated lab work area.
   d. Follow Chemical Log SOP.
2. PREPARED REAGENTS
   a. Traceable by the Reagent Log number (SW#)
   b. Reagents prepared in house are traceable to reference materials and chemicals, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in a reagent bottle in designated lab work area unless otherwise noted.
      i. NOTE: Daily Reagents ʙ record on data sheet or in instrument log and dispose at the end of the day.
   d. Follow Reagent SOP.
3. Preparation Techniques
   a. Follow Personnel: Training, Basic Technical Skills SOP.

REAGENTS

1. Distilled water, Type II.
2. Diatomaceous Earth (Infusorial Earth)

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

a. Neat material.

3. TSS Standard, 100 mg/L.
   a. **Add 1 Liter of distilled water to a reagent bottle.**
   b. Weigh 0.1000 grams of Diatomaceous Earth (Infusorial Earth)
   c. **Quantitatively transfer to the reagent bottle and mix thoroughly.**
   d. Store in reagent bottle at room temperature.
4. TSS LCS, 50 mg/L.
   a. Add1 Liter of distilled water to a reagent bottle.
   b. Weigh 0.0500 grams of Diatomaceous Earth (Infusorial Earth)
   c. **Quantitatively transfer** to the reagent bottle and mix thoroughly.
   d. Store in the reagent bottle at room temperature.
5. TSS LCS, other concentrations may be prepared in a like manner.
6. Isopropyl alcohol.

SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample is collected in unpreserved glass or plastic sample, stored at **≤6°C**, and analyzed within 7 days of collection.

QUALITY CONTROL

Any quality control outside acceptable control limits will be evaluated for significance of nonconformity by the Quality Department. See Corrective Action SOP.

TSS

Type	Minimum Frequency	Acceptance Limits	Corrective Action
Method Blank	Beginning and end of set	Tare wt ± 0.0005 g	Repeat dry, cool, and weight cycle
Standard / LCS	Beginning and end of set	± 10%	Correct problem and re-analyze set
Duplicate	1 per 10 production samples	≤ 20% RPD NOTE 1	Flag NOTE 2

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

VSS

Type	Minimum Frequency	Acceptance Limits	Corrective Action
Method Blank	Beginning of set	Tare wt ± 0.0005 g	Repeat dry, cool, and weight cycle
Duplicate	1 per 10 production samples	≤ 20% RPD [NOTE 1]	Flag [NOTE 2]

NOTES
1. For sample results that are ≥5 times the reporting limit.
2. If Duplicate is outside the acceptance criteria and the LCS is within the acceptance criteria, flag the analyte with a data qualifier.

PROCEDURE

QUALITY CONTROL PREPARATION

1. Method blank B 200 mL Distilled Water
   a. First and last crucibles in set
2. TSS Standard B Diatomaceous Earth (Infusorial Earth), 100 mg/L.
   a. Second crucible in set
3. TSS LCS B Diatomaceous Earth (Infusorial Earth) appropriate concentration.
   a. Next to last crucible in set
4. Duplicate B 1 per 10 production samples
   a. Selected at random and representative of the samples in the set.
   b. If set includes VSS analysis, select a sufficient number of samples that also require VSS.

PREPARATION

1. Print TSSS list and select samples to be analyzed.
   a. Refer to Testing Priority SOP
   b. Watch for holding time, rush samples, and re-runs.
2. Start LDS set for TSS.
   a. Select random duplicates which are representative of samples in set.
   b. Arrange the set in the following order:
      i. Method Blank

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

ii. Standard
iii. VSS Samples (If any are to be analyzed)
iv. TSS Samples
v. LCS
vi. Method Blank

c. Arrange samples in numerical order.
i. Except: If there are samples which need VSS, they should be in numerical order immediately after the standard followed by samples which need TSS only in numerical order.

3. Print **data** sheet.
4. Obtain the samples to be analyzed from the cooler and arrange them on a cart in the same order as they appear on the TSS **data** sheet.
5. Allow samples to equilibrate to room temperature.

CRUCIBLE PREPARATION

1. Insert a glass fiber filter disk into the bottom of a clean uniquely numbered Gooch crucible with the wrinkle side up and the smooth side down.
   a. Prepare enough crucibles to fill a pan.
2. With a vacuum applied, rinse the filter with three small portions of distilled water.
   a. Make sure the filter is seated on the crucible and covers all of the holes.
   b. There must not be any uncovered holes or tears in the filter.
3. Remove all traces of water by continuing to apply vacuum after the water has passed through the filter.
4. Remove the crucible from the vacuum manifold, place in a pan, and cover with clean paper towel.
5. Label the set.
6. Place the pan containing the set in an oven maintained at 103-105EC.
7. Dry the crucibles with filters at 103-105EC for at least 1 hour.
8. Crucibles may be prepared ahead of time and stored either in the103-105EC oven or covered in the TSS lab area until used.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

TARE WEIGHTS (1.WEIGHT)

1. Check desiccant in desiccator.
   a. Desiccant must be dry and cool before the desiccator can be used.
   b. Replace the desiccant if necessary.
   c. If desiccant is hot, it must be cooled in the desiccator at least one hour.
2. Remove pan containing set from oven, remove cover, and place pan containing set of crucibles in desiccator.
3. Cool the crucibles with filters in the desiccator for 20 minutes.
4. Check the level on the balance before using it.
   a. If it is not level, level it.
   b. The balance must be level prior to use or weights will not be accurate.
5. Close Balance Room door when obtaining weights.
6. Close all the balance doors and tare the balance. (Set weight to 0.0000 grams.)
7. Using tongs, remove the crucibles one at a time, in order, from the desiccator and place on balance pan.
   a. Close the desiccator door between crucible weights.
8. Close the balance door, obtain and record tare weight of the crucible plus filter (1.weight).
9. Remove the crucible from the balance and close the balance door.
10. Tare balance if the weight is not 0.0000 grams.
11. Return the crucible to the pan in the desiccator and remove the next crucible.
12. Repeat steps 7-11 until all crucibles have been weighed.
13. Remove the pan of crucibles from the desiccator and cover with a clean paper towel.
14. Store covered crucibles in a clean, safe place.
15. May be obtain ahead of time and stored covered until used.

SAMPLE FILTRATION (ML)

1. Rinse all of the cylinders that will be used with distilled water. Shake or drain to remove the distilled water.
2. Drain the vacuum manifold.
3. Turn on the vacuum pump.
4. Place a pre-weighed crucible with filter onto the vacuum manifold and apply vacuum.
   a. Do not use the crucible if the filter does not cover all of the holes in the bottom of the crucible or if the filter is torn.

ANALAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@anc-lab.com • www.anc-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

5. Place each blank, standard, sample, or LCS in front of the crucible that it will be filtered through.
6. Using a cylinder of appropriate size, measure an appropriate volume.
7. Always shake **vigorously** immediately before obtaining measured aliquot.
   a. Method Blank - 200 mL of distilled water - first crucible
   b. Standard - 50 mL of 100 mg/L - second crucible
   c. Samples - well mixed unpreserved sample
      i. If sample presents a filtering problem, add sample in 25 mL increments until rate of filtration slows to indicate that the filter is approaching maximum capacity. Report the sum of all that was filtered.
   d. LCS - 50 mL of prepared solution - next to last crucible
   e. Method Blank - 200 mL of distilled water - last crucible
8. Transfer measured aliquot into the corresponding crucible, being careful not to overflow the crucible or spill aliquot.
9. Record volume filtered.
10. After the sample has completely filtered:
    a. Rinse the graduated cylinder and TSS filter with 3 small successive portions of distilled water.
    b. Completely filter each rinse before adding the next.
    c. Rinse organic samples with alcohol.
11. Continue to apply vacuum for a short period of time to assure that all the water has been removed.
12. Remove the crucible from the vacuum manifold and return it to the covered pan.
13. Repeat steps 6-12 until all of the samples have been filtered.
14. Check the set label. It needs to be easily visible.
15. Place the covered pan of crucibles in a drying oven at 103-105EC.

DRY WEIGHT (2.WEIGHT)

1. Dry the covered pan of crucibles with filter and residue at 103-105EC for at least 8 hours or 1 hour with repeated drying cycles to demonstrate constant dry weight.
2. Remove the crucibles from the 103-105EC drying oven and place it in a desiccator with dry desiccant.
3. Desiccator time.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

a. Target desiccator time is the same number of minutes used for Tare Weights (20 minutes).
b. Set a timer.
c. Check the weight of the Method Blank a few minutes sooner.
d. If the weight is:
   i. Less than the Tare weight (-0.0005 grams), return the flask to the desiccator and wait a few minutes longer.
   ii. Greater than the Tare weight (+0.0005 grams), return crucibles to the 103-105EC. drying oven for 30 minutes.
e. Repeat steps 1-3c until the Method Blank is within range.
   i. Range is Tare weight ∀ 0.0005 grams.

4. When Method Blank is within range, weigh all of the crucibles in the exact same order and manner as the Tare weights were obtained. (LDS Set B1)
5. If repeat drying cycles are used,
   a. Place the covered pan of crucibles in a drying oven at 103-105EC and repeat steps1-4 until crucibles reach a constant dry weight (+/- 0.0005 grams).
6. Check LDS Set Reading >Difference= to compare the current dry weights and the previous dry weights. (bn and bn-1).
7. If weight loss is:
   a. <0.5 mg of the previous weight, constant dry weight was obtained. Go to step 8.
   b. >0.5 mg of the previous weight, constant dry weight has not been obtained, repeat steps 1-7a. (LDS Set: Weights B2, B3, etc.)
8. Cover the crucibles flasks with a clean paper towel or other protective covering.

VSS

1. Preheat a muffle furnace to 550C ± 50
2. Remove the crucibles with filter and TSS residue that require VSS analysis.
3. Place in the preheated furnace for 15 minutes (ignition of residue)

IGNITED WEIGHT (3.WEIGHT)

1. Transfer to a desiccator with dry desiccant for about 20 minutes.
   a. CAUTION: crucibles will be very hot.

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

2. Repeat Dry Weight steps 3-8, obtaining and recording the ignited weights (LDS Set Weights C1, C2, C3, etc.)
3. The loss of weight on ignition is the volatile residue.

CLEANING CRUCIBLES

1. After TSS and VSS results have been verified, clean the crucibles by removing the used filter and wiping the inside of the crucible with a paper towel moistened with isopropyl alcohol and distilled water.
2. Store crucibles in a pan.
3. **Cover with a paper towel.**

DATA ANALYSIS AND CALCULATIONS

QUALITATION AND QUANTITATON

1. **TSS -- SM 2540 D, 20th Edition.**
2. **VSS -- SM 2540 E, 20th Edition.**

CALCULATION

1. All weights are measured in grams.
2. Amount of sample volume is mL of sample filtered.

$$\text{mg/L, TSS} = \frac{\text{2.weight - 1.weight * 1000 * 1000}}{\text{mL}}$$

$$\text{mg/L, VSS} = \frac{\text{2.weight - 3.weight * 1000 * 1000}}{\text{mL}}$$

EVALUATION

1. If the TSS residue weight is <1.0 mg, the sample volume should be increased up to a maximum volume of 200 mL (or remaining sample volume, whichever is the smallest) to

ANA-LAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

yield ∃1.0 mg of residue on the filter.
2. If the TSS residue weight is >200 mg, the sample should volume should be reduced to a volume that will yield #200 mg of residue.
3. If VSS was determined, compare TSS and VSS values.
   a. TSS should be ∃VSS.

DATA REPORTING INSTRUCTIONS

1. TSS and VSS results are usually calculated and reported in mg/L with 3 significant figures.
2. If required, report the appropriate data qualifier with the result.

DATA ENTRY AND REVIEW

1. Using LDS Sets program, create a set.
   a. Opening a set assigns a set number
2. Enter data into LDS.
3. Calculate and post data.
4. Print verification sheet and review flags.
5. Submit data and verification sheet for second level of review and verification.

RECORD MANAGEMENT

1. Follow Record Management SOP
2. Record will contain all necessary information including links to supporting data.
3. Record maintenance in the appropriate log(s).
4. Data is scanned into the network and archived electronically.
5. Electronic records have multiple backups.

METHOD PERFORMANCE

1. **TSS -- SM 2540 D, 20th Ed.**
2. **VSS -- SM 2540 E, 20th Ed.**

POLLUTION CONTROL

1. Employ techniques to reduce or eliminate the quantity or toxicity of waste generation.

ANALAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

2. Quantity of chemicals purchased is based of expected usage and shelf life.
3. Reagent preparation volumes reflect anticipated usage and reagent stability.

WASTE MANAGEMENT

1. Follow Disposal SOPs.

REFERENCES

1. APHA, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 2540 D.
2. APHA, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 2540 E.
3. NMX-AA-034-SCFI-2001. Water Analysis - Determination of Salts and Solids Dissolved in Natural, Wastewaters, and Wastewaters Treated - Test Method.
4. Equipment Manual(s).

APPROVED BY

Bill Posey — **02/01/2008**

Technical Director — Date

Revised by:	Date	Reviewed by:	Date
NGT, Sr. Quality Tech	April 2007	MRM, Project Manager	Feb. 2008

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

TSS AND VSS / TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS, REVISION 07

File Name: J:\word\SOP\Active\TSS_VSS_Total_&_Volatile_Suspended_Solids_07.doc
Date Initiated: 05/16/1994
Date Revised: **02/01/2008**

Appendix I

Training Requirements
Technical Skills

1. **Completion of Basic Technical Skills training.**
   a. **Correct use of an analytical balance.**
   b. **Correct use of mechanical pipettes with disposable tips.**
   c. **Correct preparation of standard/LCS using a volumetric flask.**
2. **Use filtration apparatus correctly.**
3. **Measure sample aliquots accurately.**
4. **Analyze standard/LCS within acceptance criteria.**
5. **Record data accurately and enter into LDS.**

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

METHODS

Potable Water: ..... SM 2540 C
Nonpotable Water: ..... **SM 2540 C** /EPA 160.1
Solid/Hazardous Waste: ..... **SM 2540 C** /EPA 160.1
Mexican Method: NMX-AA-034-SCFI-2001

SCOPE AND APPLICATION

Procedure determines Total Dissolved Solids (TDS) in aqueous samples. Typical detection limit is 5 mg/L. TDS of samples with high levels of dissolved solids can be determined by reducing the sample size that is analyzed. Reporting limit will vary depending upon the amount of sample analyzed.

Data objectives for precision, bias, representativeness, comparability and completeness are predetermined. Refer to Quality Control acceptance limits.

***The client's DQOs take precedence if they differ from those stated in this SOP **and apply only to samples governed by the client's DQOs. If client's DQOs are less stringent than the referenced method or NELAC requirements, the analysis is flagged on the analytical report as not meeting NELAC requirements because the client's supplied DQO's govern.**

Procedure is performed by trained personnel with current demonstration of capability and authorization. Refer to Appendix I for training needs.

SUMMARY

TDS is defined as the solids that pass through a glass fiber filter. A well mixed sample aliquot is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C. The residue is calculated as TDS and reported in mg/L.

DEFINITIONS

1. BATCH – 1 to 20 production samples of like matrix plus associated quality control; processed as a unit.
2. Data Qualifier – used to flag and qualify the use of data when a data quality objective was

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

exceeded.

3. DQO (DATA QUALITY OBJECTIVE) – identifies and defines the type, quality, and quantity of data need to satisfy a specified use; qualitative and quantitative statements.
4. Duplicate - replicate of the sample, quantifies precision.
5. Holding Time – time allowed between sample collection and analysis.
6. LCS (Laboratory Control Sample) – reagent water or other blank matrices spiked with a known quantity of the target analyte(s) and carried through preparation and analytical procedures exactly like a sample; determines usability of the data; verifies that bias and precision of the analytical process are within control limits.
7. LDS (LABORATORY DATA SERVICES) – in-house LIMS; computer software.
8. METHOD BLANK – reagent water or other blank matrices processed simultaneously with and under the same conditions as samples and carried through preparation and analytical procedures exactly like a sample; monitors contamination present in the laboratory environment, equipment or reagents.
9. PRODUCTION SAMPLE – Sample logged-in to LDS with a unique sample number.
10. QC STANDARD – used to confirm the accuracy of an analytical process; independent of the calibration, if applicable.
11. REPORTING LIMIT – lowest technically valid value.
12. SET – processed as a unit; an analytical group / analytical batch.
13. Weigh Blank–an empty beaker carried through the heating and cooling cycles of the experiment, and used to determine when the other beakers can be weighed. It stays in the pan at all times except when being weighed.

INTERFERENCES

1. Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic
   a. May require prolonged drying, desiccation and rapid weighing.
2. Samples containing high concentrations of bicarbonate
   a. May require careful and prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
3. Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying.
   a. Total residue should be limited to about 200 mg.

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

SAFETY

1. Follow Chemical Hygiene Plan for routine laboratory practices.
2. Follow MSDSs for safe handling of solvents and target analytes.
3. Wear appropriate personal protective clothing and equipment.

EQUIPMENT AND SUPPLIES

1. Glass beakers, 150 mL.
2. Desiccator equipped with dry Calcium Sulfate desiccant or equal.
3. Drying oven maintained at 180° ± 2° C
4. Thermometer, 1° C increments.
5. **Water bath**
6. Glass fiber filter disk, Whatman 934AH or equivalent.
7. Gooch crucibles, appropriate size.
8. Vacuum flask, 500 mL, equipped with Gooch crucible adapter.
9. Vacuum.
10. Graduated cylinders.
11. **Volumetric flasks.**
12. Pipettes, with disposable tips.
13. Analytical Balance.
14. Conductivity meter with a TDS mode.
15. Plastic cups.
16. Tongs.

SUPPLEMENTAL EQUIPMENT AND SUPPLIES

1. Computer with LDS software and printer.
2. Equipment manual(s).
3. Maintenance Log.
4. Testing list for applicable test codes.
5. Data sheets
6. Notebook or file folder for completed data.
7. Ballpoint pen, black waterproof ink.
8. Permanent marker, Sharpie or equivalent.
9. Label tape.

ANA-LAB CORP.® THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

REAGENTS

GENERAL

1. PURCHASED REAGENTS
   a. Traceable by the Chemical Log number. (C#)
   b. Purchased reference materials and chemicals are traceable to NIST and to CoAs, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in the chemical or the solvent storage room or in the designated lab work area.
   d. Follow Chemical Log SOP.
2. PREPARED REAGENTS
   a. Traceable by the Reagent Log number **(SW#)**
   b. Reagents prepared in house are traceable to reference materials and chemicals, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in a reagent bottle in designated lab work area unless otherwise noted.
      i. **NOTE: Daily Reagents – record on data sheet or in instrument log and dispose at the end of the day.**
   d. Follow Reagent SOP.
3. Preparation Techniques
   a. Follow Personnel: Training, Basic Technical Skill SOP.

REAGENTS

1. Distilled water, Type II.
2. NaCl, dried at 180°C for at least one hour.
3. QC Standard, 100 mg/L.
   a. Dissolve 0.200g dry NaCl in 2 Liters of distilled water.
   b. Mix well and store in a reagent bottle.
   c. Verify concentration using conductivity probe.
4. LCS, 200 mg/L.
   a. Dissolve 0.400g dry NaCl in 2 Liters of distilled water.
   b. Mix well and store in a reagent bottle.
   c. Verify concentration using conductivity probe.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

SAMPLE COLLECTION, PRESERVATION, STORAGE, HOLDING TIME

Aqueous sample is collected in 1/2 gal plastic unpreserved container, stored at 4°C ± 2, and analyzed within 7 days of collection.

QUALITY CONTROL

Any quality control outside acceptable control limits will be evaluated for significance of nonconformity by the Quality Department. Refer to Corrective Action SOP.

Type	Minimum Frequency	Acceptance Limits	Corrective Action
Weigh Blank	1 per batch NOTE 1	±0.0005 g	Repeat dry, cool, and weigh steps for the complete set.
Method Blank	1 per batch NOTE 1	**<5.0 mg/L**	See QC Dept
QC Standard	1 per batch NOTE 1	± 10%	Correct problem and re-analyze
LCS	1 per batch NOTE 1	± 15%	Correct problem, re-prep, re-analyze
Duplicate	1 per 10 production samples	< 20% RPD	Note 2

NOTES
1. A batch is 20 production samples, or less, of like matrix.
2. RPD for sample results that are ≥5 times the reporting limit

PROCEDURE

QUALITY CONTROL

1. Weigh Blank the first beaker in the set. This beaker stays in the pan except when weighed.
2. Method blank
   a. **Place** a filter in a Gooch crucible and filter **the same amount of distilled water as the largest volume of production sample used. (Minimum of 50mL)**
   b. Transfer filtrate to the second beaker in the set then rinse vacuum flask with three small portions of distilled water and pour each portion into the beaker.

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

3. QC standard
   a. Filter 50 mL of the 100 mg/L standard and transfer to third beaker in the set.
   b. Rinse the vacuum flask three times with distilled water and add each rinse to the beaker.
4. LCS
   a. Filter 50 mL of the 200 mg/L standard and transfer to last beaker in the set.
   b. Rinse the vacuum flask three times with distilled water and add each rinse to the beaker.
5. Duplicate
   a. Selected at random, but typically the first sample in the set.
   b. Filter a second sample aliquot using the same amount of sample.
6. Refer to QC chart for frequency.

PREPARATION

1. Print TDS list and select samples to be analyzed.
   a. Refer to Testing Priority SOP
   b. Watch for holding time, rush samples, and re-runs.
2. Start LDS set for TDS.
   a. Refer to Data Entry: Sets, Gravimetric SOP.
   b. Select random duplicates which are representative of samples in set.
   c. Typical set arrangement:
      i. Weigh Blank
      ii. Method Blank
      iii. QC Standard
      iv. Samples, in numerical order
      v. LCS
3. Print data sheets.
4. Allow samples to equilibrate to room temperature.
5. Using a meter, measure and record the approximate TDS of each production sample.

BEAKER PREPARATION

1. Number a clean glass beaker for each QC and production sample in the set.
2. Place beakers in a pan in numerical order and label the set.
3. Place the pan and beakers in a drying oven at 178-182°C for at least an hour.

ANALAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

TARE WEIGHTS (1.WEIGHT)

1. Check desiccant in desiccator.
   a. Desiccant must be dry and cool before the desiccator can be used.
   b. Replace the desiccant if necessary.
   c. If desiccant is hot, it must be cooled in the desiccator at least one hour.
2. Remove pan containing the beakers from oven and place in desiccator.
3. Cool the beakers for **45** minutes.
4. Check the level on the balance before using it.
   a. If it is not level, level it.
   b. The balance must be level prior to use or weights will not be accurate.
5. Close Balance Room door when obtaining weights.
6. Close all the balance doors and tare the balance. (Set weight to 0.0000 grams.)
7. Using tongs, remove the beakers one at a time, in order, from the desiccator and place on balance pan.
   a. Close the desiccator door between balance weights.
8. Close the balance door
9. Obtain and record tare weight of the beaker to the nearest 0.0001 grams. **(A)**.
10. Remove the beaker from the balance and close the balance door.
11. Tare balance if the weight is not 0.0000 grams.
12. Return the beaker to the pan in the desiccator and remove the next beaker.
13. Repeat steps 7-11 until all beakers have been weighed.
14. Remove the pan of beakers from the desiccator and cover with a clean paper towel.
15. Store covered beakers in a clean, safe place.
16. Beaker weights may be obtain ahead of time and stored covered until used.

ESTIMATION OF TDS USING CONDUCTIVITY METER

1. The TDS of all samples is estimated using a conductivity meter in the TDS mode before filtering any samples.
2. Samples are shaken and then poured into plastic cups.
3. The conductivity meter is calibrated according to the Conductivity (CONL/CONS) SOP.
4. The calibration is checked with the appropriate standards.
5. The meter is set to the TDS mode.
6. The probe is placed in the sample, stirred briefly then held steady until the meter reads "Ready."

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

7. The TDS value is recorded and used to determine the amount sample that will be filtered according to Appendix II.

CRUCIBLE AND FILTER PREPARATION

1. Use clean vacuum flasks and crucibles.
2. Place a glass fiber filter disk with wrinkled side up into a Gooch crucible.
3. Place Gooch crucible onto a vacuum flask equipped with Gooch crucible adapter.
4. With a vacuum applied, rinse the filter with three small portions of distilled water.
   a. Make sure the filter is seated on the crucible and covers all of the holes.
   b. There must not be any uncovered holes or tears in the filter.
5. Remove all traces of water by continuing to apply vacuum after the water has passed through the filter.
6. Discard rinses; vacuum flask must be empty before filtering the sample.

FILTRATION

1. Use the approximate TDS value obtained from the conductivity meter as a guide to select an appropriate sample volume according to Appendix II.
2. **Shake sample**
3. Using a graduated cylinder or pipette, measure sample volume to be filtered and record volume. **(C)**
4. Transfer measured sample into a prepared Gooch crucible with glass fiber filter.
   a. If sample clogs the filter quickly, change filter or setup multiple filtrations. Combine filtrate from multiple filtrations. Record the total volume of sample filtered.
   b. If more than10 minutes are required to complete the filtration, start the filtration over with a smaller sample volume.
   c. Remember to record the sample volume actually used.
5. Apply vacuum until sample is completely filtered.
6. Rinse the graduated cylinder into the glass fiber filter with 3 successive small volumes of distilled water, allowing complete drainage between each washing. Continue suction until all liquid has passed through the filter.
7. Transfer the filtrate in the vacuum flask to the appropriate beaker.
8. Rinse the vacuum flask with 3 small volumes of distilled water and add each rinse to the beaker.

ANALAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

EVAPORATION AND DRYING

1. Place beakers in a water bath.
   a. Water in water bath should be hot but less than 100°C.
2. If the sample boils, it can splatter out of the beaker.
3. Evaporate until there is no apparent liquid in the beaker.
4. Remove each beaker from the water bath when it is evaporated
5. Place beakers in numerical order in the pan.
6. Place pan and beakers with residue in 178-182°C drying oven for at least 8 hours or 1 hour with repeated drying cycles to demonstrate constant dry weight.

DRY WEIGHT (2.WEIGHT)

1. Check desiccant in desiccator.
   a. Desiccant must be dry and cool before the desiccator can be used.
   b. Replace the desiccant if necessary.
   c. If desiccant is hot, it must be cooled in the desiccator at least one hour prior to use.
2. Remove pan and beakers from the 178-182°C drying oven and place in desiccator.
3. Desiccator time should be the same number of minutes used for Tare Weights (**45** min).
   a. Set a timer.
   b. Check the weight of the Weigh Blank a few minutes sooner.
      i. Weigh in the same manner as Tare Weights.
   c. If the weight is:
      i. Less than Tare weight (-0.0005 g), return beaker to desiccator and wait a few minutes longer.
      ii. Greater than Tare weight (+0.0005 grams), return all beakers to 178-182°C drying oven for 30 minutes.
   d. Repeat steps 1-3c until the Weigh Blank is within range.
4. When Weigh Blank is within range, (± 0.0005 grams), then weigh and record the weight of all beakers in the exact same order and manner as the Tare weights were obtained above. (**B1**)

REPEAT DRYING CYCLE

1. If repeat drying cycles are required,
   a. Dry, cool, and weigh in the same manner as above.
   b. Enter dry weights in LDS as (**B2**).

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

2. Check LDS Set Reading 'Difference' to compare the **B2** and **B1**.
3. If weight loss is:
   a. <0.5 mg of the previous weight, constant dry weight was obtained.
   b. >0.5 mg of the previous weight, constant dry weight has not been obtained, repeat drying, cooling, and dry weights as above until dry weight is constant.
   c. Enter dry weights in LDS as (**B3**), (**B4**) etc.)

DATA ANALYSIS AND CALCULATIONS

QUALITATION AND QUANTITATON

Refer to EPA method 160.1 and SM 2540 C.

CALCULATION

$$\text{mg TDS / L} = \frac{(B-A) * 1000000}{C}$$

Where: A = tare weight of beaker, g
B = dry weight of sample plus beaker, g, either **B1** or **B2**.
C = sample volume, mL

DATA REPORTING INSTRUCTIONS

1. Results are usually calculated and reported with 3 significant figures.
2. Typical units mg/L
3. If required, report the appropriate data qualifier with the result.

DATA ENTRY AND REVIEW

1. Using LDS Sets program, create a set.
   a. Opening a set assigns a set number
2. Enter data into LDS.
3. LDS will calculate data and post.
4. Print verification sheet and review flags.
5. Submit data for review and verification.

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

RECORD MANAGEMENT

1. Follow Record Management SOP.
2. Record will contain all necessary information including links to supporting data.
3. Record maintenance in the appropriate log.
4. Complete all required data sheets.
5. After verification, data is scanned into the network and archived on CD.
6. LDS has multiple backups.

METHOD PERFORMANCE

Refer to the appropriate section in EPA method 160.1 or SM 2540 C.

POLLUTION CONTROL

1. Employ techniques to reduce or eliminate the quantity or toxicity of waste generation.
2. Quantity of chemicals purchased should be based on expected usage and shelf life.
3. Reagent preparation volumes should reflect anticipated usage and reagent stability.

WASTE MANAGEMENT

Follow Disposal SOPs.

REFERENCES

1. APHA, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 2540 C.
2. EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 Revised March 1983, Method 160.1
3. Mexican Method. NMX-AA-034-SCFI-2001. Water Analysis - Determination of Salts and Solids Dissolved in Natural, Wastewaters and Wastewaters Treated - Test Method.
4. Equipment manual(s).

ANALAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

APPROVED BY

Bill Reary 11/28/2006

Technical Director Date

Revised by:	Date:	Reviewed by:	Date
LLW, Tech TDD, Tech	Nov. 2006 Nov. 2006	MRM, Manager	Nov. 2006

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

APPENDIX I

Training Needs

1. Proper use of the analytical balance
2. Preparation of standards using volumetric glassware.
3. Proper use of conductivity meter

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

TDS / TOTAL DISSOLVED SOLIDS, REVISION 07

File Name: J:\Word\SOP\Active\TDS_Dissolved_Solids_07.Doc
Date Initiated: 05/16/1994
Date Revised: 11/28/2006

APPENDIX II

Sample volume to be filtered

Probe reading (mg/L)	mL of sample
0-100	100
100-300	50
300-500	25
500-5000	10
5000-10,000	5
>10,000	1

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

METHODS

Potable Water:..... SM 2320B
Nonpotable Water:..... EPA 310.1
Solid/Hazardous Waste:..... EPA 310.1
Mexican Method:.....NMX-AA-036-SCFI-2001

SCOPE AND APPLICATION

Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For total alkalintiy, titration is done to pH 4.5, for partial alkalinity a pH 8.3 endpoint is used. This method is applicable to aqueous samples and extracts. It is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid titrations greater buret capacity.

***The client's DQOs take precedence if they differ from those stated in this SOP and apply only to samples governed by the client's DQOs. If client's DQOs are less stringent than the referenced method or NELAC requirements, the analysis is flagged on the analytical report as not meeting NELAC requirements because the client's supplied DQO's govern.

Procedure is performed by trained personnel with current demonstration of capability and authorization. Refer to Appendix I for training needs.

SUMMARY

A 100 ml aliquot of sample is added to a beaker and initial pH is recorded. The partial alkalinity of the sample is titrated with a standardized acid solution to a pH of 8.3, the amount of titrant is recorded. The titration is continued to pH of 4.5, the amount of titrant is recorded. An Automated as well as a Manual procedure are offered in this SOP.

DEFINITIONS

1. BATCH – 1 to 20 production samples of like matrix plus associated quality control; processed as a unit.
2. Duplicate - replicate of the sample, quantifies precision.
3. Holding Time – time allowed between sample collection and analysis.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

4. LDS (LABORATORY DATA SERVICES) – in-house LIMS; computer software.
5. METHOD BLANK – reagent water or other blank matrices processed simultaneously with and under the same conditions as samples and carried through preparation and analytical procedures exactly like a sample; monitors contamination present in the laboratory environment, equipment or reagents.
6. **ISV (INITIAL STANDARDIZATION VERIFICATION) – used to confirm the accuracy of an analytical process; independent of original standard , if applicable.**
7. **CSV (Continuing Standardization Verification) - used to confirm the accuracy of an analytical process and is of the same standard used in standardization.**
8. MS (MATRIX SPIKE) – same amount of target analyte added to the LCS is added to a second aliquot of sample; quantifies matrix bias.
9. PARTIAL ALKALINITY - "phenolphthalein alkalinity: the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination.
10. Production Sample – Sample logged-in to LDS with a unique sample number.
11. QC (QUALITY CONTROL) – is the overall system of technical activities that measures the attributes and performance of a process against defined standards to verify that they meet the stated requirements of the client.
12. QC STANDARD – used to confirm the accuracy of an analytical process; independent of the calibration, if applicable.
13. SET – processed as a unit; an analytical group / analytical batch.

INTERFERENCES

1. Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response.
   a. Allow addition time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

SAFETY

1. Follow Chemical Hygiene Plan for routine laboratory practices.
2. Follow applicable MSDSs.
3. Wear appropriate personal protective equipment and clothing.

ANALAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

EQUIPMENT AND SUPPLIES

1. pH Meter and probes.
2. Beakers.
3. Magnetic stirrer and teflon coated stir bars.
4. Pipets and disposable tips, appropriate volumes.
5. Burets, borosilicate glass
6. 100 mL graduated cylinder.
7. Auto titration system: Schott TitroLineTA50 plus with sample changer and TitriSoft 2.5 software.

SUPPLEMENTAL EQUIPMENT AND SUPPLIES

1. Computer with LDS software and printer.
2. Testing list for applicable test codes.
3. Laboratory notebook with data sheets.
4. Notebook or folder for completed data.
5. Ballpoint pen, black waterproof ink.
6. Permanent marker, Sharpie or equivalent.

REAGENTS

1. PURCHASED REAGENTS
   a. Traceable by the Chemical Log number. (C#)
   b. Purchased reference materials and chemicals are traceable to NIST and to CoAs, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in the chemical or the solvent storage room or in the designated lab work area.
   d. Follow Chemical Log SOP.
2. PREPARED REAGENTS
   a. Traceable by the Reagent Log number (SW#)
   a. Reagents prepared in house are traceable to reference materials and chemicals, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   a. Stored in a reagent bottle in designated lab work area unless otherwise noted.

ANALAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

i. NOTE: Daily Reagents - record on data sheet or in instrument log and dispose at the end of the day.

d. Follow Reagent SOP.

3. Preparation Techniques
   a. Follow Personnel: Training, Basic Technical Skills SOP

REAGENTS

1. Distilled water, Type II, pH adjusted to 4.5+/-0.1 prepared fresh daily by Titroline or by manual adjustment with 0.2N sulfuric acid.
2. Sodium carbonate Standard (Na_2CO_3) - 0.05N (2500 ppm as CaCO3), purchased or Prepared by dissolving 2.5+/- 0.2 grams of Na2CO3 (dried at 250 C over night then cooled in a desiccator) in distilled water and dilute to 1 liter final volume.
3. Standard sulfuric acid (H_2SO_4) - 0.2N, purchased or prepared by diluting 5.6 mL of Concentrated H2SO4 to 1 L with distilled water.

SAMPLE COLLECTION, PRESERVATION AND STORAGE

Aqueous sample is collected in an unpreserved ½ gallon plastic container, stored at 4°±C, and analyzed within 14 days of collection.

Non-aqueous sample is collected in unpreserved glass sample bottles with Teflon lined lids, stored at 4°C ± 2, extracted and analyzed within 14 days of collection.

QUALITY CONTROL

Any quality control outside acceptable control limits will be evaluated for significance of nonconformity by the Quality Department. See Corrective Action SOP.

TYPE	MINIMUM FFREQUENCY	ACCEPTANCE LIMITS	CORRECTIVE ACTION
TITER STANDARDIZATION	DUPLICATE: DONE DAILY	PASS ICV CRITERIA RPD<4%	Correct problem and re-analyze
ISV	AFTER EACH TITER DETERMINATION	± 10%	Correct problem and re-analyze
CSV	After each calibration After each 10 production	± 10%	Correct problem and re-analyze

ANA-LAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

	samples At the end of the set		
BLANK	1 per batch [NOTE 1]	< Reporting Limit	Note 3
DUPLICATE	1 per 10 production samples	≤ 20 % RPD[Note2]	Note 3
MATRIX SPIKE	1 per 10 production samples	± 10%	Note 3

NOTES
1. A batch is 20 production samples, or less, of like matrix.
2. Reject and re-analyze readings between failed standard and previous acceptable standard.
3. If Duplicate or MS is outside the acceptance criteria and the QC Standard is within the acceptance criteria, flag the analyte with a data qualifier (possible matrix interference).

AUTOMATED PROCEDURE (OPTION 1)

pH Calibration: TitroLine TA50 plus Meter
Two point Calibration (pH 4 and 7)

0. Press {Escape} on the keypad of the Schott TitroLineTA50 plus. Continue pressing escape until the top line of the screen reads "Titroline ready".
0. Press the "CAL" button {F8}. This will bring you to a Calibration screen.
0. Press {Enter} with on "measuring channel A".
0. You will be instructed to "rinse electrode" and "dip into Buffer 4.00 pH". Make sure that the air vent on the electrode is in the open position.
0. Press {Enter} to begin calibrating the meter at pH 4.00.
0. You will be prompted to "rinse electrode" and "dip into Buffer 7.00 pH".
0. Press {Enter} to begin calibrating the meter at pH 7.00.
0. The "result of calibration" will be displayed. The slope will be greater than 95% if the electrode is clean and in good working condition. If slope values of less than 95% are obtained, clean the electrode and recalibrate the meter beginning at step 1.
0. Press {Enter} to complete the calibration process.

Cleaning procedure for the pH Probe:
-Rinse probe with distilled water
-Dip probe in isopropyl alcohol wipe with kimwipe

ANA-LAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

-Soak probe 10 minutes in 1:1 HCl
-Rinse probe with water
-Equilibrate probe for 15 minutes in pH 7 buffer

Create a TitriSoft 2.5 Alkalinity Worklist from LDSClient.

0. Log-on to LDSClient from a computer work
0. From the menu bar click "Sets", then "Instruments" and then "Upload".
0. Select the TitriSoft instrument "003229 TitriSoft".
0. Press the "Test" button option.
0. Select "Alkalinity" from the drop down menu.
0. Choose the alkalinity test code "AlkT" under the "Test Selection" menu. This can be done by pressing the fetch button {...}, type AlkT and press {Enter} twice.
0. The Alkalinity worklist should be ready for use at the TitriSoft work station.

UpLoad LDSClient Worklist into TitriSoft 2.5

0. Start the TitriSoft 2.5 software on the titration workstation computer.
0. Login using your three charactor initials and password.
0. Click the "Titration Center" button.
0. Click on the "Worklists" tab.
0. Click on the "Worklist" drop down menu and select "Import".
0. A list of potential worklists will appear.
0. Choose the one that you just created in LDSClient and click "Open". The file name format is of the type "test_date_timecreated". Example "alkalinity_20060907_1159".
0. The new worklist will appear under the "TL alpha plus" directory on the left hand side of the screen. Scroll down, find your new worklist and select it.
0. The run sequence with QC samples and production samples will appear under the "Sample List" tab.
0. Load the sample changer according to the sequence, fill the wash station beakers with fresh distilled water (positions 15 and 16) and press "Go" to start the run.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

QC PREPARATION

Prepare each of the following standards in 150 mL beakers then place them in the autosampler in the appropriate sample position. Be sure to verify the sample changer position with the sample ID.

19. Calibration check, pH 6 buffer.
20. Calibration check, pH 10 buffer.
21. System purge standard: Same as Titer determination standard.
22. Titer determination standard: 10 mL of 0.05N carbonate standard in about 90 mL of pH adjusted distilled water.
23. ISV standard: 1 mL of 0.05 N carbonate standard in about 100 mL of pH adjusted distilled water. (This standard is from an independent lot than that used to determine the titer value.)
24. CSV standard: 1.0 mL of 0.05 N carbonate standard in about 100 mL of pH adjusted distilled water. (This standard should be from the same lot used to determine the titer value.)
25. Blank is 100 mL of pH adjusted distilled water.
26. Duplicate is a second 100 mL aliquot of a sample.
27. Matrix Spike is a 100 mL aliquot of sample spiked with 1.0 mL of standard added.

Dilute high level samples with pH adjusted distilled water so that less than 30 mL but more than 0.01 mL of titrant is used to achieve the endpoint pH.

For soil/organic samples

1. To prepare extract refer to pH SOP, except use pH adjusted water.
2. Use aqueous layer and follow general procedure listed below.

MANUAL PROCEDURE (OPTION 2)

GENERAL

1. Add 100 ml of sample to a beaker.
2. Place the pH electrode and temperature probe into this sample and record the initial pH of

ANA-LAB CORP. THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

the sample.

3. Partial Alkalinity
   a. While stirring gently, titrate with 0.02 N acid solution to a pH of 8.3. Record the amount of acid, 'A', in ml used for this end point. When close to end point, add titrant slowly.
4. Total Alkalinity
   a. Continue titration to a pH of 4.5. When close to end point, add titrant slowly. Record this volume of acid, 'B', in ml.

DATA ENTRY

27. Enter the data into LDS.
27. Print verification sheet and review
27. Submit data for review and verification.

RECORD MANAGEMENT

1. Follow Record Management SOP
2. Record will contain all necessary information including links to supporting data.
3. Record maintenance in the appropriate log.
4. After verification, data is scanned into the network and archived on CD.
5. LDS has multiple backups.

DATA ANALYSIS AND CALCULATIONS

QUALITATION AND QUANTITATON

10. Refer to methods referenced.

CALCULATION

$$\text{'Total' Alkalinity, mg } CaCO_3/L = \frac{B \times N \times 50{,}000}{C}$$

$$\text{'Partial' Alkalinity, mg } CaCO_3/L = \frac{A \times N \times 50{,}000}{C}$$

where:

A = ml of titrant (standardized H_2SO_4) at pH 8.3
B = ml of titrant at pH 4.5
N = Normality of acid used

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

C = ml of sample

DATA REPORTING INSTRUCTIONS

0. AlkT/AlkP is usually calculated and reported in mg $CaCO_3$/L with 3 significant figures.
0. Liquid sample – report mg/L
0. Solid sample – report mg/kg
0. If required, report the appropriate data qualifier with the result.

GENERAL

0. Add 100 ml of sample (or an appropriate aliquot diluted to 100 ml) to a beaker and insert a magnetic stirring bar. Aliquot used should be of a size so that titration is less than 20 ml on the 25ml buret.
0. Place the pH electrode and temperature probe into this sample and record the initial pH of the sample.
0. Partial Alkalinity
   . While stirring gently, titrate with 0.02 N acid solution to a pH of 8.3. Record the amount of acid, >A=, in ml used for this end point. When close to end point, add titrant slowly.
0. Total Alkalinity
   . Continue titration to a pH of 4.5. When close to end point, add titrant slowly. Record this volume of acid, >B=, in ml.

DATA ENTRY

0. Enter the data into LDS.
0. Print verification sheet and review
0. Submit data for review and verification.

RECORD MANAGEMENT

0. Follow Record Management SOP
0. Record will contain all necessary information including links to supporting data.
0. Record maintenance in the appropriate log.
0. After verification, data is scanned into the network and archived on CD.
0. LDS has multiple backups.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

DATA ANALYSIS AND CALCULATIONS

QUALITATION AND QUANTITATON

0. Refer to methods referenced.

CALCULATION

'Total' Alkalinity, mg $CaCO_3/L = \frac{B \times N \times 50{,}000}{C}$

'Partial' Alkalinity, mg $CaCO_3/L = \frac{A \times N \times 50{,}000}{C}$

where:

A = ml of titrant (standardized H_2SO_4) at pH 8.3
B = ml of titrant at pH 4.5
N = Normality of acid used
C = ml of sample

DATA REPORTING INSTRUCTIONS

9. AlkT/AlkP is usually calculated and reported in mg $CaCO_3/L$ with 3 significant figures.
9. Liquid sample B report mg/L
9. Solid sample B report mg/kg
9. If required, report the appropriate data qualifier with the result.

METHOD PERFORMANCE

5. Refer to methods referenced.

POLLUTION CONTROL

5. Employ techniques to reduce or eliminate the quantity or toxicity of waste generation.
5. Quantity of chemicals purchased should be based of expected usage and shelf life.
5. Reagent preparation volumes should reflect anticipated usage and reagent stability.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914

Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

WASTE MANAGEMENT

5. Follow Disposal SOPs.

REFERENCES

5. EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 Revised March 1983, Method 310.1
5. APHA, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 2320B.
5. Mexican Method. NMX-AA-036-SCFI-2001. Water Analysis - Determination of Acidity and Alkalinity Total in Natural, Wastewaters and Wastewaters Treated.
5. Equipment Manual(s).

APPROVED BY

Bill Peary 10/10/2008

Technical Director Date

Revised by:	Date:	Reviewed by:	Date:
FGO, Lab Manager	October 2008	TWV, Asst. QA Mgr	October 2008

ANA-LAB CORP.
THE COMPLETE SERVICE LAB
P.O. BOX 9000 - KILGORE, TEXAS 75663-9000 - 903/984-0551 - FAX 903/984-5914
Analytical Chemistry • Email: corp@ana-lab.com • www.ana-lab.com

Standard Operating Procedure

ALKT OR ALKP/ TOTAL AND PARTIAL ALKALINITY, REV. 06

File Name: J:\Word\SOP\Active\Alkt_Alkp_Alkalinity_06.Doc
Date Initiated: 01/15/1994
Date Revised: 10/10/2008

APPENDIX I

Training Needs

7. Manual pipette calibration and use
7. Burette usage
7. pH meter use and maintenance
7. Schott Tritoline TA-50 (automated system only)

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

METHODS

Potable Water: ..... EPA 200.8, Rev 5.4
Non potable Water: ..... EPA 200.8, Rev 5.4
Solid/Hazardous Waste: ..... EPA 6020

SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-ppb (ug/L) concentrations of metals in aqueous and non-aqueous samples and in filtrates, extracts, leachates, etc.

ICP-MS has been applied to the determination of over 60 elements in various matrices. Refer to **Appendix II**. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, and operating conditions. If ICP-MS is used to determine any analyte not listed in **Appendix II**, accuracy and precision of the method in the sample matrix is demonstrated.

This method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. Higher silver concentrations require dilution prior to digestion.

CAS numbers: REFER TO **APPENDIX II**.

Sensitivity: Refer to EPA 200.8 and 6020 tables.

Data objectives for precision, bias, representativeness, comparability and completeness are predetermined. Refer to Quality Control acceptance limits.

***The client's DQOs take precedence if they differ from those stated in this SOP **and apply only to samples governed by the client's DQOs. If client's DQOs are less stringent than the referenced method or NELAC requirements, the analysis is flagged on the analytical report as not meeting NELAC requirements because the client's supplied DQO's govern.**

Procedure is performed by trained personnel with current demonstration of capability and authorization. **Refer to Appendix I for training needs.**

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

SUMMARY

This method describes the multi-element determination of trace elements by ICP-MS. Aqueous solutions are introduced by pneumatic nebulization via a spray chamber into a radio frequency argon plasma. Desolvation, atomization and ionization create predominantly singly-charged cations which are identified and quantitated by the use of a quadrupole mass spectrometer. Potential interferences from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundances. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

Acid digestion prior to filtration and analysis is required to obtain total (acid-leachable) metal results for aqueous and non-aqueous samples. Extractions, leachates, etc also require acid digestion prior to analysis.

Digestion is not required prior to analysis for dissolved elements or drinking water samples with a turbidity of <1 NTU. Direct analysis does require acid preservation prior to analysis.

DEFINITIONS

1. Additional or expanded definitions may be found in:
   a. APHA Standard Methods, Part 1000.
   b. EPA SW846, Chapter One, 5.0 Definitions.
   c. References.
2. ALIQUOT - measured, representative portion of a sample used for analysis; subsample.
3. ANALYTICAL SAMPLES – analytical readings excluding calibration standards, calibration verifications, and calibration blanks; includes method blanks, LCSs, production samples, spikes, and replicates.
4. AWRL (AMBIENT WATER REPORTING LIMIT) - low level QC standard: independent of curve.
5. BATCH – 1 to 20 production samples of like matrix plus associated quality control; processed as a unit.
6. CALIBRATION CURVE – graphical relationship between the known values, such as concentrations, of a series of calibration standards and their analytical response.
7. CALIBRATION STANDARDS – prepared by successively diluting a stock standard to produce working standards which cover the working range of the instrument.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

8. CCB (CONTINUING CALIBRATION BLANK) – reagent blank; analyzed after each CCV.
9. CCV (CONTINUING CALIBRATION VERIFICATION) – same standard used to prepare the curve; typically a mid-range concentration; verifies the continued validity of the calibration curve.
10. DATA QUALIFIER – used to flag and qualify the use of data when a data quality objective is exceeded.
11. DILUTION FACTOR – Final Volume / Initial amount; used in calculations.
12. DOC (DEMONSTRATION OF CAPABILITY) - initial and on-going demonstration of acceptable performance.
13. DQO (DATA QUALITY OBJECTIVE) – identifies and defines the type, quality, and quantity of data need to satisfy a specified use; qualitative and quantitative statements.
14. DUPLICATE - replicate of the sample, quantifies precision.
15. FINAL VOLUME – the volume at the end of the process; dilution factor = Final / Initial.
16. HOLDING TIME – time allowed between sample collection and analysis.
17. ICB (INITIAL CALIBRATION BLANK) – reagent blank; analyzed after the ICV.
18. ICL (INSTRUMENT CALIBRATION LIMIT) – re-analysis of the highest point of the calibration curve; verifies instrument performance.
19. ICS (INTERFERENCE CHECK SOLUTION) – contains known concentrations of interfering elements; used to demonstrate impact of interference upon sample analysis
20. ICV (INITIAL CALIBRATION VERIFICATION) – standard independent of the curve; typically a mid-range concentration; verifies validity of the calibration curve prior to analysis of samples.
21. IDL (INSTRUMENT DETECTION LIMIT) – 99% confidence that the signal is not random noise.
22. INITIAL AMOUNT – amount of sample used to start the process; dilution factor = Final / Initial.
23. IS (INTERNAL STANDARD) – analyte(s) that is not a sample component is added to a sample, extract, or standard solution in a known amount and is used to measure the relative responses of other method analytes that are components of the same sample or solution.
24. LCS (LABORATORY CONTROL SAMPLE) - reagent water or other blank matrices that is spiked with a known quantity of target analyte(s) and carried through preparation and analytical procedures exactly like a sample; typically a mid-range concentration; verifies that bias and precision of the analytical process are within control limits; determines usability of the data.
25. LCSD (LABORATORY CONTROL SAMPLE DUPLICATE) – replicate LCS; analyzed when there is insufficient sample for duplicate or MSD; quantifies accuracy and precision.
26. LDS (LABORATORY DATA SERVICES) – in-house LIMS; computer software.
27. LOD (Limit of Detection) - estimate of the minimum amount that an analytical process can reliably detect.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

28. LOQ (Limit of Quantitation) - the minimum level of a target analyte that can be reported with a specified degree of confidence; lowest technically valid value.
29. LR (LINEAR RANGE) – upper limit of calibration range; usually the highest concentration in the calibration curve; may be extended with demonstration of linearity
30. MDL (METHOD DETECTION LIMIT) – 99% confidence that the analyte concentration is greater than zero; carried through preparation and analytical procedures exactly like a sample.
31. METHOD BLANK – reagent water or other blank matrices processed simultaneously with and under the same conditions as samples and carried through preparation and analytical procedures exactly like a sample; monitors contamination present in the laboratory environment, equipment or reagents.
32. MS (MATRIX SPIKE) – same solution and amount of target analyte added to the LCS is added to a second aliquot of sample; quantifies matrix bias.
33. MSD (MATRIX SPIKE DUPLICATE) – replicate of the matrix spike; same amount of target analyte is added to a third aliquot of sample; quantifies matrix bias and precision.
34. NEAT MATERIAL - pure or close to pure manufactured product, 99% pure product; not diluted.
35. PRODUCTION SAMPLE – sample logged-in to LDS with a unique sample number.
36. QC SPECIFIC - client request that specific QC procedures be applied to their sample or project.
37. QCCS (QUALITY CONTROL CHECK SAMPLE) – certified external reference material of known concentration in a clean matrix demonstrates acceptable laboratory, method, instrument and/or personnel performance; used to verify stock standards and calibration standards and to confirm analytical process accuracy.
38. REFERENCE MATERIAL – calibration standard.
39. REPRESENTATIVE SAMPLE – subsample that is representative of the sample as a whole.
40. RL (Report Limit) – refer to LOQ.
41. RPD (RELATIVE PERCENT DIFFERENCE) – demonstration of precision..
42. RSD (RELATIVE STANDARD DEVIATION) – measurement of reproducibility expressed in percent.
43. RUN – instrument run; all readings.
44. SD (Standard Deviation) – determines the width or spread of the normal distribution and is used to set confidence limits (±)
45. SET – processed as a unit; an analytical group / analytical batch.
46. STOCK STANDARD – known quantity of target analyte(s) in solution or homogeneous matrix; traceable with a certificate of analysis.
47. TRACEABILITY – an unbroken chain of comparisons to national or international standards.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS:

1. Spectroscopic Interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass to charge (m/z ratio as the analyte elements. They can be isobaric, polyatomic, refractory oxide, and doubly charged Ions. Isobaric interferences are caused by isotopes of other elements or polyatomic species which have the same nominal mass/charge ratio as the analyte element. These can be managed by the selection of an alternate Isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobar interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca, in this case the use of ^{43}Ca or ^{44}Ca is recommended. Polyatomic isobaric interference is $^{40}Ar^{35}Cl$ on ^{75}As. In this case the use of an equation based on the isotopic abundances of $^{35}Cl/^{37}Cl$ would be used. A detailed description on the theory and use of elemental equations is contained in chapter 4 of the HP 4500 Application Handbook along with recommended equations and their derivations.
   a. Most commonly used corrections for isobaric interferences are already included as the default equations in the default EPA method included with this SOP. A list of the correct equations used is located in **APPENDIX IV.**
   b. Care must be taken that any isotope used for correction purposes is itself not subject to uncorrected isobaric interferences.
2. Physical Interferences are associated with the physical processes which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the samples and calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects).
   a. To minimize some of these effects, acid composition and concentration need to be matched for all standards, blanks and samples. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

need to display similar analytical behavior to the elements being determined. To this end, internal standards need to be matched as closely as possible to the analyte elements in mass, ionization potential, solubility, boiling point and reactivity tot he various components in the sample introduction system. The recommended internal standards are listed in **APPENDIX VI** TABLE 2.

3. Memory Interferences result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition may occur is dependent on the sample and may need to be minimized through the use of a rinse blank between samples.
   a. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run need to be recognized and suitable rinse times need to be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If memory interference is suspected, the sample needs to be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.
4. For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust etc. Standards, samples and blanks need to be exposed to the laboratory environment as little as possible.
   a. The use of preparation blanks and spikes need to be used to verify the absence of sources of contamination and loss. If necessary, polypropylene sample tubes need to be rinsed and stored in dilute acid prior to use. Note: Chromic acid must not be used for cleaning glassware for trace metal analysis.

SAFETY
1. Follow Chemical Hygiene Plan for routine laboratory practices.
2. Follow manufacturer's operating instructions.
3. Follow applicable MSDSs.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

4. Wear appropriate personal protective equipment and clothing.
5. Reagents might be TOXIC or CARCINOGENS.
6. Aqua Regia is very CORROSIVE. Quickly treat any spills with baking soda.
7. Liquid argon represents a potential cryogenic and suffocation hazard.
8. The HP 4500 is fully interlocked to prevent user exposure to harmful electrical voltages, radio frequency emissions, ultraviolet radiation, high temperatures and other hazards.

EQUIPMENT AND SUPPLIES
1. Hewlett-Packard HP 4500 ICP-MS system with Cetac ASX-500 Autosampler.
2. Argon gas supply (high purity grade gas or liquid, 99.9%)
3. Instrument Consumables: Refer to **APPENDIX III.**
4. Calibrated pipettes with disposable tips, appropriate ranges.
5. Dilution water dispenser
6. 10 mL plastic culture tubes
7. 50 mL polypropylene centrifuge tubes used for standards and samples.
8. Parafilm
9. Whatman Filter paper #41
10. Equipment manual(s)

SUPPLEMENT EQUIPMENT AND SUPPLIES
1. Computer with HP 4500 ICP-MS ChemStation and LDS software and printer.
2. Equipment manual(s).
3. Equipment Maintenance Log.
4. Function Log.
5. Testing list for applicable test codes.
6. Data sheets
7. Ballpoint pen, black waterproof ink.
8. Permanent marker, Sharpie or equivalent.
9. Label tape.
10. General office supplies.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

REAGENTS

GENERAL

1. PURCHASED REAGENTS
   a. Traceable by the Chemical Log number (C#).
   b. Purchased reference materials and chemicals are traceable to NIST and to CoAs, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in the chemical or the solvent storage room or in the designated lab work area.
   d. Follow Chemical Log SOP.
2. PREPARED REAGENTS
   a. Traceable by the Reagent Log number (SW#)
   b. Reagents prepared in house are traceable to reference materials and chemicals, meet the specified requirement of the analytical method, and cannot be used past the expiration date.
   c. Stored in a reagent bottle in designated lab work area unless otherwise noted.
      i. **NOTE: Daily Reagents – record in ICP-MS log and dispose at the end of the day.**
   d. Follow Reagent Log SOP
3. Preparation Techniques
   a. Follow Personnel: Training, Basic Technical Skills SOP.

REAGENTS

*Due to the high sensitivity of ICP-MS, high-purity reagents must be used whenever possible.
*Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences.
*Use Class A volumetric flasks to prepare reagents unless otherwise noted.

1. Distilled water, ASTM Type I
2. Nitric acid, (HNO_3) concentrated "Trace Metal" grade
3. Nitric acid, 2% and 5% (vol/vol)
4. Tuning Solution: 10 ug/L Li, Ce, Y, Tl in 2% HNO_3.
   a. Pipet 0.25 mL of 10 ug/mL stock Tuning Solution into 250 mL of 2% Nitric acid.
   b. Mix well.
5. EPA Tune Check Solution: 100 ug/L ^{7} Li, Be, Mg, Co, In, Pb, Tl.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

a. Pipet 2.5 mL of a 10 ug/mL stock Tuning solution for Method 200.8 (VHG LABS products no.: LTS2008D -100) and 2.5 mL of a 10 ug/mL single element stock solution of Li and Tl into a 250 mL Nalgene bottle.
b. Dilute to 250 mL mark with 2% Nitric acid.
c. Mix well.

6. Internal Standard Solution: 0.4 mg/L ^{6}Li, Sc, Y, In, Tb, and Bi.
   a. Pipet 1.0 mL of a 100 ug/mL stock Internal standard Solution (VHG Labs product no.: LIS-100) into a Nalgene bottle.
   b. Dilute to 250 mL mark with 2% Nitric acid.
   c. Mix well.
7. Calibration standard #1, 200 ug/L:
   a. Pipet 1.0 mL of a 10 ug/mL stock Environmental Calibration standard (Agilent Part #: 5183-4688, contains Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn) into a 50 mL centrifuge tube
   b. Dilute to final volume of 50 mL with 2% nitric acid.
   c. Mix well.
8. Calibration standard #2, 300 ug/L:
   a. Pipet 1.5 mL of a 10 ug/mL stock Environmental Calibration Standard (Agilent Part#: 5183-4688, contains Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn) into a 50 mL centrifuge tube
   b. Dilute to 50mL final volume with 2% nitric acid.
   c. Mix well.
9. ICV, 100 ug/L, independent source:
   a. Pipet 0.5 mL of 100 ug/mL stock Environmental Calibration Standard (Agilent Part #:5183-4682, contains Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Tl, V, Zn) into a 50 mL centrifuge tube
   b. Dilute to 50mL final volume with 2% nitric acid..
   c. Mix well.
10. CCV, 300 ug/L:
    a. Pipet 1.5 mL of a 10 ug/mL stock Environmental Calibration Standard (Agilent Part#: 5183-4688, contains Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn) into a 50 mL centrifuge tube
    b. Dilute to 50 mL final volume with 2% nitric acid.
    c. Mix well.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

11. ICS-A, Al, Ca, Fe, K, Mg, Na, P and S @ 100,000 µg/L, Cl @ 10,000 µg/mL, C @ 2,000 µg/mL and Mo and Ti @ 20.0 µg/mL:
    a. Pipet 5 mL of 6020 Interference Check Mix A solution (Hewlett Packard Part #: 8500-6998) into a 50 mL centrifuge tube
    b. Dilute to 50mL final volume with 2% nitric acid.
    c. Mix well.
12. ICS-AB, ICS-A plus 10 ug/L of each Ag, As, Cd, Co, Cr, Cu, Mn, Ni and Zn:
    a. Pipet 5 mL of 6020 Interference Check Mix A solution (Agilent Part #: 8500-6998) and 100 uL of 10 ug/mL 6020 Interference Check Mix 2 (Agilent Part #: 8500-7001) into a 50 mL centrifuge tube.
    b. Dilute to 50 mL final volume with 2% nitric acid.
13. Calibration Blank: 2% (v/v) nitric acid.
14. Rinse Blank: 5% (v/V) nitric acid.
15. Pulse to Analog (P/A) Calibration Solution: Same as solution in 7.1.8 (ICV).

SAMPLE COLLECTION, PRESERVATION AND STORAGE

Prior to sample collection, consideration needs to be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation, etc., needs be performed at the time of sample collection or as soon thereafter as practically possible.

1. For the determination of dissolved elements, the sample is filtered through a 0.45 µm membrane filter. The filtrate is preserved to pH <2. 1+1 HNO_3 acid immediately following filtration, stored at 4°C ± 2, and analyzed within 180 days of collection. Refer to Dissolved Metal Filtration SOP.
2. For the determination of total recoverable elements:
    i. Aqueous sample is collected in a glass or plastic sample bottle, preserved to pH <2 with 1+1 HNO_3, stored at 4°C ± 2, and analyzed within 180 days of collection.
    ii. Non-aqueous sample and extractable sample, such as TCLP, are collected in unpreserved plastic or glass sample bottle stored at 4°C ± 2, and analyzed within 180 days of collection.
3. Extracts, leachates, etc. are preserved and stored according to specific SOPs.
4. Digestions are stored in the metals lab.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

NOTE: Aqueous samples that cannot be acid preserved at time of collection because of sampling limitations or transport restrictions, are acidified to pH<2 with 1+1 HNO_3 upon receipt in the laboratory. Following acidification, the sample is held for 16 hours before processing.

QUALITY CONTROL

Any quality control outside acceptable control limits will be evaluated for significance of nonconformity by the Quality Department. See Corrective Action SOP.

Type	Minimum Frequency	Acceptance Limits	Corrective Action
IDL	Initially When conditions change At least quarterly	> 0	If≤O, re-determine IDL.
LOD	Initially When conditions change At least annually	Approximately, 2x IDL and ½ MDL	Re-determine LOD
LR	Initially When conditions change At least every 6 months	90% of highest measured level	Repeat linear range study
MDL	Initially When conditions change At least annually	≤Regulatory limit	Repeat MDL study
QCCS	Initially When conditions change At least quarterly	±10% of known values	Re-analyze. If still unacceptable, correct problem before continuing analysis

Type	Minimum Frequency	Acceptance Limits	Corrective Action
Calibration	Initially Repeat as needed	±10% of known values	Correct problem and re-calibrate
Mass Calibration	Each calibration	<0.1amu	Correct problem and re-calibrate
Mass Resolution	Each calibration	<0.9 amu	Correct problem and

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

	full with at 10% peak ht		re-calibrate
Tune Verification	Beginning of run	≤5% RSD	Correct problem and re-calibrate
ICV	After each calibration	±10% of known values	Correct problem and re-calibrate
ICB	After each ICV	< ±3x IDL	Correct problem and re-calibrate
CCV	Beginning of run After each 10 production samples End of run	±10% of known values	Correct problem and re-analyze NOTE 4
CCB	After each CCV	< ±3x IDL	Correct problem and re-analyze
AWRL	After each calibration	±25% of known values	Correct problem and re-calibrate
ICS-A and ICS-AB	Beginning of run Every 12 hours End of run	±10%	NOTE 5
Internal Standards minimum of 3	Each analysis	30-120% intensity of internal std for sample ±20% of original response in calibration blank and verification standards	If not within limits, dilute a fresh aliquot of sample 2x, add internal std, re-analyze. If not within limits, terminate run.
Method Blank	1 per batch NOTE 1	< Reporting Limit	NOTE 6
LCS	1 per batch NOTE 1	Lab limits; Equal to or better than 85-115% R	Correct problem and re-analyze
LCSD	1 per batch NOTE 2	Lab limits; Equal to or better than 85-115% R ≤ 20% RPD NOTE 3	Correct problem and re-analyze

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

MS	1 per 10 production samples	Lab limits; Equal to or better than 70-130% R	NOTE 7
MSD	1 per 10 production samples	Lab limits; Equal to or better than 70-130% R ≤ 20% RPD NOTE 3	Analyze post digestion spike NOTE 7
Post Digest Spike	As needed	Lab limits; Equal to or better than 85-115% R	NOTE 7
Dilution Test	1 per batch NOTE 1	± 10% of original sample	NOTE 8

NOTES
1. A batch is 20 production samples, or less, of like matrix.
2. If insufficient sample for MSD, duplicate the LCS.
3. Applicable to sample results that are ≥5 times the reporting limit.
4. Re-analyze readings between failed standard and previous acceptable standard.
5. If interference is present, report with an appropriate data qualifier.
6. If Method Blank is > 2.2 MQL, the lowest sample concentration in the associated batch must be at least 10 times the concentration in the Method Blank or MQL. Re-analyze all samples that are > 2.2 MQL and < 10 times the Method Blank. Method Blank in excess of 2.2 times the MDL indicates possible contamination.
7. If MS or MSD is outside the acceptance criteria and the LCS is within the acceptance criteria, flag the analyte with an appropriate data qualifier.
8. Report result with an appropriate data qualifier.

PROCEDURE

Routine operation and maintenance procedures for the HP 4500 are described in the HP 4500 ChemStation Operator's Manual, the HP 4500 ChemStation Administration and Maintenance Manual and in the HP 4500 Application Handbook.

QUALITY CONTROL PREPARATION

1. Process QC samples with the digestion batch.
   a. Method Blank – 1 per batch.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

b. LCS – 2 per batch, includes each element to be analyzed
   i. MS – 1 per each 10 production samples, spiked with each element to be analyzed.
   ii. MSD – replicate of each MS.
2. **Dissolved metals**
   a. **A filtered method blank - 1 per batch**
   b. **Direct MS – 1 per each 10 production samples, spiked with each element to be analyzed.**
   c. **Direct MSD – replicate of each MS.**
   d. **If sample is not digested, LCS is not required.**
3. **Direct analysis of drinking water with <1 NTU**
   a. **Direct MS – 1 per each 10 production samples, spiked with each element to be analyzed.**
   b. **Direct MSD.- replicate of each MS**
   c. **If sample is not digested, LCS is not required.**

SAMPLE PREPARATION
1. Follow applicable digestion SOP.
2. **Dissolved metals and direct analysis of drinking water with <1 NTU do not require digestion; although, samples may be digested. Contact a supervisor for assistance.**

STANDARDIZATION AND CALIBRATION
1. Follow manufacturer instructions and EPA 200.8 and 6020 requirements.
2. Verify calibration.
3. Refer to QC chart for frequency and acceptance limits.

DEMONSTRATION OF CAPABILITY (DOC)
1. **Refer Method Evaluation SOP.**
2. **Initial prior to sample analysis, when conditions change, and at specified intervals.**
   a. **Refer to QC chart for frequency and acceptance criteria**
3. **Instrument performance**
   a. **Instrument Detection Limit (IDL)**
   b. **Limit of Detection (LOD)**
   c. **Linear Range (LR)**

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

d. **QC Check samples (QCCS)**

4. **Method performance**
   a. **Method Detection Limit (MDL)**
   b. **Limit of Quantitation (LOQ)**

LINEAR RANGE

1. Calibrate the instrument as described in HP 4500 ChemStation Operators Manual section 9.2 and 10.1.
2. Run a series of standards at increasing concentrations beginning at 10 ppm at intervals of 10 ppm. Multi-element standard solutions.
3. The Upper Linear Dynamic Range is the maximum concentration for each element for which the measured concentration is within 10% of the actual value.
4. The Upper Linear Dynamic Range is re-determined whenever one of the following occurs:
   a. Twelve months have passed since last determination
   b. A new detector is installed
   c. The instrument is tuned for significantly different sensitivity.

INTERNAL STANDARD RESPONSES

1. The analyst is expected to monitor the responses form the internal standards throughout the sample set being analyzed.
   a. Ratios of the IS responses against each other are monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample.
   b. The absolute response of any one internal standard cannot deviate more than 60-125% of the original response in the calibration blank. If deviations greater than this are observed, use the following test procedure:
2. Flush the instrument with the rinse blank and monitor the responses in the calibration blank.
3. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two and re-analyze.
4. If the responses of the IS are not within the limit, or if it is a blank or calibration standard that is out of limits, terminate the analysis, and determine the cause of the drift. Possible causes of drift may be due to gradual accumulation of sample matrix on the interface (cones,

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

extraction lenses) or a change in the state of tune of the instrument.

TYPICAL RUN SEQUENCE

Calibration curve
ICV
CCV
CCB
AWRL
Method Blank
LCS
Samples
Dilution Test
CCV and CCB after each 10 analytical samples and at end of run.

ANALYSIS

1. HP 4500 ICP-MS Method Data Acquisition Parameters
2. See the HP 4500 ChemStation Operators manual for detailed instructions on setting up the following conditions.
3. Interference Equations: K):
   a. The following interference equations are used to correct for isobaric elemental and polyatomic interferences.
4. Acquisition Mode: Spectrum
   a. Points per Mass: 3
   b. Number Replicates: 3
   c. Integration Time: 0.1 sec for all elements except As, Se, Cd, Hg and their correction masses
   d. Integration Time: 0.3 sec for As, Se, Cd and associated correction masses
5. Peristaltic Pump Program:
   a. Uptake speed: 0.5 rps
   b. Uptake time: 60 sec
   c. Stabilization Time: 50 sec
   d. Rinse Port Speed: 0.3 rps
   e. Rinse Port Time: 5 sec (after standards and samples)
   f. Optional Rinse Speed: 0.3 rps

ANALAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

g. Optional Rinse Time: 60 sec
6. Acquisition Masses: Refer to **APPENDIX V**

METHOD DATA ANALYSIS PARAMETERS

1. Calibration Levels:
   a. Blank
   b. 200ppb for trace elements, 20,000ppb for Na, K, Mg, Ca, and Fe
   c. **300ppb for trace elements, 30,000ppb for Na, K, Mg, Ca,Fe.**
   d. Internal standard concentrations are **40** ppb for all levels.
2. Internal Standard References
   a. Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. Internal standards must be present in all samples, standards, and blanks at identical levels.
   b. This is achieved by directly adding the internal standard stock solution (1.0 ppm in 1% HNO3) to all samples, standards, and blanks by on-line addition prior to nebulization using a second peristaltic pump and a mixing Y-connector.
   c. Refer to Appendix VI for a list of internal standard references.
3. Calibration Curve Fits
   a. All quantitation masses y=ax + (blank)
   b. All internal standard masses (excluded)
   c. All interference correction masses (exlcluded)
   c. All monitor masses (not for quant) (excluded)
4. Reporting Parameters:
   QC Reports On - printer
   All Other Reports Off
   QC Criteria for Smart Sequencing and EnviroQuant reports:

HP 4500 TUNING AND TUNE VERIFICATION

1. After initiating the plasma, allow the instrument to warm up while aspirating a blank solution for at least 15 minutes.
2. During this warm-up, select Tune>>Sensitivity>>Start so that the instrument is scanning. After the 15 minute warm-up, aspirate the HP Tune Solution (20 ppb Li, Y, Ce, Tl) and check for responses and RSDs.
3. Generate and evaluate a tune report.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

4. The following are suggested guidelines for an acceptable tune.Suggested Tune Specifications:
   a. Sensitivity:
      i. Li >5,000 cts/0.1 sec/20 ppb
      ii. Y >10,000 cts/0.1 sec/20 ppb
      iii. Tl >5,000 cts/0.1 sec/20 ppb
   b. Precision:
      i. Li <15% RSD (0.1 sec integration time)
      ii. Y <15% RSD (0.1 sec integration time)
      iii. Tl <15% RSD (0.1 sec integration time)
   c. Oxides: <1%
   d. Ce^{++}/Ce^{+}: 5.0%
   e. Background:
      i. Li <30 cps
      ii. Y <15 cps
      iii. Tl <15 cps
   f. Mass Resolution: W-10% 0.7-0.8 AMU
   g. Mass Axis: nominal mass +/- 0.1 AMU for ^{7}Li, ^{89}Y and ^{205}Tl
5. Tune Verification for EPA Methods:
   a. After warm-up and verification of instrument tune, compliance with method tune criteria must be demonstrated.
   b. This is achieved by analyzing the EPA Tune Check Solution using the TN-EPA.m method.
6. Resolution at low mass is indicated by magnesium isotopes 24, 25, 26.
7. Resolution at high mass is indicated by lead isotopes 206, 207, 208.
8. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height.
9. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.
10. Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.
11. A tune compliance report will be automatically generated flagging any out of control results.

CALIBRATION AND STANDARDIZATION

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

1. Acceptable initial calibration is required before any samples are analyzed and periodically throughout sample analysis as dictated by results of calibration verifications.
2. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, and at requisite intervals.
3. Calibration must include a calibration blank and 1 calibration point for each element.
4. Initial calibration accuracy must be evaluated before any samples are analyzed through the analysis of an ICV which includes all analytes of interest. The ICV must quantitate within 10% of the expected value.
5. Calibration drift is monitored through the analysis of a CCV at the beginning of the sample block, after every 10 analytical samples and again at the end of samples.
   a. It must quantitate within 10% of expected value.
   b. If it is >10% out, the system must be recalibrated and the last 10 samples re-analyzed.

STARTUP

1. Verify argon supply and pressure.
2. Turn on water chiller and exhaust fan.
3. Insure that the internal standard solution bottle is adequately full (consumption is approximately 40 uL/min or 25 min/mL).
4. Verify contents of ALS rinse port reservoir(s).
5. Insure that the drain reservoir is not full.
6. Insure that all peristaltic pump tubes are in good condition and correctly clamped into the peristaltic pumps. Verify that the flow of sample and internal standard solutions through the uptake lines and into nebulizer is free from pulsations by introducing a bubble into each line and observing its progress.
7. Initiate the plasma and allow at least 15 minutes of warm-up while scanning the mass analyzer. The tuning procedures are carried out during the next 15 minutes of warm-up.

TUNING

1. Verify the basic instrument tune as per HP 4500 Tuning and Tune Verification - page 12. Generate and file the tune report.
2. Aspirate a 100 ppb solution for all analyte elements and run P/A Autotune. File P/A report with tune report.
3. Aspirate a new rinse blank for 5-10 minutes to eliminate any carry-over into the calibration blank.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

4. Load the method TN_EPA.m.
   a. Run the tune2008.m method on the EPA Tune check Solution, including data acquisition and data analysis. The TN_EPA tune report will be generated.
5. Procedure - Automated Calibration, Quality Control and Sample Analysis
   a. Prepare calibration standard, blanks, spikes, samples, and QC samples as per Reagents - page 5 - 8.
   b. Autobuild a QC Sequence using sequence template EPA.s
   c. Create the sample list using the sequence autobuilder, imported form a CSV file. See the EnviroQuant users manual for the instructions on how to use the sequence autobuilder.
6. Exit sequence autobuilder, and print the vial position guide.
7. Make any changes to the newly created sequence such as editing the sample types for spikes and spike reference samples.
   Note: an Xfactor is appended to the sample number for any dilutions made to the sample (i.e. X10 for a 1:10 dilution).
8. Load the ALS according to the vial position guide.
9. Select Sequence >>Run

TROUBLESHOOTING

1. The following section describes some commonly occurring problems and recommended solutions:
2. Poor recovery for selected analytes in spikes.
   a. Several conditions can cause poor recovery of certain analytes in spiked samples.
      i. Ag is especially insoluble in the presence of CL^-
      ii. If Ag concentration is greater that 100 ppb, diluted before digestion.
   b. Several elements (Zn, As, Se, Cd, Hg) have relatively high first ionization potentials and may not be as effectively ionized in samples with high concentrations of easily-ionizable elements such as Na and K.
      i. Diluting the sample if possible, or selecting an alternative internal standard with a higher inonization potential may help. Possible alternative internal standards include Ge, Te, and Au.
3. Poor calibration linearity.
   a. Contaminated blanks, reagent water and acids are a common cause of poor linearity, especially for common elements such as Na, K, Ca, Mg, Fe, Al, and Zn.
   b. Incorrectly set P/A factors can also cause linearity problems fore those elements which

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

include analog points in the calibration curve.

c. When analyzing samples with expected analyte concentrations above a few hundred ppb, update P/A factors each day **that tuning parameters are changed.**

4. Poor agreement between standard calibration curve and QC sample.
   a. Check dilutions and preparation for each.
   b. Remake stock solutions.
   c. Verify that acid composition and concentration are the same in both.
   d. For Ca, uncorrected interference from Sr^{++} in one but not the other calibration mix can cause significant interference.
5. Carryover or memory interference.
   a. Several elements are prone to memory effects for various reasons.
   b. Ag, Mo, and Tl tend to stick to surfaces in the sample introduction system and slowly rinse into subsequent samples.
      i. Keeping the sample introduction system (sample tubing, peri pump tubing, nebulizer, spray chamber, torch, and cones) clean will help minimize carry-over.
      ii. Also, rinsing between samples with relatively high acid concentration rinse blanks (i.e. 5% HNO_3) will help.
      iii. If possible, avoid introducing samples or standards with concentrations of these elements above a few hundred ppb.
   c. Use of a Babington nebulizer will also reduce carryover of these elements.
   d. Li, when analyzed for extended periods of time or in very high concentrations, tends to accumulate on the back sides of the interface cones.
      i. Cleaning the cones will usually reduce Li background and carryover.
   e. Volatile elements, or elements with volatile hydrides such as Hg and Sb can also carryover due to off-gassing form droplets on the spray chamber walls.
      i. Steps to reduce the volatility of these species are helpful.
         a. The addition of gold to samples and standards to be analyzed for Hg will reduce carryover at low Hg concentrations (<10ppb).
         b. Maintaining oxidizing conditions in the sample solutions will reduce the formation of volatile hydrides.
6. Calibration Drift over time.
   a. Insure that the instrument is adequately warmed up before initial calibration (warm-up, while scanning in tune for 15 minutes).
   b. Insure that laboratory temperature does not vary by more than 3 degrees C per hour.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

c. Check cones for signs of sample deposits that will affect the size and shape of the cone orifices. Clean if necessary.
d. Check peri-pump tubing for signs of excessive wear or flattening.

7. Poor internal standard recoveries in samples.
   a. Reduction in internal standard signal is usually caused by high matrix concentration in samples (especially Na, and K).
      i. Dilute the samples.
      ii. It is also desirable to tune the instrument with a matrix matched tune solution containing appropriate levels of the matrix elements to minimize the effect of any matrix induced suppression of ionization.
   b. High relative standard deviations (RSDs) for analyte or internal standard elements during sample analysis.
   c. Usually caused by insufficient sample uptake or stabilization time.
      i. A worn peri-pump tubing or bubbles in either the sample uptake or internal standard uptake tubing will cause problems.
      ii. Check the connections at the ISTD addition "Y" and replace the peri-pump tubing.
      iii. Adjust shoe pressure on the peri-pump to be just tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).
8. High RSDs during tune.
   a. Incorrectly tuned plasma parameters such as carrier gas or blend gas flow, peri-pump speed or sample depth.
   b. Dirty cones. Worn peri-pump tubing.
   c. Incorrect shoe pressure on peri-pump.
      i. Adjust shoe pressure on the peri-pump to be just tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).

DATA ANALYSIS AND CALCULATIONS

QUALITATION AND QUANTITATION

Refer to EPA 200.8 and 6020.

EVALUATION

1. If an element has more than one monitored isotope,

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

a. Examine the concentration calculated for each isotope, or the isotope rations for spectral interference.
b. Consider both primary and secondary isotopes in the evaluation of the element concentration.

2. In some cases, secondary isotopes are be less sensitive or more prone to interferences than the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.
3. If sample analysis is above the curve, either dilute and re-analyze, analyze a higher standard, or refer to linear range.

CALCULATION

All calculations necessary to convert raw spectral intensity data into quantitative results are performed by the HP 4500 ChemStation software.

Calibration is established by using y=ax+(blank) curve fit.

ppb = sample concentration x instrument dilution x digestion factor

Digestion factor: Final volume / initial sample amount

DATA REPORTING INSTRUCTIONS

1. Results are usually calculated and reported with 3 significant figures.
2. Typical units

Prep	ppb	ppm
Direct analysis	ug/L	mg/L
301L	ug/L	mg/L
301S	ug/Kg	mg/Kg
TCLP/SPLP	-----	mg/L

3. Direct analysis - do not report a result below the IDL.
4. Digested analysis - do not report a result below the MDL.

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure
ICP- MS / METAL ANALYSIS, REVISION 05
File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

5. Report results for a solid sample on a dry weight basis unless instructed otherwise by the data user.
6. Environmental Lead samples may require specialized reporting including unit conversions.
   a. Refer to Environment Lead SOPs.
2. If required, report the appropriate data qualifier with the result.

DATA ENTRY AND REVIEW
1. Using LDS Sets program, create a set.
   a. Opening a set assigns a unique set number.
2. Calculate and post data into LDS.
3. Print verification sheet and review
4. Submit data for **second level of** review and verification.

RECORD MANAGEMENT
1. Follow Record Management SOP.
2. Record will contain all necessary information including links to supporting data.
3. Record maintenance in the appropriate log(s) or LDS note associated with the equipment..
4. After verification, data is scanned into the network and archived on electronically.
5. Electronic records have multiple backups.

METHOD PERFORMANCE
1. Refer to EPA 200.8 and 6020.
2. Refer to current detection limits.

POLLUTION CONTROL
1. Employ techniques to reduce or eliminate the quantity or toxicity of waste generation.
2. Quantity of chemicals purchased is based of expected usage and shelf life.
3. Reagent preparation volumes reflect anticipated usage and reagent stability.

WASTE MANAGEMENT
1. Follow Disposal SOPs.

ANA-LAB CORP. THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

REFERENCES

1. EPA, Methods for the Determination of Metals in Environmental samples, EPA/600/R-94/111, Supplement 1, Method 200.8, Revision 5.4, May 1994.
2. EPA, Test Methods for Evaluating Solid Waste, SW846, Volume 1A, Chapter 3, Section 3.3, Method 6020, Revision 0, September 1994.
3. Equipment manual(s)

APPROVED BY

Bill Posey 04/26/2006

Technical Director Date

Revised by:	Date	Reviewed by:	Date
MRM, Project Manager	Feb. 2006	NGT, Sr. Quality Tech	April. 2006

ANA-LAB CORP.® THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

Appendix I

Training Requirements

The ability to perform the following analytical operations with precision and accuracy is required for this procedure and is part of the demonstration of capability.

1. **Completion of Basic Technical Skills training**
2. **Prepare and use reagents associated with this SOP.**
3. **Use equipment associated with this SOP.**
4. **Perform troubleshooting procedures.**
5. **Perform routine maintenance.**
6. **Analyze QC and production samples.**
7. **Evaluate and download data into LDS.**

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

Appendix II

ELEMENT		CHEMICAL ABSTACT SERVICES REGISTRY NUMBERS (CASRN)
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-39-3
Cadmium	Cd	7440-43-9
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Lead	Pb	7439-92-1
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Thallium	Tl	7440-28-0
Thorium	Th	7440-29-1
Uranium	U	7440-61-1
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

ANA-LAB CORP.® THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

Appendix III

HP 4500 CONSUMABLE PARTS AND SUPPLIES

Part Number	Description
G1820-65215	Peri-Pump Tubing (Tygon)
G1820-65216	Peri-Pump Tubing (ISAMAPRENE)
G1820-65220	Peri-Pump Tubing (ISTD)
G1820-65104	Tygon Tubing (500 mm)
G1820-65106	Y Connectors
G1820-65036	Babington Nebulizer Assembly
5063-5261	Babington Nebulizer
G1820-65199	O-Rings (for Babington Neb.)
5063-5262	Adapter for Babington Nebulizer (Cap Assembly)
G1820-65198	O-Rings (for Caps)
G1820-650093	Meter Teflon Tube (Sample)
G1820-80234	Spray Chamber (Pyrex)
G1820-80236	Spray Chamber (Quartz)
G1820-65028	Torch (Quartz)
G1820-65061	Work Coil
G1820-65206	Sample Cone (Nickel)
G1820-65025	O-Ring for Sampling Cone
G1820-65212	Skimmer Cone (Nickel)
G1820-65205	Sampling Cone (Platninum)
G1820-65207	Skimmer Cone (Platinum) with Brass Base
G1820-XXX	Electron Multiplier

ANA-LAB CORP. THE COMPLETE SERVICE LAB
PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914
Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

Appendix IV

RECOMMENDED ELEMENTAL INTERFERENCE EQUATIONS FOR ISOBARIC ELEMENTAL AND POLYATOMIC INTERFERENCES

Ca*	(1.000)(44C)-(0.0271)(88C)
V	(1.000)(51C)-(3.127)(53C)+(0.353)(52C)
As	(1.000)(75)-(3.127)(77C)+(2.736)(82C)-(2.760)(83C)
Mo	(1.000)(98C)-(0.146)(99C)
Cd	(1.000)(111C)-(1.0723)(108C)+(0.764)(106C)
In	(1.000)(115C)-(0.016)(118C)
Pb	(1.000)(208C)+(1.000)(207C)+(1.000)(206C)

*Doubly-charged Strontium interferes with Calcium at m/z 43 and 44, the correction factor for $^{88}Sr^{++}$ / $^{88}Sr^{+}$ must be determined daily or any time the tune conditions are changed.

ANALAB CORP.® THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

APPENDIX V

ACQUISITION MASSES FOR EACH ELEMENT WITH INTEGRATION TIMES

Mass	Element	Integration Time Det. Mode	Per point	Per mass
9	Be	Auto	0.1000	0.3000
27	Al	Auto	0.1000	0.3000
45	Sc	Auto	0.1000	0.3000
51	V	Auto	0.1000	0.3000
52	(V)	Auto	0.1000	0.3000
53	Cr	Auto	0.1000	0.3000
55	Mn	Auto	0.1000	0.3000
59	Co	Auto	0.1000	0.3000
60	Ni	Auto	0.1000	0.3000
62	Ni	Auto	0.1000	0.3000
63	Cu	Auto	0.1000	0.3000
65	Cu	Auto	0.1000	0.3000
66	Zn	Auto	0.1000	0.3000
67	Zn	Auto	0.1000	0.3000
68	Zn	Auto	0.1000	0.3000
75	As	Auto	0.3000	0.9000
77	(As)	Auto	0.3000	0.9000
82	Se	Auto	0.3000	0.9000
83	(Se)	Auto	0.3000	0.9000
89	Y	Auto	0.1000	0.3000
95	Mo	Auto	0.1000	0.3000
97	Mo	Auto	0.1000	0.3000
98	Mo	Auto	0.1000	0.3000

Mass	Element	Integration Time Det. Mode	Per point	Per mass
99	Ru	Auto	0.1000	0.3000
105	Pd	Auto	0.1000	0.3000
107	Ag	Auto	0.1000	0.3000
108	(Cd)	Auto	0.3000	0.9000
109	Ag	Auto	0.1000	0.3000
111	Cd	Auto	0.3000	0.9000
114	Cd	Auto	0.3000	0.9000
115	In	Auto	0.1000	0.3000
118	Sn	Auto	0.1000	0.3000
121	Sb	Auto	0.1000	0.3000
123	Sb	Auto	0.1000	0.3000
135	Ba	Auto	0.1000	0.3000
137	Ba	Auto	0.1000	0.3000
159	Tb	Auto	0.1000	0.3000
202	Hg	Auto	1.0000	3.0000
203	Tl	Auto	0.1000	0.3000
205	Tl	Auto	0.1000	0.3000
206	Pb	Auto	0.1000	0.3000
207	Pb	Auto	0.1000	0.3000
208	Pb	Auto	0.1000	0.3000
209	Bi	Auto	0.1000	0.3000
232	Th	Auto	0.1000	0.3000
238	U	Auto	0.1000	0.3000

ANA-LAB CORP.
THE COMPLETE SERVICE LAB

PO Box 9000 • Kilgore, Texas 75663-9000 • Phone: (903)984-0551 • Fax: (903)984-5914

Analytical Chemistry

Standard Operating Procedure

ICP- MS / METAL ANALYSIS, REVISION 05

File Name: J:\Word\SOP\Active\ICP_MS_Metal_Analysis_05.Mtl.Doc
Date Initiated: 06/30/1999
Date Revised: 04/26/2006

APPENDIX VI

INTERNAL STANDARDS AND ASSOCIATED ELEMENTS

ISTD	Analytes
^{6}Li	Be
Sc	Na-Ca
Ge	V-Cd
Tb	Sb-Ba
Bi	Tl-U