

# PROFICIENCY TESTING

## Evaluation Report

### Scheduled Study

**DMRQA 42**

Study Type

WPCHEM\_MICRO

**Open Date**

2022-04-15

**Close Date**

2022-07-15

**Report Generated**

2022-08-03

**Laboratory**

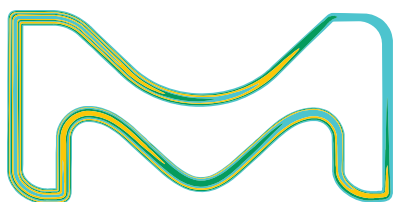
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**US EPA Lab Code**

AR01039



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**Authorized release of the report**

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(PT coordinator)

Sign: Handwritten signature of Alexis Horton in blue ink.

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Sigma-Aldrich RTC, Inc. is accredited by ANAB to provide PT programs for the scope of accreditation under ANAB Certificate # AP-1469.

All batch numbers of proficiency testing samples, including microbiological materials, are manufactured and tested in accordance with ISO/IEC 17043 requirements. For further information on proficiency testing samples, please check the PT product code information on each product detail page located on our website.



## Accreditors

Evaluations of this study will be sent to the accreditor(s) listed below. If any of the information listed below is not correct, please contact Sigma-Aldrich RTC immediately.

No accreditors were selected to receive this report.

**Summary Results for DMRQA 42**  
**PE1210-20ML pH - WP - 20ML**  
**- Intended use Water Pollution/Waste Water -**  
**LRAD1058**

This proficiency testing sample was produced in accordance with ISO/IEC 17043:2010.

Analyte	Reported Value	Assigned Value	Acceptance Window	z-score*
<b>SM 4500-H+ B 19th ED (1990) 20104603</b>				
Miscellaneous Analytes				
pH <sup>1,2</sup> 1900	7.48 Units	7.50 Units	6.75 - 8.25 Units	<b>-0.1</b> Acceptable
Analyst: EP Analysis Date: 2022-07-08	Evaluation Criteria – 1* Parameters*: a:1, b:0, c:0, d:0.066667			
<b>Group Analysis Summary</b>	Acceptable: 1/1		<b>Score: 100% - Acceptable</b>	

\* Evaluation parameters used for the statistical analysis: explanation at the end of report; a yellow highlighted results is acceptable but to be checked.

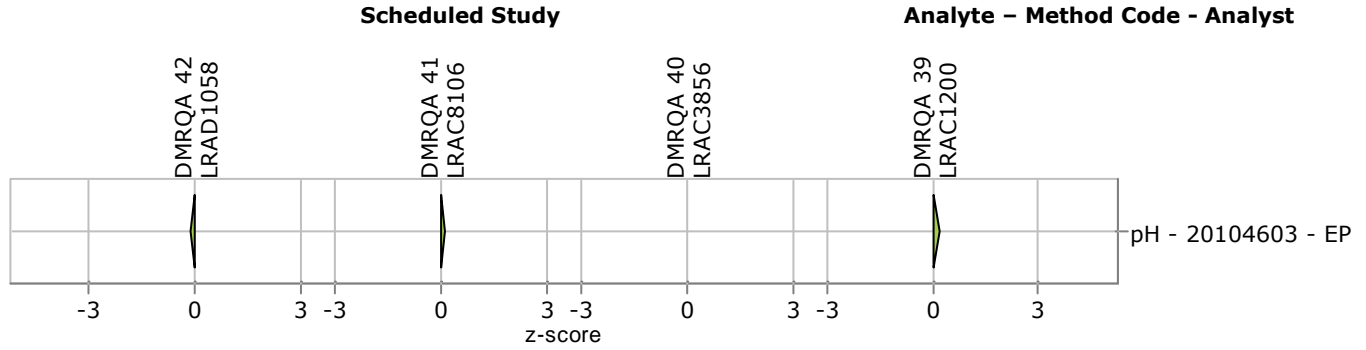
\*\* Unable to calculate a study mean due to <4 data points being received, therefore an effective evaluation could not be performed.

<sup>1</sup> TNI Compliant, covered by Sigma-Aldrich RTC's ANAB Proficiency Testing Provider accreditation, Cert. AP-1469

<sup>2</sup> ISO/IEC 17043 Accredited, covered by Sigma-Aldrich RTC's ANAB Proficiency Testing Provider accreditation, Cert AP-1469

### Graphical z-score Overview for DMRQA 42 PE1210-20ML pH - WP - 20ML

#### z-score Overview\* for DMRQA 42 and the Previous three Scheduled Studies of this Study Type



\* Evaluation parameters used for the statistical analysis; explanation at the end of report

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## **1 Aim of the Proficiency Test**

This interlaboratory study is a proficiency test for the assessment of laboratory performance. It was conducted in the framework of external quality assurance and the report provides an external appraisal of the participant laboratories' competence in the particular testing field.

## 2 Sample Information

**PE1210-20ML pH - WP - 20ML**  
**- Intended use Water Pollution/Waste Water -**  
**LRAD1058**

Analyte	Unit	Gravimetric Value	PTRL	Study Mean*	Study Std. Dev.*
pH 1900	Units	7.50	---	7.56	0.0846

\* If there are not enough data available to provide Study mean and Study Std. Dev, this is indicated by "---".



### 3 Data Availability

#### PE1210-20ML pH - WP - 20ML LRAD1058

Analyte	Number of participating laboratories		Number of data points	
	in total	with quantitative data points only*	in total	quantitative only*
pH 1900	103	103	112	112

\* Only quantitative values are taken into account in the calculation of study mean and study std.dev. (i.e. without missing results, without less-than results, without larger-than results).

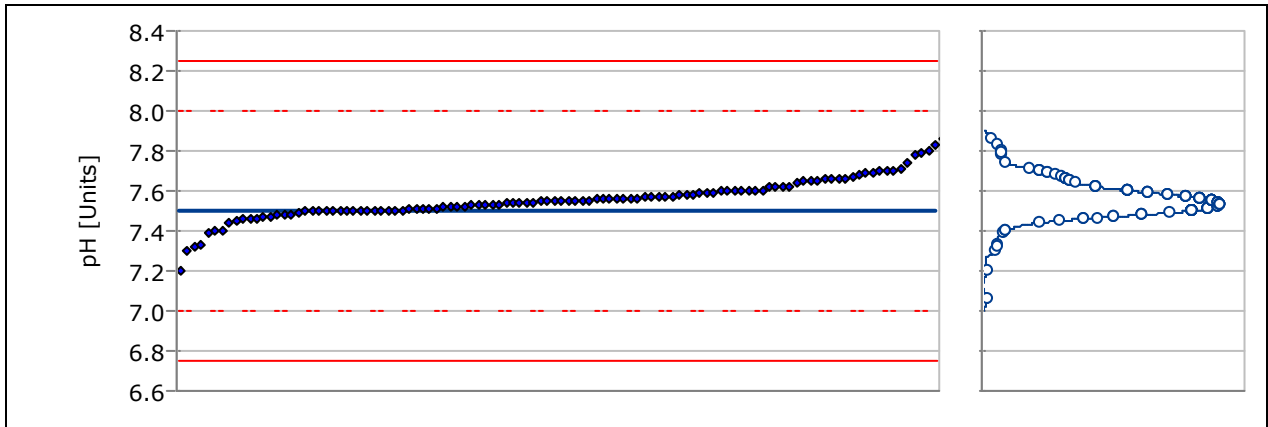
## 4 Results

### 4.1 PE1210-20ML pH - WP - 20ML / LRAD1058

This proficiency testing sample was produced in accordance with ISO/IEC 17043:2010.

#### 4.1.1 pH

No. of participating laboratories (in total / with quant. data points only)	103 / 103
No. of data points (in total / quantitative)	112 / 112
Assigned value	7.50 Units
Proficiency std. dev.	0.0667 Units
Acceptance window	6.75 - 8.25 Units



## 5 Statistical Analysis

### 5.1 Definitions and Interpretation

#### Reported Value

The participant's result.

#### Assigned Value

Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose. See ISO/IEC 17043 for additional information. In general, the assigned value is the value used to assess proficiency and may or may not be the made to value (gravimetric value).

#### Acceptance Window

The range of values that constitute acceptable performance for a laboratory participating in this PT study.

#### z-score

A z-score shows how a single data point compares to normal data. A z-score says not only whether a point was above or below average, but how unusual the measurement is. Generally, a method result with a z-score less than |2| is considered to be in control and 'Acceptable'; a z-score between |2| and |3| is considered 'Questionable', but still within control and 'Acceptable' and a z-score greater than |3| is considered 'Not Acceptable' and the method is out of control. For WS studies, a z-score greater than |2| is not acceptable.

Calculated as  $z = (\text{Reported Value} - \text{Assigned Value}) / \text{Proficiency Std. Dev.}$

A z-score cannot be provided

- (1) for presence/absence data,
- (2) for identification data and other categorial data,
- (3) where the analyte is not present in the sample,
- (4) for "less than" and "greater than" values,
- (5) NOEC analytes (in the framework of WETT analysis).

In cases (1) to (3) the participant's result is only evaluated by "acceptable" if it matches with the assigned value. Otherwise the result is indicated as "not acceptable". In case the analyte is not present in the sample and a PTRL is available, the participant's result is indicated as "acceptable" as long the result is less than the PTRL.

In case (4) the following evaluation rules will be applied:

- “less than” values:
  - When the analyte is not present in the sample the result is always “acceptable”.
  - When the analyte is truly present in the sample, the result is only “acceptable” if the “less than” value is greater than the lower limit of the acceptance window.
- “greater than” values:
  - When the analyte is not present in the sample the result is always “not acceptable”.
  - When the analyte is truly present in the sample, the result is only “acceptable” if the “greater than” value is less than the upper limit of the acceptance window.

In case (5) the result is indicated as “acceptable” if it lies within the acceptance window, otherwise the result is indicated as “not acceptable”.

#### **Proficiency Std. Dev.**

Standard deviation calculated based on Evaluation Criteria.

#### **PTRL**

Proficiency Testing Reporting Limit

#### **Study Mean**

Statistical study mean calculated using a robust statistical model. Robust statistical techniques are used to minimize the influence extreme results can have on estimates of the mean and standard deviation. NOTE - These techniques assign less weight to extreme results, rather than eliminate them from a data set.

Choice of statistical technique: In case of quantitative data points from at least 12 laboratories, Algorithm A (ISO 13528, Section C.3.1), and in case of quantitative data points of 4 to 11 laboratories, the Hampel estimator (ISO 13528, Section C.5.3) is applied. A study mean cannot be calculated in case there are quantitative data points from less than 4 laboratories available.

### **Study Std. Dev.**

Standard deviation calculated from study data using robust statistics.

In case of quantitative data points from at least 12 laboratories, Algorithm A (ISO 13528, Section C.3.1), and in case of quantitative data points of 4 to 11 laboratories, the Q method (ISO 13528, Section C.5.2) is applied. A study standard deviation cannot be calculated in case there are quantitative data points from less than 4 laboratories available.

### **Gravimetric Value**

The 'prepared to' value, determined by gravimetric means. The uncertainty associated with this value is the standard uncertainty and based on Sigma-Aldrich RTC's gravimetric tolerances.

### **Analytical Value**

The measured value, determined after preparation. The uncertainty associated to this value is the standard uncertainty and based on the measurement process.

## 5.2 Evaluation Criteria

### 1 - Regression Equation

Acceptance windows based on TNI adopted equation of proficiency value  $\pm 3$  proficiency standard deviations and check limits of proficiency value  $\pm 2$  proficiency standard deviations. Proficiency value and proficiency standard deviation are calculated from gravimetric variables a, b, c & d as proficiency value =  $a * \text{gravimetric} + b$  and proficiency standard deviation =  $c * \text{gravimetric} + d$ .

### 2 - Study Robust Mean and c, d regression

Acceptance windows based on TNI adopted equation of proficiency value  $\pm 3$  proficiency standard deviations and check limits of proficiency value  $\pm 2$  proficiency standard deviations. Proficiency value and proficiency standard deviation calculated from robust study mean and variables c & d as proficiency value = robust mean and proficiency standard deviation =  $c * \text{proficiency value} + d$ .

### 3 - Fixed Limits

Acceptance windows based on span of gravimetric percentage from gravimetric as  $\text{gravimetric} \pm \text{gravimetric} * \text{percentage}$ .

### 4 - Adjustable Fixed Limits

Acceptance windows based on a span of gravimetric percentage from gravimetric as  $\text{gravimetric} \pm \text{gravimetric} * \text{lowPercentage}$  where  $\text{gravimetric} < \text{break}$  and  $\text{gravimetric} \pm \text{gravimetric} * \text{highPercentage}$  where  $\text{gravimetric} \geq \text{break}$ .

### 5 - Study Statistics

Acceptance windows based on a number of standard deviations span from the study mean as  $\text{study mean} \pm (\text{deviations} * \text{standard deviation})$ .

### 6 - Log Transform Statistics

Acceptance windows based on lognormal distributed data. Acceptance windows =  $\text{mean}(\text{lognormal}) \pm \text{span} * \text{standard deviation}(\text{lognormal})$ .

### 7 - Regression Equation 2SD

Acceptance windows based on EPA equation of proficiency value  $\pm 2$  proficiency standard deviations. Proficiency value and proficiency standard deviation are calculated from gravimetric variables a, b, c & d as proficiency value =  $a * \text{gravimetric} + b$  and proficiency standard deviation =  $c * \text{gravimetric} + d$ . Generally reserved for drinking water studies.

### 8 - Study Median and Dilution Levels

Acceptance windows based on study median  $\pm 1$  dilution. If the median falls between two test dilutions, then the assigned value is set at the higher value, and the lower acceptance limit is the second test dilution below the median, and the upper acceptance limit is the second test dilution above the median. Generally reserved for NOEC analytes (in the framework of WETT analysis).

### 9 - Fixed Limits based on Analytical Value

Acceptance windows based on span of analytical value from measurements.

## 6 Notes on the Interpretation of the Results

### z score Overview

The z-scores are presented as colored triangles. For each item, the z-scores of all analytes of the current and the previous (up to three) scheduled studies of this study type. The z-scores depend on the lot, analytical method used, and analyst (if given). A red cross is shown if no z-score is available.

For the assessment of participants by means of z-scores according to ISO/IEC 17043:2010 [2], the triangles were colored as follows:

$ z  \leq 2$	green
$2 <  z  < 3$	yellow (WS studies, WETT samples: red)
$ z  \geq 3$	red.

For  $|z| \geq 3$ , the corresponding triangles are displayed as -3 or 3. For  $|z| > 2$ , the value of the z score is displayed next to the triangle (yellow or red). A z-score = 0 is shown as a light blue vertical bar.

#### Interpretation of the z-scores' overview:

A z-score  $< 0$ , i.e. the triangle points to the left, means that the measurement result is lower than the assigned value.

A z-score  $> 0$ , i.e. the triangle points to the right, means that the measurement result is higher than the assigned value.

A z-score = 0, i.e. a light blue vertical bar is shown, means that the measurement result coincides with the assigned value.

### Figures per Combination of Item, Lot and Analyte

The *diagram on the left* shows the participant results by means of blue diamonds.

The horizontal blue line indicates the assigned value.

Both the acceptance and the check limits for the participant results are calculated based on z-scores.

The acceptance limits are displayed as solid lines and correspond to z-scores of  $\pm 3$ . For WS studies and non-NOEC analytes (in the framework of WETT analysis), the acceptance limits correspond to a z-score  $\pm 2$ . For NOEC analytes (in the framework of WETT analysis), the acceptance limits correspond to  $\pm 1$  dilution.

The check limits are displayed as dashed lines and correspond to z-scores of  $\pm 2$ . They are only calculated if a rule is given by the evaluation criterion.

In case there are at least 8 laboratories with quantitative data points are available: The *diagram on the right* is a kernel density estimation of the distribution of the participant results. The measurement values are indicated as small circles. The kernel width is determined by the ISO 13528 formula from section 10.3.2 i) a).

## 7 Proficiency Test Item Preparation, Homogeneity and Stability Assessment

Sigma-Aldrich RTC uses proprietary and published methods for the manufacture, homogeneity and stability testing of proficiency test items. Sigma-Aldrich RTC's proficiency test materials meet the requirements of ISO 17034. For more information contact Sigma-Aldrich RTC. Additionally, Sigma-Aldrich RTC complies with the TNI Volume 3 'General Requirements for Environmental Proficiency Test Providers', EL-V3-2016, for all TNI Fields of Proficiency Testing analytes.

## 8 Metrological Traceability

All preparations are made using balances calibrated annually traceable to NIST standards. Where appropriate analytical measurements are traceable through an unbroken chain to NIST standards, or a Certified Reference Material manufactured under ISO 17034 in conjunction with ISO/IEC 17025.

## 9 Additional Information

Go to [supelco-pt.com](http://supelco-pt.com) for additional information on summary statistics for specific methods, advice on the interpretation of the statistical analysis and additional comments/recommendations. Sigma-Aldrich RTC recommends that you contact your accreditation body for specific instruction.

## 10 References

- [1] ISO 13528: Statistical methods for use in proficiency testing by interlaboratory comparison, August 2015
- [2] ISO/IEC 17025:2017: General requirements for the competence of testing and calibration laboratories
- [3] ISO/IEC 17043:2010: Conformity assessment - General requirements for proficiency testing, May 2010
- [4] S. Uhlig und P. Henschel (1997): Limits of tolerance and z-scores in ring tests. *Fresenius' J. Anal. Chem.*, Vol. 358, pp. 761-766.
- [5] ISO 17034:2016: General requirements for the competence of reference material producers.



**This section of the report is for informational purposes only. If you are unsure about specific accreditation requirements, please contact your state coordinator.**

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## Unacceptable Analytes

No unacceptable analytes

<sup>1</sup> TNI Compliant, covered by Sigma-Aldrich RTC's ANAB Proficiency Testing Provider accreditation, Cert. AP-1469

<sup>2</sup> ISO/IEC 17043 Accredited, covered by Sigma-Aldrich RTC's ANAB Proficiency Testing Provider accreditation, Cert AP-1469

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Lit. No. MS\_BR1761EN  
2018 - 10431  
06/2018