

Report No. 1147

**Air & Emissions Proficiency Testing
Program**

Round 14

Sulphuric Acid in Impinger Solution

July 2019

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Mr F Fleeer, Helix Environmental. Also, our thanks go to Environmental Resource Associates (ERA), USA for the supply of the samples.

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1. FOREWORD

This report summarises the results of a proficiency testing program on the determination of sulphuric acid in impinger solution. It constitutes the fourteenth round of an ongoing series of programs associated with the methods used to monitor process emissions to air. This program is accredited to ISO/IEC 17043:2010 “*Conformity assessment - General requirements for proficiency testing*” by International Accreditation New Zealand (IANZ).

The program was conducted in May/June 2019 by Proficiency Testing Australia (PTA). The aim of the program was to assess laboratories’ abilities to competently perform the prescribed analyses.

The Program Coordinator was Mrs K Weller and the Technical Adviser was Mr F Fler. This report was authorised by Mrs K Cividin, Quality Manager.

2. FEATURES OF THE PROGRAM

- (a) Participants were provided with one impinger solution labelled PTA AE14 containing sulphuric acid at 5 – 150 mg/dscm.
- (b) A total of 9 laboratories received samples and returned results, comprising:
 - 2 Australian participants; and
 - 7 overseas participants, including Egypt and New Zealand
- (c) Laboratories were provided with the *Instructions to Participants and Results Sheet* (see Appendix C). Laboratories were requested to perform the tests according to their routine methods and to record their results on the *Results Sheet*.
- (d) Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity. Based on the results of this testing (see Appendix B), the homogeneity of the samples was established.
- (e) Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only.
- (f) Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, uncertainty of the median, normalised interquartile range, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed). Measurement Uncertainty (MU) is also presented where supplied by participants. Please note that this information is presented for

information purposes only and has not been used for the formal evaluation of results.

- (g) A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 4). Robust z-scores, z-score charts relevant to each test are presented in Appendix A.
- (h) The document entitled *Guide to Proficiency Testing Australia, 2016* (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.
- (i) A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 4.

3. FORMAT OF THE APPENDICES

- (a) Appendix A contains the analysis of results reported by laboratories for the samples. This section contains the following for each determinant, where appropriate:
 - a table of results and calculated z-scores;
 - a list of summary statistics;
 - ordered z-score charts; and
- (b) Appendix B contains details of the homogeneity and stability testing.
- (c) Appendix C contains copies of the *Instructions to Participants* and *Results Sheet*.

4. STATISTICAL DESIGN OF THE PROGRAM

- (a) Outlier Results and Z-scores

In order to assess laboratories' testing performance, a robust statistical approach, using z-scores, was utilised. Z-scores give a measure of how far a result is from the consensus value (i.e. the median), and gives a "score" to each result relative to the other results in the group.

A z-score close to zero indicates that the result agrees well with those from other laboratories, whereas a z-score with an absolute value greater than or equal to 3.0 is considered to be an outlier and is marked by the symbol "§".

The table on page 4 summarises the outlier results detected.

(b) Results Tables and Summary Statistics

Each of these tables contains the results returned by each laboratory, including the code number for the method used, and the robust z-score calculated for each result.

Results have been entered exactly as reported by participants. That is, laboratories which did not report results to the precision (i.e. number of decimal places) requested on the Results Sheet have not been rounded to the requested precision before being included in the statistical analysis.

A list of summary statistics appears at the bottom of each of the tables of results and consists of:

- the number of results for that test/sample (*No. of Results*);
- the median of these results, i.e. the middle value (*Median*);
- the uncertainty of the median; a robust estimate of the standard deviation of the *Median*;
- the normalised interquartile range of the results (*Normalised IQR*);
- the robust coefficient of variation, expressed as a percentage (*Robust CV*) - i.e. $100 \times \text{Normalised IQR} / \text{Median}$;
- the minimum and maximum laboratory results; and
- the range (*Maximum - Minimum*).

The median is a measure of the centre of the data.

The normalised IQR is a measure of the spread of the results. It is calculated by multiplying the interquartile range (IQR) by a correction factor which converts the IQR to an estimate of the standard deviation. The IQR is the difference between the upper and lower quartiles (i.e. the values above and below which a quarter of the results lie, respectively).

For normally distributed data, the uncertainty of the median is approximated by:

$$\sqrt{\frac{\pi}{2}} \times \frac{\text{normIQR}}{\sqrt{n}} \quad n = \text{number of results}$$

Please see reference [1] for further details on these robust summary statistics.

(c) Ordered Z-Score Charts

On these charts each laboratory's robust z-score is shown, in order of magnitude, and is marked with its code number. From these charts, each laboratory can readily compare its performance relative to the other laboratories.

These charts contain solid lines at +3.0 and -3.0, so that outliers are clearly identifiable as those laboratories whose "bar" extends beyond these "cut-off" lines. The y-axis of these charts has been limited, so very large z-scores appear to extend beyond the chart boundary.

The following table summarises the results submitted by participants for the program.

TABLE A: SUMMARY STATISTICS - Sulfuric Acid (mg/dscm)

No. of Results	Median	Normalised IQR
9	58.2	2.97

5. OUTLIER RESULTS

Laboratories reporting outlier results are listed in the following table:

TABLE C: SUMMARY OF STATISTICAL OUTLIERS - Sulfuric Acid (mg/dscm)

Laboratory Code No.
1, 7

6. PTA AND TECHNICAL ADVISER'S COMMENTS

Metrological Traceability and Measurement Uncertainty of Assigned Values

Sample preparation was undertaken according to Environmental Resource Associates' (ERA) Standard Operating Procedures to ensure samples were fit-for-purpose, homogenous and stable.

The Certified Value (Reference Value) are the actual "made-to" concentrations confirmed by ERA analytical verification.

The Uncertainty is the total propagated uncertainty at the 95% confidence interval. The uncertainty is based on the preparation and internal analytical verification of the product by ERA, multiplied by a coverage factor. The uncertainty applies to the product as supplied and does not take into account

any required or optional dilution and/or preparations the laboratory may perform while using this product.

The PT Data/Traceability data include the mean value, percent recovery and number of data points reported by the laboratories in ERA's Proficiency Testing study compared to the Certified Values. In addition, where NIST Standard Reference Materials (SRMs) are available, each analyte has been analytically traced to the NIST SRM listed. This product is traceable to the lot numbers of its starting materials. All gravimetric and volumetric measurements related to its manufacture are traceable to NIST through an unbroken chain of comparisons.

Traceability Recovery (%) = $[(\% \text{ recovery certified standard}) / (\% \text{ recovery NIST SRM})] * 100$

The traceability data shown were compiled by analyzing the ERA standards or their associated stock solutions against applicable NIST SRMs.

After reviewing the results for this round and the certificate of analysis provided for the sample, it was determined that assessing results using robust z-scores would be more appropriate than using En scores, which was the statistical analysis procedure originally stated in the instructions to participants.

The matter of unrealistic claims for measurement uncertainty has, however, been raised previously and continues to be an issue. It is again strongly recommended that laboratories review their methodology for establishing measurement uncertainty.

7. REFERENCE

- [1] *Guide to Proficiency Testing Australia, 2016* (This document can be found on the PTA website, www.pta.asn.au)

APPENDIX A

Results and Data Analysis

Sulphuric Acid.....	A1
Ordered Robust Z-Score Chart.....	A2

Sulphuric Acid in Impinger Solution

Sample PTA AE14

Sulfuric Acid (mg/dscm)

Laboratory Code	Result (mg/dscm)	±MU	Robust Z-score	Method
1	16.1	2	-14.16 §	Based on Method 8, analysis by APHA 4110B IC
2	57	1	-0.40	barium-thorin titration method
3	58.11	5.30	-0.02	Method 8 EPA
5	61.88	6.2	1.24	USEPA Method 8
6	60.1	1.8	0.65	Method 8
7	41	6	-5.78 §	USEPA Method 8
8	60.4	1.3	0.75	ICP-OES
9	60.5	3.9	0.78	USEPA 8
10	58.18	2.69	0.00	SM4110

Note:

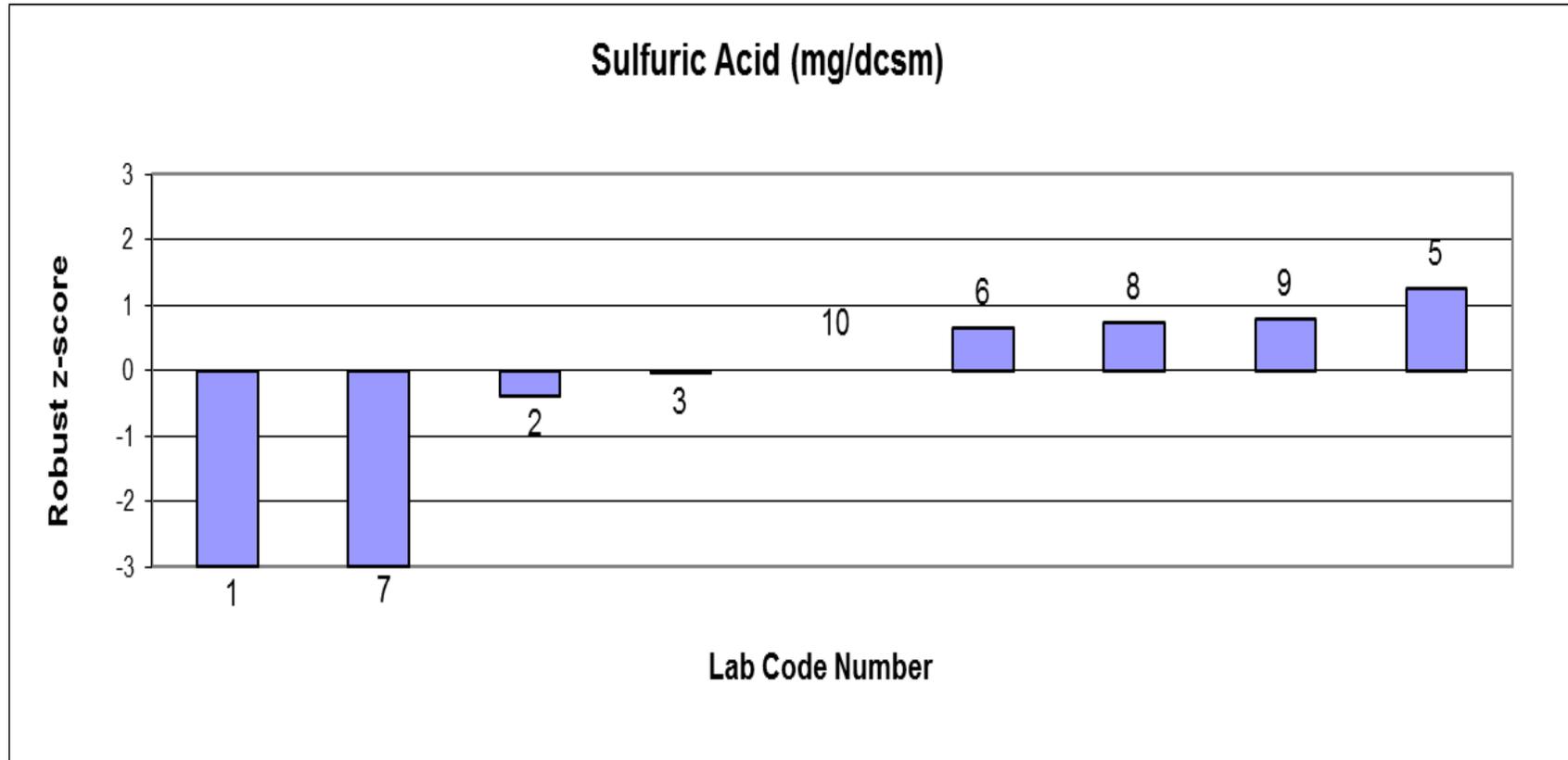
- § denotes an outlier (i.e. $|z\text{-score}| \geq 3.0$).

Summary Statistics
Sample - PTA AE14

No. of Results	9
Median	58.2
Norm IQR	2.97
Uncertainty (Median)	1.2
Robust CV	5.1%
Minimum	16.1
Maximum	61.9
Range	45.8

A2

**Sulphuric Acid (mg/dscm)
Ordered Robust Z-Score Chart**



APPENDIX B

Homogeneity and Stability Testing

Homogeneity and Stability Testing

Samples for this program were obtained from Environmental Resource Associates (ERA), USA. As such, all samples were subjected to rigorous homogeneity and stability testing. On the basis of this testing, the samples utilised for this program were considered to be homogenous and stable.

TABLE C: HOMOGENEITY AND STABILITY

Analysis	Certified Value¹ (mg/dscm)	Uncertainty² (%)	Mean (mg/dscm)	Recovery (%)	No. of Samples
Sulphuric Acid	62.5	2.58	60.8	97.3	12

Note: ERA certification and analytical verification data issued 27 June 2018

¹ The Certified Values are the actual “made-to” concentrations confirmed by ERA analytical verification.

² The stated Uncertainty is the total propagated uncertainty at the 95% confidence interval. The uncertainty is based on the preparation and analytical verification of the product by ERA, multiplied by a coverage factor. The uncertainty applies to the product as supplied and does not take into account any required or optional dilution and/or preparations the laboratory may perform while using this product.

APPENDIX C

Documentation

Instructions to Participants C1
Results Sheet C2

PROFICIENCY TESTING AUSTRALIA

Proficiency Testing Program Air & Emissions (Round 14)

INSTRUCTIONS TO PARTICIPANTS

Please read the following carefully before commencing testing.

Please note:

- The sample is packaged in a 15 mL screw-top vial containing approximately 14 mL of standard concentrate.
 - The sample is not preserved
 - The sample may be stored at room temperature
 - The sample contains Sulfuric Acid in the range 5 to 150 mg.
 - When calculating final results, assume a dry gas volume of 1 dscm
- 1) To ensure the appropriate analysis of results, participants are asked to adhere carefully to the following dilution instructions:
 - a) Add 100-200 mL of deionized water and 30mL of 30% hydrogen peroxide to a clean 1000mL class A volumetric flask.
 - b) Shake the Sulfuric Acid in Impinger Solution vial prior to opening.
 - c) Using a clean, dry, class A pipet, volumetrically pipet 5.0mL of the concentrate into the 1000mL volumetric flask.
 - d) Dilute the flask to final volume with deionized water.
 - e) Cap the flask and mix well.
 - f) Immediately analyse the diluted sample by your normal procedures and calculate the total mass in the concentrate provided.
 - 1) This sample is designed for sulfuric acid analysis by USEPA method 8. Alternate methods can be used if they are determined to be comparable to the stated method for each sample.
 - 3) For each determination, one test result for the sample is to be reported on the Results Sheet to the reporting basis indicated. The method used for each test is to be stated. Attach additional comments if necessary.
 - 4) Laboratories are also required to calculate and report an estimate of uncertainty of measurement (MU) for each reported result. All estimates of uncertainty of measurement must be given as a 95% confidence interval (coverage factor $k \approx 2$) and reported as mg/dscm. **Please note En scores will be reported for this round so it is essential that MU values are reported with the result. Please ensure MU values are reported as mg/dscm.**
 - 5) All laboratories are asked to return the Results Sheet by **10th June 2019** to:
Kathy Weller
Proficiency Testing Australia
Phone: +61 7 3721 7373
Fax: +61 7 3217 1844 **Email:** Kathy.Weller@pta.asn.au

**PROFICIENCY TESTING AUSTRALIA****Air & Emissions (Round 14) - Proficiency Testing Program****Results Sheet**Lab Code:

Sulfuric Acid (mg/dscm)	±MU (mg/dscm)	Method

Comments: _____

Signed: _____

Date: _____

Please return results no later than **Monday 10th June 2019**, to:

Kathy Weller
Proficiency Testing Australia

Phone: +61 7 3721 7373

Fax: +61 7 3217 1844

Email: Kathy.Weller@pta.asn.au