

Report No. 1126

**Air & Emissions Proficiency Testing
Program**

Round 13

Particulate Matter on Filter Paper

February 2019

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Mr F Flee, 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 gravimetric determination of total solid particulate matter collected on filters. It constitutes the thirteenth 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 November 2018 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 filter paper sample labelled PTA AE13 containing particulate matter at 50-600 mg/filter.
- (b) A total of 16 laboratories received samples, comprising:
 - 10 Australian participants; and
 - 6 overseas participants, including Indonesia and New Zealand

Of these 16 laboratories, one was unable to submit results by the due date.

- (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) The results for each sample as reported by participants are presented in Appendix A, together with calculated E_n numbers and graphical presentations of the data.

- (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.

3. FORMAT OF THE APPENDICES

- (a) Appendix A

For each sample set, the following information is provided for each sample.

- (i) The weight determination (in mg) as reported by participating laboratories, together with their reported uncertainties of measurement at the 95% confidence level (U).
 - (ii) The reference value is in mg.
 - (iii) The calculated E_n number for each participant's weight determinations.
 - (iv) A graph for each sample, displaying each participant's value, represented by a black diamond, together with their reported uncertainty of measurement, represented by bars extending above and below its value.
- (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

Measurement results submitted by the participating laboratories, compared to the reference values, are presented in Appendix A in the tables.

A summary of results returned by the participating laboratories, compared to the reference values, appears in Appendix A. Measurement performance is judged on the basis of an E_n number for each measurement. The E_n number is an internationally accepted method for determining the agreement of individual results with the reference values in relation to the uncertainties of measurement of each. That is, the E_n number indicates whether laboratories are within their particular uncertainty of measurement of the reference value.

The E_n ratio is defined as:

$$E_n = \frac{\text{LAB} - \text{REF}}{\sqrt{(U_{\text{LAB}})^2 + (U_{\text{REF}})^2}}$$

where: LAB is the participating laboratory's result
 REF is the Reference Laboratory's result
 U_{LAB} is the participating laboratory's reported uncertainty
 U_{REF} is the Reference Laboratory's reported uncertainty

with the uncertainty of measurement reported at a 95% confidence level. For the results to be acceptable, values of $|E_n| \leq 1.0$ are required.

5. **OUTLIER RESULTS**

In order to achieve the program aim of assessing laboratory testing performance, E_n numbers have been calculated for each participant's weight determination. The E_n number indicates whether laboratories are within their particular uncertainty of measurement of the reference value. For the result to be considered acceptable, the E_n number must lie between -1.0 and +1.0 (i.e. $|E_n| \leq 1.0$).

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 (%) = [(% recovery certified standard)/(% recovery NIST SRM)]*100

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

The matter of unrealistic claims for measurement uncertainty has been raised previously, with the use of E_n number as a method of evaluating proficiency test results highlighting the issue. The results for six of the 15 laboratories were unacceptable, with $|E_n|$ values greater than 1.0. 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

Particulate Matter on Filter Paper.....	A1
Graphical Representation of Participants' Results.....	A2

Particulate Matter on Filter Paper Results

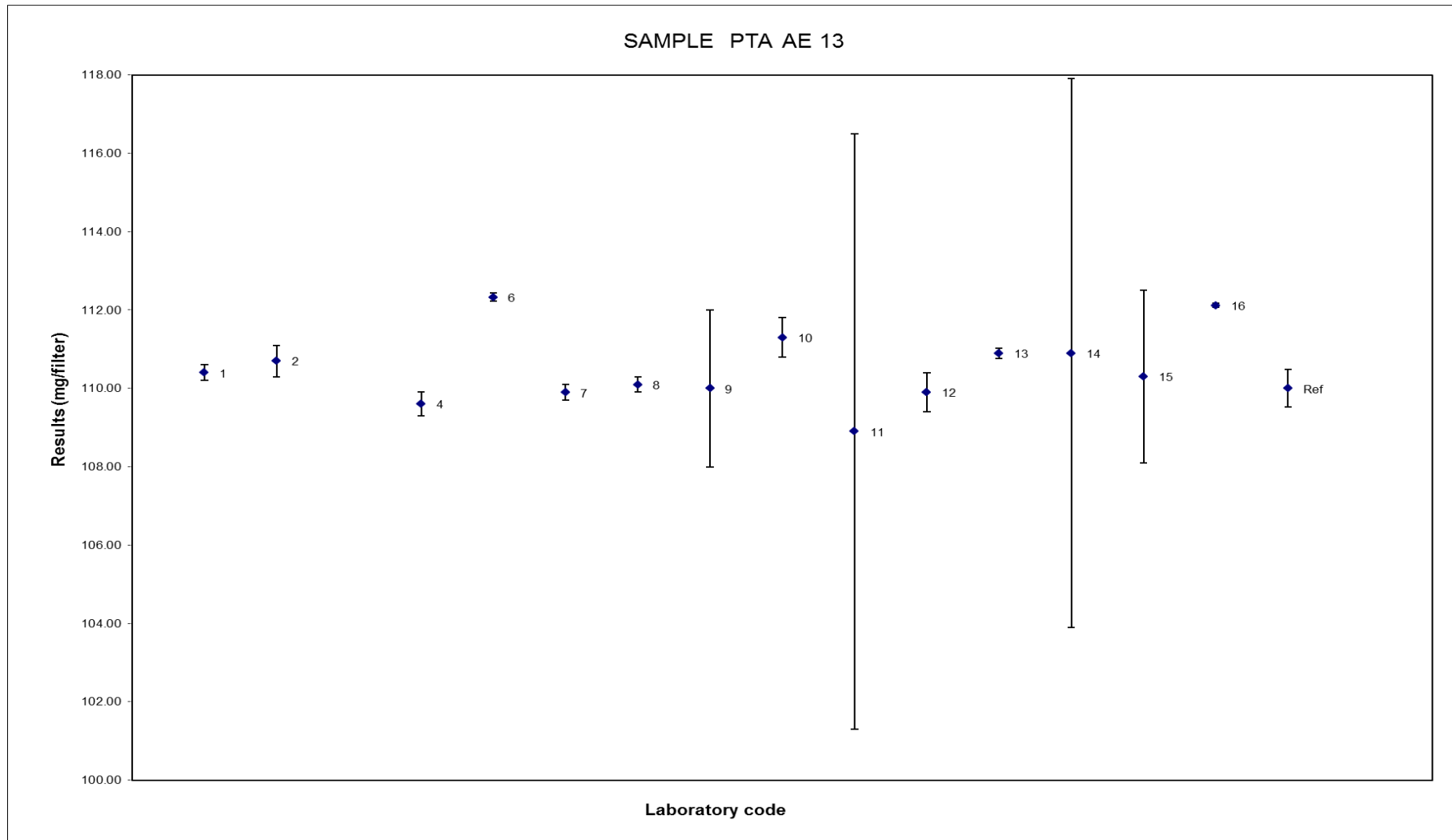
Sample PTA AE13

Particulate Matter on Filter Paper (mg/filter)

Laboratory Code	Result (mg/filter)	U _{LAB} (mg/filter)	LAB - REF	En Score	Balance Used	Method
1	110.4	0.2	0.40	0.78	5	AS4323.2:1995
2	110.7	0.4	0.70	1.13	4	USEPA Method 5
3	1.6	0.3	-108.40	-192.95	4	In house
4	109.6	0.3	-0.40	-0.71	4	USEPA Method 5
6	112.33	0.1	2.33	4.80	5	USEPA Method 5
7	109.894	0.2	-0.11	-0.21	6	USEPA Method 5
8	110.1	0.2	0.10	0.19	4	AS4323.2:1995
9	110	2	0.00	0.00	4	In house (based on AS4323.2:1995)
10	111.3	0.5	1.30	1.88	4	USEPA Method 5
11	108.9	7.6	-1.10	-0.14	4	USEPA Method 5
12	109.9	0.5	-0.10	-0.14	4	ISO9096:2017
13	110.9	0.13	0.90	1.83	4	USEPA Method 5
14	110.9	7	0.90	0.13	5	AS3640:2009
15	110.3	2.2	0.30	0.13	4	USEPA Method 5
16	112.12	0.05	2.12	4.44	5	USEPA Method 5
Reference Results	Certified Value	U _{REF}				
	110	0.475				

Notes:

1. E_n refers to Error Normalised. An E_n number between -1.0 and +1.0 is considered satisfactory (i.e. |E_n| ≤ 1.0).
2. Unsatisfactory scores (i.e. |E_n| > 1.0) are highlighted in red
3. U_{LAB} refers to uncertainty of measurement at the 95% confidence level.
4. Result (mg/filter) and U_{LAB} in the above table are shown 'as reported' by participants.
5. LAB - REF refers to Participating Laboratory's result minus the Reference Laboratory's result.
6. Reference U is reported here in mg/filter whereas in Appendix B the Reference uncertainty is reported as a percentage (%)

Graphical Presentation of Participants' Results

Note: The result for Laboratory Code 3 lies outside the scale of this graph.

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 stability and homogeneity 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/filter)	Uncertainty² (%)	Mean (mg/filter)	Recovery (%)	No. of Samples
Particulate Matter	110	0.432	111	101	38

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 13)

INSTRUCTIONS TO PARTICIPANTS

Please read the following instructions carefully before commencing testing.

Please Note:

- The sample is not preserved.
- The sample can be stored at room temperature.
- Tare weight for filter alone is provided for use in calculating your results.
- When calculating measurement uncertainty, please assume the provided initial filter weight as a routine measurement performed in your laboratory.

To ensure the appropriate analysis of results, participants are asked to adhere carefully to the following instructions:

- 1) This sample is ready for analysis as received.
- 2) Analyse the sample following the procedure specified in CARB Method 5, USEPA Methods 5, 5A, 5B, 5D, 5F and 17 or equivalent.

Please Note:

- You will need to dry the filter as per your method and record a dried weight of the filter. To obtain the Particulate Matter value, subtract the tare weight listed on the label from the dried weight.
- 3) For the determination, one test result for the sample is to be reported on the Results Sheet, to the reporting basis indicated. The method used for the test is to be stated, together with details of the balance used (i.e 4, 5 or 6 figures). Attach additional comments if necessary.
 - 4) Laboratories are also requested 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/filter. **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/filter.**
 - 5) All laboratories are asked to return the Results Sheet by **7th December 2018** to:

Kathy Weller Proficiency Testing Australia PO Box 1122 ARCHERFIELD BC QLD 4108 AUSTRALIA Phone: +617 3721 7373 Fax: +617 3217 1844 Email: Kathy.Weller@pta.asn.au
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PROFICIENCY TESTING AUSTRALIA

Air & Emissions (Round 13) - Proficiency Testing Program

Results Sheet

Lab Code:

Test	Sample PTA - AE13 (mg/filter)	\pm MU* (mg/filter)	Method	Balance Used (4,5 or 6 figures)
Particulate Matter				

- i) For each sample only a single result is requested.
- ii) Report results in milligrams per filter (mg/filter).
- iii) MU* Laboratories Measurement Uncertainty (MU). Please report in corresponding unit of measurement. **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/filter.**
- v) Report the number of figures for the balance used.

Comments: _____

Signed: _____

Date: _____

Return results **no later than 7th December 2018** to:

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