

Report No. 1236

Air & Emissions Proficiency Testing Program

Round 17

Particulate Matter on Filter Paper

January 2021

Acknowledgments

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CONTENTS

1. FOREWORD.....	1
2. FEATURES OF THE PROGRAM.....	1
3. FORMAT OF THE APPENDICES.....	2
4. STATISTICAL DESIGN OF THE PROGRAM	2
5. PTA AND TEHCNICAL ADVISER'S COMMENTS	4
6. OUTLIER RESULTS.....	5
7. REFERENCE.....	5

APPENDIX A – Results and Data Analysis

Particulate Matter on Filter Paper.....	A1
Ordered Robust Z-Score chart	A2

APPENDIX B – Homogeneity and Stability Testing

Homogeneity and Stability	B1
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APPENDIX C – Documentation

Instructions to Participants.....	C1
Results Sheet.....	C2

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 17th 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 2020 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 Fleer. This report was authorised by Mr P Briggs, General Manager.

2. FEATURES OF THE PROGRAM

- (a) Participants were provided with one filter paper sample labelled PTA AE15 containing particulate matter at 50-600 mg/filter.
- (b) A total of 19 laboratories received samples, comprising:
 - 11 Australian participants; and
 - 6 overseas New Zealand participants.

17 laboratories submitted 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. Please note that one laboratory reported results for two samples and, therefore, their code number (with letters) appear several times in the data set.
- (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*, 2019 (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

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 "§".

(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

Analysis	No. of Results	Median \pm Uncertainty of the Median (mg/filter)	Normalised IQR
Particulate Matter on Filter Paper	18	121.6 \pm 0.2	0.72

From the results sheets it was noted that eleven participants reported using a four figure balance, five participants reported using a five figure balance and two participants reported using a six figure balance.

5. PTA AND TECHNICAL ADVISER'S COMMENTS

Metrological Traceability and Measurement Uncertainty of Assigned Values

Consensus values (median) derived from participants' results are used in this program. These values are not metrologically traceable to an external reference.

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

The samples were stable and homogenous, and the median value obtained from this proficiency round was in good agreement with the expected level (manufacturer's certified value), as shown in Table B.

As the assigned value for this program is the median of the results submitted by the participants, the uncertainty of the median has been calculated and is presented below.

**TABLE B: COMPARISON OF EXPECTED LEVEL
AND PROFICIENCY MEDIAN**

Analysis	Expected Level (mg/filter)	Median (mg/filter)	Uncertainty of the Median (mg)
Particulate Matter on Filter Paper	121	121.6	0.2

Analysis of Results by Method Groups

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. As there were less than 11 results submitted for each method, reliable conclusions cannot be drawn from analysing grouped methods on this occasion. Therefore, results from all method groups have been pooled for analysis.

The matter of unrealistic claims for measurement uncertainty has been raised previously, however, the issue remains. It is strongly recommended that laboratories review their methodology for establishing measurement uncertainty.

6. OUTLIER RESULTS

No outlier results were reported this round.

7. REFERENCE

- [1] *Guide to Proficiency Testing Australia*, 2019 (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
Ordered Robust Z-Score chart.....	A2

Particulate Matter on Filter Paper Results

Sample PTA AE17

Particulate Matter on Filter Paper (mg/filter)

Laboratory Code	Result (mg/filter)	MU (mg/filter)	Robust Z-Score	Balance Used	Method
2	122	0.05	0.55	6	USEPA 5
4	120.6	0.3	-1.38	4	USEPA method 5
5	121.45	0.5	-0.21	5	USEPA M5
6	122.19	0.1	0.81	6	USEPA Method 5
8	121.6	0.5	0.00	4	USEPA 5
9	122	*	0.55	4	AS 3580.9.3 3580.9.6
10	120.64	0.01	-1.32	5	AS4323.2
15	120.3	0.4	-1.79	4	USEPA Method 5
16A	121.4	1	-0.28	4	USEPA 5
16B	121.1	0.1	-0.69	4	USEPA 5
18	121.6	0.5	0.00	4	ISO 9096:2017
21	121.46	0.0002	-0.19	5	AS4323.3 LTM1450
25	122.53	0.06	1.28	5	In house method based on AS 3580.9 (3+6)
26	122.17	7.7	0.79	5	AS2985 - 2009
27	122.3	0.2	0.97	4	AS4323.2 - 1995
28	120.1	2.4	-2.07	4	ES.ESM.0012 (AS 4323.2)
29	122.2	0.13	0.83	4	USEPA Method 5/17 (Gravimetric)
30	122.1	2.4	0.69	4	USEPA Method 5

Note:

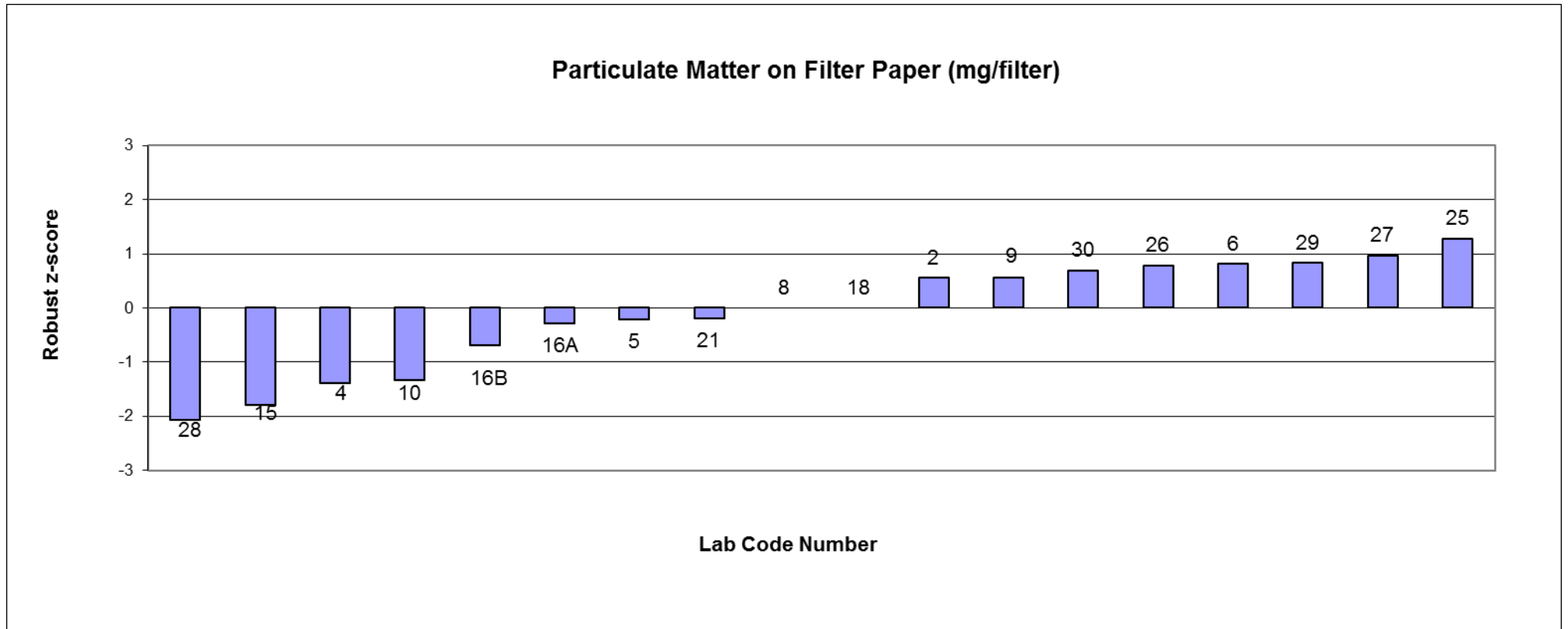
- * denotes no result reported for MU.

Summary Statistics

No. of Results	18
Median	121.6
Norm IQR	0.72
Uncertainty (Median)	0.2
Robust CV	0.6%
Minimum	120.1
Maximum	122.5
Range	2.4

A2

**Particulate Matter on Filter Paper (mg/filter)
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 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	121	1.97	121	100	26

Note: ERA certification and analytical verification data issued 17 June 2020.

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

² The stated Uncertainty represents an expanded uncertainty and approximates a 95% confidence interval. The uncertainty is based on the characterization, homogeneity and stability characteristics of the product, multiplied by a coverage factor (k=2). 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 formula used to calculate the expanded uncertainty is:

$$U_{\text{expanded}} = k * \text{SQRT}((U_{\text{char}})^2 + (U_{\text{homogen}})^2 + (U_{\text{LTS}})^2 + (U_{\text{STS}})^2 + (U_{\text{RSS}})^2)$$

Where:

U_{expanded} = Expanded uncertainty.

k = Coverage factor.

U_{char} = Combined standard uncertainty of the manufacturing and/or analytical verification assessment.

U_{homogen} = Standard uncertainty of the homogeneity assessment.

U_{LTS} = Standard uncertainty associated with long-term stability.

U_{STS} = Standard uncertainty associated with short-term (transport) stability.

U_{RSS} = Standard uncertainty associated with repeated sampling of the product (where permitted by product use instructions).

APPENDIX C

Documentation

Instructions to Participants	C1
Results Sheet	C2

PROFICIENCY TESTING AUSTRALIA
Proficiency Testing Program
Air & Emissions (Round 17)

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 AS 4323.2, 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 if possible and report an estimate of uncertainty of measurement 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. Note that the estimate of uncertainty if reported is tabled in the final report only and not used to evaluate individual laboratory performance.
 - 5) All laboratories are asked to return the Results Sheet by **Monday 30th November 2020** to:

Kathy Weller Proficiency Testing Australia Phone: +617 3721 7373 Email: Kathy.Weller@pta.asn.au

PROFICIENCY TESTING AUSTRALIA**Air & Emissions (Round 17) - Proficiency Testing Program****Results Sheet**

Lab Code:

Test	Sample PTA - AE17 (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) if known for the result. Please report in corresponding unit of measurement.
- iv) Report the number of figures for the balance used.

Comments: _____

Signed: _____

Date: _____

Return results by **30th November 2020** to:

Kathy Weller
Proficiency Testing Australia
Phone: +61 7 3721 7373

Email: Kathy.Weller@pta.asn.au

- *End of Report* -