



Report No. 837

**Air & Emissions Proficiency Testing
Round 4
Particulate Matter on Filter Paper**

November 2013

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Mr F Fleeer, Golder Associates Pty Ltd, Australia. This assistance included the design of the program, technical advice and discussion in the final report. Also our thanks go to the Environmental Resource Associates (ERA), USA, for the supply of 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 fourth round of an ongoing series of programs associated with the methods used to monitor process emissions to air.

The program was conducted in September 2013 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 Ms D Mihaila and the Technical Advisor was Mr F Flee, Golder Associates Pty Ltd, Australia. This report was authorised by Mr P Briggs, PTA General Manager.

2. FEATURES OF THE PROGRAM

- (a) Participants were provided with one filter paper sample labelled PTA AE4 containing particulate matter at 50-600mg/filter.
- (b) A total of 22 laboratories received samples, comprising:
 - 19 Australian participants; and
 - 3 overseas participants (Indonesia, New Zealand and United Arab Emirates).

All laboratories submitted the 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 the results on the *Results Sheet*.
- (d) Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity and stability. Based on the results of this testing (see Appendix B), the homogeneity and stability 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 more than one set of results and, therefore, their code number (with index) could appear several times in the same data set. Also, one laboratory received two sets of samples and their code number was marked with letter "a", corresponding to the sample analysed.

- (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 3). Robust z-scores and z-score charts are presented in Appendix A.
- (h) The document entitled *Guide to Proficiency Testing Australia, 2012* (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 8.

3. FORMAT OF THE APPENDICES

- (a) Appendix A contains the analysis of results reported by laboratories for the sample provided. This section contains the following:
 - a table of results and calculated z-scores;
 - a list of summary statistics; and
 - an ordered z-score chart.
- (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 with an absolute value less than or equal to 2.0 is considered to be satisfactory, 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 8 summarises the outlier results detected.

(b) Results Table and Summary Statistics

The results table 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 significant figures) 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 the table of results and consists of:

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. $100 \times \text{Normalised IQR} / \text{Median}$;
- *Minimum*: the lowest laboratory result;
- *Maximum*: the highest laboratory result; and
- *Range*: the difference between the *Maximum* and *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:

$$\sqrt{\frac{\pi}{2}} \times \frac{\text{normIQR}}{\sqrt{n}}$$

n = number of results

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

(c) Ordered Z-score Chart

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

The chart contains 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 the chart 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 ± Uncertainty of the Median (mg/filter)	Normalised IQR
Particulate Matter on Filter Paper	22	126.0 ± 0.2	0.6

5. PTA AND TECHNICAL ADVISOR'S COMMENTS

5.1 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 homogeneous, 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 also presented in Table B.

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	126	126.0	0.2

The program is also considered to have addressed the major issues associated with previous gravimetric analysis proficiency testing programs in which a standard metal mass was used. The filter paper was tissue quartz and the particulate matter sodium chloride, consequently both materials are slightly hygroscopic, better representing the weighing of actual samples.

Overall, the performance of participants in this round was very good, with a robust CV less than 1%. Out of 22 reported results, two were deemed to be outliers.

5.2 Analysis of Round 4 Results

This study included 22 laboratories with one laboratory reporting eight sets of results, bringing the total number of reported results to 29. However, to avoid the possibility of the summary statistics being affected by laboratory bias, only one result from each laboratory was included in the data set for statistical analyses and associated comments below.

The testing of Particulate Matter on Filter Paper was successfully carried out, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 124.8 – 127.2 mg/filter. Out of 22 participants, two outlier results ($|z\text{-scores}| \geq 3.0$) were obtained (laboratories 13 and 14a). No questionable results ($2.0 < |z\text{-scores}| < 3.0$) were reported in this round.

Figure 1 exhibits the spread of results and the methods used for Particulate Matter on Filter Paper testing in this round.

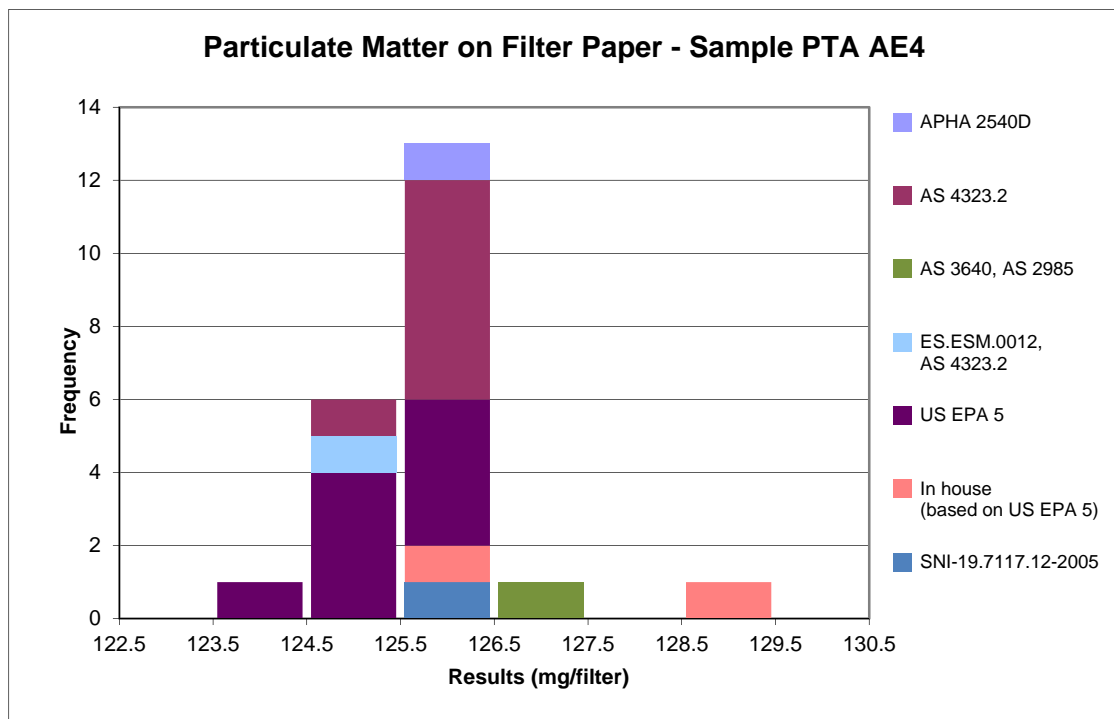


Figure 1. Spread of results for Particulate Matter on Filter Paper testing of Sample PTA AE4, with a median of 126.0 mg/filter.

Out of 22 participants, nine used US EPA Method 5 and seven used the Australian Standard AS 4323.2 method. Additionally, two laboratories reported using an in-house method based on US EPA Method 5 and one laboratory quoted method AS 4323.2 together with another method (ES. ESM.0012).

Other methods reported by participants were APHA 2540D, AS 2985, AS 3640 and SNI-19.7117.12-2005.

The measurement uncertainty (MU) reported by participants can be seen in Figure 2, displayed by the methods used. With one exception, all other participant laboratories reported MU estimations associated with their test result in this round.

A t-test of all results indicated the overall reproducibility for particulate matter on filter paper testing was 125.8 ± 1.1 mg/filter for sample PTA AE4 (95% CI).

Laboratories may use this reproducibility data as a comparison to internal estimations.

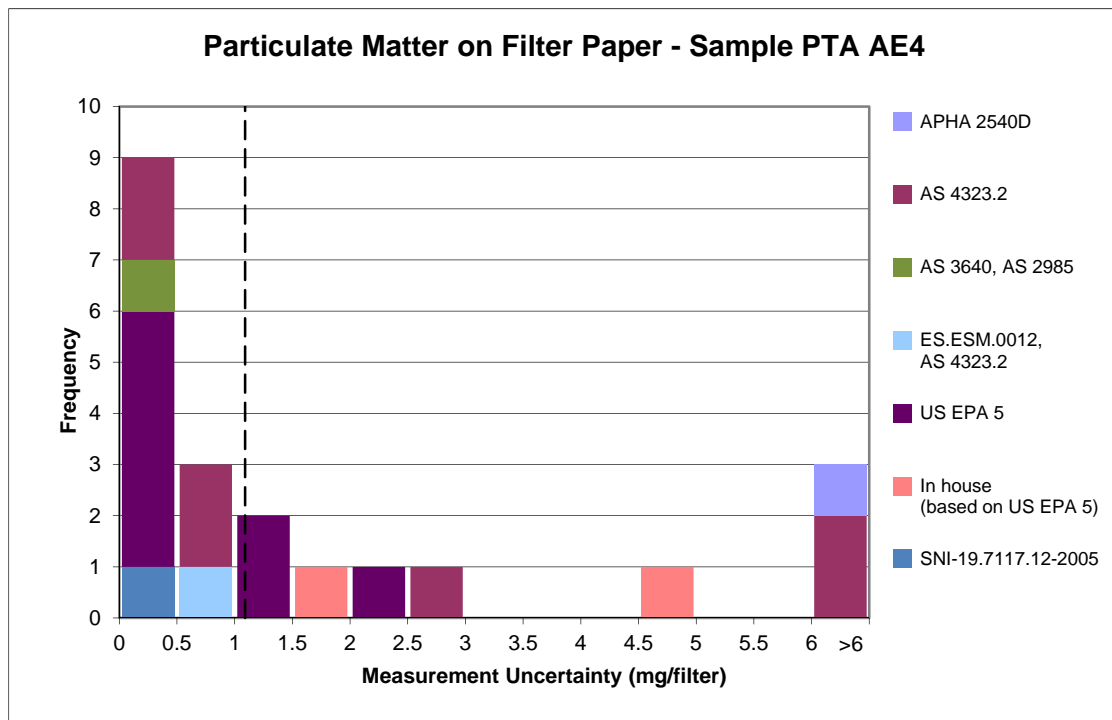


Figure 2. MU for Particulate Matter on Filter Paper testing of sample PTA AE4, compared with 95% confidence interval for overall reproducibility ± 1.1 mg/filter in this round, shown as dashed line.

Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample. Laboratories 1, 13, 14a, 17, 20 and 27 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU.

6. OUTLIER RESULTS

Laboratories reporting results that have been identified as outliers are listed by code number in Table C below.

TABLE C: SUMMARY OF STATISTICAL OUTLIERS

Analysis	Outlier results
Particulate Matter on Filter Paper	Lab Code 13 Lab Code 14a

7. Reference

- [1] *Guide to Proficiency Testing Australia, 2012* (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
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Particulate Matter on Filter Paper Results

Sample PTA AE4

Particulate Matter on Filter Paper
Results by Laboratory Code

Sample PTA AE4					
Lab Code	Result	±	MU ¹	Robust z-score ²	Method
	(mg/filter)				
1	127	±	0.016	1.59	AS 3640, AS 2985
3	126	±	5	0.00	In-house Method ³
6	126	±	19	0.00	AS 4323.2
7	126	±	16	0.00	APHA 2540D
10	126	±	1	0.00	AS 4323.2
11	126	±	0.1	0.00	AS 4323.2
12	125	±	1	-1.59	ES.ESM.0012, AS 4323.2
13	124	±	0.012	-3.17	§ US EPA 5
14a	129	±	2	4.76	§ In-house Method ³
15	126	±	0.12	0.00	US EPA 5
17	125	±	0.01	-1.59	US EPA 5
18	125	±	1.5	-1.59	US EPA 5
19	126	±	8	0.00	AS 4323.2
20	125.1	±	0.015	-1.43	US EPA 5
21	126	±	0.0005	0.00	SNI-19.7117.12-2005
22	126	±	1.3	0.00	US EPA 5
23	125.3		#	-1.11	US EPA 5
24	126	±	1	0.00	AS 4323.2
26	126	±	0.2	0.00	US EPA 5
27	125	±	0.2	-1.59	AS 4323.2
29	125.7	±	2.5	-0.48	US EPA 5
30	126	±	2.65	0.00	AS 4323.2

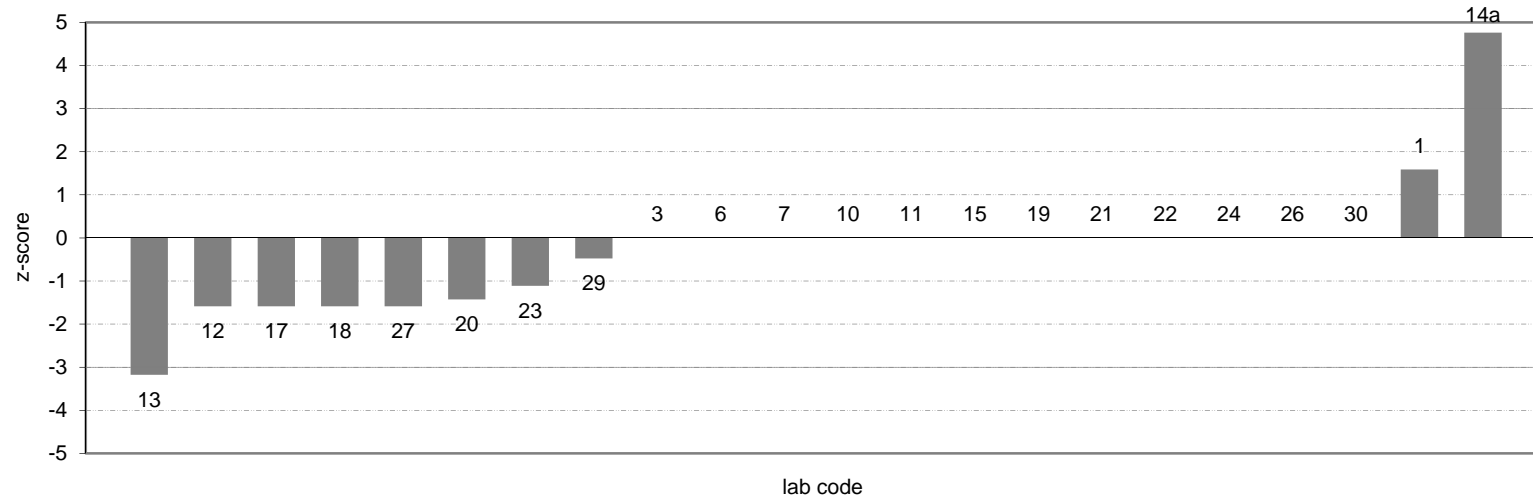
<i>No of Results:</i>	22
<i>Median:</i>	126.0
<i>Uncertainty of the Median:</i>	0.2
<i>Normalised IQR:</i>	0.6
<i>Robust CV:</i>	0.5%
<i>Minimum:</i>	124
<i>Maximum:</i>	129
<i>Range:</i>	5

- 1 Where reported, results are shown with their corresponding measurement uncertainty (MU).
- 2 "§" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.
- 3 In-house Method based on US EPA Method 5.

Note:

Laboratory 1 reported eight results for sample PTA AE4. To avoid the possibility of the summary statistics being affected by laboratory bias, only the first result submitted by this laboratory was included in the data set for calculating the median, uncertainty of the median, normalised IQR and robust CV. Please refer to page A3 for a complete list of results submitted by Laboratory 1.

Particulate Matter on Filter Paper - Sample PTA AE4 - Robust Z-scores



Particulate Matter on Filter Paper - Sample PTA AE4
Ordered Robust Z-score Chart

A2

Complete List of Results submitted by Laboratory 1

Particulate Matter on Filter Paper

Results by Laboratory Code

Lab Code	Sample PTA AE4				
	Result	±	MU ¹	Robust z-score ²	Method
1	127	±	0.016	1.59	AS 3640, AS 2985
1.1	127	±	0.016	1.59	AS 3640, AS 2985
1.2	127	±	0.016	1.59	AS 3640, AS 2985
1.3	127	±	0.016	1.59	AS 3640, AS 2985
1.4	127		#	1.59	In-house Method ³
1.5	127	±	0.016	1.59	AS 3640, AS 2985
1.6	127	±	0.016	1.59	In-house Method ³
1.7	127	±	0.016	1.59	In-house Method ³

- 1 Where reported, results are shown with their corresponding measurement uncertainty (MU).
- 2 "\$" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.
- 3 In-house Method based on AS 3640, AS 2985.

Note:

Laboratory 1 reported eight results for sample PTA AE4. To avoid the possibility of the summary statistics being affected by laboratory bias, only the first result submitted by this laboratory was included in the data set for calculating the median, uncertainty of the median, normalised IQR and robust CV.

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 homogeneous and stable.

Table D below presents the certification data and analytical verification results prior sample release.

TABLE D: HOMOGENEITY AND STABILITY

Analysis	Certified Value ¹ (mg/filter)	Uncertainty ² (%)	Pre - Release Testing		
			Mean (mg/filter)	Recovery (%)	No. of samples
Particulate Matter	126	0.822%	126	99.6%	28

Note: ERA certification and analytical verification data issued 12 February 2013.

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 4)

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, EPA Methods 5, 5A, 5B, 5D, 5F, AS 4323.2 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 dried weight from the tare weight listed on the label.
- 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. 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 **11 October 2013** to:

Delfina Mihaila Proficiency Testing Australia PO Box 7507 SILVERWATER NSW 2128 AUSTRALIA Phone: +612 9736 8397 Fax: +612 9743 6664 Email: dmihaila@pta.asn.au
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PROFICIENCY TESTING AUSTRALIA**Air & Emissions (Round 4) - Proficiency Testing Program****Results Sheet**Lab Code:

Test	Sample PTA - AE4 (mg/filter)	\pm MU* (mg/filter)	Method
Particulate Matter			

- i) For each sample only a single result is requested.
- ii) Report results using three significant figures (e.g. 63.4 mg/filter; 274 mg/filter).
- iii) Report results in milligrams per filter (mg/filter).
- iv) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in corresponding unit of measurement.

Comments: _____

Signed: _____

Date: _____

Return results **no later than 11 OCTOBER 2013** to:

Delfina Mihaila
 Proficiency Testing Australia
 PO Box 7507
 SILVERWATER NSW 2128
 AUSTRALIA

Phone: +61 2 9736 8397
Fax: +61 2 9743 6664
Email: dmihaila@pta.asn.au

INSTRUCT AE4 PROF TEST PROG

- End of Report -