Report No. 1193

PCBs in Oil

Round 12

Proficiency Testing Program

June 2020

PO Box 7507 SILVERWATER   NSW   2128,   Australia

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1. FOREWORD

This report summarises the results of a proficiency testing program on the determination of polychlorinated biphenyls (PCBs) in oil. It constitutes the twelfth round of an ongoing series of programs. 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 April 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 Dr M Li and the Technical Advisor was Mr G Ienco from Transformer Fitness Pty Ltd. This report was authorised by Mrs K Cividin, PTA Quality Manager.

2. FEATURES OF THE PROGRAM

2.1. Participants were provided with one sample labelled PTA Sample A, consisting of approximately 4ml of oil containing PCBs.

2.2. A total of 4 Australian laboratories received samples for this study. Of these 4 laboratories, 8 sets of results were submitted for analysis.

2.3. 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.

2.4. 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.

2.5. 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.

2.6. 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 (where appropriate, 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.

2.7. A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and z-score charts relevant to each test are presented in Appendix A.

2.8. 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.

2.9. A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 6.

3. FORMAT OF THE APPENDICES

3.1. 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; and

- ordered z-score charts.

3.2. Appendix B contains details of the homogeneity testing.

3.3. Appendix C contains copies of the *Instructions to Participants* and *Results Sheet.*

4. STATISTICAL DESIGN OF THE PROGRAM

4.1 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 6 summarises the outlier results detected.

4.2   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 where appropriate, 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.

If appropriate, a list of summary statistics appears at the bottom of each of the tables of results and consists of:
- the <u>number</u> of results for that test/sample (*No. of Results*);
- the <u>median</u> of these results, i.e. the middle value (*Median*);
- the <u>uncertainty of the median</u>;
- the <u>normalised interquartile range</u> of the results (*Normalised IQR*);
- the <u>robust coefficient of variation</u>, expressed as a percentage (*Robust CV*) -
  i.e. 100 x *Normalised IQR* / *Median*;
- the <u>minimum</u> and <u>maximum</u> laboratory results; and
- the <u>range</u> (*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:

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

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

4.3   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

Analyte	Summary Statistics	PTA Sample A
Total PCBs	No. of Results Median * Normalised IQR *	8 40.50 12.05
Aroclor 1016	No. of Results	2
Aroclor 1221	No. of Results	2
Aroclor 1232	No. of Results	2
Aroclor 1242	No. of Results Median * Normalised IQR *	6 39.00 11.81
Aroclor 1248	No. of Results	2
Aroclor 1254	No. of Results	6
Aroclor 1260	No. of Results	4
Aroclor 1262	No. of Results	2
Aroclor 1268	No. of Results	2

NOTE: * value determined based on previous rounds of the program.

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.

As the assigned value for this program is the median of the results submitted by the participants, where appropriate, the median and the uncertainty of the median have been calculated and they are presented below.

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Analyte	Median (mg/kg)	Uncertainty of the median (mg/kg)
Total PCBs	40.50	2.54
Aroclor 1242	39.00	2.43

5.2 Legislation-Environmental

In 2000, the Victorian Environment Protection Act 1970 was varied to include PCBs as a notifiable chemical. As stated in this order - "polychlorinated biphenyls" are any material or waste containing "polychlorinated biphenyls" at a concentration of more than 2 mg/kg.

The Victorian EPA publication 693b (2001) states that a waste containing greater than 50mg/kg is a prescribed waste (schedule PCB) and must undergo treatment. A concentration of less than 50mg/kg but greater than 2mg/kg is classified as containing 'non-schedule PCBs'. If the concentration is less than 2mg/kg then it is classified as 'PCB-free' as described in the National Management Plan (ANZEC). Therefore we have three levels in which critical decisions are made about a waste material and how it will be disposed of and potentially treated. These levels are greater than 50mg/kg, less than 50mg/kg but greater than 2mg/kg, and less than 2mg/kg. For this assessment, it is critical that the PCB values reported at these three critical levels are accurate and precise.

5.3 False Negative / Positive Results and Misidentification

No false negative or false positive results were reported for PTA Sample A.

5.4 PCB Mixtures

Mixtures of PCBs are very difficult to identify and quantitate using standard techniques for profiling. PTA Sample A was a real environmental sample that contained complex mixtures of three different PCBs (Aroclor: 1242, 1254 and 1260). Laboratory codes 1A, 1B, 3A, 3B, 5A and 5B identified Aroclor 1242. Laboratory code 3B reported an outlier for Aroclor 1242. This oil sample also contained low levels of Aroclor 1254 (6.70mg/kg) and Aroclor 1260 (2.50mg/kg). Laboratory codes 1A, 1B, 3A, 3B, 5A and 5B identified Aroclor 1254 and Laboratory codes 1A, 1B, 5A and 5B identified Aroclor 1260.

5.5 General Comments

Overall, the performance of participants in this round was good, with two results for Total PCBs being identified as statistical outliers (Laboratory codes 3A & 3B) and one result for Aroclor 1242 being identified as a statistical outlier (Laboratory Code 3B).

For specific Aroclors and Total PCBs, two of the four laboratories which submitted results have reported one or more outlier results (z-scores outliers) which should be investigated. Likewise, laboratories are also encouraged to review results which have an absolute z-score value between two and three (i.e. $2.0 < |z| < 3.0$).

Many of the participant laboratories did not perform the analysis for one or more individual Aroclors requested in this trial. Laboratories should have use of the different PCBs standards. If a laboratory is performing analysis of environmental samples there is concern that they could misidentify PCB type (which leads to errors in quantitation) if they do not include in analysis common Aroclors. All laboratories carrying out environmental testing of Aroclors should obtain these commonly available standards.

All laboratories reported using the method Gas Chromatography/Electron Capture Detection. Due to the misidentification by some laboratories it appears that they are not conducting extensive clean-ups during the preparative steps. This may add variation to the overall results.

Laboratories have clearly performed better where the oil sample was spiked with a single Aroclor. In real waste oil containing mixtures of PCBs, many laboratories have problems with misidentification and low levels detection.

The poor results obtained from this trial for the real oil samples clearly demonstrates that there is merit in having real samples to test and indicates the necessity of including these type of samples in future proficiency studies.

6. OUTLIER RESULTS

Laboratories reporting outlier results are listed in the following table:

TABLE B: SUMMARY OF STATISTICAL OUTLIERS

Analyte	Outlier Type	Laboratory Code No.
Total PCBs	$|z\ score| \geq 3.0$	3A, 3 B
Aroclor 1242	$|z\ score| \geq 3.0$	3B

7. Reference

[1]   *Guide to Proficiency Testing Australia*, 2020 (This document can be found on the PTA website, www.pta.asn.au)

APPENDIX A

Results and Data Analysis

Total PCBs Results

PTA Sample A

Analysis for Total PCBs

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU	Robust z-score	
1A	50.93	3	0.87	
1B	46.63	3	0.51	
2A	12.4	1	-2.33	
2B	11.8	1	-2.38	
3A	87	23	3.86	§
3B	112	28	5.94	§
5A	47.4	19	0.57	
5B	47.4	19	0.57	

No. Results:	**8**
Median* :	**40.50**
Uncertainty of the median* :	**2.52**
Normalised IQR* :	**12.05**
Robust CV:	**29.7%**
Minimum:	**11.8**
Maximum:	**112**
Range:	**100.2**

NOTE: * Value was determined based on previous rounds of the program

Total PCBs - Robust Z-Scores
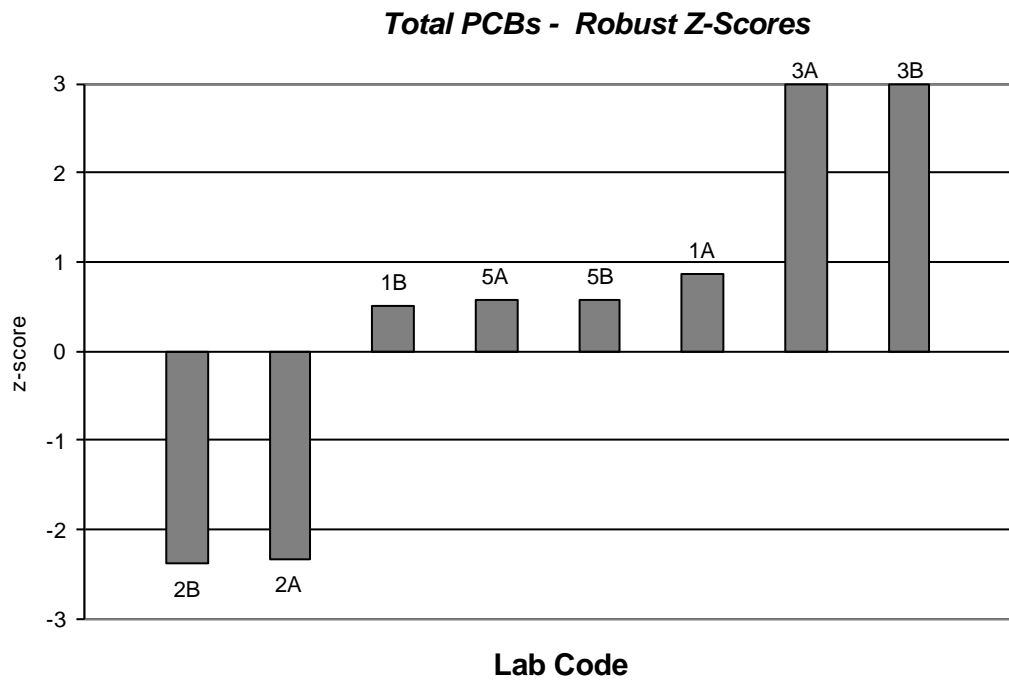
Lab Code

Aroclor 1016 Results

PTA Sample A

Aroclor 1016

Results by Laboratory Code

Lab Code	Result(mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results **2**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values

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Aroclor 1221 Results

PTA Sample A

Aroclor 1221

Results by Laboratory Code

Lab Code	Result(mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	
No. Results	**2**	

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

Aroclor 1232 Results

PTA Sample A

Aroclor 1232

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results **2**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

Aroclor 1242 Results

PTA Sample A

Analysis for Aroclor 1242

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU	Robust z-score	
1A	50.93	3	1.01	
1B	46.63	3	0.65	
2A	nt			
2B	nt			
3A	73	18	2.88	
3B	99	24	5.08	§
5A	47.4	19	0.71	
5B	47.4	19	0.71	

No. Results:	**6**
Median* :	**39.00**
Uncertainty of the median* :	**2.43**
Normalised IQR* :	**11.81**
Robust CV:	**30.3%**
Minimum:	**46.63**
Maximum:	**99**
Range:	**52**

NOTE: * Value was determined based on previous rounds of the program.

Aroclor 1242
Ordered Robust Z-Score Chart

Aroclor 1242 - Robust Z-Scores

Lab Code

Aroclor 1248 Results

PTA Sample A

Aroclor 1248

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results **2**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

Aroclor 1254 Results

PTA Sample A

Aroclor 1254

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	<2	
1B	<2	
2A	nt	
2B	nt	
3A	14	5
3B	13	4
5A	<10	
5B	<10	

No. Results **6**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the majority of results were reported "less than" values.

Aroclor 1260 Results

PTA Sample A

Aroclor 1260

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	<2	
1B	<2	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results: **4**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

Aroclor 1262 Results

PTA Sample A

Aroclor 1262

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results **2**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

Aroclor 1268 Results

PTA Sample A

Aroclor 1268

Results by Laboratory Code

Lab Code	Result (mg/kg)	± MU
1A	nt	
1B	nt	
2A	nt	
2B	nt	
3A	nt	
3B	nt	
5A	<10	
5B	<10	

No. Results **2**

NOTES: nt = not tested

No statistical analysis was conducted for this Aroclor as the results were reported as "less than" values.

APPENDIX B

Homogeneity Testing & Stability
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Homogeneity Testing

PTA Sample A was a real contaminated waste lubricating oil that contained a complex mixture of Aroclor 1242 (major), 1254 and 1260 (minor).

The concentrations employed were set out to determine the laboratories' ability to meet regulatory requirements for waste classification of PCB containing oils.

Statistical analyses showed that all samples were sufficiently homogenous so that any results later identified as outliers should not be attributed to any sample variability.

Sample Identification: PTA Sample A
Oil Type: Real waste lubricating oil
Contaminated oil 'Aroclors present'.
Mixed Aroclor

Analyte	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	Mean	SD	CV
Aroclor 1016	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Aroclor 1221	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Aroclor 1232	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Aroclor 1242	38	41	42	41	40	38	44	45	44	44	41.70	2.54	6.1%
Aroclor 1248	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Aroclor 1254	6.0	6.0	7.0	6.0	6.0	7.0	7.0	8.0	7.0	7.0	6.70	0.67	10.1%
Aroclor 1260	2.0	2.0	2.0	2.0	2.0	3.0	3.0	3.0	3.0	3.0	2.50	0.53	21.1%
Aroclor 1262	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Aroclor 1268	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Total PCBs	46	49	51	49	48	48	54	56	54	54	50.90	3.38	6.6%

Stability Testing

Due to the nature of the sample it was not considered necessary to perform stability testing.

APPENDIX C

Documentation

Proficiency Testing Australia

PCBs in Oil Proficiency Testing Program

Round 12

INSTRUCTIONS TO PARTICIPANTS

To ensure that all results from this program are analysed appropriately, participants are asked to read and adhere carefully to the following instructions:

1. One 10 ml bottle of oil containing Polychlorinated Biphenyls (PCBs) is supplied.
2. The sample is labelled: PTA Sample A
3. Carefully open the PCBs in Oil.
4. Take a clean, dry 10ml class A volumetric flask.
5. Transfer approximately 1.0g of the PCBs in Oil sample to the flask and record the weight.
6. Dilute the flask to the line with pesticide grade hexane and mix well.
7. Cap the flask and mix by inverting two or three times.
8. Immediately analyse the diluted sample by your normal procedures.
9. The sample is to be tested for the Aroclor types listed on the results sheet, and the amounts of each Aroclor type quantified in mg/kg.
10. Results are to be recorded to the accuracy and reporting basis indicated on the *Results Sheet:*

    Please do not leave empty boxes on the results sheet.

    i)   results are to be reported in mg/kg, to at least two significant figures.
    ii)   levels less than your level of detection may be reported as a "<" value.
    iii)   for the AROCLOR types tested and not detected, report "Not Det".
    iv)   for the AROCLOR types not tested, report "Not tested".

11. Laboratories are also requested to calculate and report an estimate of measurement uncertainty for each reported result. All estimates of uncertainty of measurement must be provided as a 95% confidence interval (coverage factor $k \approx 2$) and reported in mg/kg.

12. On the *Results Sheet* record the appropriate method code number:
    1.   Gas Chromatography/Electron Capture Detection
    2.   Gas Chromatography/Mass Spectrometric Detection
    3.   Other (please specify)

13. Testing may commence as soon as samples are received. Please return results, **NO LATER THAN 23 April 2020,** to:

> Dr Michael LI
> Proficiency Testing Australia
> PO Box 7507
> Silverwater NSW 2128
> Email: michael.li@pta.asn.au
> TEL: (02) 9736 8397 FAX: (02) 9743 6664

PROFICIENCY TESTING AUSTRALIA
PCBs in Oil Proficiency Testing Program

Round 12

Results Sheet

Lab Code: #

RESULTS (mg/kg)	PTA Sample A	±MU
AROCLOR TYPE 1016		
AROCLOR TYPE 1221		
AROCLOR TYPE 1232		
AROCLOR TYPE 1242		
AROCLOR TYPE 1248		
AROCLOR TYPE 1254		
AROCLOR TYPE 1260		
AROCLOR TYPE 1262		
AROCLOR TYPE 1268		
TOTAL PCBs		

Please do not leave empty boxes on the results sheet.

    i)   results are to be reported in mg/kg, to at least two significant figures.
    ii)   levels less than your level of detection may be reported as a "<" value.
    iii)   for the AROCLOR types tested and not detected, report "Not Det".
    iv)   for the AROCLOR types not tested, report "Not tested".

METHOD (Please tick):

☐ Gas Chromatography/Electron Capture Detection

☐ Gas Chromatography/Mass Spectrometric Detection

☐ Other (please specify)

Print name: _____ Signature: _____ Date: _____

Please return by 23 April 2020 to: Dr Michael Li Email: michael.li@pta.asn.au
TEL: (02) 9736 8397 FAX: (02) 9743 6664

- End of Report -