Report No. 1210

Waters Proficiency Testing Program

Round No. 262

- Total Recoverable Oil and Grease -

August 2020

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). Also our thanks go to Global Proficiency Ltd (New Zealand) and to Global Proficiency Pty Ltd (Australia) for the supply and distribution of the samples.

PO Box 7507 SILVERWATER NSW 2128, Australia

SD 9.17.13

CONTENTS

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Total Recoverable Oil and Grease in waters. This is round 262 in a planned series of programs involving the analysis of chemical and physical parameters of waters. This program is accredited to ISO/IEC 17043:2010 "*Conformity assessment - General requirements for proficiency testing"* by International Accreditation New Zealand (IANZ).

The exercise was conducted in June 2020 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Program Coordinator was Mrs D Mihaila and the Technical Adviser was Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). This report was authorised by Mrs K Cividin, PTA Quality Manager.

2. Program Features and Design

2.1 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 a number of laboratories reported more than one set of results and, therefore, their code numbers (with letter) could appear several times in the same data set.

2.2 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.

2.3 Participants were provided with two glass vials (labelled PTA 1 and PTA 2) for analysis of Total Recoverable Oil and Grease.

2.4 A total of 31 laboratories received samples, comprising:

- 19 Australian participants; and
- 12 overseas participants, including:
    - Indonesia (1), Malaysia (7), Mali West Africa (1), Papua New Guinea (2), Thailand (1).

Of these 31 laboratories, 2 were unable to submit results by the due date.

2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, uncertainty of the median, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).

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

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.

2.7 A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 11.

2.8 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) it was considered that the samples utilised for this program were homogeneous and stable. As such, any results later identified as outliers could not be attributed to any notable sample variability.

3. Statistical Format

For each test, where appropriate, the following information is given:

- a table of results and calculated z-scores;
- a list of summary statistics; and
- ordered z-score charts.

3.1 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 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 "§". Laboratories are also encouraged to review results which have an absolute z-score value between 2.0 and 3.0 (i.e. $2.0 < |z\text{-score}| < 3.0$). These are considered to be questionable results.

In this study, high biasing results which have a z-score ≥ 3.0 and have been marked with a "‡" are considered questionable results. Results which have a z-score value between two and three ($2.0 < z\text{-score} < 3.0$) and have been marked with a "†" are considered satisfactory results.

Each determination was examined for outliers with all methods pooled. The table on page 11 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

The tables in Appendix A contain 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 results tables and consists of:

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. 100 x *Normalised IQR* / *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:

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

n = number of results.

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

In this round, the robust CV values were considered inappropriate to calculate robust z-scores, therefore a target coefficient of variation (target CV) was used. The target coefficient of variation was based on historical data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median.

The robust z-score (denoted by z) for a laboratory's sample A result was calculated as:

$$\mathrm{z} = \frac{\mathrm{A} - \mathrm{median(A)}}{\mathrm{target\ SD(A)}}$$

where A is a sample in a testing program.

3.3 Ordered Z-score Charts

The charts in Appendix A indicate each laboratory's robust z-score, in order of magnitude, marked with its laboratory 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.

4. PTA and Technical Adviser's Comments

4.1 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 Global Proficiency Ltd's Standard Operating Procedures to ensure samples were fit-for-purpose, homogeneous and stable. Weight checks were undertaken on all samples to ensure that the variability on doping concentrations was less than 3%. Dope concentrations presented in Table 1 illustrate the average oil and grease sample weight and the 95% confidence interval for weight variation at manufacturing, as ± 2SD (standard deviations).

Sample PTA 1 was prepared from high purity mineral oil and stearic acid (which has a low viscosity) in distilled water. Sample PTA 2 was prepared from a mixture of vegetable oil, anhydrous milk fat (AMF) and stearic acid in distilled water. Samples were prepared as ready-to-test (500 mL) samples, packaged in PP capped glass bottles and preserved with acid to pH 2.

Solutions were stable and homogeneous, and medians obtained from this proficiency round gave average recoveries of 86.3% for sample PTA 1 and 82.8% for sample PTA 2, with respect to the expected levels (dope concentration), as shown in Table 1. These were close to published precision data, which indicated that laboratories should be able to yield an average recovery of 84.2% - 93% with the Liquid-Liquid Partition Gravimetric method (APHA 5520 B), a recovery of 87.1% - 92.5% with the Solid Phase Partition Gravimetric method (APHA 5520 B), and a recovery of 98.7% for Soxhlet Extraction method (APHA 5520 D) [2].

Table 1. Comparison of expected levels (dope concentration) and proficiency medians. The values of the calculated uncertainty of the median are also presented.

Analysis	Sample	Dope Concentration ± 2SD (mg/L)	Median (mg/L)	Uncertainty of the median (mg/L)
Total Recoverable Oil and Grease	PTA 1	89.04 ± 0.97	76.80	4.74
	PTA 2	74.66 ± 0.98	61.80	3.21

As the assigned value for each sample in this program is the median of the results submitted by the participants, the uncertainty of the median for each sample has been calculated and is also presented in the Table 1.

4.2 Analysis of Round 262 Results

4.2.1 Total Recoverable Oil and Grease

Table 2 compares the Total Recoverable Oil and Grease medians and robust CVs from this round to those obtained in previous PTA rounds. Historically, CVs have been in the vicinity of 18.6% when the levels of Oil and Grease were not too close to the limit of quantitation (~20 mg). CVs in this round were wider than this historical variability. Published precision from the APHA 5520 B and US EPA 1664 interlaboratory method validation study, indicated laboratories should be able to achieve CVs of 8.7% (APHA, 23rd Ed & US EPA 1664 B) [2, 3].

Table 2. Comparison of current round variability and proficiency median of Total Recoverable Oil and Grease testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	76.80	26.5	29
	PTA 2	61.80	22.3	29
Report 1182	PTA 1	57.10	31.8	21
	PTA 2	42.40	36.7	21
Report 1160	PTA 1	63.30	47.1	34
	PTA 2	41.55	34.4	38

Bias / Accuracy

The Total Recoverable Oil and Grease testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 50.0 – 114 mg/L for sample PTA 1 and between 41 – 91 mg/L for sample PTA 2.

Out of 29 participants, two low biasing questionable results (2.0 < |z-score| < 3.0) were reported, for sample PTA 2 (laboratory codes 222 and 740). Laboratory code 742A reported a high biasing result (statistical outlier |z-score| ≥ 3.0) that was considered questionable in this study.

Three low biasing and two high biasing outlier results (|z-score| ≥ 3.0) were obtained for sample PTA 1, requiring follow-up action by laboratory codes 163, 218, 421, 425 and 471. For sample PTA 2, one low-biasing outlier result was obtained, requiring follow-up action by laboratory code 421.

Please note that the robust CV values for Total Recoverable Oil and Grease were considered inappropriate to calculate robust z-scores, therefore a target CV of 18.6% was used, based on data from previous PTA rounds.

The data sets for samples PTA 1 and PTA 2 formed approximately normal distributions (Figures 1 and 2). The method most frequently used for Total Recoverable Oil and Grease testing in this round was APHA 5520 B (Liquid-Liquid, Partition-Gravimetric Method), which was used by 55% of participants.

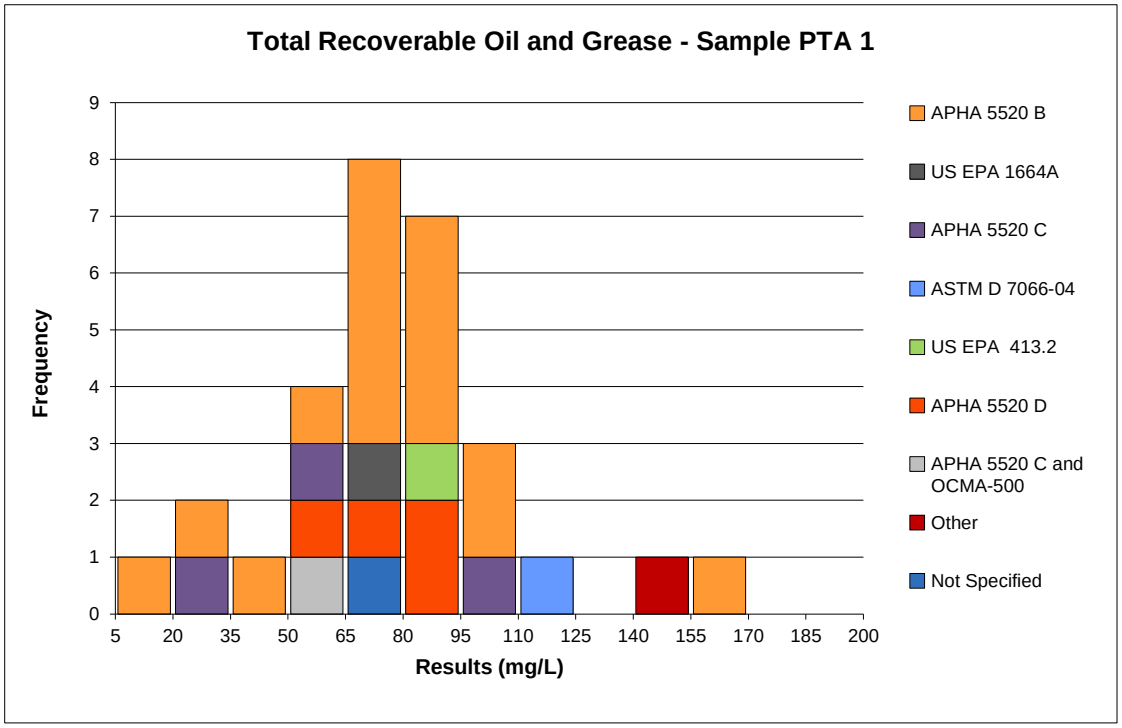


Figure 1. Spread of results for Total Recoverable Oil and Grease testing of sample PTA 1, with a median of 76.80 mg/L.

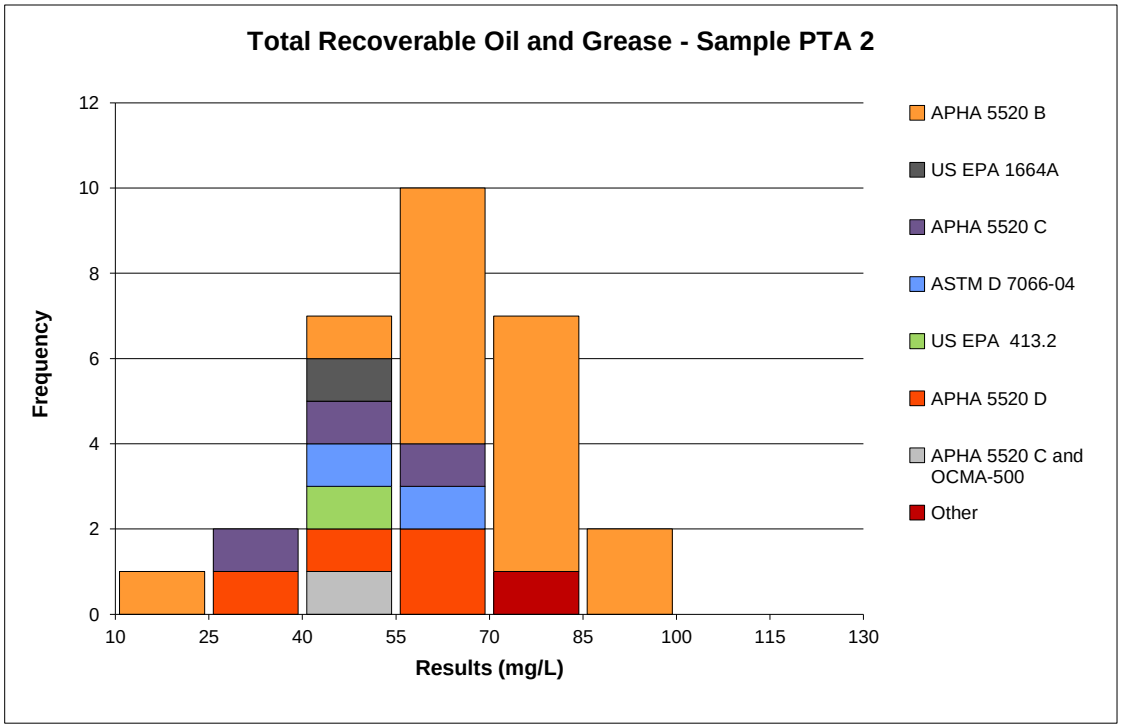


Figure 2. Spread of results for Total Recoverable Oil and Grease testing of sample PTA 2, with a median of 61.80 mg/L.

Laboratories concerned about their results may note that APHA 5520 A.4.b. recommends laboratories adhere strictly to sample drying times to standardize the gradual loss of weight due to volatilization of short-chain hydrocarbons and simple aromatics. APHA 5520 B includes special precautions regarding temperature and

solvent vapour displacement to minimize the effect of oxidation of unsaturated fats and fatty acids. Low biasing results can also occur if samples form emulsions that are difficult to break. APHA 5520 B.4 recommends centrifuging the emulsion for 5 minutes at 2400 rpm, if this is a potential problem [2]. APHA 5020 B also recommends QC for all Oil and Grease methods include use of Method Blanks, Laboratory Fortified Blanks, and Laboratory Fortified Matrix with Duplicates, in addition to QC practices specific to your method.

Laboratories that reported outlier results may try and replicate the samples presented in this round to check their recoveries are within expected APHA limits mentioned earlier. Sample PTA 1 consisted of: 90% mineral oil, 10% stearic acid – dispensing 44 mg of the Oil and Grease mix into a 500mL glass vessel, or double this into a 1L glass vessel. Sample PTA 2 consisted of: 30% Anhydrous milk fat, 60% Sunflower oil, 10% Stearic acid – dispensing 37 mg of the Oil and Grease mix into a 500mL glass vessel, or double this into a 1L glass vessel.

Additional suggestions for improving the quality of results can be found in US EPA Method 1664 (2010), which gives an excellent description of the Initial Demonstration of Laboratory Capability as well as ongoing Quality Control [3].

Measurement Uncertainty (MU)

The MUs reported by participants can be seen in Figures 3 and 4. Out of 29 participants, 18 (62%) and 19 (66%) submitted MU information for samples PTA 1 and PTA 2, respectively.

Some laboratories may have notably underestimated their MU, as they indicated that their MU was less than two times the uncertainty of the median (refer to Table 1), however, their results were further from the median than this value.

Conversely, laboratories which indicated a MU which was greater than three times the normalised IQR may have overestimated their MU.[1]

The majority of laboratories reporting MUs that successfully encompassed the median or doping concentration (Figures 3 and 4), indicated their MU was between 8.6% - 25.3% (8 mg/L – 23 mg/L).

If laboratory codes 163, 218, 222, 251, 323, 335, 421, 425, 529, 682, 740 and 742A find that their MU does not encompass the median or doping concentration for samples in successive rounds, they are recommended to reassess their measurement uncertainty using a passive empirical approach incorporating QC, RM and Proficiency results (Eurachem 2012) [4].

[1] MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [5]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

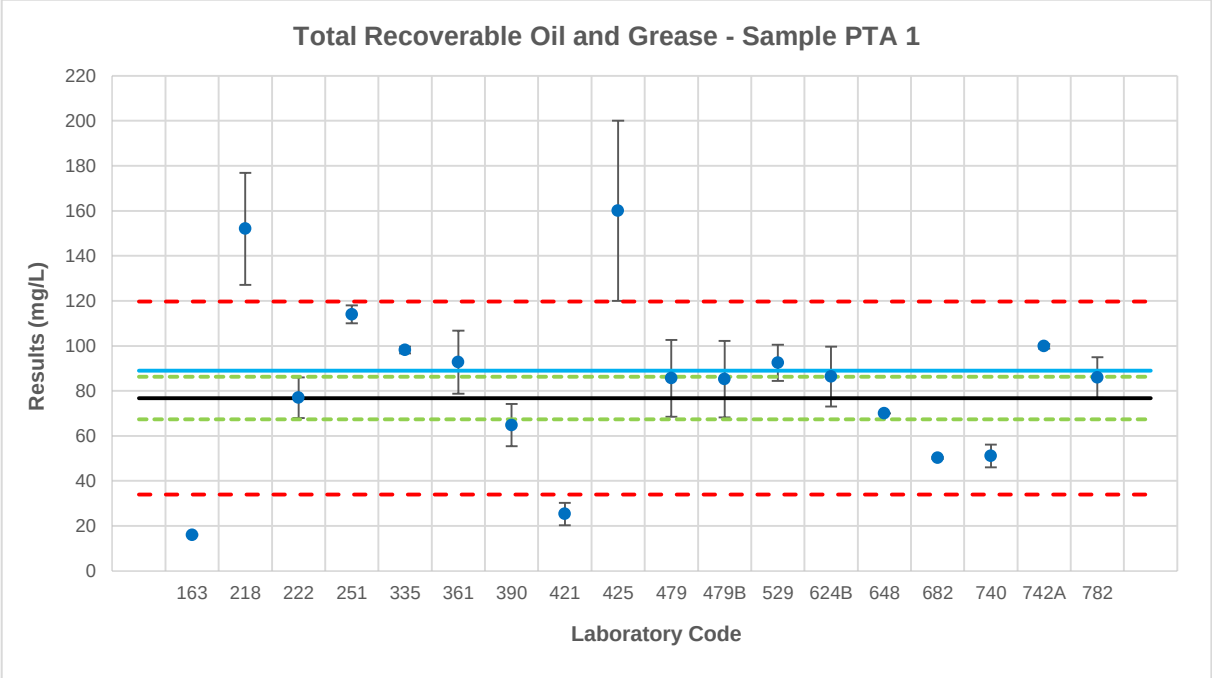


Figure 3. Laboratory MU for Total Recoverable Oil and Grease testing of sample PTA 1, including the median (——), uncertainty of the median (- - -), doping concentration (——), and 3xNIQR U_{max} (- - -).

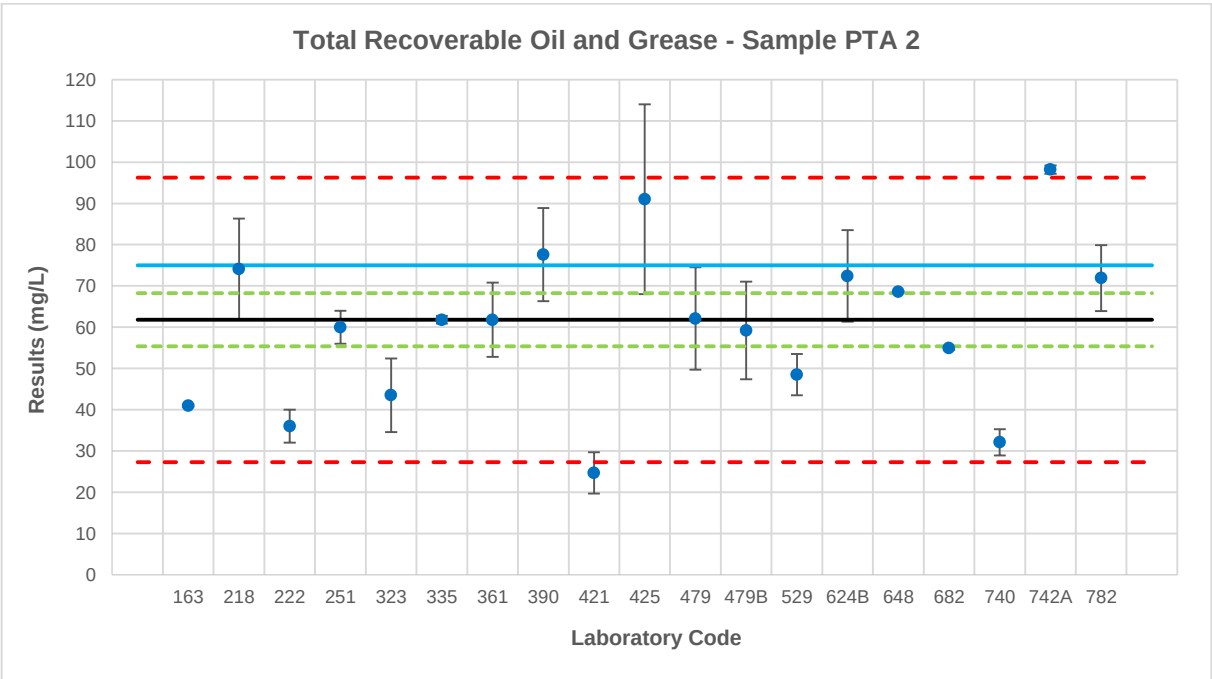


Figure 4. Laboratory MU for Total Recoverable Oil and Grease testing of sample PTA 2, including the median (——), uncertainty of the median (- - -), doping concentration (——), and 3xNIQR U_{max} (- - -).

4.4 Analysis of Results by Method Groups

Further analysis of results by method groups was undertaken to provide specific information on individual method performance.

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. Please note that, for methods other than the one presented below, there were less than 11 results submitted for each method and reliable conclusions cannot be drawn from analysing them on this occasion.

The method APHA 5520 B (Liquid-Liquid, Partition-Gravimetric Method - method code 1), was most frequently employed for both samples.

Table 3 below presents the median and uncertainty of the median for results obtained by method 1. Results for both samples were less variable than the overall dataset (CV_{PTA1}: 26.5%, CV_{PTA2}: 22.3%), but still much more variable than the published precision for this method (8.7%).

Table 3. Variability and proficiency medians obtained by method 1.

Sample	Method code	Participants	Median ± Uncertainty of the Median (mg/L)	Robust CV (%)
PTA 1	1	16	73.40 ± 4.84	21.1
PTA 2	1	16	70.25 ± 3.04	13.8

The median result for laboratories using APHA 5520 B (Liquid-Liquid, Partition-Gravimetric Method) in comparison to the doping concentrations from Table 1 (PTA 1: 89.04 mg/L and PTA 2: 74.66 mg/L) gave average recoveries of 82.4% and 94.1% respectively. These compared well to published precision data, which indicated that laboratories should be able to yield an average recovery of 84.2% on a mineral oil samples (APHA 5520 B, 20th Edition) using the Liquid-Liquid Partition Gravimetric method, or up to 93% recovery as was found in the interlaboratory method validation study (APHA 5520 B 23rd Edition and US EPA 1664 B) [2, 3].

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 4 below.

Table 4. Laboratory results identified as outliers for each sample tested.

Lab Code	Total Recoverable Oil and Grease	
	PTA 1	PTA 2
163	§	
218	§	
421	§	§
425	§	
471	§	

Note:
1. A "§" indicates the occurrence of a z-score outlier result (i.e. those results for which |z-score| ≥ 3.0).

6. References

[1] *Guide to Proficiency Testing Australia*, 2019 (This document can be found on the PTA website, www.pta.asn.au)

[2] *APHA Standard Methods for the Examination of Water and Wastewater,* 1998 - 20th Edition, 2012 - 22nd Edition, & 2017 - 23rd Edition.

[3] *US EPA Method 1664 Revision B: n-Hexane Extractable material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry,* February 2010. https://www.epa.gov/sites/production/files/2015-08/documents/method_1664b_2010.pdf

[4] EURACHEM / CITAC Guide CG 4 (2012). *Quantifying Uncertainty in Analytical Measurement; S. Ellison & A. Williams (Eds), Third Edition, Section 7.8, pg 20.* https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf

[5] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

APPENDIX A

Results and Data Analysis

Total Recoverable Oil and Grease Results

Samples PTA 1 and PTA 2

Total Recoverable Oil and Grease

Results by Laboratory Code

Laboratory Code	Sample PTA 1				
	Result ± mg/L	MU[1]	Robust z-score[2, 3, 4]		Method Code[5]
122	50.0	#	-1.88		1
154	89.4	#	0.88		1
163	16	0.28	-4.26	§	1
218	152	24.9	5.26	§	11
222	77	9	0.01		9
240	68.6	#	-0.57		1
251	114	4	2.60	†	5
252	68.6	#	-0.57		1
272	97	#	1.41		1
280	66.8	#	-0.70		1
291	66	#	-0.76		3
335	98.1	1.5	1.49		4
361	92.8	14	1.12		9
390	64.8	9.4	-0.84		1
421	25.3 ±	5.0	-3.61	§	1
425	160 ±	40	5.82	§	1
471	25.8	#	-3.57	§	4
479	85.6 ±	17.1	0.62		9
479B	85.2 ±	17.0	0.59		1
529	92.5 ±	8.0	1.10		7
624B	86.4 ±	13.3	0.67		1
648	70.0 ±	0.1	-0.48		1

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] Each z-score marked with a "§" is an outlier and indicates an absolute z-score value |z-score| ≥ 3.0. Please note that the robust CV values were considered inappropriate to calculate robust z-scores, therefore a target CV of 18.6% was used, based on data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median. Robust *z-scores* are calculated *as: z* = (*A* - *median*) ÷ *target SD*, where *A* is the participant laboratory's result.

[3] Laboratories are encouraged to review results which have been marked with a "‡". These results have a z-score ≥ 3.0 and, in this study, are considered questionable results

[4] In this study, results which have a z-score value between two and three (2.0 < z-score < 3.0) and have been marked with a "†" are considered satisfactory results. These results are deemed to be satisfactory, as they are closer to the doping concentration for this sample/test.

[5] Please refer to Appendix C (page C3) for method code descriptions.

[6] "na" indicates "not applicable".

[7] "#" indicates that no result was returned for this sample/test.

Total Recoverable Oil and Grease - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 1				
	Result ± mg/L		MU[1]	Robust z-score[2, 3, 4]	Method Code[5]
652	65.0		#	-0.83	9
682	50.2	±	0.4	-1.86	4, 10
731	74.8		#	-0.14	#
740	51.1	±	5.1	-1.80	4
742A	99.8	±	1	1.61	1
782	85.9	±	9	0.64	1
795	76.8		#	0.00	1

No of Results:	29
Median:	76.80
Normalised IQR:	20.39
Uncertainty of the Median:	4.74
Robust CV:	26.5%
Target SD:	14.28
Target CV:	18.6%
Minimum:	16
Maximum:	160
Range:	144

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] Each z-score marked with a "§" is an outlier and indicates an absolute z-score value |z-score| ≥ 3.0. Please note that the robust CV values were considered inappropriate to calculate robust z-scores, therefore a target CV of 18.6% was used, based on data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median. Robust *z-scores* are calculated *as: z* = (*A* - *median*) ÷ *target SD*, where *A* is the participant laboratory's result.

[3] Laboratories are encouraged to review results which have been marked with a "‡". These results have a z-score ≥ 3.0 and, in this study, are considered questionable results

[4] In this study, results which have a z-score value between two and three (2.0 < z-score < 3.0) and have been marked with a "†" are considered satisfactory results. These results are deemed to be satisfactory, as they are closer to the doping concentration for this sample/test.

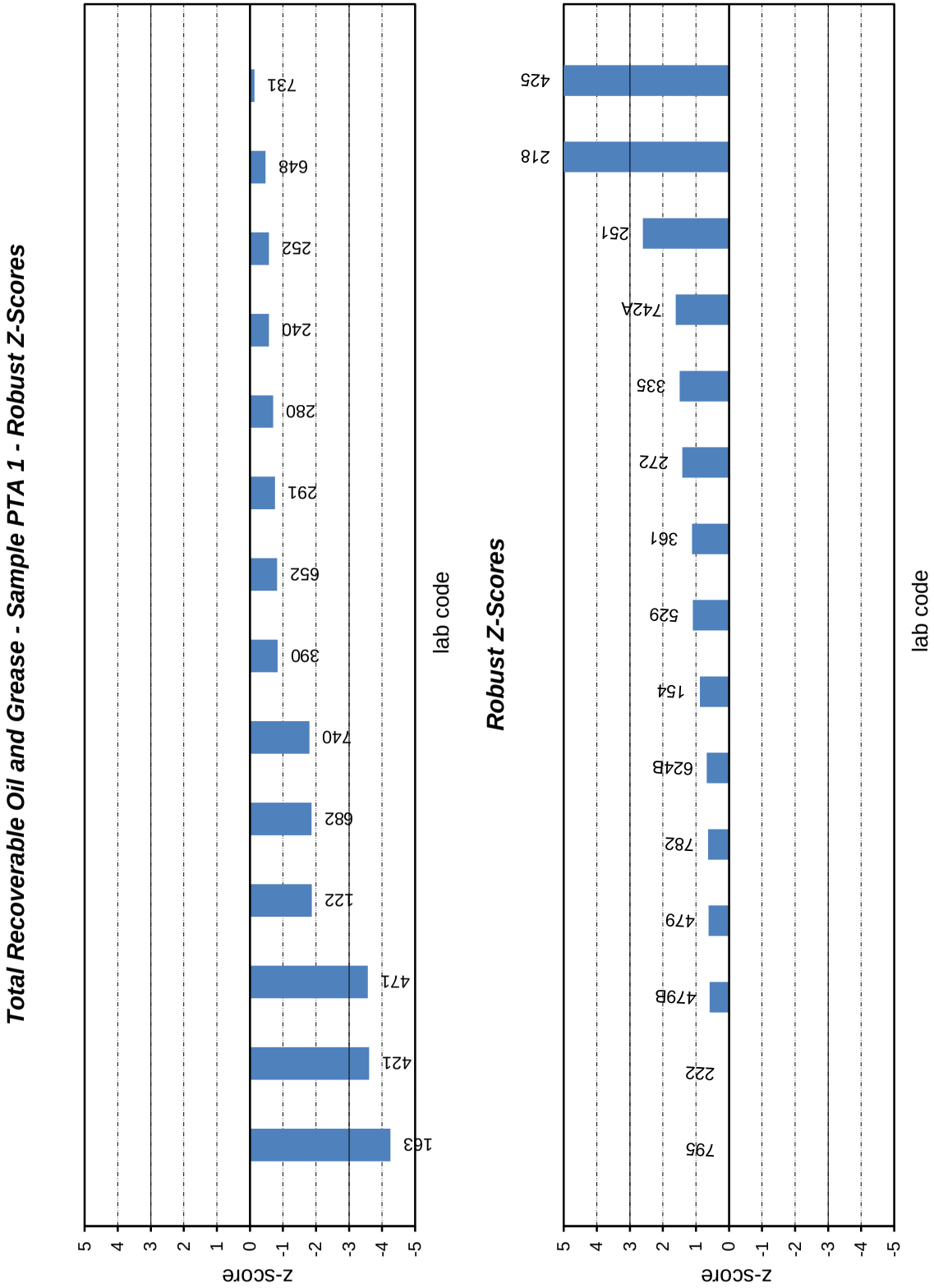
[5] Please refer to Appendix C (page C3) for method code descriptions.

[6] "na" indicates "not applicable".

[7] "#" indicates that no result was returned for this sample/test.

Total Recoverable Oil and Grease - Sample PTA 1

Ordered Robust Z-Score Charts



Total Recoverable Oil and Grease

Results by Laboratory Code

Laboratory Code	Sample PTA 2				
	Result ± mg/L		MU[1]	Robust z-score[2, 3, 4]	Method Code[5]
122	66.2		#	0.38	1
154	77.6		#	1.37	1
163	41		0.28	-1.81	1
218	74.1		12.2	1.07	11
222	36		4	-2.24	9
240	61.8		#	0.00	1
251	60		4	-0.16	5
252	63.8		#	0.17	1
272	76		#	1.24	1
280	72.4		#	0.92	1
291	42		#	-1.72	3
323	43.5		8.9	-1.59	5
335	61.8		0.9	0.00	4
361	61.8		9	0.00	9
390	77.6		11.3	1.37	1
421	24.7	±	5.0	-3.23 §	1
425	91	±	23	2.54 †	1
471	54.0		#	-0.68	4
479	62.1	±	12.4	0.03	9
479B	59.2	±	11.8	-0.23	1
529	48.5	±	5.0	-1.16	7
624B	72.4	±	11.1	0.92	1

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] Each z-score marked with a "§" is an outlier and indicates an absolute z-score value |z-score| ≥ 3.0. Please note that the robust CV values were considered inappropriate to calculate robust z-scores, therefore a target CV of 18.6% was used, based on data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median. Robust *z-scores* are calculated *as: z* = (*A* - *median*) ÷ *target SD*, where *A* is the participant laboratory's result.

[3] Laboratories are encouraged to review results which have been marked with a "‡". These results have a z-score ≥ 3.0 and, in this study, are considered questionable results

[4] In this study, results which have a z-score value between two and three (2.0 < z-score < 3.0) and have been marked with a "†" are considered satisfactory results. These results are deemed to be satisfactory, as they are closer to the doping concentration for this sample/test.

[5] Please refer to Appendix C (page C3) for method code descriptions.

[6] "na" indicates "not applicable".

[7] "#" indicates that no result was returned for this sample/test.

Total Recoverable Oil and Grease - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result ± mg/L		MU[1]	Robust z-score[2,3,4]		Method Code[5]
648	68.6	±	0.1	0.59		1
652	53.8		#	-0.70		9
682	54.9	±	0.4	-0.60		4, 10
740	32.1	±	3.2	-2.58		4
742A	98.2	±	1	3.17	‡	1
782	71.9	±	8	0.88		1
795	67.4		#	0.49		1

No of Results:	29
Median:	61.80
Normalised IQR:	13.79
Uncertainty of the Median:	3.21
Robust CV:	22.3%
Target SD:	11.49
Target CV:	18.6%
Minimum:	24.7
Maximum:	98.2
Range:	73.5

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] Each z-score marked with a "§" is an outlier and indicates an absolute z-score value |z-score| ≥ 3.0. Please note that the robust CV values were considered inappropriate to calculate robust z-scores, therefore a target CV of 18.6% was used, based on data from previous PTA rounds. The target standard deviation (target SD) is calculated as the target CV multiplied by the median. Robust *z-scores* are calculated *as: z* = (*A* - *median*) ÷ *target SD*, where *A* is the participant laboratory's result.

[3] Laboratories are encouraged to review results which have been marked with a "‡". These results have a z-score ≥ 3.0 and, in this study, are considered questionable results

[4] In this study, results which have a z-score value between two and three (2.0 < z-score < 3.0) and have been marked with a "†" are considered satisfactory results. These results are deemed to be satisfactory, as they are closer to the doping concentration for this sample/test.

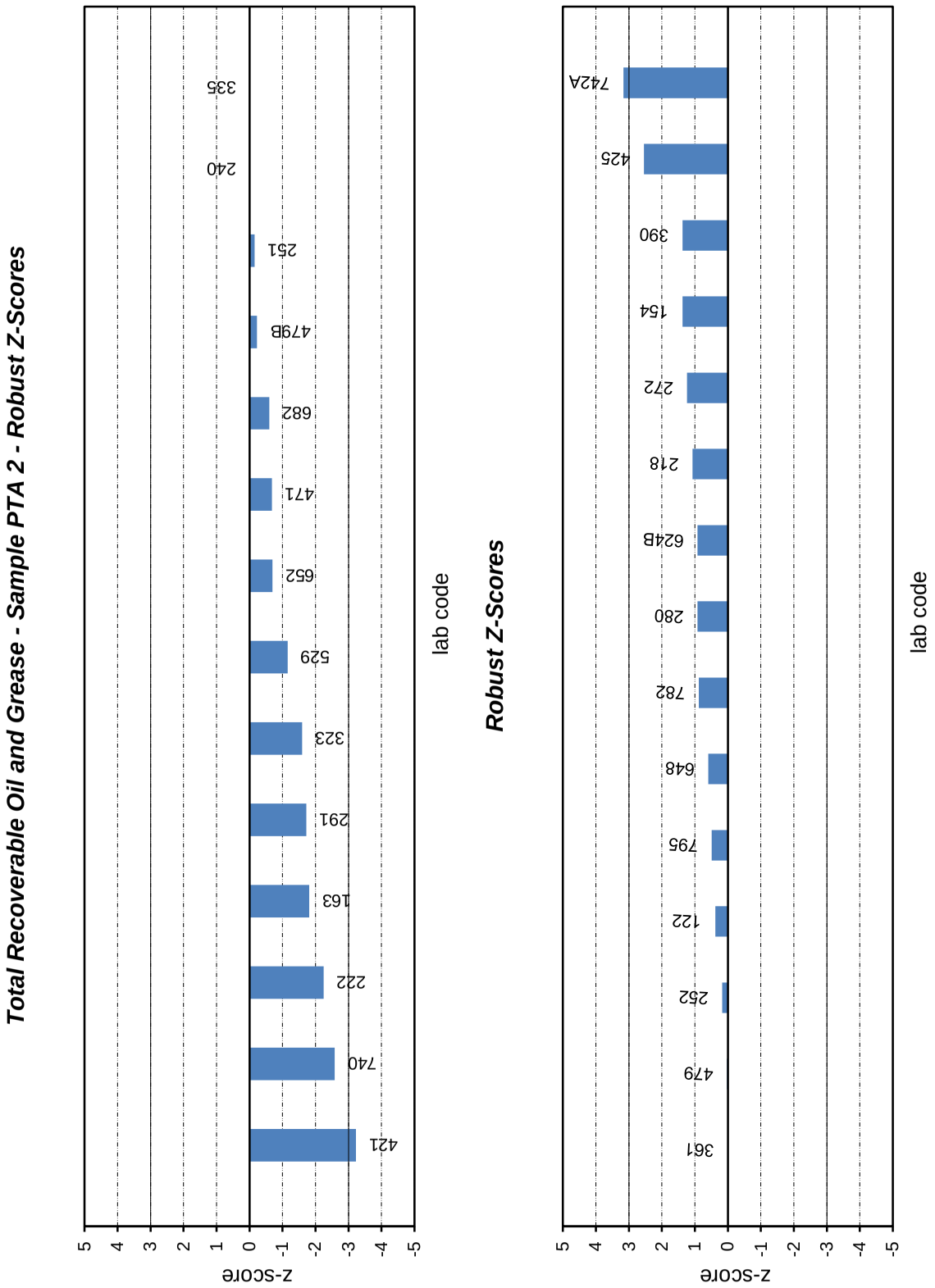
[5] Please refer to Appendix C (page C3) for method code descriptions.

[6] "na" indicates "not applicable".

[7] "#" indicates that no result was returned for this sample/test.

Total Recoverable Oil and Grease - Sample PTA 2

Ordered Robust Z-Score Charts



APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing

Samples for this program were obtained from Global Proficiency Ltd, New Zealand. As such, all samples were subjected to rigorous quality control and homogeneity / stability testing. Sample PTA 1 was doped with 44.52 ± 0.49 mg (95% CI) of mineral oil and stearic acid in a 500mL bottle, and sample PTA 2 was doped with 37.33 ± 0.49 mg (95% CI) of a mixture of vegetable oil, anhydrous milk fat and stearic acid. All samples were acidified to pH < 2 using HCl.

Samples were manufactured with QC weight checks on all samples. A random selection of ten samples was chosen from samples PTA 1 and PTA 2 for homogeneity and stability testing. Seven of these were stored chilled at 4°C and the remaining three were subjected to 35°C for three days, for an accelerated ageing stability trial. Samples were then analysed for Oil and Grease by Eurofins, New Zealand, using the Partition-Gravimetric method APHA 5520 B (modified) Online Edition.

All stability samples showed no notable differences when compared to homogeneity samples. These data combined with the recommendations in APHA 1060 C that samples should have a pH < 2 and temperature < 6°C to give a recommended maximum storage of 28 days.

From statistical analyses based on the results of this testing and rigorous quality control, it was considered that all samples were sufficiently homogeneous and stable, so that any results later identified as outliers should not be attributed to any notable sample variability.

The results of homogeneity and stability testing, and QC checks, are presented in Table B1 below. Please note that the mean results for these tests are not intended to be used as reference values.

Table B1. Homogeneity and stability testing of PTA 1 and PTA 2 samples.

Round PTA 262		**Total Recoverable Oil and Grease (g/m^3)**			
	Sample ID	Sample PTA 1		Sample PTA 2	
		Test Result	Quality Control	Test Result	Quality Control
Homogeneity	H1	90	88.4	75	75.4
	H2	99	89.6	72	74.8
	H3	95	88.8	73	75.0
	H4	98	89.4	78	74.0
	H5	87	88.6	77	74.4
	H6	82	88.8	75	75.2
	H7	85	89.4	73	74.0
Stability	S1	82	89.8	79	75.4
	S2	84	89.4	72	74.6
	S3	78	88.8	71	74.6
Median		86	89.1	74	74.7
RSD		8.2%	0.5%	3.7%	0.7%
Recovery		97%		99%	

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 262 **JUNE, 2020**

Total Recoverable Oil and Grease

INSTRUCTIONS TO PARTICIPANTS

*****Please record (on the Results Sheet) the approximate temperature of the samples upon receipt*****

Please note the following before commencing the analysis of the samples.

1. Samples

i) Two 500 mL glass bottles, labelled PTA 1 and PTA 2, supplied by Global Proficiency Ltd. The bottles contain oil and grease (in water) in the range of 10-50 milligrams (mg). These have been acid preserved and should be refrigerated until ready to test.

ii) The sample must be thoroughly mixed prior to analysis. Please take extra care as the sample may be strongly adhered to the glass neck and shoulder of the bottle.

Please Note: Where possible, proficiency testing samples should be treated as a routine laboratory sample.

2. Sample Preparation

Caution: Analysis must begin immediately after bottle is opened.

i) Adjust bottle temperature to 20º C.

ii) Record bottle ID number.

iii) Shake the bottle prior to opening.

iv) Each bottle is ready to test according to your normal procedures.

Note: Please treat as “unknown oil”.

3. Tests Requested

i) Total Recoverable Oil and Grease.

If unable to perform the above please note this on your Results Sheet.

4. Safety

i) Samples are for laboratory use only.

ii) Participants should have sufficient experience and training to take the necessary precautions when handling the samples and reagent chemicals and during disposal.

iii) Use of safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

i) Report results using one decimal place.

ii) Report results in milligrams per litre (mg/L).

iii) Do not correct results for recovery.

iv) Select the appropriate method code from the Method Code Table and record it on the Results Sheet.

v) Calculate the measurement uncertainty (MU) for each reported result. All estimates of MU must be given as a 95% confidence interval (coverage factor k ≈ 2) and reported in mg/L. Report MU using the same number of decimal places as for the result.

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 3 JULY 2020** 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

7. For this program your laboratory has been allocated the code number shown on the attached Results Sheet. All reference to your laboratory in reports associated with the program will be through this code number, thus ensuring the confidentiality of your results.

8. As a guide, ranges for the samples can be expected to be (in mg/L):

Analyte	Range
Total Recoverable Oil and Grease	20 – 100 mg/L

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD	METHOD DESCRIPTION	CODE
Total Recoverable Oil and Grease	Partition-Gravimetric	APHA 5520 B. Liquid-Liquid, Partition-Gravimetric Method	1
		APHA 5520 G. Solid-Phase, Partition-Gravimetric Method	2
	Hexane Extraction & Gravimetry	US EPA 1664A Oil & Grease (HEM/SGT-HEM) by extraction	3
	Infrared	APHA 5520 C. Partition-Infrared Method	4
		ASTM D 7066-04 Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination	5
		ASTM D 3921-96 Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water	6
		US EPA 413.2 Oil & Grease, Total Recoverable - Spectrophotometric, Infrared)	7
		US EPA 418.1 Petroleum Hydrocarbons, Total Recoverable	8
	Soxhlet Extraction	APHA 5520 D. Soxhlet Extraction Method	9
	HORIBA	OCMA-500	10
	Other	Please specify	11

Method Reference Key

i) APHA APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19, 20, 21, 22, 23 Edition) (http://www.standardmethods.org/).

ii) ASTM American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 11.01 and Vol. 11.02.

iii) US EPA U.S Environmental Protection Agency. (http://www.epa.gov/osa).

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 262

Total Recoverable Oil and Grease

JUNE, 2020

RESULTS SHEET
(mg/L)

Laboratory Code	

*Approximate temperature of samples upon receipt:	

ANALYSIS	**SAMPLE PTA 1**		**SAMPLE PTA 2**		**METHOD CODE**
	Result (mg/L)	**±MU (mg/L)**	**Result (mg/L)**	**±MU (mg/L)**	
Total Recoverable Oil and Grease					

Please note: Where possible, proficiency testing samples should be treated as a routine laboratory sample.

i) For each sample only a single result is requested.

ii) Report results using one decimal place.

iii) Report results in milligrams per litre (mg/L).

iv) Do not correct results for recovery.

v) MU* Laboratories Measurement Uncertainty (MU) if known for the result.
Please report in mg/L and use a coverage factor of k=2.

DATE: _____ **SIGNATURE:** _____

Return results **NO LATER THAN 3 JULY 2020** 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

- End of Report -