Results of Proficiency Test Total Per- & Polyfluoroalkyl Substances (PFAS) in Textile March 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis21T02

May 2021

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1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluoroalkyl substances (PFAS). The hazard profile of PFOA is well-known: PFOA is a persistent, bio accumulative and toxic substance, which may cause severe and irreversible adverse effects on the environment and human health. PFOA was the first PFAS to be identified as substance of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in 2014. Besides PFOA also other fluorinated substances have properties of concern. Perfluorooctanesulfonic Acid (PFOS) is listed as persistent organic pollutant (POP) in Annex B of the Stockholm Convention, implemented now by Regulation (EU) 2019/1021. In July 2020 regulation EU 2020/784 was implemented for PFOA and its related compounds.
In addition to mandatory environmental standards and requirements for textiles, some Eco-labelling schemes are imposing environmental requirements for textile products on a voluntary basis, e.g. Bluesign© system substances list (BSSL) (Switzerland) and OEKO-TEX© Standard 100 (Switzerland). The results of this interlaboratory study are compared to the OEKO-TEX® requirements and Bluesign® regulations on Textiles in paragraph 5.

Since 2017 the Institute for Interlaboratory Studies organizes a proficiency scheme for the analysis of Total Per- & Polyfluoroalkyl Substances (PFAS) in Textile every year. During the annual proficiency testing program 2020/2021 it was decided to continue the proficiency test for the analysis of Total Per- & Polyfluoroalkyl Substances (PFAS) in textile.

In this interlaboratory study 51 laboratories in 21 different countries registered for participation. See appendix 4 for the number of participants per country. In this report the results of the Total Per- & Polyfluoroalkyl Substances (PFAS) in textile proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send 2 different textile samples positive on PFAS of approximately 5 grams each and labelled #21530 and #21531 respectively. The participants were requested to report rounded and unrounded test results and some details of the test methods used. The unrounded test results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

For the first sample a batch of green cotton was selected which was made positive on PFOA and PFDA by a third-party. This batch was cut into small pieces. After homogenization the batch was divided over 100 subsamples in small bags of approximately 5 grams each and labelled #21530.
The homogeneity of the subsamples was checked by determination of Total PFOA and Total PFDA using an in-house test method on eight stratified randomly selected subsamples.

	Total PFOA in mg/kg	Total PFDA in mg/kg
Sample #21530-1	7.37	7.31
Sample #21530-2	6.97	7.13
Sample #21530-3	7.17	7.33
Sample #21530-4	7.14	7.46
Sample #21530-5	7.27	7.50
Sample #21530-6	7.25	7.26
Sample #21530-7	6.95	7.07
Sample #21530-8	7.17	7.50

Table 1: homogeneity test results of subsamples #21530

From the above test results the repeatabilities were calculated and compared with 0.3 times the estimated reproducibilities calculated with the Horwitz equation in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Total PFOA in mg/kg	Total PFDA in mg/kg
r (observed)	0.40	0.46
reference method	Horwitz (n=2)	Horwitz (n=2)
0.3 x R (reference method)	1.01	1.03

Table 2: evaluation of the repeatabilities of subsamples #21530

The calculated repeatabilities are in agreement with 0.3 times the estimated reproducibilities calculated with the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of pink cotton was selected which was made positive on PFOS. This batch was cut into small pieces. After homogenization the batch was divided over 100 subsamples in small bags of approximately 5 grams each and labelled #21531. The homogeneity of the subsamples was checked by determination of Total PFOS using an in-house test method on nine stratified randomly selected subsamples.

	Total PFOS in mg/kg
Sample #21531-1	7.47
Sample #21531-2	7.77
Sample #21531-3	7.63
Sample #21531-4	7.79
Sample #21531-5	7.97
Sample #21531-6	7.56
Sample #21531-7	7.83
Sample #21531-8	7.67
Sample #21531-9	7.54

Table 3: homogeneity test results of subsamples #21531

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility calculated with the Horwitz equation in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Total PFOS in mg/kg
r (observed)	0.45
reference method	Horwitz (n=3)
0.3 x R (reference method)	1.32

Table 4: evaluation of the repeatability of subsamples #21531

The calculated repeatability is in agreement with 0.3 times the estimated reproducibility calculated with the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one textile sample labelled #21530 and one textile sample labelled #21531 were sent on February 10, 2021.

2.5 ANALYZES

The participants were requested to determine on samples #21530 and #21531 the concentrations of Perfluorooctanoic acid (Total PFOA), Perfluorooctanesulfonic acid (Total PFOS), Perfluorononanoic acid (Total PFNA), Perfluorodecanoic acid (Total PFDA), Perfluorobutanesulfonic acid (Total PFBS), Perfluorooctadecanoic acid (Total PFODA), Perfluorododecanoic acid (Total PFDoA) and Other Per- and Polyfluorinated compounds. It was requested to report if the laboratory was accredited for the requested components that were determined and to report some analytical details. It was noted in the instructions of this PT to use no less than 0.5 grams per determination to ensure the homogeneity.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results, but report as much significant figures as possible. It was also requested not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 and 2 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.
According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

3.3 z-scores

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ISO reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.
The z-scores were calculated according to:

$z_{(target)}$ = (test result - average of PT) / target standard deviation

The $z_{(target)}$ scores are listed in the test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

	|z|	< 1	good
1 <	|z|	< 2	satisfactory
2 <	|z|	< 3	questionable
3 <	|z|		unsatisfactory

4 Evaluation

In this proficiency test some problems were encountered with the dispatch of the samples. Three participants reported test results after the final reporting date and three other participants did not report any test results. Not all participants were able to report all tests requested.
In total 48 participants reported 131 numerical test results. Observed were 2 outlying test results, which is 1.5%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Not all data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the reported test results are discussed per sample and per component. The test methods which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable.
These test methods are also in the tables together with the original data. The abbreviations, used in these tables, are explained in appendix 5.

For the determination of Per- and Polyfluorinated compounds in textile, the CEN-TS 15968 method may be considered to be the official EC test method. Regretfully, the CEN-TS 15968 method does not mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation based on two or three components (see paragraph 5).

Please note that by the term “Total” is meant the sum of linear and branched isomers (see paragraph 5).

Sample #21530

Total PFOA: This determination was not problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the estimated reproducibility calculated with the Horwitz equation for 2 components.

Total PFDA: This determination was not problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in full agreement with the estimated reproducibility calculated with the Horwitz equation for 2 components.

For other Per- and Polyfluorinated compounds, the majority of the participants agreed on a concentration near or below the limit of detection. Therefore, no z-scores were calculated for these compounds. The reported test results are given in appendix 2.

Sample #21531

Total PFOS: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in full agreement with the estimated reproducibility calculated with the Horwitz equation for 3 components.

For other Per- and Polyfluorinated compounds, the majority of the participants agreed on a concentration near or below the limit of detection. Therefore, no z-scores were calculated for these compounds. The reported test results are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the estimated target reproducibility calculated with the Horwitz equation and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility estimated using the Horwitz equation are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(target)
Total PFOA	mg/kg	46	5.74	2.02	2.80
Total PFDA	mg/kg	35	5.37	2.80	2.64

Table 5: reproducibilities of components on sample #21530

Component	unit	n	average	2.8 * sd	R(target)
Total PFOS	mg/kg	48	7.78	4.76	4.43

Table 6: reproducibilities of components on sample #21531

Without further statistical calculations, it can be concluded that for all tests there is a good compliance of the group of participants with the reference method.

4.3 COMPARISON OF PROFICIENCY TEST OF MARCH 2021 WITH PREVIOUS PTS

	March 2021	March 2020	March 2019	March 2018	March 2017
Number of reporting laboratories	48	62	54	49	72
Number of test results	131	123	189	132	263
Number of statistical outliers	2	7	5	8	17
Percentage of statistical outliers	1.5%	5.7%	2.6%	6.1%	6.5%

Table 7: comparison with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency tests was compared, expressed as relative standard deviation (RSD) of the PTs, in the next table.

Component	March 2021	March 2020	March 2019	March 2018	March 2017	Target
Total PFOA	13%	23%	22% - 24%	18%	18% - 31%	25% - 16%
Total PFOS	22%	18%	25% - 33%	11%	15% - 27%	31% - 20%
Total PFDA	19%	n.e.	19%	n.e.	n.e.	31% - 20%

Table 8: development of uncertainties (RSD) over the years

The uncertainty of Total PFOA in this PT has improved while the uncertainty of Total PFOS or PFDA is in line when compared to the uncertainties with previous PTS.

The target value for the precision of the Total PFOA, PFOS or Total PFDA determination in textile is based on the Horwitz equation for 2 or 3 components.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The participants were asked to provide some analytical details which are listed in appendix 3. Based on the reported answers the following can be summarized:

- 81% mentioned that they are ISO/IEC17025 accredited to determine the reported components.
- 57% further cut the samples prior to analysis while 43% used the samples as received. See page 17 for further analysis on the determination of PFOS. Cutting the sample has a positive effect on the observed reproducibility in this PT.
- 94% used between 0.5 - 1 grams of sample intake of which 52% around 0.5 grams and 42% around 1 gram. No profound effect has been observed.
- 94% used Ultrasonic technique to extract/release the components from the samples.
- 96% used Methanol as extraction solvent and some others used a mixture of Methanol/ACN or Methanol/Toluene.
- 81% used an extraction/release temperature of 60°C, 13% used a lower temperature and 6% used a higher temperature to extract/release.
- 83% used an extraction/release time of 120 minutes, 15% used 60 minutes or less.

About 75% of the reporting participants mentioned to use test method CEN/TS15968 for the determination of the Per- and Polyfluorinated compounds. About 15% of the participants reported to have used in house method and 10% of the reporting participants used a different test method.
Test method CEN/TS15968 mentions to use at least 2 grams of sample intake. However, a vast majority of the participants reported to use a sample intake between 0.5 - 1 grams.

5 DISCUSSION

In legislation and in the limits set for PFOA, PFDA and PFOS it is clear that **Total** amounts for these compounds are meant. However, in the available test methods this is less clear. Test method CEN/TS15968 mentions the existence of linear and branched isomers and the possibility to separate these isomers. It is also mentioned that branched isomers should be based on the response factor of the linear isomer. But method CEN/TS15968 is not clear whether the sum of linear and branched isomers should be reported.

For most laboratories, it is not clear whether the sum or the linear isomer is determined. Therefore, it was decided not to ask for linear and branched isomers in this proficiency test but only the sum of linear and branched isomers. Therefore, the term “Total” was used.

In the 2017 PT on PFOA/PFOS in textile (iis17A05) it became clear that both components have branched and linear isomers. And in the 2017 PT more data were collected over the amount of linear, branched and total PFOA/PFOS. Next to this data also the chromatograms were collected from the participating laboratories in 2017. Based on the chromatograms the Horwitz equation was calculated based on 2 components for PFOA (in general two peaks were visible in the chromatograms) and on 3 components for PFOS (in general three peaks were visible). It was decided to use n=2 in the Horwitz equation to estimate the target reproducibility for all PFAS other than PFOS.

When the results of this interlaboratory study were compared to the OEKO-TEX® requirements and Bluesign® regulations on Textiles (table 9), it is noticed that all of the reporting laboratories would reject sample #21530 and #21531 for containing too much Total PFOA, Total PFDA or Total PFOS. Only one laboratory would accept sample #21530 for Total PFDA.

	OEKO-TEX®	Bluesign® BSSL v11.0
Total PFOA	<1.0 µg/m^2	<1.0 µg/m^2 (corresponds with <0.01 mg/kg)
Total PFDA	<0.05, <0.1, <0.5 mg/kg (different categories)	<0.05 mg/kg
Total PFOS	<1.0 µg/m^2	<1.0 µg/m^2 (corresponds with <0.01 mg/kg)

Table 9: Ecolabelling Standards for Textiles in EU

Sample #21530 was also used in a previous proficiency test iis19A02 as sample #19513. The obtained PT results are in line with the previous PT, see the next table.

Component	unit	Sample #21530			Sample #19513		
		n	average	2.8 * sd	n	average	2.8 * sd
PFOA	mg/kg	46	5.74	2.02	51	5.86	3.59
PFDA	mg/kg	35	5.37	2.80	39	5.43	2.90

Table 10: comparison sample #21530 vs #19513

6 CONCLUSION

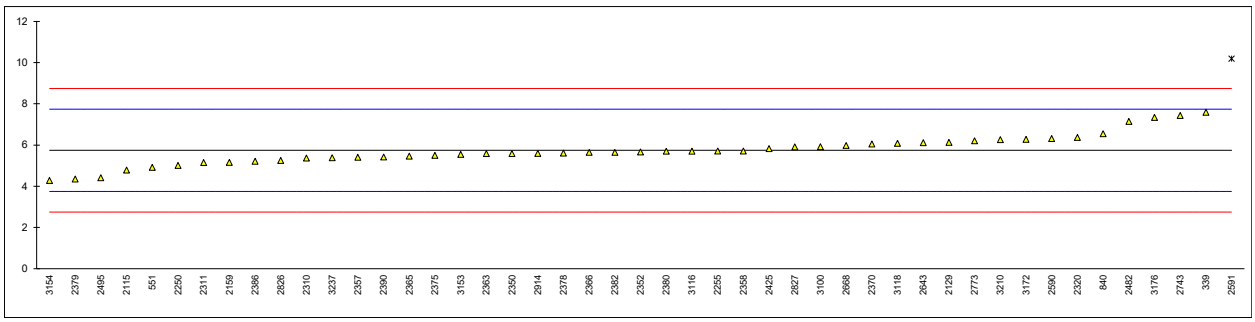
Although it can be concluded that the majority of the participants has no problem with the determination of Total Per- & Polyfluoroalkyl Substances (PFAS) in the textile samples of this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of Total PFOA on sample #21530; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	7.59		1.85	
551	ISO23702-1	4.919		-0.83	
840	CEN-TS15968	6.55		0.81	
2115	CEN-TS15968	4.78		-0.96	
2129	CEN-TS15968	6.128		0.38	
2159	CEN-TS15968	5.16		-0.58	
2250	CEN-TS15968	5.01		-0.73	
2255	CEN-TS15968	5.71		-0.03	
2293		-----		-----	
2310	CEN-TS15968	5.37		-0.37	
2311	CEN-TS15968	5.15		-0.59	
2320	CEN-TS15968	6.3654		0.62	
2350	CEN-TS15968	5.584		-0.16	
2352	CEN-TS15968	5.66		-0.08	
2357	CEN-TS15968	5.401		-0.34	
2358	CEN-TS15968	5.71		-0.03	
2363	CEN-TS15968	5.58		-0.16	
2365	CEN-TS15968	5.461		-0.28	
2366	CEN-TS15968	5.64		-0.10	
2370	CEN-TS15968	6.05		0.31	
2375	CEN-TS15968	5.5		-0.24	
2378	CEN-TS15968	5.61		-0.13	
2379	CEN-TS15968	4.345		-1.40	
2380	CEN-TS15968	5.7		-0.04	
2382	CEN-TS15968	5.64		-0.10	
2386	CEN-TS15968	5.2146750		-0.53	
2390	CEN-TS15968	5.42		-0.32	
2425	In house	5.83		0.09	
2482	CEN-TS15968	7.14		1.40	
2495	CEN-TS15968	4.415		-1.33	
2561		-----		-----	
2590	CEN-TS15968	6.312		0.57	
2591	In house	10.190	R(0.01)	4.45	
2643	KS M9722	6.11		0.37	
2668	CEN-TS15968	5.98		0.24	
2743	CEN-TS15968	7.428		1.69	
2773	CEN-TS15968	6.21		0.47	
2826	DIN38414-14Mod.	5.253		-0.49	
2827	CEN-TS15968	5.91		0.17	
2886		-----		-----	
2914	In house	5.596		-0.15	
3100	GB/T31126	5.913		0.17	
3116	CEN-TS15968	5.703		-0.04	
3118	In house	6.08		0.34	
3153	CEN-TS15968	5.55		-0.19	
3154	ISO/WD24640draft	4.277531		-1.47	
3172	CEN-TS15968	6.2738		0.53	
3176	In house	7.34		1.60	
3210	In house	6.263		0.52	
3222		-----		-----	
3237	CEN-TS15968	5.38		-0.36	
	normality	OK			
	n	46			
	outliers	1			
	mean (n)	5.7437			
	st.dev. (n)	0.72279	RSD=13%		
	R(calc.)	2.0238			
	st.dev.(Horwitz 2 comp)	0.99899			
	R(Horwitz 2 comp)	2.7972			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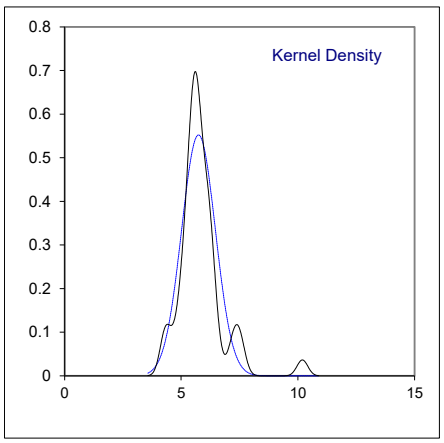
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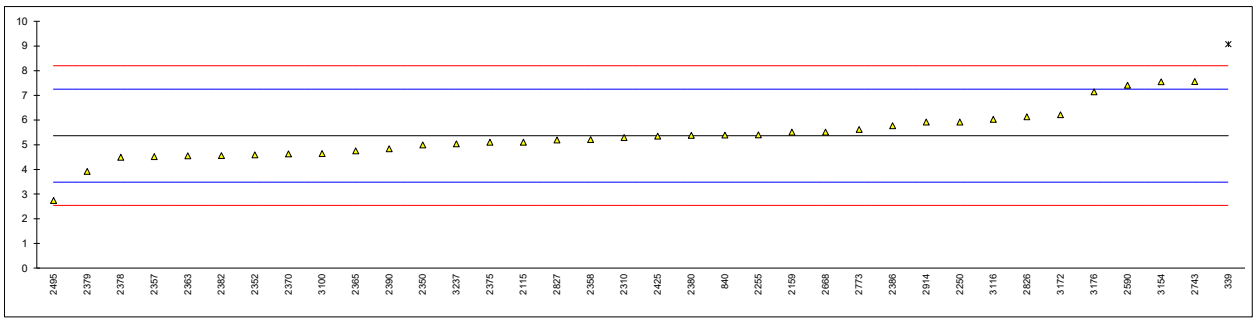
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15

Determination of Total PFDA on sample #21530; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	9.071	R(0.05)	3.92	
551		-----		-----	
840	CEN-TS15968	5.39		0.02	
2115	CEN-TS15968	5.10		-0.29	
2129	CEN-TS15968	<0,01	f-?	<-5.68	possibly a false negative test result?
2159	CEN-TS15968	5.51		0.15	
2250	CEN-TS15968	5.92		0.58	
2255	CEN-TS15968	5.40		0.03	
2293		-----		-----	
2310	CEN-TS15968	5.29		-0.08	
2311		-----		-----	
2320		-----		-----	
2350	CEN-TS15968	4.990		-0.40	
2352	CEN-TS15968	4.59		-0.83	
2357	CEN-TS15968	4.521		-0.90	
2358	CEN-TS15968	5.21		-0.17	
2363	CEN-TS15968	4.55		-0.87	
2365	CEN-TS15968	4.753		-0.65	
2366		out capability		-----	
2370	CEN-TS15968	4.63		-0.78	
2375	CEN-TS15968	5.1		-0.29	
2378	CEN-TS15968	4.49		-0.93	
2379	CEN-TS15968	3.918		-1.54	
2380	CEN-TS15968	5.38		0.01	
2382	CEN-TS15968	4.56		-0.86	
2386	CEN-TS15968	5.7719		0.43	
2390	CEN-TS15968	4.83		-0.57	
2425	In house	5.35		-0.02	
2482		-----		-----	
2495	CEN-TS15968	2.740		-2.79	
2561		-----		-----	
2590	CEN-TS15968	7.407		2.16	
2591		-----		-----	
2643		-----		-----	
2668	CEN-TS15968	5.51		0.15	
2743	CEN-TS15968	7.564		2.33	
2773	CEN-TS15968	5.62		0.27	
2826	DIN38414-14Mod.	6.133		0.81	
2827	CEN-TS15968	5.19		-0.19	
2886		-----		-----	
2914	In house	5.919		0.58	
3100	GB/T31126	4.641		-0.77	
3116	CEN-TS15968	6.028		0.70	
3118		-----		-----	
3153		-----		-----	
3154	ISO/WD24640draft	7.550330		2.31	
3172	CEN-TS15968	6.2122		0.89	
3176	In house	7.14		1.88	
3210		-----		-----	
3222		-----		-----	
3237	CEN-TS15968	5.04		-0.35	
	normality	suspect			
	n	35			
	outliers	1			
	mean (n)	5.3700			
	st.dev. (n)	1.00169	RSD=19%		
	R(calc.)	2.8047			
	st.dev.(Horwitz 2 comp)	0.94348			
	R(Horwitz 2 comp)	2.6418			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3100
2365
2390
2360
3237
2375
2115
2827
2358
2310
2425
2380
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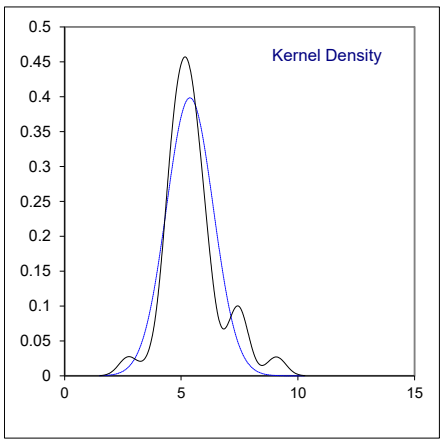
3116
2826
3172
3176
2590
3154
2743
339

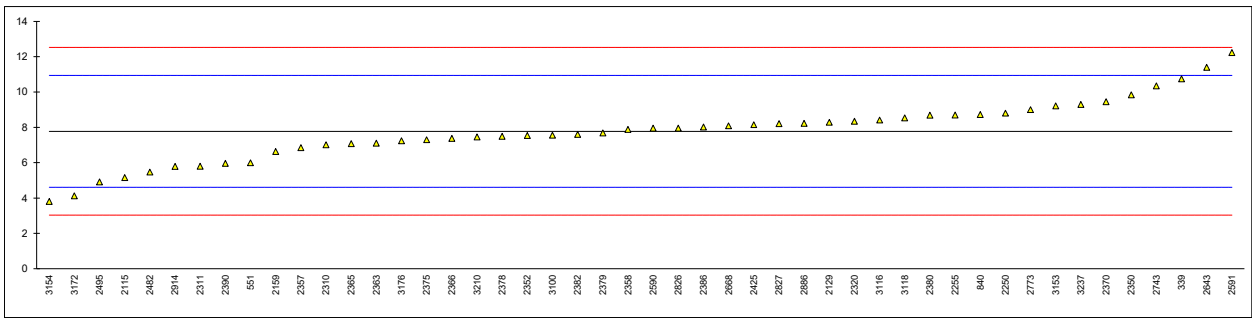

Kernel Density
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15

Determination of Total PFOS on sample #21531; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	10.748		1.88	
551	ISO23702-1	5.992		-1.13	
840	CEN-TS15968	8.72		0.59	
2115	CEN-TS15968	5.16		-1.65	
2129	CEN-TS15968	8.2875		0.32	
2159	CEN-TS15968	6.63		-0.73	
2250	CEN-TS15968	8.8		0.64	
2255	CEN-TS15968	8.70		0.58	
2293		-----		-----	
2310	CEN-TS15968	7.01		-0.49	
2311	CEN-TS15968	5.799		-1.25	
2320	CEN-TS15968	8.3429		0.36	
2350	CEN-TS15968	9.838		1.30	
2352	CEN-TS15968	7.54		-0.15	
2357	CEN-TS15968	6.850		-0.59	
2358	CEN-TS15968	7.88		0.06	
2363	CEN-TS15968	7.1		-0.43	
2365	CEN-TS15968	7.074		-0.45	
2366	CEN-TS15968	7.38		-0.25	
2370	CEN-TS15968	9.45		1.06	
2375	CEN-TS15968	7.3		-0.30	
2378	CEN-TS15968	7.49		-0.18	
2379	CEN-TS15968	7.683		-0.06	
2380	CEN-TS15968	8.69		0.58	
2382	CEN-TS15968	7.60		-0.11	
2386	CEN-TS15968	8.0173166670		0.15	
2390	CEN-TS15968	5.96		-1.15	
2425	In house	8.15		0.23	
2482	CEN-TS15968	5.47		-1.46	
2495	CEN-TS15968	4.910		-1.81	
2561		-----		-----	
2590	CEN-TS15968	7.948		0.11	
2591	In house	12.230		2.81	
2643	KS M9722	11.40		2.29	
2668	CEN-TS15968	8.09		0.20	
2743	CEN-TS15968	10.348		1.62	
2773	CEN-TS15968	9.0		0.77	
2826	DIN38414-14Mod.	7.954		0.11	
2827	CEN-TS15968	8.21		0.27	
2886	In house	8.2265		0.28	
2914	In house	5.791		-1.26	
3100	GB/T31126	7.552		-0.14	
3116	CEN-TS15968	8.415		0.40	
3118	In house	8.53		0.47	
3153	CEN-TS15968	9.22		0.91	
3154	ISO/WD24640draft	3.802420		-2.51	
3172	CEN-TS15968	4.1268		-2.31	
3176	In house	7.24		-0.34	
3210	In house	7.455		-0.20	
3222		-----		-----	
3237	CEN-TS15968	9.3		0.96	

				sample used as received		sample further cut	
	normality	OK		OK		OK	
	n	48		20		26	
	outliers	0		0		0	
	mean (n)	7.7794		7.1572		8.3122	
	st.dev. (n)	1.70010	RSD=22%	2.03245	RSD=28%	1.28285	RSD=15%
	R(calc.)	4.7603		5.6909		3.5920	
	st.dev.(Horwitz 3 comp)	1.58316		1.47493		1.67481	
	R(Horwitz 3 comp)	4.4329		4.1298		4.6895	

For this component the effect of sample pre-preparation was further investigated. It seems that further cutting the sample prior to analysis helps to yield a higher level of Total PFOS with less variation between results.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6
4
2
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3154
3172
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2115
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2914
2311
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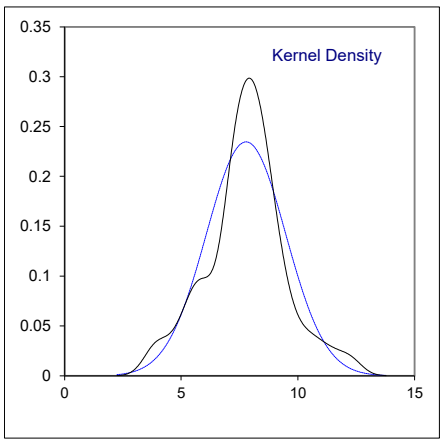
2310
2365
2363
3176
2375
2366
3210
2378
2352
3100
2382
2379
2358
2590
2626
2386
2668
2425
2627
2886
2129
2320
3116
3118
2380
2255
840
2250
2773
3153
3237
2370
2350
2743
339
2643
2591


Kernel Density
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15

APPENDIX 2: Other reported test results

Determination of Total PFOS, Total PFNA, Total PFBS, Total PFODA, Total PFDoA and Other Per- and Polyfluorinated compounds on sample #21530; in mg/kg

lab	Total PFOS	Total PFNA	Total PFBS	Total PFODA	Total PFDoA	Other Per- and Polyfluorinated compounds
339	0.145	<0.1	<0.1	-----	-----	-----
551	0.085	-----	-----	-----	-----	-----
840	not detected	not detected	not detected	not detected	not detected	not detected
2115	0.052	-----	-----	-----	-----	PFHpA 0.125, PFHxA 0.012
2129	0.09	<0,01	<0,01	not analyzed	<0,01	0.2655
2159	<0,01	<0,01	<0,01	Not applicable	<0,01	Not applicable
2250	0.0848	-----	-----	-----	-----	PFHpA 0.0516
2255	n.d	n.d	n.d	n.d	n.d	n.d
2293	-----	-----	-----	-----	-----	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	-----
2311	<0.1	-----	-----	-----	-----	-----
2320	0.09077	-----	-----	-----	-----	-----
2350	<1.00	<1.00	<1.00	N/A	<1.00	N/A
2352	0.07	-----	-----	-----	-----	-----
2357	0.0740	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
2365	0.051	<0.010	<0.010	<0.010	<0.010	<0.010
2366	<1	out capability	out capability	out capability	out capability	out capability
2370	0.119	<0.01	<0.01	Out Capability	<0.01	PFHpA=0.0786
2375	-----	-----	-----	-----	-----	-----
2378	0.07	-----	-----	-----	-----	-----
2379	0.074	not detected	not detected	not detected	not detected	-----
2380	<0.1	<0.1	<0.1	<0.1	<0.1	-----
2382	0.056	<0.010	<0.010	<0.010	<0.010	<0.010
2386	0.032786750	0.0026	not detected	not detected	not detected	0.0809
2390	Not detected	Not detected	Not detected	-----	Not detected	Not Deteted
2425	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2482	0.0627	0.00628	-----	-----	-----	-----
2495	0.031	<0.005	<0.005	-----	<0.005	0.070
2561	-----	-----	-----	-----	-----	-----
2590	0.024	-----	-----	-----	-----	-----
2591	not detected	-----	not detected	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2743	0.080	not detected	not detected	-----	not detected	not detected
2773	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2826	Not detected	Not detected	Not detected	Not analyzed	Not detected	Not applicable
2827	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2886	0.1046	-----	-----	-----	-----	-----
2914	0.030	-----	-----	-----	-----	0.056
3100	<0.1	<0.1	<0.1	-----	<0.1	<0.1
3116	0.0135	-----	-----	-----	-----	-----
3118	<0.01	-----	-----	-----	-----	-----
3153	<0.01	-----	-----	-----	-----	-----
3154	0.022855	-----	-----	-----	-----	0,0674655 PFHpA
3172	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-----
3176	-----	-----	-----	-----	-----	-----
3210	0.0340	-----	-----	-----	-----	-----
3222	-----	-----	-----	-----	-----	-----
3237	-----	-----	-----	-----	-----	5.29

Determination of Total PFOA, Total PFNA, Total PFDA, Total PFBS, PFODA, PFDoA and Other Per- and Polyfluorinated compounds on sample #21531; in mg/kg

lab	Total PFOA	Total PFNA	Total PFDA	Total PFBS	Total PFODA	Total PFDoA	Other Per- and Polyfluorinated compounds
339	<0.1	<0.1	<0.1	<0.1	-----	-----	-----
551	-----	-----	-----	-----	-----	-----	-----
840	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2115	-----	-----	-----	-----	-----	-----	PFBA 0.037, PFHpS 0.102, PFHxS 0.084
2129	<0,01	<0,01	<0,01	<0,01	not analyzed	<0,01	0.1625
2159	<0,01	<0,01	<0,01	<0,01	not applicable	<0,01	not applicable
2250	0.00673	-----	-----	-----	-----	-----	0.125
2255	n.d	n.d	n.d	n.d	n.d	n.d	n.d
2293	-----	-----	-----	-----	-----	-----	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2311	Not Detected	-----	-----	-----	-----	-----	-----
2320	0.003144	-----	-----	-----	-----	-----	-----
2350	<1.00	<1.00	<1.00	<1.00	N/A	<1.00	N/A
2352	-----	-----	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2365	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2366	<1	out capability	out capability	out capability	out capability	out capability	out capability
2370	<0.01	<0.01	<0.01	<0.01	Out Capability	<0.01	PFHxS=0.108, PFHpS=0.108
2375	-----	-----	-----	-----	-----	-----	-----
2378	-----	-----	-----	-----	-----	-----	-----
2379	not detected	not detected	not detected	not detected	not detected	not detected	-----
2380	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-----
2382	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2386	0.00586920	not detected	0.0016	0.0012	not detected	not detected	0.1929
2390	Not Detected	Not Detected	Not Detected	Not Detected	-----	Not Detected	Not Detected
2425	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2482	0.0231	0.00295	-----	-----	-----	-----	-----
2495	0.008	<0.005	<0.005	<0.005	-----	<0.005	0.176
2561	-----	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----	-----
2591	not detected	-----	-----	not detected	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2743	0.046	not detected	0.038	not detected	-----	not detected	not detected
2773	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2826	Not detected	Not detected	Not detected	Not detected	Not analyzed	Not detected	Not applicable
2827	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2886	-----	-----	-----	-----	-----	-----	-----
2914	-----	-----	-----	-----	-----	-----	0.061
3100	<0.1	<0.1	<0.1	<0.1	-----	<0.1	<0.1
3116	-----	-----	-----	-----	-----	-----	-----
3118	<0.01	-----	-----	-----	-----	-----	-----
3153	<0.01	-----	-----	-----	-----	-----	-----
3154	0.008453	-----	0.012254	-----	-----	-----	0,056294 PFHxS; 0,05436 PFHpS
3172	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-----
3176	-----	-----	-----	-----	-----	-----	-----
3210	<0.01	-----	-----	-----	-----	-----	-----
3222	-----	-----	-----	-----	-----	-----	-----
3237	-----	-----	-----	-----	-----	-----	-----

APPENDIX 3 Analytical details

lab	Accredited to ISO/IEC 17025	Sample preparation prior to analysis	Sample intake (g)	Technique to release/ extract the analyte(s)	Solvent used	Extraction Temperature (°C)	Extraction Time (min)
339	No	Further cut	0.5	Ultrasonic	Methanol/toluene	60	120
551	No	Used as received	1	Ultrasonic	Methanol	120	50
840	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2115	Yes	Used as received	0.5	Ultrasonic	Methanol	60	120
2129	Yes	Used as received	1	Ultrasonic	Methanol	22	30
2159	Yes	Used as received	1	Ultrasonic	meOH	60	120
2250	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2255	Yes	Further cut	0.5	Ultrasonic	Methanol/ACN	70	120
2293	---	---	---	---	---	---	---
2310	Yes	Used as received	1.0	Ultrasonic	Methanol	60	120
2311	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2320	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2350	Yes	Further cut	0.5	Ultrasonic	methanol	60	120
2352	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2357	---	---	---	---	---	---	---
2358	Yes	Used as received	0.5	Ultrasonic	Mathanol	60	120
2363	Yes	Further cut	1	Ultrasonic	methonal	60	120
2365	Yes	Further cut	0.5	Ultrasonic	methanol	60	120
2366	No	Further cut	0.5	Soxhlet	methanol	60	120
2370	Yes	Further cut	0.5	Ultrasonic	5 mL	60	120
2375	---	---	0.5	---	Methanol	60	120
2378	No	Used as received	2	Other	methanol	60	120
2379	No	Further cut	1	Ultrasonic	Methanol	60	120
2380	Yes	Further cut	1.00	Ultrasonic	Methanol	60	120
2382	Yes	Further cut	1.0	Ultrasonic	CH3OH	60	120
2386	Yes	Used as received	1	Ultrasonic	Methanol	60	120
2390	Yes	Further cut	1	Ultrasonic	Methanol	60	120
2425	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2482	Yes	Used as received	0.5	Ultrasonic	Methanol	60	120
2495	Yes	Used as received	1	Ultrasonic	MeOH	60	120
2561	No	Further cut	0.5-0.6	Ultrasonic	methanol	40	60
2590	Yes	Used as received	1	Mechanical Shaking	MeOH	60	120
2591	No	Used as received	1.0	Ultrasonic	Methanol	60	120
2643	Yes	Further cut	0.5	Ultrasonic	methanol	60	120
2668	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2743	Yes	Used as received	0.7	Ultrasonic	Methanol	60	120
2773	No	Further cut	2.0025	Ultrasonic	Methanol	60	120
2826	Yes	Used as received	1	Ultrasonic	Methanol	60	60
2827	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
2886	Yes	Used as received	0.5	Ultrasonic	Methanol	60+	120
2914	No	Used as received	0.5	Ultrasonic	Methanol	Room temp.	2x15
3100	Yes	Further cut	1.0	Ultrasonic	Methanol	Room temp.	40
3116	Yes	Used as received	1	Ultrasonic	methanol	60	120
3118	Yes	Further cut	1	Ultrasonic	methanol	60	120
3153	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120
3154	Yes	Used as received	0.5	Ultrasonic	MeOH	60	120
3172	Yes	Used as received	0.15	Ultrasonic	Methanol	25	120
3176	Yes	Further cut	1	Ultrasonic	MeOH	40	30
3210	Yes	Used as received	1	Ultrasonic	Methanol	60	90
3222	---	---	---	---	---	---	---
3237	Yes	Further cut	0.5	Ultrasonic	Methanol	60	120

APPENDIX 4

Number of participants per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	DENMARK
2 labs in	FRANCE
5 labs in	GERMANY
1 lab in	GUATEMALA
4 labs in	HONG KONG
5 labs in	INDIA
1 lab in	INDONESIA
6 labs in	ITALY
8 labs in	P.R. of CHINA
1 lab in	PAKISTAN
2 labs in	SOUTH KOREA
1 lab in	SPAIN
1 lab in	SRI LANKA
1 lab in	SWITZERLAND
1 lab in	TAIWAN
1 lab in	THAILAND
4 labs in	TURKEY
1 lab in	UNITED KINGDOM
1 lab in	VIETNAM

APPENDIX 5

Abbreviations

C = final test result after checking of first reported suspect test result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected

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