Results of Proficiency Test
PFOA/PFOS
September 2015

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Worldwide, many consumer products are produced that contain Teflon parts. In the production of Teflon, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used. PFOA/PFOS persist indefinitely in the environment. It is a toxicant and carcinogen in animals.
In order to protect health and environment, the European Union promulgated Directive 2006/122/EC on 27 December 2006 [ref. 12], in which the placing on the market and the use of perfluorooctane sulfonate (C8F17SO2X, where X may be OH, being PFOA) is restricted: “Semi-finished products or articles, or parts thereof, if the concentration of PFOS is equal or greater than 0.1% by mass” and “May not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005 % by mass.”
Also the migration from food packaging has been subject of investigations [ref. 13, 14].
On request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of PFOA and PFOS content in the 2012 PT program. This PT was continued each following year. In the interlaboratory study of September 2015, 56 laboratories from 20 different countries participated (See appendix 4). In this report, the results of the proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, The Netherlands, was the organiser of this proficiency test. It was decided to send 2 different plastic samples (approximately 3 gram each), positive (artificially fortified) on PFOS and labelled #15154 and #15155 respectively. Participants were also requested to report a number of details of the test method used.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie, see also www.RVA.nl). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially 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 organisation 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 April 2014 (iis-protocol, version 3.3 [ref 3]). This protocol is electronically available through the iis internet site 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

Two different samples, #15154 artificially fortified to be positive on PFOS and #15155 artificially fortified with PFOS, were selected. The materials were divided over plastic bags, approx. 3 grams for each sample.
The homogeneity of the subsamples was checked by determination of PFOS content on a number of stratified randomly selected subsamples. For sample #15154, the test results for PFOS varied between 350 and 368 mg/kg. For sample #15155, the test results for PFOS varied between 660 and 691 mg/kg.
From the results of the homogeneity test, the relative between sample standard deviations RSD_r were calculated and compared with 0.3 times the relative proficiency target standard deviations RSD_R in agreement with the procedure of ISO 13528, Annex B2 [ref. 4] in table 1 below.

	PFOS in #15154	PFOS in #15155
RSD_r (observed)	2.1%	1.6%
target	Horwitz	Horwitz
0.3 x RSD_R (target)	2.0%	1.8%

Table 1: Relative repeatability standard deviations of PFOS contents of the subsamples #15154 and #15155

The calculated variation coefficients RSDr are close to or in agreement with the estimated targets, calculated using the Horwitz equation, for both samples. Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples, (1* sample #15154 and 1* sample #15155) was sent on August 12, 2015.

2.5 ANALYSIS

The participants were requested to determine PFOA and PFOS content on both samples. It was explicitly requested to treat the samples as routine samples and to report the analytical results using the indicated units on the report form in the data entry portal and not to round the results, but report as much significant figures as possible. It was also requested not to report ‘less than’ results, which are above the detection limit, because such results can not be used for meaningful statistical calculations.
To get comparable results a detailed report form, on which the units were prescribed as well, as a letter of instructions were prepared and made available for download on the data entry

portal www.kpmd.co.uk/sgs-iis-cts/. A form to confirm receipt of the samples and instructions were also included into the sample package. The laboratories were requested to complete a questionnaire on the data entry portal with some details of the sample pre-treatment used.

3 RESULTS

During four weeks after sample dispatch, the results of the individual laboratories were received. The original data are tabulated per sample in the appendices 1 and 2 of this report. The laboratories are represented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that did not report results at that moment. Shortly after the deadline the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test [ref. 5]) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. If appropriate, additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

The statistical calculations were performed as described in the procedures in the report ‘iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation’ of April 2014 (iis-protocol, version 3.3 [ref. 3]). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as ‘<…’ or ‘>…” were in general not used in the statistical evaluation.

First, the normality of the distribution of the 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. In case that a data set proved **not** to have a normal distribution the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 [ref. 6] and 1994 [ref. 7]) the original results per determination were submitted subsequently to Dixon, Grubbs and or Rosner General ESD outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test [ref. 8]. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

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.

3.2 GRAPHICS

In order to visualise 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 analysis results are plotted. The corresponding laboratory numbers are under 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 standard. 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 [ref. 9] and [ref. 10]. Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. In order to be able to have an objective evaluation of the performance of each participant, it was decided to evaluate this performance against the literature requirements. Therefore the z-scores were calculated using a target standard deviation. This target standard deviation was calculated from the literature reproducibility by division with 2.8.

The standard uncertainly (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6:

$$u_x = 1.25 * (\text{st.dev (n)}) / \sqrt{n}$$

In ISO13528 is stated that if $u_x \geq 0.3$ * standard deviation for proficiency testing, the uncertainly of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. Therefore in this PT report z'-scores were calculated in stead of the usual z-scores. The z'(target)-scores were calculated in accordance with ISO13528 paragraph 7.6:

$$z'(\text{target}) = (\text{result} – \text{mean of PT}) / \sqrt{((\text{target standard deviation})^2 + (u_x)^2)}$$

The z'(target) scores are listed in the result tables in appendix 1.

In general 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

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.

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Eight participants reported test results after the final reporting date and five other participants did not report any test result at all. Finally, the 51 reporting laboratories reported 135 numerical results. No outlying results were observed. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

A normal distribution was found for the data sets of reported PFOS test results for both samples #15154 and #15155.

For the determination of PFOA/PFOS, the CEN-TS 15968 method [ref. 11] is considered to be the official EC test method by the majority of the participating laboratories. However the scope of this method is more for extractable/migratable PFOS and not for total PFOS content, see also the discussion in paragraph 4.3. Also the CEN-TS 15968 method does not mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation.

Furthermore, it was decided to use assigned consensus values for the PFOS determination based on a sub set of test results, determined after exploring the effect of sample pre-treatment as reported by the participants. It appears that more PFOS is determined and the variation between test results decreases when the samples were reduced in combination of extraction with Soxhlet in DCM/MeOH or in Ultrasonic bath in MeOH, see paragraphs 4.3 and 5 for more discussion.

4.1 Evaluation per sample and test

In this section the results are discussed per sample and per test.

#15154: PFOA

All of the 49 reporting participants agreed on the absence of PFOA on a concentration level lower than 10 mg/kg. The majority (59%) reported n.d. or lower than 1 (or lower) mg/kg. 16 participants reported a value for PFOA, however all reported a result lower than 1 mg/kg.
The material had not been spiked with PFOA and it was decided not to calculate a z-score for this determination.

#15154: PFOS

Severe analytical problems were observed in determining the concentration level of PFOS in the evaluated material. The reported PFOS concentration varies over a large range from 21 to 429 mg/kg and consequently a high variation (RSD 58%) is calculated. No extreme test results are observed.
Due to the large variation compared to the target reproducibility (R(lit)) based on the Horwitz equation it was decided to calculate z'-scores based on Horwitz adapted values for this determination, see paragraph 3.3 for more background.

#15155: PFOA

All of the 49 reporting participants agreed on the absence of PFOA on a concentration level lower than 10 mg/kg. The majority (57%) reported n.d. or lower than 1 (or lower) mg/kg. 17 participants reported a value for PFOA, however 15 participants reported a result lower than 1 mg/kg.
The material had not been spiked with PFOA and it was decided not to calculate a z-score for this determination.

#15155: PFOS

Severe analytical problems were observed in determining the concentration level of PFOS in the evaluated material. The reported PFOS concentration varies over a large range from 31 to 861 mg/kg and consequently a high variation (RSD 61%) is calculated. No extreme test results are observed.
Due to the large variation compared to the target reproducibility (R(lit)) based on the Horwitz equation it was decided to calculate z'-scores based on Horwitz adapted values for this determination, see paragraph 3.3 for more background.

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

The calculated reproducibilities and the target reproducibilities derived from the literature standards, here Horwitz, and based on all received test results, are compared in table 2 below.

	unit	n	Average	2.8 * sd	R'(Horwitz)
PFOA in #15154	mg/kg	49	Not detected or <10	n.a.	n.a.
PFOS in #15154	mg/kg	50	189	305	66
PFOA in #15155	mg/kg	49	Not detected or <10	n.a.	n.a.
PFOS in #15155	mg/kg	50	401	690	142

Table 2: Performance overview for all received test results on samples #15154 and #15155

Without further statistical calculations, it can be concluded that there is no good compliance of the group of participating laboratories with the target reproducibility.

4.3 EVALUATION OF THE TEST METHODS USED

Almost the half of the participants (48%) reported to have used an 'in house' test method and 44% of the participants reported to have used the CEN/TS 15968 method for the determination of PFOA/PFOS. Another four participants reported to have used EPA3540C or EPA3550C methods. The reported details of the methods that were used by the participants are listed in appendix 2. The effect of the used method reported on the PFOS determination is explored and shown in table 1 of appendix 3. In general the participants that used the CEN/TS 15968 method, determined on average lower amounts of PFOS than participants that used an in-house method. The CEN/TS 15968 method is considered as the standard EC standard by the majority of the participants (see also paragraph 4.0). The CEN/TS 15968 method is very comprehensive in the description of the analytical part after the sample pre-treatment and quite brief about the sample pre-treatment and extraction from polymers. This description about sample pre-treatment is mainly the extraction from materials such as paper or textile by ultrasonic bath in Methanol for 2h at 60°C. 42% of the participants reported to use this pre-treatment of ultrasonic bath in Methanol for 2h at 60°C. For the reduction of solid polymers by grinding, the CEN/TS 15968 method refers to EN ISO 6427 and to ISO 9113 for a list of extractions conditions dependent on a type of plastic.

The effect of pre-treatment of the granulate on the PFOS determination is given in table 2 of appendix 3. In general more PFOS is determined when the granulate is milled or grinded. Cutting of the granulate releases PFOS from the matrix as well, but the effectiveness is highly dependent on the used extraction technique, see table 3 below. Cutting the granulate in combination with Soxhlet/DCM/MeOH extracts almost the same amount on average than grinding or milling in combination with Ultrasonic bath/MeOH.

			PFOS #15154			PFOS #15155		
Pathway to extract PFOS from the matrix		**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
as received	Ultrasonic bath with MeOH	11	103.23	120.548	117%	184.19	237.415	129%
Cut	Ultrasonic bath with MeOH	11	116.42	60.562	52%	245.88	137.713	56%
Milled/Grinded	Ultrasonic bath with MeOH	8	268.06	78.694	29%	566.68	173.933	31%
as received	Soxhlet with DCM/MeOH	3	331.01	85.702	26%	719.57	88.504	12%
Cut	Soxhlet with DCM/MeOH	10	255.88	53.730	21%	592.76	114.223	19%
Several other combinations		5	208.07	53.230	26%	443.14	149.356	34%
n (total in analysis)		50	188.72	108.836	58%	400.91	246.260	61%

Table 3: Effect of sample pre-treatment on the determination of PFOS for samples #15154 and #15155

No data is available to draw conclusions on the combination; Milling/grinding in combination of Soxhlet extraction. Participants either use Ultrasonic bath in combination with MeOH or Soxhlet in combination with DCM/MeOH. In table 4 of appendix 3 the effect of solvent is explored and it seems that DCM/MeOH is more effective than MeOH alone. One should realize that the choice of solvent is always in combination with the choice of extraction technique and no hard conclusions can be drawn on the choice of solvent alone.

The effect of extraction time is given in table 5 of appendix 3. Further study shows that the choice extraction time is in combination of choice of pre-treatment path way; 27 participants have reported to extract PFOS for 2 hours and 22 of them (81%) reported to use ultrasonic bath in MeOH at 60°C. 11 participants reported to extract PFOS for 6 hours and all have used a Soxhlet in DCM/MeOH at presumable reflux temperature (see next discussion about the effect of temperature). So no hard conclusions can be drawn about the choice of extraction time.

The effect of the reported extraction temperature is explored as well and this is given in table 6 of appendix 3. No strong correlation is found between temperature and amount PFOS determined. Some participants reported temperature settings >100°C. This appears to be the setting of the heating device of the oil bath. The boiling points of DCM and MeOH are about 40°C and 65°C respectively. Therefore it is assumed that in case the sample is heated above the boiling points the extraction will be at the reflux temperature of the solvent mixture used. In this case one could argue that the higher temperature the more PFOS will be found, when the other conditions are kept equal, but more data is needed to underpin this.

4.4 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2015 AGAINST PREVIOUS PTS

The observed variation expressed as relative standard deviation (RSD) in the test results in the 2015 PT is in line with the observations in previous PTs, see table 4 below.

RSD%	*2015*	*2014*	*2013*	*2012*	*2011*	*Target Horwitz 100-1000 mg/kg*
PFOA sample 1	n.d.	n.d.	n.d.	30%	15%	6 - 8%
PFOA sample 2	n.d.	144%	29%	Not in PT	19%	6 - 8%
PFOS sample 1	25[s] - 58%[a]	62[s] - 128%[a]	162%	141%	Not in PT	6 - 8%
PFOS sample 2	24[s] - 61%[a]	27[s] - 53%[a]	n.d.	Not in PT	Not in PT	6 - 8%

Table 4: Development of uncertainties, reported as RSD, over **all (a**) or over **subset (s)** of results against previous PTs

For PFOA/PFOS the target value for the precision of the PFOA and PFOS content determination in polymers is based on the Horwitz equation. This target value of 6 - 8% appears to be very optimistic. Based on the subset as discussed in paragraph 4.3 above a value of 25 - 27% for the variation coefficient is durable when participants use an effective method for sample pre-treatment and extraction (see also paragraph 5 for more discussion and exploration sample pre-treatment in appendix 3).

The observed recovery of PFOS compared to the “expected” concentration of PFOS of the 2015 proficiency test was compared against previous PTs, see table 5 below.

Recovery%	*2015*	*2014*	*2013*	*2012*	*2011*
PFOA sample 1	n.e.	n.e.	n.e.	68% (PVC)	70% (PVC)
PFOA sample 2	n.e.	n.e.	80% (PVC)	Not in PT	80% (PVC)
PFOS sample 1	72[s] - 52%[a] (PVC)	2.5[s] - 1.5%[a] (PP)	10% (PP)	17% (PP)	Not in PT
PFOS sample 2	86[s] - 59%[a] (PVC)	78[s] - 67%[a] (PVC)	n.e.	Not in PT	Not in PT

Table 5: Development of recovery calculated over **all (a)** or over **subset (s)** of results against previous proficiency tests

In general the recovery is about 70% or higher in a PVC matrix. The recovery in the PP samples (in 2012, 2013 and 2014) is remarkably low. The PFOS extraction from the PP matrix is obviously very difficult. The presence of a plasticizer in the PVC matrix may possibly facilitate the extraction of PFOS and thus explain the observed difference in behaviour between PVC and PP.

5 DISCUSSION

Based on the amount PFOS determined on average and the variation between the reported results it is observed that reproducible pathways to release PFOS from the polymer are possible. In this PT these are; milling or grinding the sample in combination with ultrasonic bath in MeOH or cutting the granules in combination with Soxhlet extraction in a DCM/MeOH mixture (see table 5 above). In total 36% of the participants had used either one of those two pathways to pre-treat the samples and the RSD found is 24-25% (see table 6 below). This is a significant reduction of the RSD compared to the RSD found over all participants (RSD 58-61%).

Therefore it was decided to use these two pathways to calculate the consensus values for the z'-score calculation as mentioned earlier in paragraph 4 above. The pathway using the granulates as received in combination of Soxhlet/DCM/MeOH may also be very effective but this is based on only 3 participants and therefore not included into the selected group.

		PFOS #15154			PFOS #15155		
Group	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
Selected group	18	261.29	64.165	25%	581.17	139.793	24%
No	32	147.90	108.110	73%	299.51	235.924	79%
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%

Table 6: Comparison selected pathways to others on the determination of PFOS for samples #15154 and #15155

The conclusion is that the majority of the participants is able to determine PFOS in the polymer matrix, but a huge variation is found between participants. This variation is highly dependent on the chosen sample pre-treatment and extraction. Fortunately, the determination of PFOS becomes more reproducible when sample pre-treatments are chosen which releases PFOS more effectively from the polymer. Such pathways could be cutting, milling or grinding the polymer prior the extraction. However it is important to realize what kind of determination is requested by the applicant. In case of a migration request the cutting or grinding may not be appropriate and the material should probably best be treated as received. In the case of a total content determination request the polymer matrix should be reduced to facilitate the release of PFOS from the matrix.

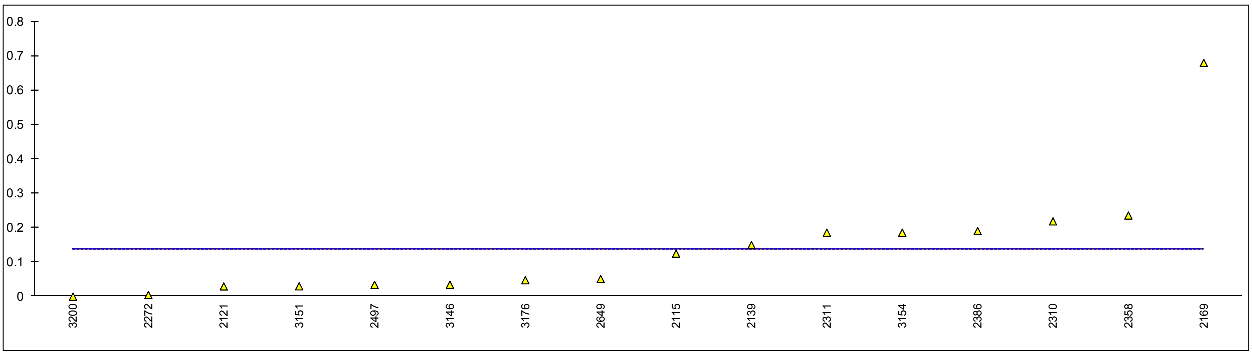
APPENDIX 1

Determination of PFOA on sample #15154; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	in house	<10		-----	
339	in house	<0.100		-----	
623	in house	n.d.		-----	
2115	in house	0.12518		-----	
2121	in house	0.0297		-----	
2139	CEN-TS15968	0.15		-----	
2169	in house	0.68		-----	
2172	in house	<0.0001		-----	Probably reported in %M/M
2201	CEN-TS15968	n.d.		-----	
2255	in house	n.d.		-----	
2271	CEN-TS15968	<1		-----	
2272	CEN-TS15968	0.00474		-----	Reported: matrix interference occured
2290	CEN-TS15968	<1.0		-----	
2310	CEN-TS15968	0.219		-----	
2311	CEN-TS15968	0.186		-----	
2350	in house	<1.0		-----	
2352	EPA3540C/8321B	n.d.		-----	
2358	in house	0.236		-----	
2363	INH-243	<10		-----	
2365	EPA3540C	<10		-----	
2369		-----		-----	
2370	INH-219	n.d.		-----	
2379	CEN-TS15968	n.d.		-----	
2380	in house	n.d.		-----	
2384	EPA3540C	n.d.		-----	
2386		0.1908		-----	
2390	INH-219	n.d.		-----	
2410	CEN-TS15968	<1		-----	
2415	in house	n.d.		-----	
2425	CEN-TS15968	n.d.		-----	
2482	CEN-TS15968	n.d.		-----	
2492		-----		-----	
2493		-----		-----	
2497	CEN-TS15968	0.0342		-----	
2510		-----		-----	
2532	in house	<0.1		-----	
2549	in house	n.d.		-----	
2566	CEN-TS15968	n.d.		-----	
2590	CEN-TS15968	<L.O.Q.		-----	
2649	in house	0.051		-----	
2710		-----		-----	
3118	INH-ref. to CEN-TS 15968	<1		-----	
3146		0.0345		-----	
3151	CEN-TS15968	0.030		-----	
3154	CEN-TS15968	0.186		-----	
3163		-----		-----	
3172	CEN-TS15968	<0.01		-----	
3176	CEN-TS15968	0.0477		-----	
3182	CEN-TS15968	n.d.		-----	
3190	CEN-TS15968	n.d.		-----	
3197	CEN-TS15968	n.d.		-----	
3200	EPA3550C/8321B	0		-----	
3209	in house	n.d.		-----	
3214	CEN-TS15968	<1		-----	
3220		-----		-----	
3225		<10		-----	

Summary

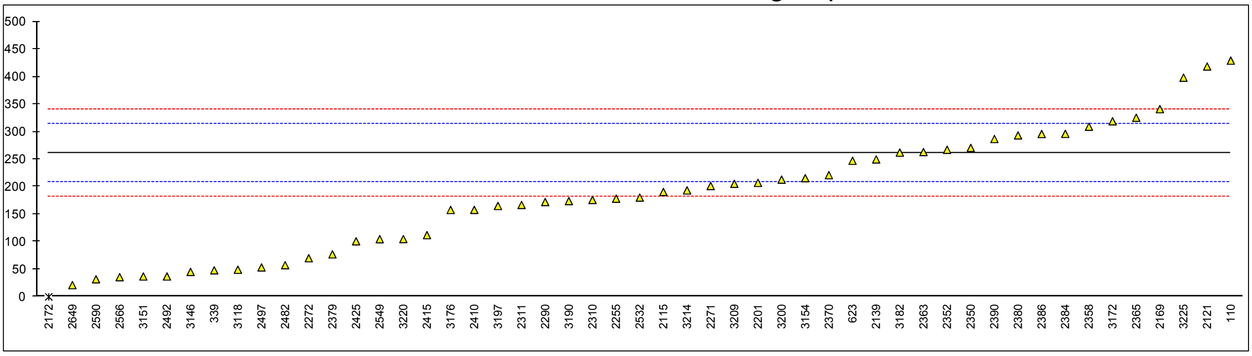
18 reported n.d. and 1 reported < L.O.Q.	normality	n.a.
10 reported < 1 (or lower) mg/kg	n	49
This is in total 29 out of 49 reported results (59%)	outlier	n.a.
4 reported < 10 mg/kg	mean (n)	<10mg/kg
16 reported a value for PFOA	st.dev. (n)	n.a.
	R(calc.)	n.a.
	R(Horwitz)	n.a.

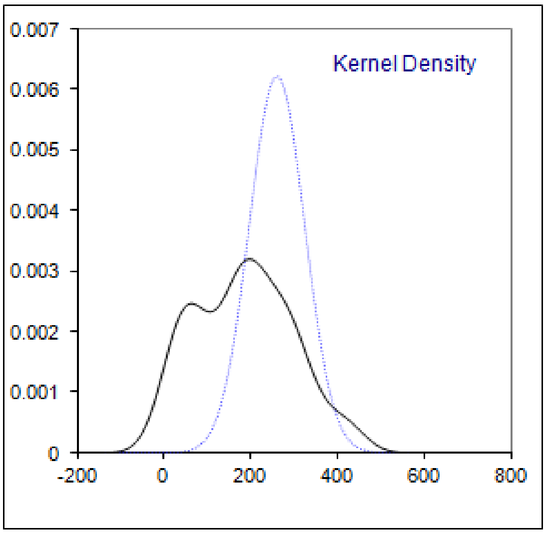

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
3200
2272
2121
3151
2497
3146
3176
2649
2115
2139
2311
3154
2386
2310
2358
2169

Determination of PFOS on sample #15154; results in mg/kg

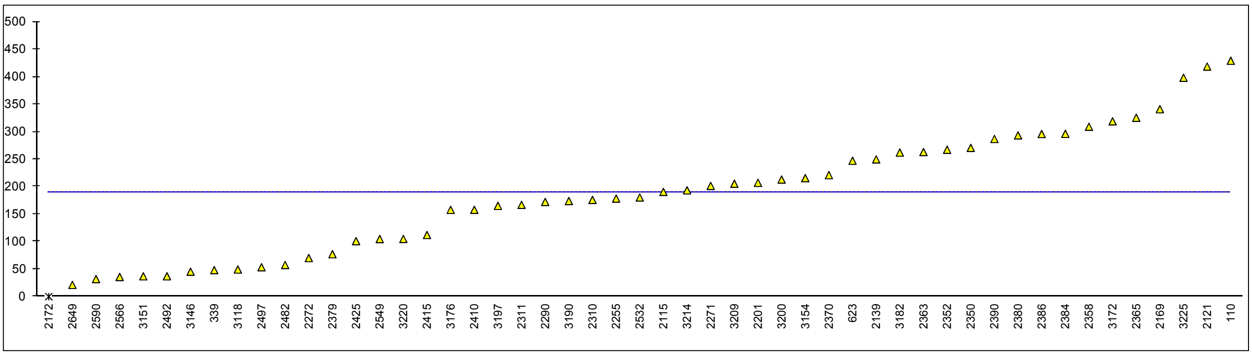
lab	method	value	mark	z'(targ)	remarks
110	in house	429.1		6.41	
339	in house	48.278		-8.14	
623	in house	247.22		-0.54	
2115	in house	190.5268		-2.70	
2121	in house	418.517		6.01	
2139	CEN-TS15968	249.7		-0.44	
2169	in house	341		3.05	
2172	in house	0.0130	ex	-9.99	Probably reported in %M/M
2201	CEN-TS15968	207.1		-2.07	
2255	in house	178.4		-3.17	
2271	CEN-TS15968	201.4		-2.29	
2272	CEN-TS15968	70.2		-7.30	Reported: matrix interference occured
2290	CEN-TS15968	172.3		-3.40	
2310	CEN-TS15968	176		-3.26	
2311	CEN-TS15968	167		-3.60	
2350	in house	270.628		0.36	
2352	EPA3540C/8321B	267.2		0.23	
2358	in house	309		1.82	
2363	INH-243	263		0.07	
2365	EPA3540C	325.4		2.45	
2369		-----		-----	
2370	INH-219	221		-1.54	
2379	CEN-TS15968	77.20		-7.04	
2380	in house	293.3		1.22	
2384	EPA3540C	296.14		1.33	
2386		295.8		1.32	
2390	INH-219	286.80		0.97	
2410	CEN-TS15968	158		-3.95	
2415	in house	112.1		-5.70	
2425	CEN-TS15968	100.96		-6.13	
2482	CEN-TS15968	57.533		-7.79	
2492	in house	37.09		-8.57	
2493		-----		-----	
2497	CEN-TS15968	53.51		-7.94	
2510		-----		-----	
2532	in house	180.4		-3.09	
2549	in house	104.8		-5.98	
2566	CEN-TS15968	35.8		-8.62	
2590	CEN-TS15968	31.92		-8.77	
2649	in house	21.375		-9.17	
2710		-----		-----	
3118	INH-ref. to CEN-TS 15968	49.319		-8.10	
3146		45.4		-8.25	
3151	CEN-TS15968	37.00		-8.57	
3154	CEN-TS15968	215.6		-1.75	Dilution 1:50
3163		-----		-----	
3172	CEN-TS15968	319		2.21	
3176	CEN-TS15968	157.85		-3.95	
3182	CEN-TS15968	262.1		0.03	
3190	CEN-TS15968	174		-3.34	
3197	CEN-TS15968	165.2		-3.67	
3200	EPA3550C/8321B	213.0		-1.85	
3209	in house	205.42		-2.14	
3214	CEN-TS15968	193.4		-2.59	
3220		105.0		-5.97	
3225		398.153		5.23	
		Selected group (see paragraph 4, 4.3 or 5)			**All data**
	normality	OK			OK
	n	18			50
	outliers	0			0+1ex
	mean (n)	261.29			188.72
	st.dev. (n)	64.165			108.836
	R(calc.)	179.66			304.74
	R(Horwitz')	73.26			66.17

Mean values and 2s-3s lines calculated based on selected group





Mean value over all data (n=50)

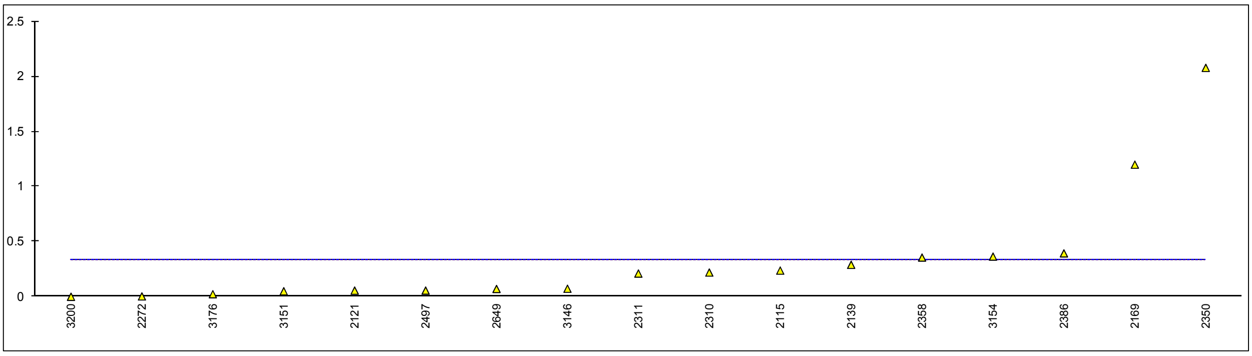


Determination of PFOA on sample #15155; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	in house	<10		-----	
339	in house	<0.100		-----	
623	in house	n.d.		-----	
2115	in house	0.23776		-----	
2121	in house	0.0561		-----	
2139	CEN-TS15968	0.29		-----	
2169	in house	1.2		-----	
2172	in house	<0.0001		-----	Probably reported in %M/M
2201	CEN-TS15968	n.d.		-----	
2255	in house	n.d.		-----	
2271	CEN-TS15968	<1		-----	
2272	CEN-TS15968	0.00313		-----	Reported: matrix interference occured
2290	CEN-TS15968	<1.0		-----	
2310	CEN-TS15968	0.22		-----	
2311	CEN-TS15968	0.211		-----	
2350	in house	2.079		-----	
2352	EPA3540C/8321B	n.d.		-----	
2358	in house	0.356		-----	
2363	INH-243	<10		-----	
2365	EPA3540C	<10		-----	
2369		-----		-----	
2370	INH-219	n.d.		-----	
2379	CEN-TS15968	n.d.		-----	
2380	in house	n.d.		-----	
2384	EPA3540C	n.d.		-----	
2386		0.3942		-----	
2390	INH-219	n.d.		-----	
2410	CEN-TS15968	<1		-----	
2415	in house	n.d.		-----	
2425	CEN-TS15968	n.d.		-----	
2482	CEN-TS15968	n.d.		-----	
2492		-----		-----	
2493		-----		-----	
2497	CEN-TS15968	0.0566		-----	
2510		-----		-----	
2532	in house	<0.1		-----	
2549	in house	n.d.		-----	
2566	CEN-TS15968	n.d.		-----	
2590	CEN-TS15968	<L.O.Q.		-----	
2649	in house	0.071		-----	
2710		-----		-----	
3118	INH-ref. to CEN-TS 15968	<1		-----	
3146		0.0729		-----	
3151	CEN-TS15968	0.050		-----	
3154	CEN-TS15968	0.365		-----	
3163		-----		-----	
3172	CEN-TS15968	<0.01		-----	
3176	CEN-TS15968	0.0232		-----	
3182	CEN-TS15968	n.d.		-----	
3190	CEN-TS15968	n.d.		-----	
3197	CEN-TS15968	n.d.		-----	
3200	EPA3550C/8321B	0		-----	
3209	in house	n.d.		-----	
3214	CEN-TS15968	<1		-----	
3220		-----		-----	
3225		<10		-----	

Summary

18 reported n.d. and 1 reported < L.O.Q.	normality	n.a.
9 reported < 1 (or lower) mg/kg	n	49
This is in total 28 out of 49 reported results (57%)	outlier	n.a.
4 reported < 10 mg/kg	mean (n)	<10 mg/kg
17 reported a value for PFOA	st.dev. (n)	n.a.
	R(calc.)	n.a.
	R(Horwitz)	n.a.

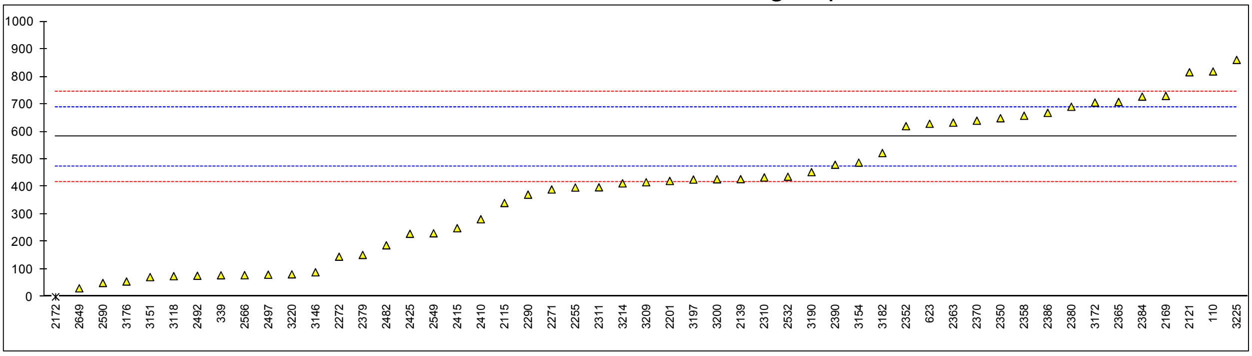

2.5
2
1.5
1
0.5
0
3200
2272
3176
3151
2121
2497
2649
3146
2311
2310
2115
2139
2358
3154
2386
2169
2350

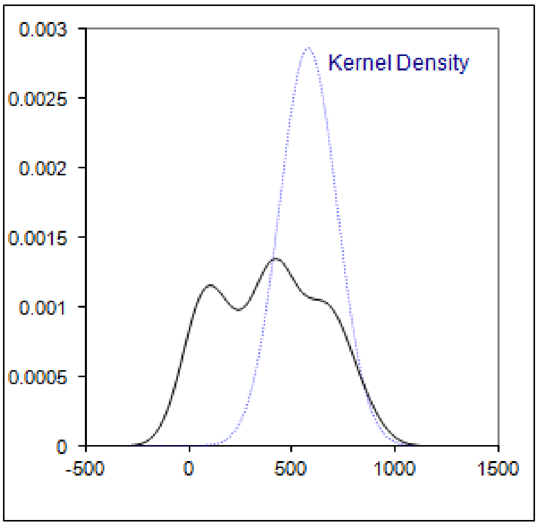
Determination of PFOS on sample #15155; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	in house	818.9		4.36	
339	in house	78.421		-9.23	
623	in house	628.76		0.87	
2115	in house	340.9852		-4.41	
2121	in house	816.050		4.31	
2139	CEN-TS15968	427.7		-2.82	
2169	in house	730		2.73	
2172	in house	0.0220	ex	-10.67	Probably reported in %M/M
2201	CEN-TS15968	421.2		-2.94	
2255	in house	397.2		-3.38	
2271	CEN-TS15968	390.1		-3.51	
2272	CEN-TS15968	146		-7.99	Reported: matrix interference occured
2290	CEN-TS15968	371.4		-3.85	
2310	CEN-TS15968	434		-2.70	
2311	CEN-TS15968	398		-3.36	
2350	in house	649.1		1.25	
2352	EPA3540C/8321B	620.2		0.72	
2358	in house	658		1.41	
2363	INH-243	633		0.95	
2365	EPA3540C	708.1		2.33	
2369		-----		-----	
2370	INH-219	640		1.08	
2379	CEN-TS15968	152.37		-7.87	
2380	in house	690.7		2.01	
2384	EPA3540C	727.42		2.68	
2386		668.5		1.60	
2390	INH-219	480.10		-1.85	
2410	CEN-TS15968	282		-5.49	
2415	in house	249.4		-6.09	
2425	CEN-TS15968	229.27		-6.46	
2482	CEN-TS15968	187.334		-7.23	
2492	in house	76.62		-9.26	
2493		-----		-----	
2497	CEN-TS15968	80.62		-9.19	
2510		-----		-----	
2532	in house	436.4		-2.66	
2549	in house	230.9		-6.43	
2566	CEN-TS15968	78.8		-9.22	
2590	CEN-TS15968	50.49		-9.74	
2649	in house	31.124		-10.09	
2710		-----		-----	
3118	INH-ref. to CEN-TS 15968	75.163		-9.29	
3146		89.20		-9.03	
3151	CEN-TS15968	71.88		-9.35	
3154	CEN-TS15968	487.8		-1.71	
3163		-----		-----	
3172	CEN-TS15968	706		2.29	
3176	CEN-TS15968	55.72		-9.64	
3182	CEN-TS15968	522.3		-1.08	
3190	CEN-TS15968	453		-2.35	
3197	CEN-TS15968	426.2		-2.84	
3200	EPA3550C/8321B	427.3		-2.82	
3209	in house	416.43		-3.02	
3214	CEN-TS15968	412.4		-3.10	
3220		82.0		-9.16	
3225		860.807		5.13	

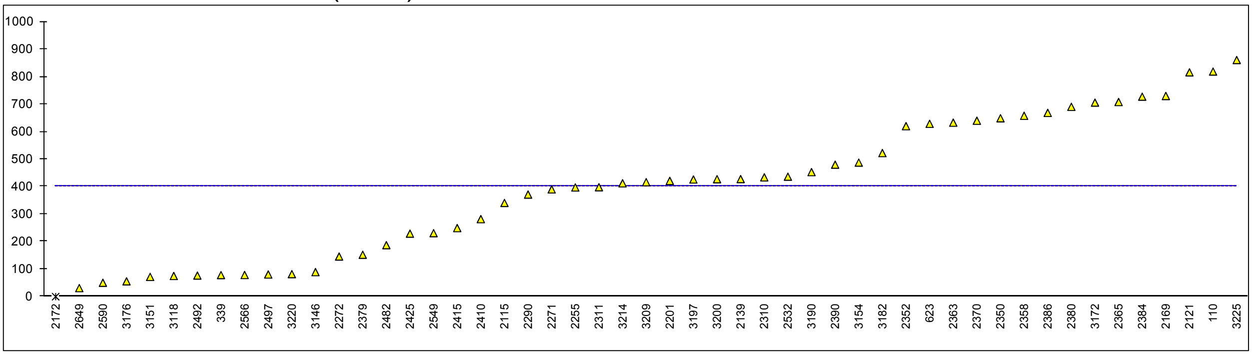
	Selected group (see paragraph 4, 4.3 or 5)	All data
normality	OK	OK
n	18	50
outliers	0	0+1 ex
mean (n)	581.17	400.91
st.dev. (n)	139.793	246.260
R(calc.)	391.42	689.53
R(Horwitz')	152.58	142.01

Mean values and 2s-3s lines calculated based on selected group





Mean value over all data (n=50)



APPENDIX 2 Analytical details

lab	method	Method to reduce the granulate or used as received	reduced to max. particle size	How particle size checked	Technique to release/extract the analyte?	Extraction solvent or mixture	Extraction time -temp. (h/°C)
110	in house	as received	---	---	Soxhlet	DCM/MeOH	6h - reflux
339	in house	as received	=< 1 mm	visual	Ultrasonic	MeOH	1h
623	in house	Cut	>1 mm	---	Soxhlet	DCM/MeOH	6h
2115	in house	as received	>1 mm	---	Ultrasonic	DCM/MeOH 1:1	2h - 50°C
2121	in house	as received	---	---	Ultrasonic	MeOH	1h – rT
2139	CEN-TS15968	Milled (cryogenic)	>1 mm	< 0.2mm	Ultrasonic	MeOH	1h - 60°C
2169	in house	Milled (cryogenic)	=< 0.5 mm	---	Ultrasonic	MeOH	1h - 30°C
2172	in house	Cut	=< 1 mm	---	Ultrasonic	MeOH	2h - 60°C
2201	CEN-TS15968	Grinded	=< 1 mm	Sieve (1mm)	Ultrasonic	MeOH	2h - 60°C
2255	in house	---	---	---	---	MeOH	2h - 60°C
2271	CEN-TS15968	Cut	=< 1 mm	---	Ultrasonic	MeOH	2h - 60°C
2272	CEN-TS15968	Cut	=< 0.5 mm	---	Ultrasonic	MeOH	2h - 60°C
2290	CEN-TS15968	Cut	=< 1 mm	---	Ultrasonic	MeOH	2h - 60°C
2310	CEN-TS15968	Cut	=< 1 mm	Caliper	Soxhlet	DCM/MeOH 1:1	6h - 70°C
2311	CEN-TS15968	Cut	=< 1 mm	Caliper	Soxhlet	DCM/MeOH	6h - 70°C
2350	in house	as received	>1 mm	---	Soxhlet	DCM/MeOH	6h
2352	EPA3540C/8321B	Cut	=< 1 mm	---	Soxhlet	DCM/MeOH 1:1	6h - 150°C
2358	in house	Cut	---	3mm x 3mm	Soxhlet	DCM/MeOH 1:1	0.5h - 105°C
2363	INH-243	Cut	>1 mm	---	Soxhlet	DCM/MeOH	6h
2365	EPA3540C	Cut	=< 1 mm	---	Soxhlet	DCM/MeOH 1:1	6h
2369	No data	---	---	---	---	---	---
2370	INH-219	Cut	=< 1 mm	ruler	Soxhlet	DCM/MeOH	1.75h - 105°C
2379	CEN-TS15968	as received	>1 mm	---	Ultrasonic	MeOH	1h - 60°C
2380	in house	as received	---	---	Soxhlet	DCM/MeOH	6h - 95°C
2384	EPA3540C	Cut	=< 0.5 mm	Sieve (0.5mm)	Soxhlet	DCM/MeOH 1:1	6h – reflux
2386	---	Milled (cryogenic)	=< 1 mm	---	Ultrasonic	Aceton:Acetonitril/80:20	1h - 40°C
2390	INH-219	Cut	=< 1 mm	Caliper	Soxhlet	DCM/MeOH	6h - 50°C
2410	CEN-TS15968	Milled (cryogenic)	=< 0.5 mm	---	Ultrasonic	MeOH/MeOH&Demi	2h - 60°C
2415	in house	Cut	=< 1 mm	Caliper	Ultrasonic	MeOH	1h - 70°C
2425	CEN-TS15968	Cut	=< 1 mm	No change of size	Ultrasonic	MeOH	2h - 60°C
2482	CEN-TS15968	as received	>1 mm	---	Ultrasonic	MeOH	2h - 60°C
2492	in house	as received	=< 0.5 mm	---	Ultrasonic	MeOH	1h - 40°C
2493	No data	---	---	---	---	---	---
2497	CEN-TS15968	Cut	=< 1 mm	---	Ultrasonic	MeOH	2h - 70°C
2510	No data	---	---	---	---	---	---
2532	in house	Cut	=< 0.5 mm	---	Soxhlet / Ultrasonic	MeOH	2h - 60°C
2549	in house	Cut	=< 0.5 mm	Caliper	Ultrasonic	MeOH	2h - 60°C
2566	CEN-TS15968	as received	---	---	Ultrasonic	MeOH	2h - 60°C
2590	CEN-TS15968	as received	---	Not reduced	Ultrasonic	MeOH	2h - 60°C
2649	in house	as received	>1 mm	---	Ultrasonic	MeOH	0.5h - 40°C
2710	No data	---	---	---	---	---	---
3118	In house	Cut	>1 mm	Caliper	Ultrasonic	MeOH	2h - 60°C
3146	---	Cut	>1 mm	measured	Ultrasonic	MeOH	2h - 60°C
3151	CEN-TS15968	as received	---	---	Ultrasonic	MeOH	2h - 60°C
3154	CEN-TS15968	as received	>1 mm	---	Ultrasonic	Acetone:Hexane/20:80	2h - 60°C
3163	No data	---	---	---	---	---	---
3172	CEN-TS15968	Milled (cryogenic)	=< 0.5 mm	---	Ultrasonic	MeOH	2h - 60°C
3176	CEN-TS15968	as received	>1 mm	---	Ultrasonic	MeOH	2h - 60°C
3182	CEN-TS15968	Milled (cryogenic)	=< 0.5 mm	Sieve	Ultrasonic	MeOH	2h - 60°C
3190	CEN-TS15968	Grinded	=< 0.5 mm	---	Ultrasonic	MeOH	2h - 60°C
3197	CEN-TS15968	Cut	=< 0.5 mm	Sieve (0.5mm)	Ultrasonic	MeOH	2h - 60°C
3200	EPA3550C/8321B	as received	---	---	Ultrasonic	MeOH	2h - 60°C
3209	in house	Cut	=< 0.5 mm	Sieve (0.5mm)	Ultrasonic	MeOH	2h - 60°C
3214	CEN-TS15968	Grinded	=< 0.5 mm	Sieve (0.5mm)	Ultrasonic	MeOH	2h - 60°C
3220	---	---	---	---	---	---	---
3225	---	Grinded	=< 0.5 mm	---	Ultrasonic	MeOH	2h - 60°C

rT = room temperature

APPENDIX 3 Exploration of different pathways of sample pre-treatment on PFOS determination

Table 1 Effect of reported determination method

		PFOS #15154			PFOS #15155		
Method	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
CEN-TS15968	22	149.22	80.836	54%	308.39	183.390	59%
in house	24	210.48	125.200	59%	449.07	277.530	62%
EPA3550C/8321B	1	213.00	---	---	427.30	---	---
EPA3540C/8321B	1	267.20	---	---	620.20	---	---
EPA3540C	2	310.77	20.690	7%	717.76	13.661	2%
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

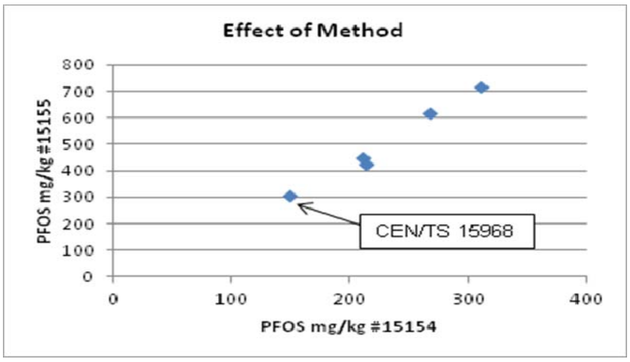


Table 2 Effect of reported methods to reduce the granulate

		PFOS #15154			PFOS #15155		
How granulate reduced	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
Used as received	16	158.42	138.364	87%	313.35	293.151	94%
Cut	22	182.72	88.516	48%	412.21	211.340	51%
Grinded	4	243.16	104.215	43%	536.85	216.673	40%
Milled (cryogenic)	6	270.93	64.994	24%	556.08	177.823	32%
not mentioned	2	141.70	51.902	37%	313.35	293.151	94%
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

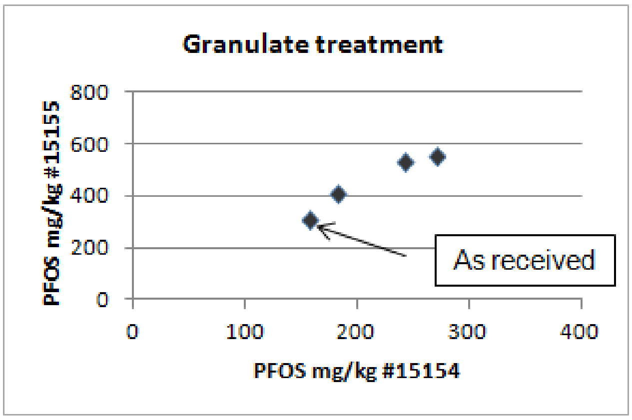


Table 3 Effect of reported extraction techniques

		PFOS #15154			PFOS #15155		
Techniques	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
Ultrasonic	34	159.43	109.759	69%	324.81	237.786	73%
Soxhlet / Ultrasonic	1	180.40	---	---	436.40	---	---
Soxhlet	13	273.21	66.895	24%	622.02	119.092	19%
Not mentioned	2	141.70	51.902	37%	239.60	222.880	93%
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

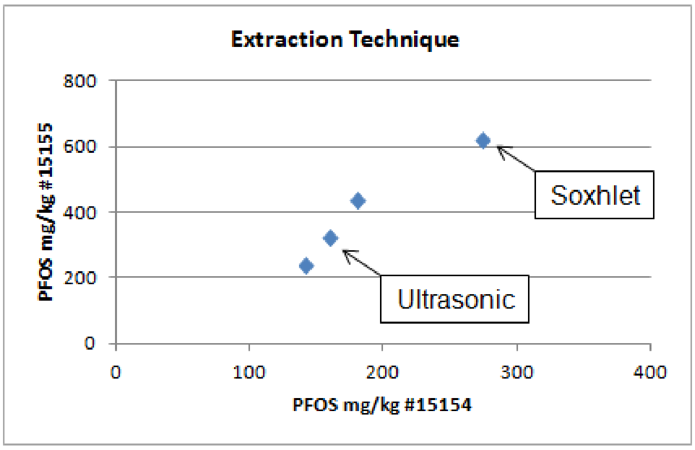


Table 4 Effect of reported extraction solvent (Note: is chosen pre-treatment pathway)

		PFOS #15154			PFOS #15155		
Solvent used to release PFOS	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
MeOH (in ultrasonic bath)	32	153.73	109.925	72%	315.56	236.511	75%
DCM/MeOH (in Soxhlet app.)	14	267.31	67.964	25%	601.95	136.870	23%
MeOH/MeOH&Demi	1	158.00	---	---	282.00	---	---
Acetone:Hexane/20:80	1	215.60	---	---	487.80	---	---
Aceton:Acetonitril/80:20	1	295.80	---	---	668.50	---	---
Not mentioned	1	105.00	---	---	82.00	---	---
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

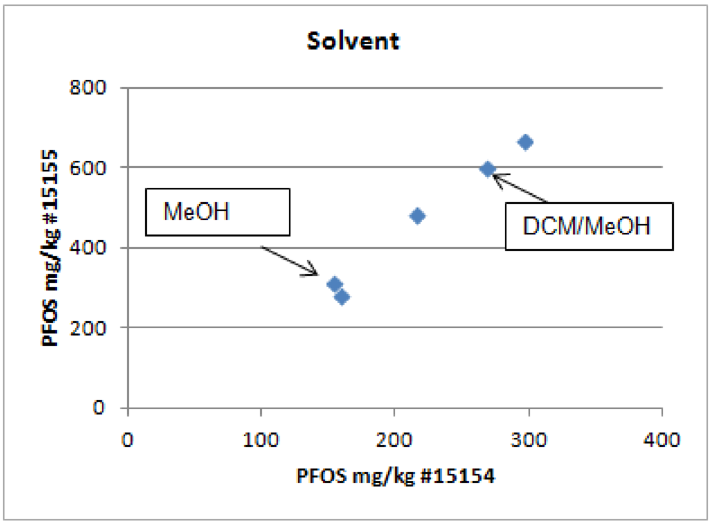


Table 5 Effect of reported extraction time (Note: is chosen pre-treatment pathway)

		PFOS #15154			PFOS #15155		
Time (h)	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
0.5	2	165.19	203.382	123%	344.56	443.268	129%
1	8	197.46	147.160	75%	399.88	303.984	76%
1.75	1	221.00	---	---	640.00	---	---
“2” (Ultrasonic bath/MeOH/60°C)	27	154.75	91.049	59%	320.26	206.140	64%
“6” (Soxhlet/DCM&MeOH/reflux T)	11	274.71	70.475	26%	617.12	129.736	21%
Not mentioned	1	105.00	---	---	82.00	---	---
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

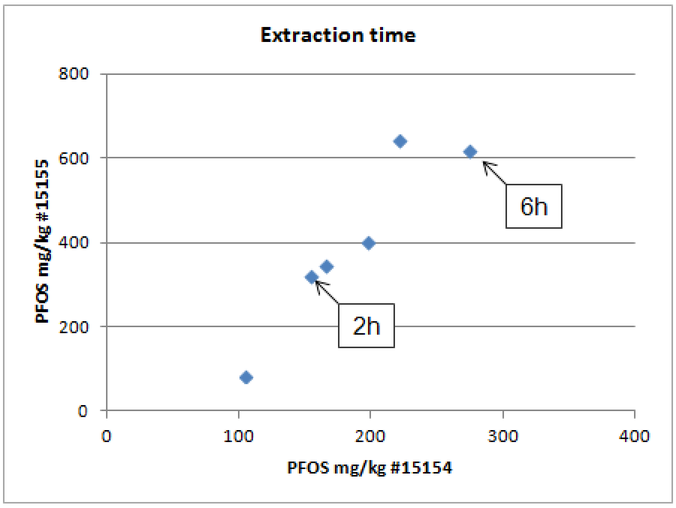


Table 6 Effect of reported extraction temperature

		PFOS #15154			PFOS #15155		
Temperature (°C)	**n**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**	**mean (mg/kg)**	**SD (mg/kg)**	**RSD (%)**
rT	1	418.52	---	---	816.05	---	---
30	1	341.00	---	---	730.00	---	---
40	3	118.09	154.103	130%	258.75	355.584	137%
50	2	238.66	68.075	29%	410.54	98.369	24%
60	27	157.82	91.732	58%	326.12	204.355	63%
“70” (reflux)	4	127.15	56.638	45%	290.51	161.129	55%
“95” (reflux)	1	293.30	---	---	690.70	---	---
“105” (reflux)	2	265.00	62.225	23%	649.00	12.728	2%
“150” (reflux)	1	267.20	---	---	620.20	---	---
reflux	2	362.62	94.017	26%	773.16	64.686	8%
Not mentioned	6	209.92	108.043	51%	463.23	298.042	64%
n (total in analysis)	50	188.72	108.836	58%	400.91	246.260	61%
n (excluded from analysis)	1	---	---	---	---	---	---
No data	5	---	---	---	---	---	---

APPENDIX 4 Number of participating laboratories per country

4 labs in	BANGLADESH
2 labs in	FRANCE
5 labs in	GERMANY
4 labs in	HONG KONG
1 lab in	HUNGARY
6 labs in	INDIA
2 labs in	INDONESIA
1 lab in	IRELAND
4 labs in	ITALY
1 lab in	JAPAN
3 labs in	KOREA
1 lab in	MALAYSIA
10 labs in	P.R. of CHINA
1 lab in	PAKISTAN
2 labs in	TAIWAN R.O.C.
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TURKEY
2 labs in	U.S.A.
2 labs in	VIETNAM

APPENDIX 5 Abbreviations and Literature

Abbreviations

C	= final result after checking of first reported suspect 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' outlier test
R(0.05)	= straggler in Rosner' outlier test
n.a.	= not applicable
n.d.	= not detected
n.e.	= not evaluated
rT	= room Temparature

Literature

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