Results of Proficiency Test on PFOA/PFOS September 2012

Organised by: Institute for Interlaboratory Studies
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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 on 27 December 2006 Directive 2006/122/EC, in which the placing on the market and the use of perfluorooctane sulfonates (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.”
On request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of PFOA in the 2011/2012 PT program and to continue this PT in 2012 with the extention to PFOS. In the interlaboratory study of September 2012, 28 laboratories from 13 different countries participated (See appendix 3). In this report, the results of the proficiency test are presented and discussed.

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 5 gram each), positive (artificially fortified) on PFOA or PFOS and labelled #12084 and #12085 respectively. Participants were also requested to report some details of the test method used.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO guide 43, ILAC-G13:2007 and ISO/IEC 17043:2010. This ensures 100% confidentially of participant’s data. Also, customer’s satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report ‘iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of January 2010 (iis-protocol, version 3.2). This protocol can be downloaded from the iis website http://www.iisnl.com.

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, #12084 artificially fortified to be positive on PFOA (theoretically 0.20%) and #12085 artificially fortified to be positive on PFOS (theoretically 0.06%), were selected. Both materials were divided over plastic bags, approx. 5 grams for each sample.
The homogeneity of the subsamples was checked by determination of PFOA content on a number of stratified randomly selected subsamples.

	%M/M PFOA in #12084	%M/M PFOS in #12085
Sample 1	0.1422	0.05706
Sample 2	0.1396	0.05751
Sample 3	0.1440	0.05722
Sample 4		0.05865
Sample 5		0.05624
Sample 6		0.05696
Sample 7		0.05830
Sample 8		0.05777

Table 1: results of the homogeneity test on the subsamples #12084 and #12085

From the above 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 in the next table:

	PFOA in #12084	PFOS in #12085
RSD_r (observed)	1.6%	1.3%
reference method	Horwitz	Horwitz
0.3 x RSD_R (reference method)	1.6%	1.8%

Table 2: relative repeatability standard deviations of PFOA/PFOS contents of the subsamples #12084 and #12085

The calculated variation coefficients RSDr are in good 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 #12084 and 1* sample #12085) was sent on August 15, 2012.

2.5 ANALYSIS

The participants were requested to determine PFOA/PFOS on both samples. It was explicitly requested to treat the samples as if it were routine samples and to report the analytical results using the indicated units on the report form 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, was sent together with each set of samples. Also, a letter of instructions was added to the package.
The laboratories were requested to complete the report form with some details of the methods used.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received.
The original data are tabulated per sample in the appendix 1 of this report.
The laboratories are represented by the 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) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. 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 January 2010 (iis-protocol, version 3.2).

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers this check was repeated.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs 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. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test. 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. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have significant consequences for the evaluation of the test results.

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 (see appendix 4; ref. 14 and 15).

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, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study.
The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) 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.
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:

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
$3 <$	$\lvert z \rvert$	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 the fit-for-useness of the reported test result. See also appendix 3; ref. 16.

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples.
Two participants reported test results after the final reporting date and two other participants did not report any test results at all.
Finally, 26 of the 28 participants submitted analysis results. The 26 reporting laboratories reported 42 numerical results. Observed were 4 outlying results, which is 8.7%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

A not-normal distribution was found for the reported PFOS test results of sample #12085.
Therefore this statistical evaluation should be used with due care.

For the determination of PFOA/PFOS, the CEN/TS 15968 method is considered to be the official EC test method. Regretfully this method does not yet mention reproducibility requirements.
Therefore, the target requirements in this study were estimated using the Horwitz equation.

4.1 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

The calculated reproducibilities and the target reproducibilities derived from the literature standards, here Horwitz, are compared in the next table.

	unit	n	Average	2.8 * sd	R (lit)
PFOA in #12084	%M/M	23	0.136	0.116	0.023
PFOS in #12085	%M/M	15	0.010	0.041	0.005

Table 3: performance overview for samples #12084 and #12085

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the target reproducibility.

4.2 EVALUATION PER SAMPLE

In this section the results are discussed per sample.

#12084: Severe analytical problems were observed at the relatively high concentration level of 0.1 - 0.2 %M/M PFOA in the evaluated material. Three statistical outliers were detected. The calculated reproducibility, after rejection of the statistical outliers, is not at all in agreement with the target requirement estimated from the Horwitz equation.

#12085: Severe analytical problems were observed at the low concentration level of 0.01-0.05 %M/M PFOS in the evaluated material. One statistical outlier was detected. The calculated reproducibility, after rejection of the statistical outlier, is not at all in agreement with the target requirement estimated from the Horwitz equation.

4.3 EVALUATION OF THE TEST METHODS USED

Most participants reported to have used an 'in house' test method. It is remarkable that only three participants reported to have used the CEN/TS 15968 method. Three other participants reported to have use THF or a THF/methanol mixture to extract the PFOA/PFOS from the plastic matrix. The test results of these three laboratories were all relatively high and close to the actual amount of PFOA/PFOS added to the plastics, thus resulting in relatively high recoveries.
The reported details of the methods that were used by the participants are listed in appendix 2.

5 CONCLUSIONS

The final assigned value of 0.136 %M/M PFOA for sample #12084, even after removal of 3 test results, may still be rather low. The theoretical value, derived from the PFOA amount used during the preparation is 0.2%, which means that only 68% may have been recovered on average.

The final assigned value of 0.0104 %M/M PFOS for sample #12085 may be very low and close to the lower detection limit of the test methods used. The theoretical value, derived from the PFOS amount used during the preparation is 0.06%, which means that only 17% may have been recovered on average.

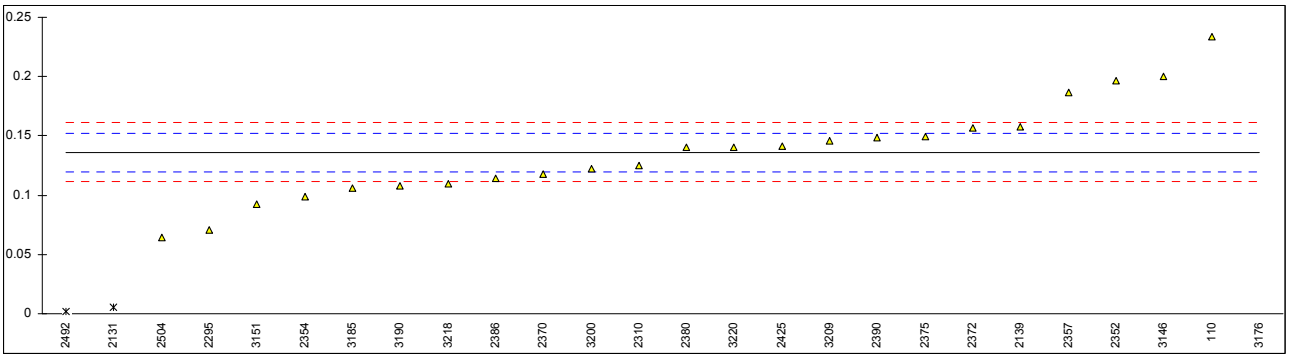
This is not unexpected as also during the preparation of the samples and the subsequent testing for suitability it was found that indeed some extra efforts may be needed to increase the recovery of PFOA and PFOS from the matrix upto an acceptable level.

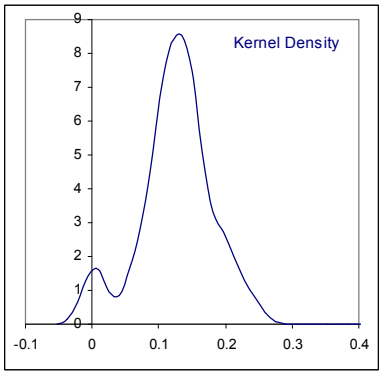
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of PFOA on sample #12084; results in %M/M

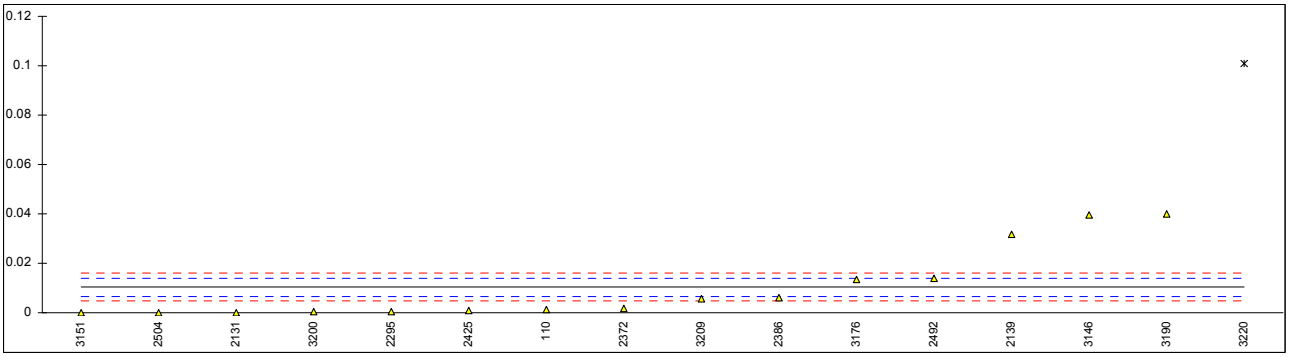
lab	method	value	mark	z'(targ)	remarks
110	INH-059	0.2341		11.84	
2115		-----		-----	
2129		-----		-----	
2131	in house	0.00514	DG(0.05)	-15.77	
2139	in house	0.1577		2.63	with other standard 0.12%M/M was calculated
2295	in house	0.0703	C	-7.91	first reported 0.043947
2310	in house	0.125		-1.32	
2352	EPA3540C/8321B	0.197		7.36	
2354	in house	0.099182		-4.43	
2357	EPA3550C/3540C	0.187		6.16	
2370	INH-219	0.118		-2.16	
2372	EPA3540C	0.1568		2.52	
2375	INH-219	0.1499		1.69	
2380	INH-122	0.14		0.49	
2386	DIN38414	0.114		-2.64	reported also the presence of a trace of PFOS
2390	in house	0.148686		1.54	
2425	in house	0.1410	C	0.61	first reported 0.2937
2492	in house	0.0018944	DG(0.05)	-16.16	
2504	in house	0.064	C	-8.67	first reported 0.0405
3146	in house	0.2004		7.77	
3151	CEN-TS15968	0.0923		-5.26	
3176		3.88	C,G(0.01)	451.44	first reported 6.93
3185	CEN-TS15968	0.1062		-3.58	
3190	in house	0.108		-3.37	
3200	EPA3550C/8321B	0.1220		-1.68	
3209	in house	0.1455		1.15	
3218	CEN-TS15968	0.1092		-3.22	
3220	in house	0.140		0.49	
	normality	OK			
	n	23			
	outliers	3			
	mean (n)	0.136	added 0.20%; recovery approx. 68%		
	st.dev. (n)	0.0414			
	R(calc.)	0.116			
	R(Horwitz)	0.021			
	U(mean)	0.011			
	R(Horwitz')	0.023			

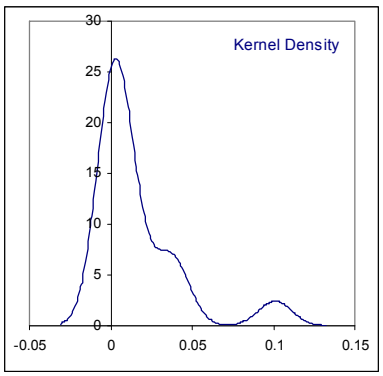




Determination of PFOS on sample #12085; results in %M/M

lab	method	value	mark	z'(targ)	remarks
110	INH-059	0.00142		-4.76	
2115		-----		-----	
2129		-----		-----	
2131	in house	0.0000126		-5.51	normally would have reported <0.1µg/cm2 (= legal requirement)
2139	in house	0.0316		11.33	
2295	in house	0.0004969		-5.25	
2310	in house	n.d		-----	
2352	EPA3540C/8321B	<0.001		<-4.99	false negative?
2354	in house	n.d		-----	
2357	EPA3550C/3540C	n.d		-----	
2370	INH-219	n.d		-----	
2372	EPA3540C	0.00163		-4.65	
2375	INH-219	<0.0002		<-5.41	false negative?
2380	INH-122	n.d		-----	
2386	DIN38414	0.00617		-2.23	reported also the presence of a trace of PFOA
2390	in house	n.d		-----	
2425	in house	0.000899		-5.04	
2492	in house	0.013784		1.83	
2504	in house	0.000122		-5.45	
3146	in house	0.0394		15.49	
3151	CEN-TS15968	0.0000523		-5.49	
3176		0.0134		1.63	reported also 0.0029%M/M PFOA
3185	CEN-TS15968	<0.0005		<-5.25	false negative?
3190	in house	0.040		15.81	
3200	EPA3550C/8321B	0.0003		-5.36	
3209	in house	0.005866		-2.39	
3218	CEN-TS15968	<0.0005		<-5.25	false negative?
3220	in house	0.101	G(0.01)	48.33	
	normality	not OK			
	n	15			
	outliers	1			
	mean (n)	0.0104	added 0.06%; recovery approx. 17%		
	st.dev. (n)	0.01462			
	R(calc.)	0.0409			
	R(Horwitz)	0.0023			
	U(mean)	0.0046			
	R(Horwitz')	0.0053			





APPENDIX 2

Analytical details for samples #12084 and #12085

Lab	Extraction method	Solvent(s) used	Detection	Corr	Other
110	Soxhlet extraction	dichloromethane/methanol	LC/MS	NO	
2115					
2129					
2131	ultrasonic extraction	methanol	LC/MS/MS	NO	
2139	ultrasonic extraction	THF/methanol	LC/MS/MS	NO	see note 1
2295	ultrasonic extraction	methanol	LC/MS/MS	YES	
2310	solvent extraction	dichloromethane/methanol	LC/MS/MS	NO	
2352	Soxhlet extraction	dichloromethane/methanol	HPLC-MSD	NO	
2354	Soxhlet extraction	dichloromethane/methanol	LC/MS/MS	NO	
2357	Soxhlet extraction	dichloromethane/methanol	LC/MS	NO	
2370	InHouse-219-3	dichloromethane/methanol	LC/MS/MS	YES	
2372	Soxhlet extraction	dichloromethane/methanol	LC/MS	NO	
2375	Soxhlet extraction	dichloromethane/methanol	LC/MS	NO	
2380	Soxhlet extraction	dichloromethane/methanol	HPLC/MS	YES	
2386	ultrasonic bath 60°C , 60 min	methanol	LC/MS/MS	NO	SPE clean-up
2390	Soxhlet extraction	dichloromethane/methanol	LC/MS	NO	
2425	Soxhlet extraction	dichloromethane/methanol	UPLC-DA-MS/MS	NO	
2492	ultrasonic extraction	methanol	LC/MS/MS	NO	
2504	solvent extraction	methanol	HPLC-MSD	NO	
3146	ultrasonic extraction	THF	LC/MS	NO	#12084 only, see note 2
3151	ultrasonic extraction	Methanol	LC-MS/Q-TOF	NO	
3176					
3185	ultrasonic extraction	methanol	HPLC/MS/MS	NO	
3190	ultrasonic extraction	THF	LC/MS/MS	NO	
3200	ultrasonic extraction	methanol	UPLC/MS/MS	NO	
3209	ultrasonic extraction	methanol	UPLC/MS/MS	NO	
3218	ultrasonic extraction	methanol	LC/MS/MS	NO	
3220	extraction	methanol	LC/MS	NO	

Note 1: laboratory 2139 encountered problem with the purchased standard

Note 2: laboratory 3146 used for sample #12085 different conditions:

3146	reflux condenser	chlorobenzene	LC/MS	NO	#12085 only

APPENDIX 3

Number of participating laboratories per country

2 labs in BANGLADESH

4 labs in GERMANY

2 labs in HONG KONG

2 labs in INDIA

1 lab in ITALY

1 lab in KOREA

7 labs in P.R. of CHINA

1 lab in PAKISTAN

1 lab in SWITZERLAND

2 labs in TAIWAN R.O.C.

1 lab in THAILAND

3 labs in TURKEY

1 lab in U.S.A.

APPENDIX 4

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
n.a. = not applicable
n.d. = not detected

Literature:

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