

## THE INTER-LABORATORY TRIAL OF PFOS AND PFOA MEASUREMENTS IN WATER SAMPLES (ISO/TC14/SC2/WG56)

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### Abstract

Perfluorinated compounds, in particular, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) have emerged as global environmental contaminants. Because of the occurrence of perfluorinated acids in waters worldwide, including drinking water, a sensitive and reliable method to determine their concentrations is needed. An inter-laboratory study was initiated to investigate consistency in reported concentrations of PFOS and PFOA in various water matrices including sea water, wastewater, river water and fortified water samples. This inter-laboratory comparison study was tied with the International Organization for Standardization's (ISO) draft international standard document (ISO/CD25101) that was voted in favor of development of standard analytical method for PFOS and PFOA in water. This international inter-laboratory exercise was organized by inviting experts from all over the world to participate in this exercise. Thirty laboratories were registered for participation and 23 of the laboratories provided the final results. Samples of seawater, river water, industrial wastewater, spiked water matrices and standard solutions were prepared and distributed to the registered participants. A published analytical method, as a guidance document, and native and labeled standards were provided to all participants. The method supplied along with the samples provided a guidance document containing important steps to consider while sample preparation and quantification of concentrations. Twenty three laboratories from 10 countries successfully completed the analysis. With the exception of a few outliers, the coefficient of variation in reported concentrations among the laboratories was <30%. Determination of PFOS and PFOA in water samples, when provided with a standard protocol/analytical method documenting appropriate QA/QC protocol, has resulted in improved accuracy and precision.

### Introduction

The first international activity to establish International Organization for Standardization (ISO) method for PFOS and PFOA in water samples, initiated in May 2005, was approved by the committee to develop a new working draft based on a previous method (blank free solid phase extraction method with HPLC tandem mass spectrometry developed by AIST<sup>1,2</sup>). The committee members represented twelve countries (Australia, Austria, Finland, France, Germany, The Netherlands, Russian Federation, Spain, Sweden, Switzerland, Turkey and United Kingdom) and the vote was positive result. The committee draft was submitted for balloting in November 2006 and the draft was accepted as an Draft International Standard (DIS) in February 2007. The inter-laboratory study for DIS was announced in November 2006. The study period was from November 2006 to February 2007, and an evaluation report was scheduled to be distributed in April 2007. The final report will be available after the next ISO meeting in Canada, during the spring of 2008. The result of this trial will be used as a basis for developing the ISO method, which is planned to be established in early 2009. Here we present the preliminary results of the inter-laboratory comparison trial of PFOS and PFOA in water samples.

### Materials and Methods

An announcement about the inter-laboratory comparison trial was sent out in November 2006 and thirty laboratories registered to participate in this exercise. However, only twenty three laboratories from 10 countries successfully completed the analysis and this include Australia: 1; Belgium: 1; Canada: 2; England: 1; Germany: 7; Italy: 1; Japan: 2; Switzerland 1; United Kingdom: 1; United States of America: 6. PFOS and PFOA were analyzed in seawater, river water, spiked river water, two levels of spiked Milli-Q water, waste water and standard solution in methanol. The test samples were as follows:

Sample 1; three bottles of sea water (each 500ml)

Sample 2; three bottles of river water (each 500ml)

Sample 3; three bottles of river water with standard spike (each 500ml)

Sample 4; three bottles of Milli-Q water with standard spike (low conc. 0.5 to 10ng/L, each 500ml)

Sample 5; three bottles of Milli-Q water with standard spike (high conc. 10 to 200ng/L, each 500ml)

Sample 6; one bottle of waste water (5,000 to 150,000ng/L, 100ml)

Sample 7; standard solution of PFOS and PFOA in methanol (0.2ml in ampoule)

Mass-labelled internal standards (Wellington Laboratories, Guelph, Canada) were provided to the participants.; these include perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanoic acid (50 µg/ml in methanol, 0.2ml) and Sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate (50 µg/ml in methanol, 0.2ml)

Participating laboratories were requested to determine the levels of PFOS and PFOA in the water samples. All determinations were required to be done in triplicate. Laboratories were requested to follow a unified analytical method, as described in the draft ISO document<sup>3</sup>. The draft ISO document was provided as a guide and this document included step by step details of analytical methods. Methods developed in individual laboratories were also accepted. A brief description of the ISO draft method is given as follows. A complete documentation of instructions, analytical methods, detailed operating procedures to enable high accuracy and precision in the analysis and professional support during analysis were provided by AIST staff to participants after registration.

1. Extraction by SPE, Oasis®WAX, Oasis®HLB, SepPak®tC18 (Waters) or comparable SPE method.
2. HPLC-MS/MS quantification by following parameters; HPLC column, Betasil C18 (Thermo Hypersil-Keystone), Ace 3 C18 (Advanced Chromatography Technologies) or comparable HPLC column.
3. Quantification by ISTD method using <sup>13</sup>C-labeled surrogates. Participants were allowed to report both external standard and internal standard based results.

This International Standard specifies a method for the determination of the linear isomers of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in unfiltered samples of drinking water, ground water and surface water (fresh water and sea water) using high performance liquid chromatography-tandem mass spectrometry (HPLC MS/MS). Other isomers may be reported separately as non-linear isomers and qualified as such. The method is applicable for a concentration range of 0.002 µg/l to 10 µg/l for PFOS and 0.02 µg/l to 10 µg/l for PFOA. Depending on the matrix, the method is also applicable to higher concentrations ranging from 0.1 µg/l to 200 µg/l after suitable dilution of the sample extracts or with small sample volume for extraction. PFOS and PFOA were the major target compounds for this trial but the method could be validated for twenty one related chemicals. Organizers of this trial plan to provide all the information in the final report.

### Results and Discussion

Results of PFOS and PFOA reported by all participating laboratories in sample 1 (seawater), sample 4 (native standard spiked Milli-Q water) and sample 7 (standard) are shown in Table 1 and Figure 1. Only those laboratories which provided internal standard recoveries were selected for this report, and the results that reported less than 50% for internal standard recoveries were rejected from data analysis. Reported value by AIST were highlighted in blue. Accuracy of the current values as represented by Coefficient of Variation (23% for PFOS, 27% for PFOA) were smaller than that reported during another calibration study (95% for PFOS, 118% for PFOA) conducted in 2005<sup>4</sup>. This improvement is considerable, particularly when considering the fact that the concentration of target chemicals in the test sample in our exercise was 10,000 times lower than the earlier study. Although the aims of inter-calibration study and round robin test are different, it can be mentioned that determination of PFOS and PFOA in water samples, when provided with a standard protocol documenting appropriate QA/QC protocol, improved the accuracy and prevision. Further information from this trial will be provided at the ISO meeting (TC147/SC2) in 2008.

# Use of trade names does not mean endorsement of the product, but for illustrative purpose only.

## References

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Table 1. Performance data for the seawater (sample 1)

Parameter	<i>l</i>	<i>n</i>	<i>n</i> <sub>AP</sub> %	$\bar{X}$ ng/l	$\eta$ %	<i>s</i> ng/l	<i>CV</i> %
PFOS (ISTD)	13	35	31,4	41,4		9,31	22,5
PFOS (ESTD)	11	33	29,8	38,2		12,1	31,6
<sup>13</sup> C <sub>4</sub> -PFOS	13	33	32,7		84,2	0,16	18,8
PFOA (ISTD)	12	36	20,0	11,1		3,04	27,3
PFOA (ESTD)	12	36	14,3	10,5		3,10	29,5
<sup>13</sup> C <sub>4</sub> -PFOA	13	36	21,7		99,2	0,17	17,1
<i>l</i>	is number of laboratories after outlier rejection;						
<i>n</i>	is number of analytical result after outlier rejection;						
<i>n</i> <sub>AP</sub>	is number of outliers;						
$\bar{X}$	is mean of results (without outliers) ;						
$\eta$	is mean of internal standard recovery;						
<i>s</i>	is standard deviation;						
<i>CV</i>	is coefficient valuation;						
ISTD	is valued by internal standard method;						
ESTD	is valued by external standard method.						

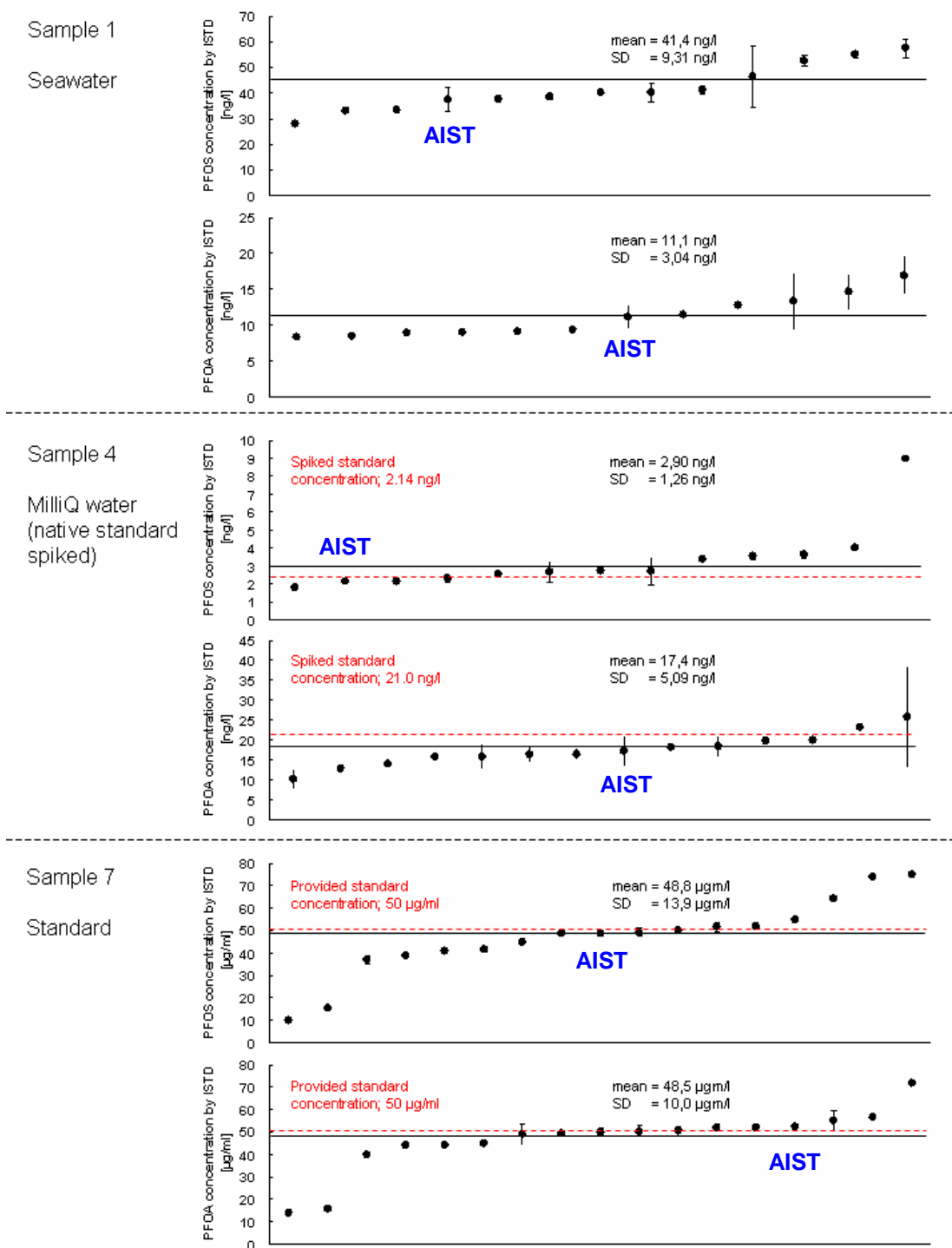


Figure 1. Graphical presentation of the results of the inter-laboratory trial of PFOS and PFOA in water: seawater, native standard spiked Milli-Q water and standard solution.