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Significant improvements in the analysis of perfluorinated compounds in water and fish: Results from an interlaboratory method evaluation study

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ABSTRACT

The 2nd international interlaboratory study (ILS) on perfluorinated compounds (PFCs) in environmental samples was organized to assess the performance of 21 North American and European laboratories on the analysis of PFCs in water and fish. A study protocol was provided to assess accuracy, precision, matrix effects and to study the use of in-house standards. The participants used shared native and mass-labelled standards that were provided for this study to quantify the PFC concentrations in the samples. Matrix effects in the determination of PFCs can be considerable and can decrease the sensitivity, the accuracy and internal standard recoveries. Therefore, two quantification methods were evaluated by all laboratories: standard addition quantification (SAQ) and solvent-based calibration curve quantification (SBCCQ; using mass-labelled internal standards (IS)). The between laboratory reproducibility (i.e. coefficient of variance) was smaller for the SBCCQ results (except for PFBS and PFHxS for which no mass-labelled analogues were available) compared to those obtained by the SAQ method. The within laboratory precision of individual laboratories is good (mean for all PFCs in water 12% and 6.8% in fish). The good performance is partially attributable to the use of well-defined native- and mass-labelled standards. Therefore, the SBCCQ method is recommended. The results show that analytical methods for PFCs in water and fish have improved considerably. Critical steps identified in this study are (i) the use of well-defined native standards for quantification, (ii) the use of mass-labelled internal standards (preferably one for each target compound) and (iii) minimization of matrix effects by a better clean up.

1. Introduction

Perfluorinated compounds (PFCs) are omnipresent in the environment [1–3]. To study the distribution of these chemicals in the environment and to assess the environmental and human exposure, many laboratories have developed methods for analysis of PFCs in environmental matrices. For several years, the quality of data obtained was a major issue of concern [4]. Identified problems in the quantification were the limited availability of high quality standards and mass-labelled standards, severe matrix effects and interferences, the occurrence of branched isomers and blank problems due to contamination from labware and instrumentation. This was reflected in the 1st interlaboratory study (ILS) conducted in 2004/2005 and organized within the framework of the European Perforce project (http://www.science.uva.nl/PERFORCE/index.htm). The between laboratory coefficients of variation for environmental samples amounted to 95% for perfluorooctane sulfonate (PFOS) in water and 125% for PFOS in a fish sample [5]. This illustrated that improvement of method performance was required in order to obtain reliable analytical results.

Meanwhile, a larger number of high quality standards has become commercially available, and the list of these standards continues to expand. Furthermore, a wide range of mass-labelled standards is available for use as internal standards. Earlier on, many laboratories used ion-pair extraction (IPE) for biota often leading to inaccurate results. Nowadays, more diverse extraction, cleanup and quantification approaches exist [6,7] with good performance characteristics. Yamashita et al. reported on a method evaluation study of PFOS and perfluorooctanoic acid (PFOA) in water (performed in the framework of an ISO technical working group) [8]. Good performance (23–32% RSDs for PFOS and 27–30% RSDs for PFOA) in seawater was reported, but this study limited to PFOS and PFOA. The present study was initiated and aimed at evaluation of the following analytical aspects:

(i) Analysis of 11 perfluoroalkyl carboxylates, 4 perfluoroalkyl sulfonates and perfluorinated sulfonamide (PFOSA).

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(ii) Comparison of results obtained by standard addition quantification (SAQ) and solvent-based calibration curve quantification (SBCCQ).
(iii) Determination of the precision of individual laboratories.
(iv) Determination of the influence of in-house standards on the quantification.
(v) Quantification of the matrix effect.

This work was performed on a fish sample and a freshwater sample.

2. Experimental

The PFCs included in this study were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA), perfluorotetradecanoic acid (PFTeA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, perfluorodecane sulfonate (PFDS) and PFOSA.

2.1. Design of the study

This study was designed to evaluate the performance of the current state-of-the art methods in terms of quantification principles, use of standards, accuracy, precision and matrix effects. The participants were invited to a 2-day workshop to stimulate exchange of expertise and receive instructions on how to conduct the experiments according to the exercise protocol. At this workshop, specialists from industries and research institutes presented their technical insights in the extraction, cleanup and analysis of PFCs in water and biota. From these discussions, the following critical factors were identified: the use of well-characterized native and mass-labelled standards, different responses of branched and linear compounds, control of method and instrumental blanks and the occurrence and influence of matrix effects. Based on these discussions, a study was designed that is shown in Table 1. A protocol was developed to provide guidance to the participants for performing the study. It included suggestions on how to improve the critical analytical aspects to obtain proper data on accuracy and precision, while avoiding, e.g. blank problems.

This design enabled the determination of performance characteristics of the two quantification methods used. SBCCQ was chosen as this is a commonly applied (routine) method in most laboratories, whereas SAQ is very suitable for unknown matrices (and matrix effects) as it intrinsically takes matrix effects into account. The SAQ method was derived from general guidelines on method validation [9,10]. Furthermore, the design of the study enabled the determination of factors contributing to method accuracy and precision (e.g. use of in-house standards and matrix interferences).

Table 1
Study design. In-house methods and instruments were used for all experiments.

Study aspect	Experimental execution
Variance due to in-house standard	Quantification of a 50-ng/mL in-house standard against the shared standard (50 ng/mL). No mass-labelled standards.
Accuracy by two different quantification methods: SBCCQ and SAQ[a]	SBCCQ: analysis of the sample using shared native and mass-labelled standards.
	SAQ: analysis of the sample by standard addition of 1, 2 and 4 times the PFC levels already present in the sample. No mass-labelled standards are used.
Precision	Triplicate analysis of the sample by SBCCQ using shared native and mass-labelled standards.
Matrix interferences in ESI–MS(/MS)	Preparation of an extract and fortification by 50 ng/mL of the shared standard. Net peak areas compared to a 50-ng/mL standard. No mass-labelled standards are used.

[a] SBCCQ: solvent-based calibration curve quantification; SAQ: standard addition quantification.

Table 2
PFCs spiked to the fish and water sample. Concentrations refer to the spiked amount.

	Fish (ng/g)	Water (ng/L)
PFBA	N.a.	25
PFPeA	N.a.	5.0
PFHxA	N.a.	5.0
PFHpA	N.a.	5.0
PFOA	22.6	25
PFNA	17.2	5.0
PFDA	21.9	5.0
PFUnA	17.8	5.0
PFDoA	20.1	5.0
PFBS	N.a.	17.7
PFHxS	N.a.	9.5
PFOS	145	23.2
PFOSA	3.2	5

2.2. Study material preparation

2.2.1. Water sample

The water sample was taken in April 2007 from the North Sea Canal (which connects Amsterdam with the North Sea) close to the Assendelft-Spaarndam ferry (The Netherlands). The water here is mainly freshwater, with a slightly elevated salinity due to the inflow of seawater from the IJmuiden locks. Five 30 L high-density polyethylene (HDPE) containers were filled with water and after transport to the laboratory they were stored at 4 °C. Residuals were allowed to settle and after 1 week, the water was slowly decanted in a large 150 L container while filtering over three stainless steel sieves with (top to bottom) 1.0, 0.53 and 0.22 μm pore sizes for removal of residual particles. The large container containing approximately 150 L of water sample was kept at 4 °C under continuous mixing using a stainless steel stirring device. All materials that came in contact with the water were rinsed three times with ultra pure methanol (JT-Baker, HPLC Analyzed) prior to use. The container and 30 L containers were all tested for blank contributions. The water sample was characterized by Omegam Laboratories (Amsterdam, The Netherlands) and the results show a typical freshwater composition (pH 6.4, conductivity 1529 mS/m, calcium 160 mg/L, magnesium 320 mg/L, dissolved organic carbon 14 mg C/L, total organic carbon 14 mg C/L and hardness 35 mequiv./L). A preliminary PFC analysis was carried out, and based on the low PFCs concentrations detected (<1 for PFNA to 20 ng/L for PFBA), it was decided to spike the water sample with relevant PFCs mentioned in Table 2. This was done so as to facilitate the detection of the target compounds by all laboratories. A stock solution of the target PFCs was made in methanol. This solution was added slowly (under continuous mixing) to the large water container containing 150 L water sample. The sample was homogenized for 48 h. Subsequently, 500 mL HDPE bottles were filled under continuous homogenization of the bulk sample. The bottles were stored at 4 °C until transportation.