

New Proposal of International Standard of Poly and Per-Fluorinated Alkyl Substances (PFASs) Measurements in Water Samples

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Introduction

Poly and per-fluorinated alkyl substances (PFASs), in particular, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are emerging global environmental contaminants. PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) were listed as restricted use chemicals (Annex B) under the Stockholm Convention. There is also growing interest in PFASs other than PFOS and PFOA because of increasing use of substitutes in place of PFOS/PFOA. Some of PFASs such as PFOA, perfluorononanoic acid (PFNA), Perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA) were listed as candidates under the Registration, Evaluation, Authorization and restriction of Chemicals (REACH). Not only PFOS but also PFOA salts and PFOA-related compounds were proposed for listing under the Stockholm Convention in 2015.

There is a lack of international standard method for the analysis of PFASs, except for PFOS and PFOA as ISO 25101:2009¹. Therefore a workable and internationally standardized method for analysis of PFASs in water is needed. There are some national and domestic standards for analytical methods for PFASs in water¹⁻⁴.

As a part of standardization and accreditation of laboratories involved in the analysis of PFASs, inter-laboratory study (ILS) trials were conducted^{5,6}. We successfully obtained several useful information about quality assurance and quality control (QA/QC) to enable accurate measurement of PFASs in water samples. The knowledge was shared with the ISO experts at the ad hoc meeting in Conshohocken, Philadelphia, USA in 2015. Fourteen experts from seven countries agreed to apply for a new proposal to establish more comprehensive international standard method for PFASs (Table 1) in water samples than ISO 25101 which only analyses for PFOS and PFOA. A new work item proposal (NWIP) on PFASs in water was submitted from Japan to the ISO/TC 147 (Water Quality) in March 2016. The NWIP was approved by fifteen countries in July 2016. The working draft (WD) was discussed at ISO/TC 147 meeting in September 2016. The committee draft (CD) was submitted in March 2017⁷, after revised WD.

In this report, several QA/QC protocols to enable accurate measure of PFASs in water samples, have been described with some recommendations for improving accuracy and precision from recent knowledge. Some recent developments to enable accurate measurement of PFASs in water samples is discussed and useful information to join to incoming round robin test of new analytical method by ISO/TC 147/SC 2/WG 74 "PFAS LC-MS/MS".

Table 1 — Analytes determinable by proposed new ISO standard for PFASs in water samples.

Analyte	Formula	Abbreviation	CAS-RN
Perfluoro-n-butanesulfonic acid	C ₄ HF ₉ O ₃ S	PFBS	375-73-5
Perfluoro-n-hexanesulfonic acid	C ₆ HF ₁₃ O ₃ S	PFHxS	335-46-4
Perfluoro-n-heptanesulfonic acid	C ₇ HF ₁₅ O ₃ S	PFHpS	375-92-8
Perfluoro-n-octanesulfonic acid	C ₈ HF ₁₇ O ₃ S	PFOS	1763-23-1
Perfluoro-n-decanesulfonic acid	C ₁₀ HF ₂₁ O ₃ S	PFDS	335-77-3
Perfluorooctanesulfonamide	C ₈ H ₂ F ₁₇ NO ₂ S	FOSA	754-91-6
N-methyl perfluorooctanesulfonamide	C ₉ H ₄ F ₁₇ NO ₂ S	N-MeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	C ₁₀ H ₆ F ₁₇ NO ₂ S	N-EtFOSA	4151-50-2
N-methyl perfluorooctanesulfonamidoacetic acid	C ₁₁ H ₆ F ₁₇ NO ₄ S	N-MeFOSAA	not available
N-ethyl perfluorooctanesulfonamidoacetic acid	C ₁₂ H ₈ F ₁₇ NO ₄ S	N-EtFOSAA	1336-61-4
Perfluoro-n-butanoic acid	C ₄ HF ₇ O ₂	PFBA	375-22-4
Perfluoro-n-pentanoic acid	C ₅ HF ₉ O ₂	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	C ₆ HF ₁₁ O ₂	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	C ₇ HF ₁₃ O ₂	PFHpA	375-85-9
Perfluoro-n-octanoic acid	C ₈ HF ₁₅ O ₂	PFOA	335-67-1
Perfluoro-n-nonanoic acid	C ₉ HF ₁₇ O ₂	PFNA	375-95-1
Perfluoro-n-decanoic acid	C ₁₀ HF ₁₉ O ₂	PFDA	335-76-2
Perfluoro-n-undecanoic acid	C ₁₁ HF ₂₁ O ₂	PFUnDA	2058-94-8
Perfluoro-n-dodecanoic acid	C ₁₂ HF ₂₃ O ₂	PFDoDA	307-55-1
Perfluoro-n-tridecanoic acid	C ₁₃ HF ₂₅ O ₂	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	C ₁₄ HF ₂₇ O ₂	PFTeDA	376-06-7
Perfluoro-n-hexadecanoic acid	C ₁₆ HF ₃₁ O ₂	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid	C ₁₈ HF ₃₅ O ₂	PFOcDA	16517-11-6
8:2 Fluorotelomer alcohol	C ₁₀ H ₅ F ₁₇ O	8:2 FTOH	678-39-7
8:2 Fluorotelomer unsaturated carboxylic acid	C ₁₀ H ₂ F ₁₆ O ₂	8:2 FTUCA	not available
8:2 Polyfluoroalkyl phosphate ester	C ₁₀ H ₆ F ₁₇ O ₄ P	8:2 PAP	57678-03-2
8:2 Polyfluoroalkyl phosphate diester	C ₂₀ H ₉ F ₃₄ O ₄ P	8:2 diPAP	678-41-1

Materials and Methods

Three ILS (ISO-2006, JIS-2008 and JIS-2009) using standard operation procedure (SOP)-were carried out during 2006 to 2010.

The ISO-2006 trial was focused on PFOS and PFOA analysis whereas JIS trials included the analysis of a variety of PFASs. Although the results of a suite of PFASs were available, the major emphasis of this article was on the analysis of PFOS and PFOA in water, because PFOS and PFOA were the main target compounds of the ISO and JIS trials.

- **ISO -2006 trial:** The ILS was conducted from November 2006 to February. The participants were required to use the draft of ISO 25101 as the SOP. The analyses were performed in river water, seawater, Milli-Q water containing low-concentration of the standard substance, Milli-Q water containing high-concentration of the standard substance, and the standard substance.

Mass-labeled internal standards of PFOS and PFOA were provided from Wellington Laboratories

- **JIS -2008 trial:** The ILS was conducted from March to July 2008, studies were conducted for tap water, seawater, river water, Milli-Q water containing low-concentration of the standard substance, Milli-Q water containing high-concentration of the standard substance, and the standard substance, using the same analysis method as ISO 25101. Participating laboratories were requested to quantify the concentrations of PFOS and PFOA in the water samples. Other PFASs, C₅ to C₁₂ PFCAs, C₄, C₆, C₁₀ PFASs were encouraged to be reported, if possible. Standard solutions were provided from Wellington Laboratories, Wako Pure Chemicals Industries and CIL

- **JIS -2009 trial:** The ILS conducted from September 2009 to January 2010, the industrial water, plant wastewater and Milli-Q water containing concentration of the standard substance were used as the main subjects of measurement for the JIS standardization which was modified from ISO 25101. Standard solutions were provided from Wellington Laboratories. Other PFASs, C₄ to C₁₄, C₁₆, C₁₈ PFCAs, C₄, C₆, C₇, C₁₀ PFASs were encouraged to be reported, if possible.

Results and Discussion

CV_R (reproducibility coefficient of variation) values for PFOS and PFOA were less than 30% (ISO criteria) for the most of samples on the three ILSs. Three ILS trials were successful and distributed SOPs were adequate to establish ISO and JIS methods. There are several criteria required to obtain reliable data, as following;

- Procedural blank < Sample concentrations / 10
- 70% < Procedural recovery < 125%
- CV_r (repeatability of coefficient variation) < 30%
- Select and use corresponding labelled internal standard for native compound i.e.) PFOA with ¹³C-PFOA not ¹³C-PFHxA
- Relative ion ratio between standard and real sample < 25%

Until now, some commercially available weak anion exchange (WAX) solid phase extraction cartridges (e.g. Oasis®WAX (150 mg, 30 µm, Waters Co.) showed acceptable recovery for most PFASs tested. However, several limitations to the use of commercially available WAX for open-ocean water were noted. Specially customized SPE cartridge was manufactured and validated for open ocean seawater samples. This brand new SPE cartridge, namely “WAXsea” with 500 mg of adsorbent and 30 µm of pore size was optimized for this purpose. “WAXsea” was validated using 1 L of open-ocean seawater collected from the Pacific Ocean and successfully detected PFOS and PFOA at 0.05 pg/L and 0.1 pg/L, respectively⁸. It is worth to list “WAXsea” as the example of SPE cartridge in the new ISO method to analyze trace levels of PFAS in open-ocean seawater.

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Announcement of incoming round robin test by ISO/TC 147/SC 2/WG 74 "PFAS LC-MS/MS" will be circulated to all member of SC2 in this year. Please contact to (s-taniyaus@aist.go.jp) for more information about ISO activity on PFASs.

References

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