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## THE NEXT STAGE OF INTERNATIONAL STANDARDIZATION OF PFAS 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 considered as emerging global environmental contaminants. PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) are 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) are listed in the candidate list 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. Therefore a workable and internationally standardized method for analysis of PFASs in water is needed. There are some national and domestic standard for analytical methods for PFASs in water<sup>1-4</sup> (Table 1).

As a part of standardization and accreditation of laboratories involved in the analysis of PFASs, inter-laboratory study (ILS) trials were conducted in Japan and published<sup>5,6</sup>. 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 new proposal to establish more comprehensive international standard methods for PFASs in water samples after the ISO 25101.

In this report, the results of three ILS trials, that involved the use of a standard method with appropriate QA/QC protocols, for the measurement of PFASs in water samples, have been described with some recommendations for improving accuracy and precision in the analysis of PFASs in water samples. Additionally, some recent developments to enable accurate measurement of PFASs in water samples is discussed as the next stage for the international standard method after ISO 25101.

### 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 ISL 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%
- CVr (repeatability of coefficient variation) < 30%
- Select and use corresponding labelled internal standard for native compound i.e.) PFOA with  $^{13}C$ -PFOA not  $^{13}C$ -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  $\mu$ m, Waters Co.) showed acceptable recovery for most PFASs tested (Figure 1). 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  $\mu$ m 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, respectively<sup>7</sup>. 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.

### Acknowledgement

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### References

1. ISO 25101:2009.
2. EPA Method 537: 2009.
3. DIN 38407-42:2011-03.
4. JIS K 0450-70-10:2011.
5. Taniyasu S et al., *Anal Chim Acta.*, 2013, 111-120.
6. Taniyasu S et al., *Synthesiology*, 2012, 261-276.
7. Yamazaki E et al., *Bunseki Kagaku*, 2015, 759-768.

Table 1 Comparison of standard method on perfluorinated alkyl substances (PFASs)

	ISO 25101:2009 <sup>1</sup>	EPA METHOD 537 Version 1.1 September 2009 <sup>2</sup>	DIN 38407-42:2011 <sup>3</sup> (ISO/WD PFC-HPLC/MS- MS)	JIS K 0450-70-10: 2011 <sup>4</sup>
<b>Title</b>	Water quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – Method for unfiltered water samples using solid phase extraction and liquid chromatography with mass spectrometry	Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS)	Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction	Testing methods for perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in industrial water and wastewater
<b>Target matrices</b>	drinking water, ground water and surface water (fresh water and sea water)	drinking water (Accuracy and precision data have been generated in reagent water, and finished ground and surface waters)	drinking water, ground water, surface water, treated waste water	industrial water and wastewater (drinking water, ground water and surface water (fresh water and sea water) as Annex: informative)
<b>Target compounds</b>	PFOS, PFOA	PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, NtEFOsAA, NMeFOsAA	PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA	PFOS, PFOA (PFBS, PFHxS, PFHpS, PFDS, FOSA, PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA as Annex: informative)
<b>Quantification</b>	Internal standard method (ISTD)	Internal standard method (ISTD)	Internal standard method (ISTD) External standard method (ESTD)	Internal standard method (ISTD) (External standard method (ESTD) as Annex)

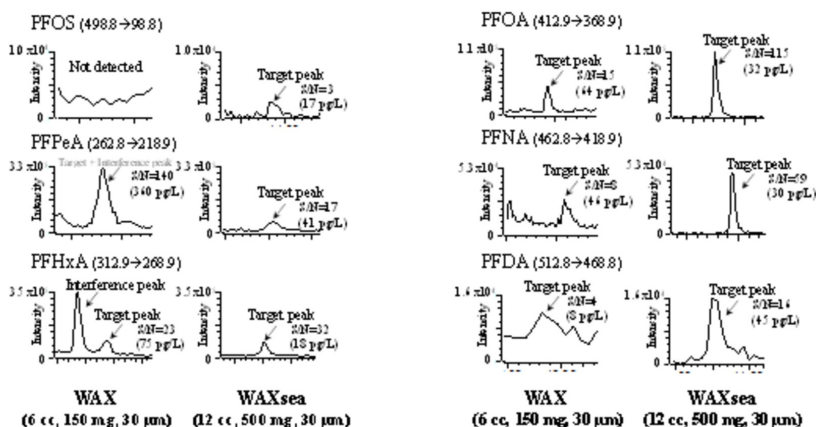


Figure 1. PFASs chromatograms of seawater samples collected from the Pacific Ocean those were extracted by WAX(150 mg, 30 μm) and WAXSea (500 mg, 30 μm)<sup>7</sup>