Interlaboratory trial for validation of ISO 21675 for per- and polyfluoroalkyl substances (PFAS) in water

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Introduction

Per- and polyfluoroalkyl substances (PFAS) have been widely used in numerous industrial and commercial applications since the 1950s. The most common PFAS are perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) which have been detected in the environment, wildlife, and humans. PFOS and its salt have been restricted under the Stockholm Convention since 2011, with only a few allowed remaining uses.

There is growing interest in PFAS other than PFOS and PFOA. In fact, additional PFAS are listed in the Candidate List as Substances of Very High Concern (SVHCs) under the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) at the European Chemicals Agency (ECHA), such as perfluorononanoic acid (PFNA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA). In addition to PFOS, PFOA salts, PFOA-related compounds, PFHxS salts, and PFHxS-related compounds were proposed for listing under the Stockholm Convention. There is currently no standard international analytical method for PFAS determination, although an analytical method for PFOS and PFOA in water has been published as ISO 25101:2009[1, 2]. Therefore, a standard method for the analysis of additional PFAS in water is needed.

A new work item proposal (NWIP) on PFAS in water was registered from Japan to ISO/TC 147 (Water Quality) in April 2016. The NWIP was approved by fifteen countries in July 2016, as *ISO 21675 Water quality — Determination of polyfluorinated alkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)*. The working draft (WD) was discussed at an ISO/TC 147 meeting in September 2016 and the committee draft (CD) was submitted in March 2017 for consideration after the WD was revised. The CD was then approved for registration as the draft international standard (DIS) in July 2017. An interlaboratory trial (ILT) was carried out to validate ISO method 21675 and determine the stability and homogeneity of PFAS in ILT water samples. In this report, the results of the stability and homogeneity study as well as the ILT validation of ISO 21675 are presented. This involved using the ISO 21675/CD (revised)[3] version of the method for the measurement of thirty-one PFAS (Table 1) in water samples.

Materials and methods

Interlaboratory trial:

The ILT was announced in August 2017. Six water samples (2 drinking water, 1 river water, 1 sea water, and 2 waste water samples) were examined and three independent replicates per sample were analyzed. All laboratories were provided calibration solutions and mass labelled stock solutions (internal standard surrogate substances) for spiking into water samples by Wellington Laboratories Inc (Guelph, Ontario, Canada). A total of 120 test sample bottles for each sample were prepared. Known concentrations of native target compounds in methanol from Wellington Laboratories Inc were spiked into each sample bottle. The water samples were shipped from Japan to participants in November 2017. An electronic data sheet for the reporting of results was provided by the organizer to participants and the results were submitted from each participant to the organizer by January 2018. This trial was a validation exercise, not a proficiency testing trial, therefore it was crucial that participants adhered to the procedure described in ISO/CD 21675 (revised). The relevant document for the trial was also circulated to participants.

Homogeneity study:
Five sample bottles in each ILT sample were selected and analyzed to check the homogeneity.

Stability study:
Five fresh samples (Day 1 or Day 2 as storage period) and three old samples (Day 42, Day 44 or Day 46) were selected and analyzed in each ILT sample to check stability during the storage. Samples were storage at 5±3 °C in the dark until analysis.

Table 1: The list of analytes validated by interlaboratory trial for ISO 21675

Abbreviation	Analyte
PFBS	Perfluoro-n-butanesulfonic acid
PFHxS	Perfluoro-n-hexanesulfonic acid
PFHpS	Perfluoro-n-heptanesulfonic acid
PFOS	Perfluoro-n-octanesulfonic acid
PFDS	Perfluoro-n-decanesulfonic acid
FOSA	Perfluorooctanesulfonamide
N-MeFOSA	*N* -methyl perfluorooctanesulfonamide
N-EtFOSA	*N* -ethyl perfluorooctanesulfonamide
N -MeFOSAA	*N* -methyl perfluorooctanesulfonamidoacetic acid
N -EtFOSAA	*N* -ethyl perfluorooctanesulfonamidoacetic acid
PFBA	Perfluoro-n-butanoic acid
PFPeA	Perfluoro-n-pentanoic acid
PFHxA	Perfluoro-n-hexanoic acid
PFHpA	Perfluoro-n-heptanoic acid
PFOA	Perfluoro-n-octanoic acid
PFNA	Perfluoro-n-nonanoic acid
PFDA	Perfluoro-n-decanoic acid
PFUnDA	Perfluoro-n-undecanoic acid
PFDoDA	Perfluoro-n-dodecanoic acid
PFTrDA	Perfluoro-n-tridecanoic acid
PFTeDA	Perfluoro-n-tetradecanoic acid
PFHxDA	Perfluoro-n-hexadecanoic acid
PFOcDA	Perfluoro-n-octadecanoic acid
8:2 FTOH	8:2 Fluorotelomer alcohol
8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acid
8:2 diPAP	8:2 Polyfluoroalkyl phosphate diester
6:2 FTSA	6:2 Fluorotelomer sulfonic acids
8:2 FTSA	8:2 Fluorotelomer sulfonic acids
HFPO-DA	2,3,3,3-Tetrafluoro-2 (heptafluoropropoxy) propanoic acid
ADONA	3H-Perfluoro-3-[(3-methoxy-propoxy) propanoic acid
9Cl-PF3ONS	2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexoxy)-1,1,2,2-tetrafluoroethanesulfonate

Results and discussion
Nearly fifty laboratories were contacted in September 2017, of which thirty-four laboratories accepted the invitation to participate in the study. Due to the requirement of the ILT to follow the method directly, only twenty-seven laboratories from eleven countries submitted results.

For validation of an ISO analytical method, labs must follow the method directly[4]. For each analyte, at least eight valid data points after elimination of outliers had to be obtained, the percentage of outliers had to be less than 20%, and the coefficient of variation ($C_{V,R}$) had to be less than 40 %. Also, the recovery rate had to lie

within acceptable limits and it was recommended to have global participation (i.e. participants from at least five countries).

The validation data for most of PFAS were generally acceptable, except for 8:2 FTOH in waste water and 8:2 FTUCA in sea water. 8:2 FTOH was validated in only one of the wastewater samples. Only two laboratories submitted data of 8:2 FTOH with low recoveries and high $C_{V,R}$. 8:2 FTOH, therefore, will be removed from ISO 21675. Results of 8:2FTUCA in drinking water, river water, and waste water were acceptable, but low recovery and high $C_{V,R}$ was obtained in sea water. Homogeneity of PFAS in prepared ILT water samples was acceptable. The stability of PFAS was also acceptable for most of compounds in the ILT samples, except for 8:2 FTUCA in the sea water sample. 8:2 FTUCA recovery was only 60% even in Day 1 sea water sample and decreased dramatically to 0% in Day 44. The low recovery of 8:2 FTUCA in the validation on ILT might caused by unstability of 8:2 FTUCA in sea water. Overall, the results of the ILT confirmed that the ISO/CD 21675 (revised) is a robust and reliable method the meets the criteria to be published by ISO and hopefully will be published as an ISO standard in 2019.

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References

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