

# APPLICATION OF CRYOGENIC MOISTURE SAMPLER AND RECENT TECHNOLOGIES IN THE ANALYSIS OF PERFLUORO ALKYL SUBSTANCES

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## Introduction

Perfluoro alkyl substances (PFASs) including perfluoro alkyl sulfonic acids (PFASAs) and perfluoro alkyl carboxylic acids (PFCAs) have been found to be global pollutants. The findings of PFASs in the environment have generated several new perspectives in the field environmental chemistry. The first is that these are emerging chemicals with stable carbon-fluorine bonds, instead of carbon-bromine and carbon-chlorine bonds in persistent organic pollutants (POPs). Although fluorination of organics was predicted to be persistent because of the knowledge generated from legacy halogenated (brominated and/or chlorinated) POPs, PFASs have remarkably different physicochemical properties in comparison with legacy POPs. Most remarkable differences are high water solubility and acid dissociation ( $pK_a$ ). These two properties led to wide distribution of PFASs in hydrosphere in combination with variable vapor pressure of PFASs precursors. Recent global monitoring and computer simulations suggested significant role of water currents including global circulation of deep seawaters in long range transportation of PFASs.

Investigations on the distribution of PFASs in the environment required comprehensive global scale concept in comparison with traditional monitoring survey in the continental and coastal areas. However, there is no sufficient sampling technique of PFASs in open ocean air before. Some trials using traditional high volume air sampling technique was applicable to volatile precursors and selected PFASs only. Because of the wide range of physicochemical properties of PFASs and their precursors, a comprehensive sampling technique for air is still not available.

Here we present a newly developed air sampler "Cryogenic Moisture Sampler: CMS" to enable large volume air collection with moisture in the open ocean. From the preliminary survey that we conducted using the new sampler and water samples collected around the global oceans, shorter chains of PFASs appeared to be significant tracers of PFASs and CMS provided accurate measure of these shorter chain PFASs. Two more recent technologies (WAXsea and PFASs free Milli-Q system) for trace level PFASs analysis are also described.

## Cryogenic moisture sampler (CMS) for PFASs in open ocean air

Traditional high volume air sampler (HVA) is used for the collection of volatile precursors and selected PFASs and there is no good sampling technique for all analogues of PFASs to date. In general, high humidity and huge amount of water in the air (aerosol), make collection of large volume of open ocean air difficult even with modified PUF in HVA. The breakthrough in the use of CMS is that it can collect all moisture into ice and adsorption solvent using electrical cryo-traps. It enables complete collection of all chemicals in the atmosphere. Theoretically this technique is applicable to any type of chemicals including PFASs, volatile organic carbons (VOCs), chloro fluoro carbons (CFCs), even legacy POPs in air. Figure 1 shows prototype of CMS (type 1st) and inlet system set on board. Polypropylene inlet tube (10 to 20m) was hung on top of



Figure 1. Cryogenic Moisture Sampler (CMS type 1st) in a laboratory and inlet system on board.

compass deck of JAMSTEC research vessels "Mirai" and "Hakuho Maru". The inlet tube was introduced in dry laboratory on board and connected to CMS. CMS type 1st comprised of three main traps, namely bubbler, mist trap and cold trap. Temperature of each part were controlled at 10 to 5°C for bubbler and mist trap, -4 to -20°C for cold trap during sample collection. Adsorption solvent was mixture of water and methanol with EDTA.

We chose PFASs as test chemicals to evaluate the performance of CMS because of specific physicochemical properties described above. Figure 2 shows results of recovery experiments using glass traps and polypropylene traps. Although glass traps showed poor recoveries, polypropylene traps showed good recoveries for most PFASs. This is remarkable and indicates clear adsorption of PFASs on to glass surface as expected. Very low recovery of longer chains compared to C4 (PFBS and PFBA) suggests "unsuitability of glass apparatus for atmospheric sampling of PFASs and PFCAs".

On the other hand, some of volatile precursors showed better recoveries in cold trap and mist trap of glass apparatus compared to polypropylene. Although the reason for this is not known, CMS can be useful not only for atmospheric sampling of PFASs but also enable useful "chamber study" that may provide some insight into environmental kinetics of PFASs at various temperatures and humidity in the environment.

After preliminary results from CMS type 1st, modified type 2nd was developed. Key modification of type 2nd was to use a suitable adsorption solvent in bubbler. Around 5% of methanol with EDTA provided acceptable recoveries (between lines in red) of shorter chain PFASs (PFOS and smaller) and PFCAs (PFUnDA and smaller) in the atmosphere.

As the second verification of CMS during above open ocean cruises, PFASs in open ocean atmosphere and seawater collected same location were analyzed. This provides useful information about PFASs partitioning between air and seawater in open ocean environment. It enables accurate estimation of global distribution according to not only their variable physicochemical properties but also under real environmental conditions.

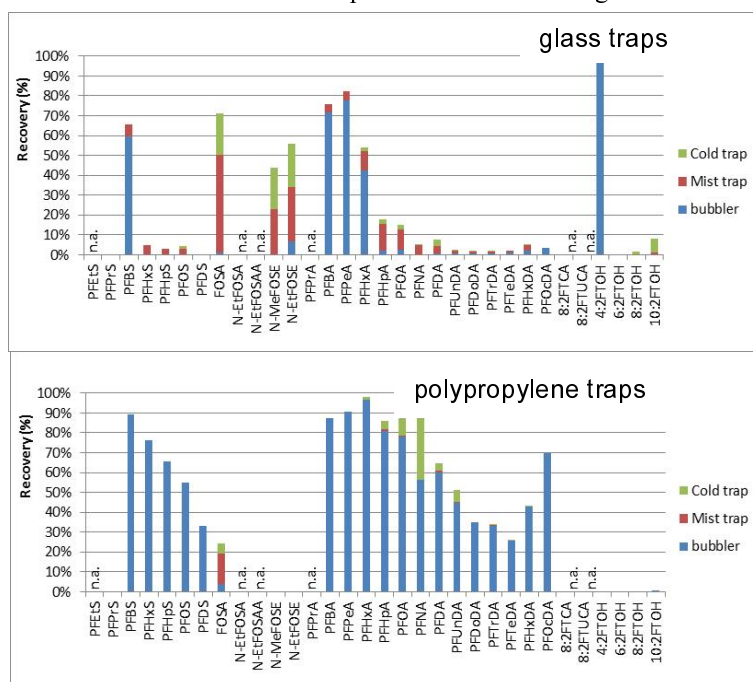


Figure 2. Recovery results for PFASs using "CMS type 1st" using glass traps (upper) and polypropylene traps (below).

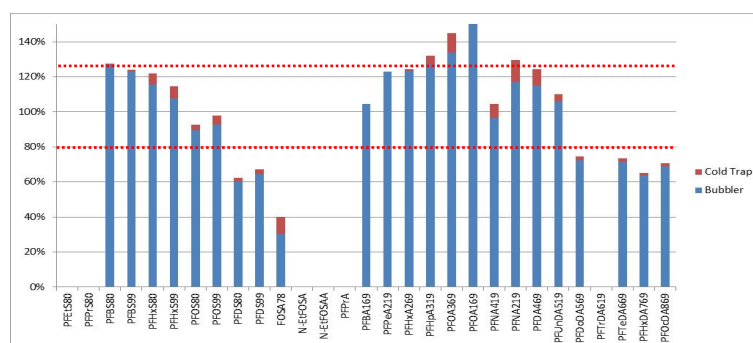


Figure 3. Recovery experiment for PFASs using "CMS type 2nd" using polypropylene apparatus and modified adsorption system.

### WAXsea: Novel WAX cartridge optimized for trace level analysis of PFASs in seawater analysis

A type of the solid phase extraction (SPE) cartridge "WAX" produced by Waters Co. and comparable weak anion exchange cartridges are widely used for PFASs analysis after the method was first development by Taniyasu et al. (2005) because this cartridge is capable not only for PFOS and PFOA but also for a serious of

PFAS analogues including shorter chain compounds (C4 and smaller). Several standard methods of water analysis, ISO25101(2009)<sup>1)</sup> and JIS K0450-70-10 (2011)<sup>2)</sup> were established according to that literature<sup>3)</sup> and this SPE cartridge is commonly used in basic clean up method of crude extract of PFASs even in biota, sediment and atmospheric samples.

However, there remains some uncertainty in PFASs analysis in seawater samples. The initial survey of PFASs in open ocean water was started in 2002 and a complete global survey of PFASs in all Oceans is fulfilled after 11 years. Contrary to our expectation, number of reports on PFASs analysis in open ocean water is very little. Shorter chain PFASs were rarely analyzed in open ocean waters because of the challenges in accurate quantification and number of reliable reports on PFASs in open ocean waters is still few. The AIST in Japan carried out several inter-laboratory calibration studies and some difficulties in the accurate use of WAX cartridge for seawater analysis were elucidated. There are two major difficulties, LOQ of PFASs in was around 100 pg/L and 1L of seawater was not enough to detect PFASs in open ocean water, which contains less than 1 pg/L, using instrument established in general laboratory. The second issue is variable SPE results depending on the type of seawaters. Salinity and pH drastically change from coastal seawater to open ocean water and the performance of SPE can vary without accurate conditioning and treatment using commercially available WAX cartridge.

Hence, we tested different types of WAX cartridges (amount of adsorbent and type of materials) and optimized for trace level seawater analysis. We introduce novel WAX cartridge optimized for PFASs analysis in seawater, namely "WAXsea" in this presentation.

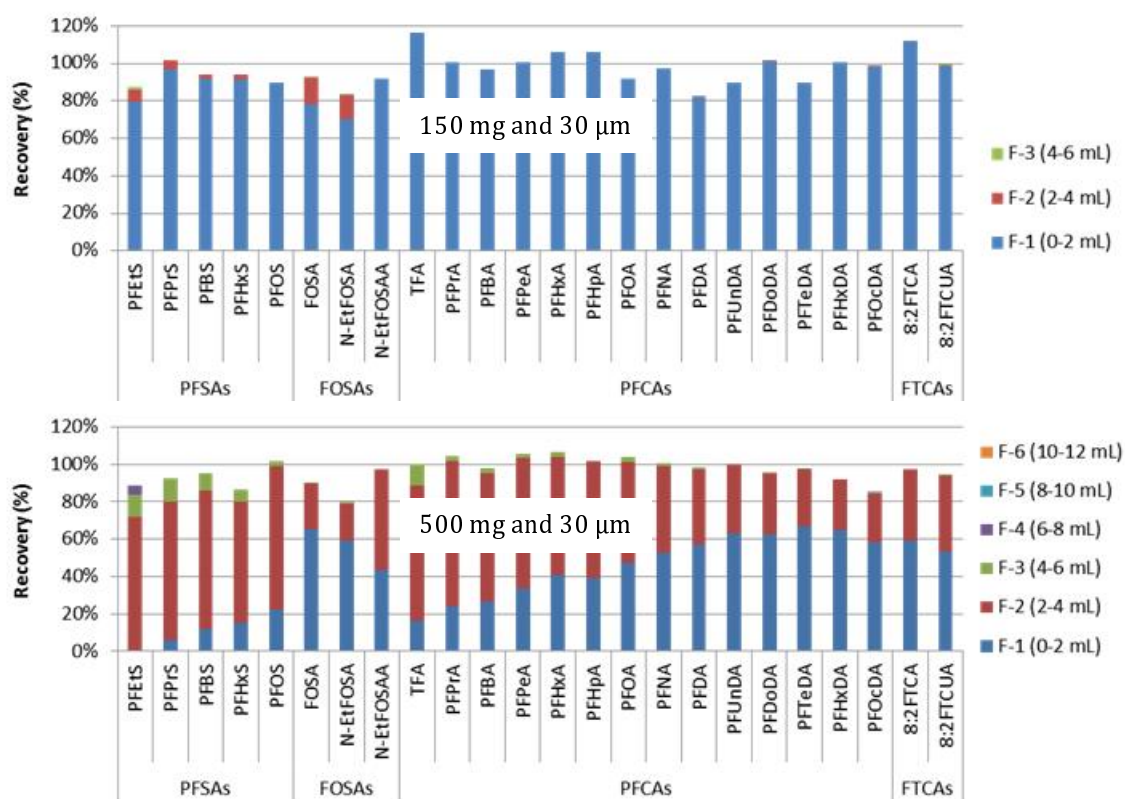


Figure 4. Elution profiles of PFASs in WAX cartridges with different volume of adsorbent but with similar particle size.

Basic conditioning and treatment of SPE cartridge is similar to that described in ISO25101 and JIS K0450-70-10. After analysis of open ocean waters collected from more than 600 locations on our planet,

several modifications to these standard methods were developed. One is demineralization of cartridge during sample loading and another is inclusion of larger volume of small particle size of adsorbent. Small volume and particle size (150 mg and 30  $\mu\text{m}$ ) of adsorbent of commercially available WAX cartridge may not have sufficient capacity for volume of water greater than 1L. However, larger volume with larger particle size (500 mg and 60  $\mu\text{m}$ ) also showed to be insufficient for shorter chain PFASs because of less active surface area on the cartridge. Hence, we customized it for larger volume water samples, but with smaller particle size (300 mg, 500 mg and 30  $\mu\text{m}$ ). Tentative results of recoveries of PFASs through modified WAX cartridge are shown in Figure 4.

Commercially available smaller volume WAX cartridge (150 mg and 30  $\mu\text{m}$ ) didn't show exact elution profile of PFASs, but larger volume cartridge revealed that it is similar to mix mode anion exchange separation with suitable mobile phase. This is a reason of better separation of shorter chain PFASs.

We tested several other parameters of conditioning and demineralization procedure and successfully developed accurate separation of PFASs from interferences in seawater samples using larger volume WAX cartridge. This could be a useful technique for the survey of PFASs in seawater sample and will enable the development of database of PFASs on a global scale.

### PFASs free Milli-Q water system

To obtain purified water that is used in analytical procedures, is very important for trace analysis of PFASs. Widely used Milli-Q water purification system is applicable to PFAS analysis in water sample at pg/L level. However, variability in water quality supplied by the commercially available system was found. For example, background levels (pg) in Milli-Q water were ranged from 0.1 to 20 for PFBS, 0.5 to 50 for PFOS, 0.1 to 100 for PFBA and 1.0 to 100 for PFOA even in processed Milli-Q water. This is the problem that a beginner may encounter when they start PFASs analysis. From the limited information, relatively dirty source of tap water (resulting from inefficient water treatment) in highly populated regions may result in high background of PFASs, even in purified Milli-Q water in laboratory. We evaluated two Milli-Q systems, namely Milli-Q advantage and Milli-Q Integral 5 to determine possible PFASs in procedural blanks after newly set up in the laboratory. Interestingly, old Milli-Q advantage system set up in 2003 showed lower blank levels compared to brand-new system.

In conclusion, recent technologies described above will enable more challenging investigations of accurate analysis of PFASs, such as partitioning between atmosphere and ocean water. PFASs research started as residue analysis in biota and moved to freshwater/coastal water and atmospheric transportation. Now many investigations suggest significant role of ocean water current to understand global transportation of PFASs. Recent technologies will reveal the next stage of PFASs research, the crossing road between atmosphere and hydrosphere.

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Commercially available "Cryogenic Moisture Sampler : CMS" plan to be announced in end of 2013 by Sibata Scientific Technology Ltd. 1-1-62, Nakane, Soka, Saitama, 340-0005 Japan, tel: +81-48-933-1582, fax: +81-48-933-1591, e-mail : overseas@sibata.co.jp. In Korea, Taewon Sibata Co., Ltd. 128-9, Sangbong-dong, Jungnang-gu, Seoul, Korea, 131-861, tel : 82-2-841-2270, fax: 82-2-841-2290, e-mail: sibata@hanmail.net

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