Non-Target Analysis of Ambient Air Using Cryogenic Air Sampler

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Introduction

Non-target analysis using Time of Flight Mass Spectrometry (TOF-MS) seems to be the recent movement of analytical chemistry. Several reports attempted to establish this concept with modern development of the instruments, application of data analysis and with relatively simple sample preparation. Unexpectedly, the last one is most important, because different standard operation protocols (SOPs) of sample preparation may only extract "selected chemicals" to be measured in the whole sample. Water, sediment and biological samples might be possible to use for non-target analysis because of their well reported sample preparation procedure, such as solid phase extraction and others.

On the other hand, the most difficult part in non-target analysis of ambient air is the air sampling devices that are generally specific to their target chemicals. Many adsorption cartridges for most common volatile organic compounds are Benzene/Toluene/Xylene, acid gas, styrene and so on. These VOCs are collected using specific commercially available sampling tube. However, there is no such single sampler for sampling both particle and gaseous phases in air. In spite of numbers of sampling devices for hundreds of chemicals in air, it is supposed to be impossible to develop non-target analysis of ambient air, because till today sampling devices like adsorption tube can only analyze "Selected Chemicals - target".

New technology, the Cryogenic Air Sampler (CAS), is a breakthrough on this issue. Concept of cryogenic collection of air has already known for non-selective collection of nitrogen and carbon dioxide using liquid helium (-269 °C). However, there is no such technology to collect wide variety of organic gases including highly volatile compounds, volatile organic gases, semi-volatile and non-volatile (partly particulate) organic chemicals in ambient air using cryogenic collection because of several industrial limitations to manufacture this sampler.

AIST and Sibata Scientific Technology Ltd. innovated a cryogenic moisture sampler (CMS) for collection of water soluble gas and particulate matter in ambient air in 2013 [1, 2]. After the industrial innovation for the last five years, most comprehensive cryogenic sampling device, namely cryogenic air sampler (CAS) for POPs (CAS-02) was manufactured and introduced to market at the Pittsburg conference (Chicago, USA) in March 2017. CAS-02 is the first available instrument to enable comprehensive collection of wide variety of organic chemicals in ambient air using single sampling device.

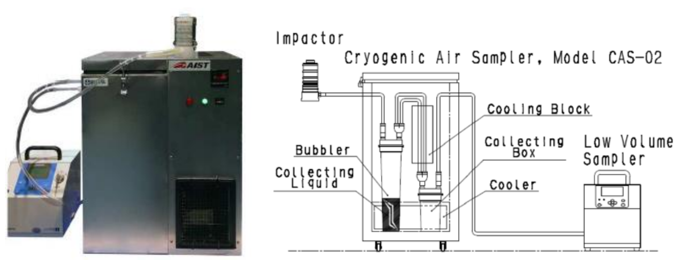
In this report, preliminary trial of non-target analysis of POPs in ambient air using CAS-02 and TOFMS is described.

Materials and methods

The Cryogenic Air Sampler for POPs (CAS-02) is a device to collect both gases of high/low boiling points and particle matters in the air simultaneously. It is also designed with a new concept which is effective for sampling of Fluorinated organic toxic substances (such as PFOS, which was the limitation of collection rate by the conventional methods) and light/temperature sensitive Brominated flame retardant (such as PBDEs) at the same time.

CAS-02 can collect different types of chemicals ranging from high & low-boiling gases (e.g., VVOC, VOC and SVOC) to particle matter (e.g., POM, PM10 and PM2.5) in work environment and ambient air. A comprehensive air sampler when connected to a classified impactor, it can collect hazardous air pollutants including both high & low-boiling gases and particle matters simultaneously. Specifications and dimensions are shown below.

After sample collection by CAS-02, liquid sample were analyzed using TOF-MS scan and Information Dependent Acquisition (IDA) by TripleTOF®4600 system equipped with Agilent 1100 HPLC.



Setting temp. range	-20 to 0 ℃
Display	Digital (℃)
Joint hose diameter	O. D. φ8 (inlet, decompression)
Safety function	Electrical leakage breaker (with overcurrent prevention)
Alarm function	Exhaust heat warning for excess heat increase, Sensor short circuit
Dimensions	460 (W) x 340 (D) x 625 (H) mm
Weight	19 kg
Power supply	AC 100V to 240V

Figure: 1. Specifications of the Cryogenic Air Sampler for POPs (CAS-02).

Results and discussion

PFASs were chosen as test chemicals to evaluate the performance of CAS-02 because of their specific physicochemical properties. Figure 2 shows the results of recovery experiments using glass traps (similar to conventional air sampler such as high volume air sampler) and polypropylene traps used for CAS-01 (previous version). Glass traps showed poor recoveries; in contrast, polypropylene traps showed good recoveries for most PFASs. This is remarkable and indicates clear adsorption of PFASs onto 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 PFSAs and PFCAs".

On the other hand, some of volatile precursors showed better recoveries for cold trap and mist trap of glass apparatus compared to polypropylene. Although the reason for this is not known, CAS-02 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.

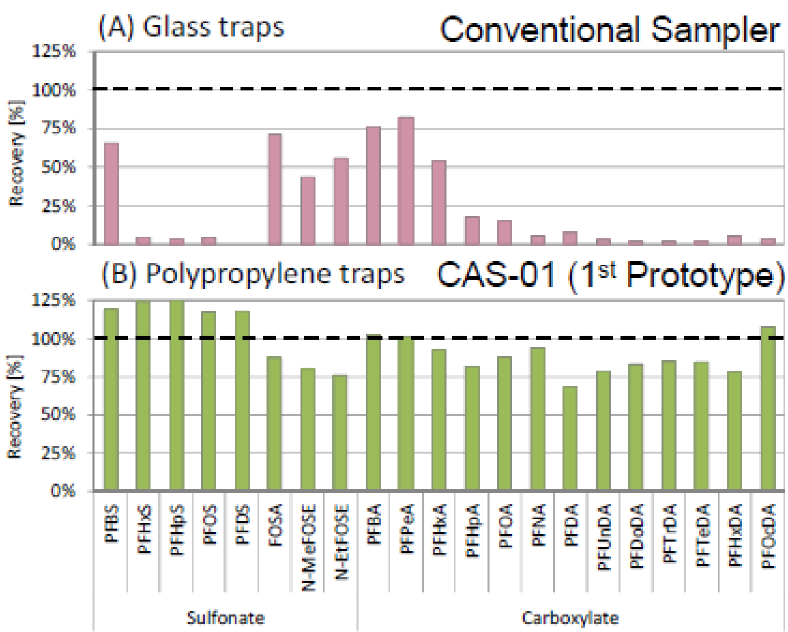


Figure: 2. Recovery results for PFASs using "CAS-01" for glass traps (upper) and polypropylene traps (below).

Several parameters for TOF-MS were optimized to obtain the higher intensities using comprehensive analysis of most PFASs in liquid extraction of ambient air collected by CAS-02. The parameters of Ion Source Gas 1 (GS1 (psi)), Ion Source Gas 2(GS2 (psi)), Curtain Gas (CUR (psi)), Temperature (TEM (°C)), Ion Spray Voltage Floating (ISVF (V)) and Declustering Potential (DP (V)) were optimized. After optimization, intensities of selected PFAS were 7.4 to 43.8 times higher than original values of parameters. In brief, liquid sample collected from ambient air using CAS-02 contained not only well-known PFASs but also several unidentified chemicals in air. including C_6HF_{11} (m/z 280.9830 as [M-H]-), proposed structure was 1,1,2,3,3,4,4,5,5,6,6-Undecafluoro-1-hexene, undecafluorocyclohexane. $C_6H_2F_{10}O_2$ (m/z 294.9822 as [M-H]-), proposed structure was 1,2,3,3,4,4,5,5,6,6-decafluoro-1,2-cyclohexanediol, 2,2,3,3,3-pentafluoropropyl pentafluoropropanoate, 1,1,1,3,5,5,5-heptafluoro-4-(trifluoromethyl)-3-pentene-2,2-diol or 2,2,2-trifluoroethyl heptafluorobutanoate. This result showed that the combination of CAS-02 and TOF-MS identification seems to be very useful technique for non-targeting analysis of chemicals in ambient air.

Conclusion: CAS-02 has several features suitable to "non-target analysis of ambient air" as below:

A) Comprehensive sampling device – capable to collect both particulate matter and gaseous materials at the same time in one compact equipment;

B) Highly accurate fine analysis - by using a functionalized resin, the CAS-02 is capable for sampling of fluorinated organic toxic substance and brominated flame retardant, which seems difficult to collect with current glass or Teflon based sampling methods;

C) LC-MS analysis ready - direct measurement is possible without further extraction, because ambient chemicals are collected in freeze/liquid sample;

D) Convenient to use at different sites - the cooling part doesn't require optional coolant such as liquid-nitrogen;

E) Applicable to humid environment - the CAS-02 does not require the removal of moisture from the atmosphere and can work in humid and foggy environment, but conventional samplers cannot; and

F) Compliance with ISO methods - the CAS-02 complies with ISO25101 (PFOS/PFOA) and on-going international standard of ISO method, TC147/SC2/WG74 "PFAS LC-MS/MS".

References

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