

EXAMINATION OF ANALYTICAL METHOD FOR FLUOROTELOMER COMPOUNDS IN AMBIENT AIR

Takemine S, Matsumura C, Suzuki M, Okada Y, Yoshida M, Tsurukwa M, Nakano T.
Hyogo Prefectural Institute of Environmental Sciences,
3-1-27, Yukihiro-cho, Suma-ku, Kobe, Hyogo, Japan, 654-0037.

Abstract

The analytical method for fluorotelomer compound in ambient air was examined. The target compounds were Fluorotelomer alcohols(FTOHs), Fluorotelomer acrylates(FTAcrylates), Fluorotelomer methacrylates(FTMethacrylates), Fluorotelomer olefin(FTOlefin), and Fluorotelomer Iodides(FTIs). Reducing the amount of the extraction solvent by using Accelerated Solvent Extractor (ASE), cleanup recovery was improved. The recovery rates at spike recovery experiments were between 18% (8:2FTMethacrylate) to 72% (8:2FTOH) by using the analytical method. Target compounds in ambient air were investigated at the roof of Hyogo prefectural institute of environmental sciences. As a result, 8:2 FTOH (270pg/m³), 10:2 FTOH (150pg/m³) and 8:2 FTAcrylates (70pg/m³) were detected.

Introduction

Perfluoro carboxylic acids (PFCAs) are widespread and persistent environmental contaminants. The environmental pollution of PFCAs has become popular through the reports on the environmental problem in the world¹⁾²⁾³⁾.

The sources of PFCAs in the environment are not fully elucidated. Fluorotelomer alcohols (FTOHs) might be indirect sources of PFCAs because it has recently been suggested that FTOHs are precursor compounds which degrade to PFCAs in the environment⁴⁾. Fluorinated oil and water repellents could be a significant source of the FTOHs released into the environment. In addition, our other studies suggested that fluorinated oil and water repellents contain FTOHs and various Fluorotelomer compounds such as Fluorotelomer acrylates(FTAcrylates), Fluorotelomer methacrylates(FTMethacrylates), Fluorotelomer olefins(FTOlefins), and Fluorotelomer Iodides(FTIs). As for Fluorotelomer compounds in environment, FTOHs and several Fluorotelomer compounds such as 6:2FTAcrylates, 8:2FTAcrylates and 8:2FTMethacrylates were analyzed⁵⁾⁶⁾⁷⁾.

In this paper, the analytical method for fluorotelomer compounds such as FTOH, FTAcrylates, FTMethacrylates, FTOlefin and FTIs in ambient air was examined. In addition, Reducing volatilization at concentration that is a problem of the conventional method, the amount of the extraction solvent was reduced by using Accelerated Solvent Extractor.

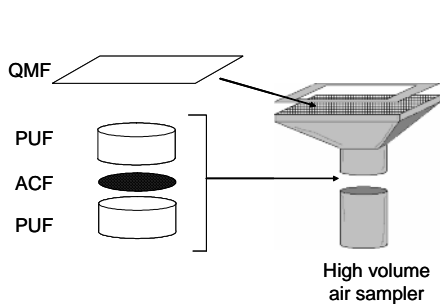
Methods and Materials

Target compounds are shown in table 1. Air sample were collected by High volume air sampler (HV-700F, SIBATA) at the roof of Hyogo prefectural institute of environmental sciences. Quartz micro fiber filters(QMF, QR-100, 203 × 254mm, ADVANTEC), Poly-urethane foams (PUF, 80mmφ, SIBATA) and activated carbon felts (ACF, Fiber AC disk, 85mmφ, Autoprep, Showa denko) were used for sampling medias. The air sampler is shown in Fig.1.

Table 1 Target compounds

compound	acronym	molecular wt.	structure
1H,1H,2H,2H-Perfluorohexan-1-ol	4:2FTOH	264.1	CF ₃ (CF ₂) ₃ CH ₂ CH ₂ OH
1H,1H,2H,2H-Perfluorooctan-1-ol	6:2FTOH	364.1	CF ₃ (CF ₂) ₅ CH ₂ CH ₂ OH
1H,1H,2H,2H-Perfluorodecan-1-ol	8:2FTOH	464.1	CF ₃ (CF ₂) ₇ CH ₂ CH ₂ OH
1H,1H,2H,2H-Perfluorododecan-1-ol	10:2FTOH	564.1	CF ₃ (CF ₂) ₉ CH ₂ CH ₂ OH
1H,1H,2H,2H-Perfluorooctyl acrylate	6:2FTAcrylate	418.2	CF ₃ (CF ₂) ₅ CH ₂ CH ₂ OC(=O)CH=CH ₂
1H,1H,2H,2H-Perfluorodecyl acrylate	8:2FTAcrylate	518.2	CF ₃ (CF ₂) ₇ CH ₂ CH ₂ OC(=O)CH=CH ₂
1H,1H,2H,2H-Perfluorooctyl methacrylate	6:2FTMethacrylate	432.2	CF ₃ (CF ₂) ₅ CH ₂ CH ₂ OC(=O)C(CH ₃)=CH ₂
1H,1H,2H,2H-Perfluorodecyl methacrylate	8:2FTMethacrylate	532.2	CF ₃ (CF ₂) ₇ CH ₂ CH ₂ OC(=O)C(CH ₃)=CH ₂
1H,1H,2H-Perfluorododec-1-ene	10:2FTOlefin	546.1	CF ₃ (CF ₂) ₉ CH=CH ₂
1H,1H,2H,2H-Perfluorohexyl Iodide	4:2FTI	374.0	CF ₃ (CF ₂) ₃ CH ₂ CH ₂ I
1H,1H,2H,2H-Perfluorooctyl Iodide	6:2FTI	474.0	CF ₃ (CF ₂) ₅ CH ₂ CH ₂ I
1H,1H,2H,2H-Perfluorodecyl Iodide	8:2FTI	574.0	CF ₃ (CF ₂) ₇ CH ₂ CH ₂ I

Extractions of the each sampling medias were performed with ethyl acetate using Accelerated Solvent Extractor (ASE200, Dionex). Conditions of ASE were shown in Table 2. All extracts were concentrated to 1ml under a gentle nitrogen stream. 1H,1H-Perfluoro -1-nonanol (1,000 ng) was added as a syringe spike. All Extracts were analyzed by GC/MS. Analytical conditions of GC/MS are shown in Table 3. SIM chromatogram of the standard mixture (1000ng/L each) under the conditions is shown in Fig. 2.



Instrument :	DIONEX ASE-200
Cell Size :	11mL(ACF), 33mL(QF, PUF)
Oven temp. :	40
Pressure :	1500psi
Static time :	10min
solvent :	Ethyl acetate
Nitrogen purge :	150psi for 100 sec.
Extraction cycle :	Three time

Fig. 1 Air sampler

Instruments :	Agilent 6890N/JEOL JMS-K9
Column :	J&W Sci. DB624 60m×0.25 I.D.(1.4µm)
Injection volume :	2µl(Splitless)
Injection port temp :	200
Column oven temp :	90 (5min) 5 /min 110 (0min) 10 /min 240 (15mi
Carrier gas :	Helium (Flow rate 1mL/min)
Ion source temp :	230
Interface temp :	200
Ionization method :	EI
Ionization energy :	70ev
Mode :	SIM

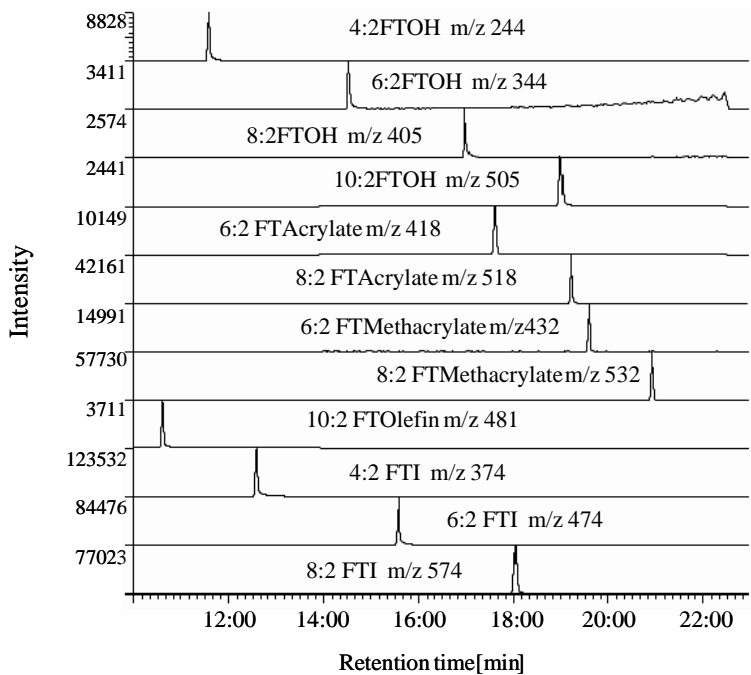


Fig.2 SIM chromatogram of the standard mixture (1000ng/mL each).

Results and discussions

Target compounds are volatile during concentrate because the boiling point of target compounds is low. ASE was used for decrease the amount of the extraction solvent and short the concentration time. Recovery experiments at the pretreatment were conducted by spiking 1000ng of target compounds onto ACF. Moreover, the recovery rates at the pretreatment of a conventional technique (medias are soaked in 50 mL×3 of ethyl acetate) was investigated. Fig.3 shows those results. The recovery rates of the pretreatment were improved by this technique compared with conventional technique

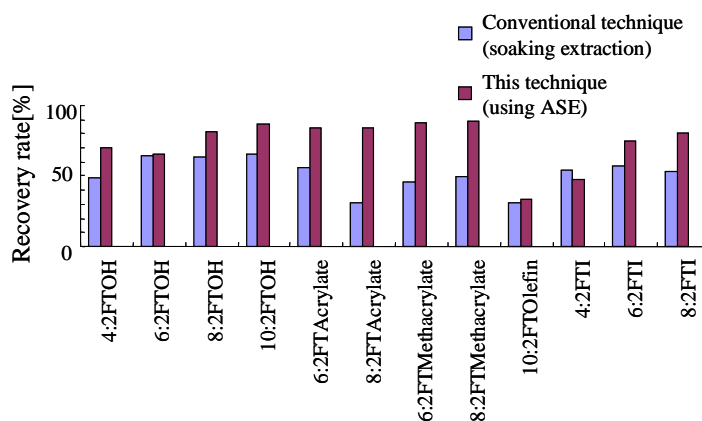


Fig.3 Recovery rates of this technique and conventional technique at pretreatment

Detection limits were defined as a peak signal-to-noise ratio 3 by GC/MS analysis of target compounds. Recovery experiments were performed by spiking 1,000ng of target compound mixtures. Moreover, the case of spiking the mixtures onto QF and the case of spiking onto PUF were compared. As a result, recovery rates of spiking onto PUF were better.

Furthermore, Target compounds were detected on only ACFs in each experiment. Table4 shows IDLs and the recovery rates.

Fig.4 shows an example of concentration of Fluorotelomer compounds in ambient air by this analysis. 8:2FTOH, 10:2FTOH and 8:2FTAcrylate were detected. However, 6:2FTOH, 6:2FTMethacrylate, 6:2FTI and 8:2FTI detected in products were not detected from ambient air in this study.

Table 4 IDLs and recovery rates

Compound	Detection Limit [pg/m ³]	Recovery rate[%]	
		(Stds were added QF,n=2)	(Stds were added PUF,n=2)
4:2FTOH	10	43	61
6:2FTOH	20	53	58
8:2FTOH	20	60	72
10:2FTOH	25	39	62
6:2FTAcrylate	3	45	52
8:2FTAcrylate	3	40	59
6:2FTMethacrylate	3	39	51
8:2FTMethacrylate	2	18	57
10:2FTOlefin	25	28	36
4:2FTI	2	26	31
6:2FTI	2	40	54
8:2FTI	1	42	54

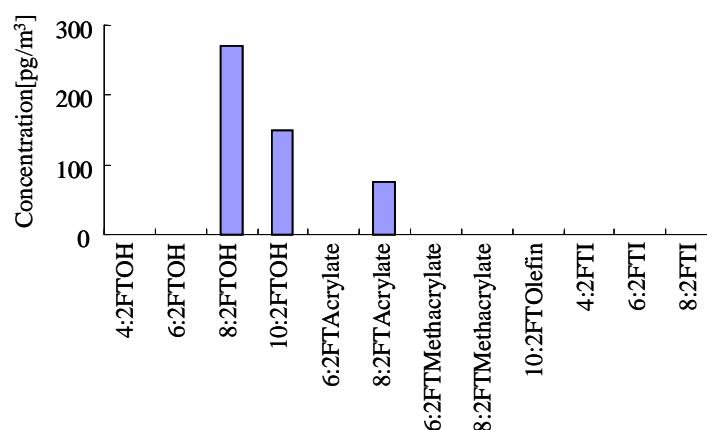


Fig.4 Concentrations of fluorotelomer compounds in ambient air(Date 2009/4/10)

Acknowledgment

This research was partially supported by the ministry of the Environment, Promotion cost of environmental technology development.

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