INVESTIGATION OF FLUORINATED TELOMER ALCOHOLS AND RELATED COMPOUNDS IN FLUORINATED OIL AND WATER REPELLENTS

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Abstract

Fluorinated Telomer Alcohols(FTOHs) and related compounds in Fluorinated oil and water repellents used for papers, textiles and cars were investigated by using Headspace GC/MS. As a result, FTOHs and related compounds were detected from 4 kinds of Fluorinated oil and water repellents used for papers and textiles industries. Moreover, the concentration patterns of FTOHs and related compounds were different. Especially, PFOA precursors such as 8:2FTOH were not detected in the products that were developed in response to 2010/2015 PFOA stewardship program.

Introduction

Perfluoro carboxylic acids (PFCAs) are widespread and persistent environmental contaminants. And the environmental pollution of PFCAs has become popular through the reports on the environmental problem in the world[1)2)3)].

The sources of PFCAs in the environment are not fully elucidated. FTOHs might be indirect sources of PFCAs, because it has recently been suggested that FTOHs are precursor compounds that degrade to PFCAs in the environment[4)]. FTOHs are volatile and spread across a wide area. FTOHs are used in the synthesis of Fluorinated polymer used for oil and water repellents. Fluorinated oil and water repellents could be a significant source of FTOHs into the environment[5)]. But Fluorinated oil and water repellents in Japan haven’t been investigated yet.

In this paper, FTOHs and related compounds in the Japanese fluorinated oil and water repellents used for papers, textiles and cars were investigated using Headspace GC/MS.

Materials and Method

Target compounds are shown in table 1. 4 kinds of Fluorinated oil and water repellents of Company A used for papers and textiles industries ,2 kinds of Fluorinated oil and water repellents of Company B used for papers and textiles industries and 3 kinds of Japanese marketed Fluorinated oil and water repellents used for cars were investigated. 10mL of distilled water was added to Head space vessels along with 10-100ml of the samples. The vessels were analyzed using by Headspace GC/MS. Analytical conditions of Headspace GC/MS are shown in table 2.

Table 1 Target compounds

compound	acronym	molecular wt.	structure
1H,1H,2H,2H-Perfluorohexan-1-ol	4:2FTOH	264.1	$CF_3(CF_2)_3CH_2CH_2OH$
1H,1H,2H,2H-Perfluorooctan-1-ol	6:2FTOH	364.1	$CF_3(CF_2)_5CH_2CH_2OH$
1H,1H,2H,2H-Perfluorodecan-1-ol	8:2FTOH	464.1	$CF_3(CF_2)_7CH_2CH_2OH$
1H,1H,2H,2H-Perfluorooctyl acrylate	6:2FTAcrylate	418.2	$CF_3(CF_2)_5CH_2CH_2OC(=O)CH=CH_2$
1H,1H,2H,2H-Perfluorodecyl acrylate	8:2FTAcrylate	518.2	$CF_3(CF_2)_7CH_2CH_2OC(=O)CH=CH_2$
1H,1H,2H,2H-Perfluorooctyl methacrylate	6:2FTMethacrylate	432.2	$CF_3(CF_2)_5CH_2CH_2OC(=O)C(CH_3)=CH_2$
1H,1H,2H,2H-Perfluorodecyl methacrylate	8:2FTMethacrylate	532.2	$CF_3(CF_2)_7CH_2CH_2OC(=O)C(CH_3)=CH_2$
1H,1H,2H-Perfluoro-1-hexene	4:2FTOlefin	246.1	$CF_3(CF_2)_3CH=CH_2$
1H,1H,2H-Perfluoro-1-octene	6:2FTOlefin	346.1	$CF_3(CF_2)_5CH=CH_2$
1H,1H,2H-Perfluoro-1-decene	8:2FTOlefin	446.1	$CF_3(CF_2)_7CH=CH_2$
1H,1H,2H-Perfluoro-1-dodecene	10:2FTOlefin	546.1	$CF_3(CF_2)_9CH=CH_2$
1H,1H,2H,2H-Perfluorohexyl Iodide	4:2FTI	374.0	$CF_3(CF_2)_3CH_2CH_2I$
1H,1H,2H,2H-Perfluorooctyl Iodide	6:2FTI	474.0	$CF_3(CF_2)_5CH_2CH_2I$
1H,1H,2H,2H-Perfluorodecyl Iodide	8:2FTI	574.0	$CF_3(CF_2)_7CH_2CH_2I$

Table 2 Analytical conditions of Headspace GC/MS

GC/MS		
Instruments	:	GCMS-QP2010
Column	:	VOCOL 60m×0.32mm I.D.(3μm)
Oven temp.	:	40℃(2min)-5℃/min-90℃(0min)-10℃/min-220℃(10min)
Carreir gas	:	He
Interface temp.	:	220℃
Ion source temp		200℃
Ionization method	:	EI
Ionization voltage	:	70ev
Mode	:	SIM
Headspace autosampler		
Instrument	:	TurboMatrix 40
Injection time	:	0.16min
Thermostic temp.	:	60℃
Thermostic time	:	30min
Pressurization time	:	1min

Results and discussions

Detection limits were defined as a peak signal-to-noise ratio 3 by GC/MS analysis. Detection limits and monitoring ions are shown in table 3. In addition, SIM chromatogram of the standard mixture (500ng/L each) is shown in Fig. 1.

6:2FTOH, 8:2FTOH, 8:2FTOlefin, 10:2FTOlefin, 8:2FTAcrylate, 8:2FTMethacrylate, 6:2FTI, 8:2FTI were detected from the fluorinated materials of Company A. On the other hand, target compounds were not detected from the fluorinated materials of Company B and the Fluorinated oil and water repellents used for cars. The concentrations of the target compounds in the Fluorinated oil and water repellents of Company A are shown in Fig. 2.

The Compounds detected in the products of Company A were intermediates in the synthesis of fluorinated polymer. Fig. 2 shows the difference of the concentration patterns of FTOHs and related compounds. It is especially product D that the pattern is different : only 6:2FTOH and 6:2FTMethacrylate were detected. The companies that relate to fluorinated polymer are doing the effort to reduce discharge of PFOA and PFOA's precursor according to the 2010/2015 PFOA Stewardship Program. Reflecting the program, Product D was produced. Therefore, it is thought that compounds such as 8:2FTOH which might degrade to PFOA were not detected in Product E

The analytical method using Head space GC-MS can easily analyze the target compounds in Fluorinated oil and water repellents, however, low-volatile compounds in target compounds such as 8:2FTMethacrylate had a low sensitivity.

Table 3 Monitoring ions and Detection limits

Compound	Monitoring ion [m/z]	Detection limit [ng/mL]
4:2FTOH	244	3
6:2FTOH	344	3
8:2FTOH	405	30
6:2FTAcrylate	418	0.4
8:2FTAcrylate	518	15
6:2FTMetacrylate	432	0.2
8:2FMetacrylate	532	200
4:2FTOlefin	181	0.2
6:2FTOlefin	281	3
8:2FTOlefin	381	1
10:2FTOlefin	481	40
4:2FTI	374	0.02
6:2FTI	474	0.03
8:2FTI	574	0.3

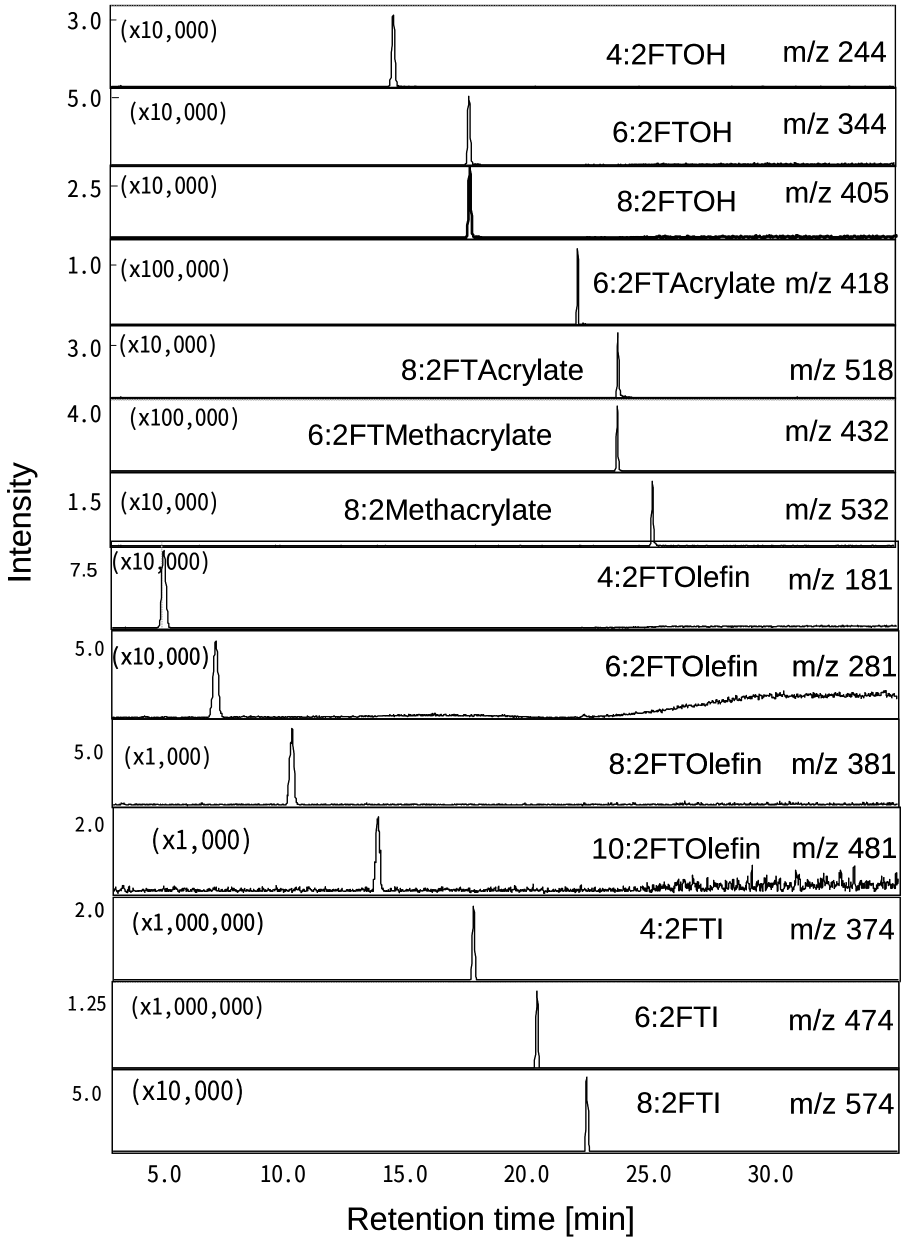

Fig. 1 SIM chromatogram of the standard mixture(500ng/ml each)

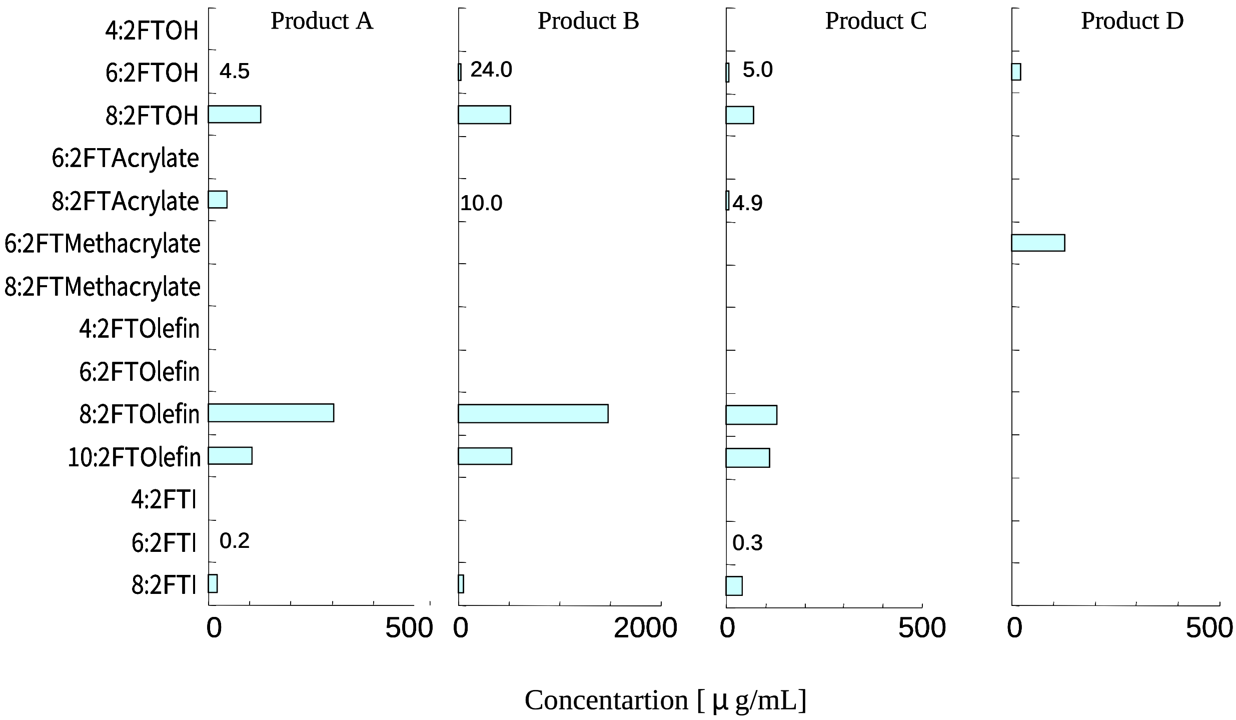

Fig. 2 Concentrations of target compounds in Fluorinated oil and water repellents of Company A

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