Journal of Chromatography A, 1217 (2010) 4439–4447

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Trace determination of airborne polyfluorinated iodine alkanes using multisorbent thermal desorption/gas chromatography/high resolution mass spectrometry

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ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form 3 April 2010
Accepted 19 April 2010
Available online 24 April 2010

Keywords:
Polyfluorinated iodine alkanes
PFC
Telomer
Thermal desorption
Tenax
Gas chromatography/high resolution mass spectrometry

ABSTRACT

A novel gas chromatography/high resolution mass spectrometry method coupled with multisorbent thermal desorption cartridges has been developed for the determination of volatile neutral polyfluorinated iodine alkanes (PFIs) in airborne samples. It allows, for the first time, simultaneous analysis of four mono-iodized perfluorinated alkanes, three diiodized perfluorinated alkanes and four mono-iodized polyfluorinated telomers in ambient air samples. 3.75 L air sample was passed through a sorbent tube packed with 150 mg of Tenax TA and 200 mg of Carbograph 1TD for analyte adsorption. Important factors during the analysis procedures, such as safe sampling volume, air sampling rate, analyte desorption and transfer strategies, were optimized and good thermal desorption efficiencies were obtained. The method detection limit (MDL) concentration ranged from 0.04 pg/L for 1H,1H,2H,2H-perfluorododecyl iodide to 1.2 pg/L for perfluorohexyl iodide, and instrument response of a seven-point calibration was linear in the range of 10–1000 pg. Travel spike recoveries ranged from 83% to 116%. Small variabilities of less than 36% were obtained near the MDLs and the differences between triplicates were even smaller (2.1–7.3%) at 200 pg spiked level. The method was successfully applied to analyze ambient air samples collected near a point source, and five PFIs were identified (10.8–85.0 pg/L), with none of the analytes detectable at the background site.

1. Introduction

Fluorinated additive materials have a wide range of applications such as in surfactants, lubricants, varnishes, pesticides and vinyl polymerization [1,2]. Regulatory efforts are underway to limit the use of some of these chemicals, mainly the perfluorinated compounds (PFCs), due to concerns over their environmental persistency, bioaccumulation ability and toxicity [3,4]. Among the PFCs, perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) are most widely detected in human [5,6] and other biological samples including those in pristine areas such as the Arctic [7,8]. Airborne fluorotelomer alcohols (FTOHs) have attracted considerable attention mainly due to their abilities for long range atmospheric transport [9,10] and can act as volatile precursors that may undergo degradation to form PFCAs and other related compounds [11,12].

Polyfluorinated iodine alkanes (PFIs) consist of an even numbered hydrophobic alkyl chain (typically C_4–C_{12}) which is fully or partially fluorinated and include an iodine atom at one or both of the ends (Table 1). They are reaction products synthesized from telomerization process by iodine pentafluoride reacting with unsaturated taxogen molecules such as tetrafluoroethylene and ethylene. PFIs are used as important industrial intermediates for the production of various PFCs, such as fluorotelomer alcohols, olefins and acrylate monomers [2,13]. Since the usage of electrochemical fluorination method has been terminated since 2002 in most countries, the telomerization process has been increasingly popular in the production of PFCs. The increase in production volume of PFIs might therefore be of particular concern as the risk subsequent release to the environment also increases [14,15]. They might possess abilities to undergo long range transport to remote areas such as the Arctic [16] and become potential precursors to form other known PFC contaminants [17] by e.g. nucleophilic attack on the iodine atom [18].

Martin et al. [19] were the first to use high volume active sampling to collect and quantify airborne FTOHs, N-alkyl perfluorooctane sulfonamides and sulfonamidoethanols by ana-

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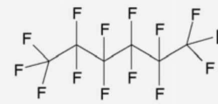
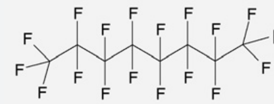
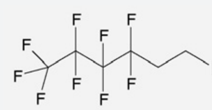
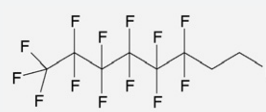
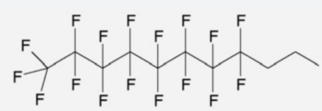
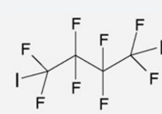
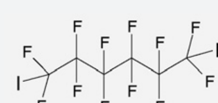
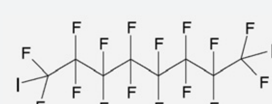
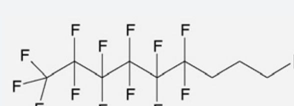
0021-9673/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.chroma.2010.04.051

Table 1
Analyte name, structure and other relevant data.

Acronym	Analyte	CAS no.	Structure	MW[a] (m/z)	VP[b] (Torr)
PFHxI	Perfluorohexyl iodide	355-43-1		445.9	20.4
PFOI	Perfluorooctyl iodide	507-06-1		545.9	3.22
PFDeI	Perfluorodecyl iodide	423-62-1		645.9	0.248
PFDoI	Perfluorododecyl iodide	307-60-8		745.9	0.122
PFHxHI	1H,1H,2H,2H-perfluorohexyl iodide	2043-55-2		373.9	15.0
PFOHI	1H,1H,2H,2H-perfluorooctyl iodide	2043-57-4		473.9	2.9
PFDeHI	1H,1H,2H,2H-perfluorodecyl iodide	2043-53-0		573.9	0.576
PFDoHI	1H,1H,2H,2H-perfluorododecyl iodide	2043-54-1		673.9	0.095
PFBuDiI	1,4-Diiodooctafluorobutane	375-50-8		453.8	5.13
PFHxDiI	1,6-Diiodooctafluorohexane	375-80-4		553.8	0.327
PFODiI	1,8-Diiodoperfluorooctane	335-70-6		653.8	0.067
IS	1H,1H,2H,2H,3H,3H-perfluorononyl iodide (internal standard)	89889-20-3		487.9	1.1

[a] Average molecular weight.
[b] Estimated vapor pressure calculated by USEPA EPI Suite V3.2.