



Isomers/enantiomers of perfluorocarboxylic acids: Method development and detection in environmental samples



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HIGHLIGHTS

- We report a method to detect up to eight PFOA isomers.
- We identify three chiral isomers with pure standards.
- Enantiomeric fractions (EFs) of the P3 isomer can be calculated.
- P3 EFs are identified in samples of biosolids, soil, plants and sediments.

ARTICLE INFO

Article history:

Received 7 May 2015

Received in revised form

1 October 2015

Accepted 19 October 2015

Available online xxx

Keywords:

Perfluorocarboxylic acids

PFCAs

PFOA

Isomers

Chiral

Enantiomers

Enantioselectivity

ABSTRACT

Perfluoroalkyl substances are globally distributed in both urban and remote settings, and routinely are detected in wildlife, humans, and the environment. One of the most prominent and routinely detected perfluoroalkyl substances is perfluorooctanoic acid (PFOA), which has been shown to be toxic to both humans and animals. PFOA exists as both linear and branched isomers; some of the branched isomers are chiral. A novel GC–NCl–MS method was developed to allow for isomer/enantiomer separation, which was achieved using two columns working in tandem; a 30-m DB-5MS column and a 30-m BGB-172 Analytik column. Samples were derivatized with diazomethane to form methyl esters of the PFOA isomers. In standards, at least eight PFOA isomers were detected, of which at least four were enantiomers of chiral isomers; one chiral isomer (P3) was sufficiently separated to allow for enantiomer-fraction calculations. Soil, sediment and plant samples from contaminated locations in Alabama and Georgia were analyzed. P3 was observed in most of these environmental samples, and was non-racemic in at least one sediment, suggesting the possibility of chirally selective generation from precursors or enantioselective sorption. In addition, the ratio of P3/linear PFOA was inversely related to distance from source, which we suggest might reflect a higher sorption affinity for the P3 over the linear isomer. This method focuses on PFOA, but preliminary results suggest that it should be broadly applicable to other chiral and achiral perfluorocarboxylic acids (PFCAs); e.g., we detected several other homologous PFCA isomers in our PFCA standards and some environmental samples.

Published by Elsevier Ltd.

1. Introduction

Fluorotelomer and perfluoroalkyl substances (PFASs) have been produced in relatively large quantities since the 1950s to impart anti-wetting and anti-staining properties to a wide range of consumer products such as carpeting, metal plating and cleaning, food

packaging, shampoos, paper, and fire-fighting foams (Prevedouros et al., 2006; Paul et al., 2009). The anti-wetting and anti-staining properties are imparted by the elemental fluorine atom, which is the most electronegative of all elements (Giesy et al., 2010). Unfortunately, these same properties cause PFASs to be environmentally persistent and, hence, have the potential to be bio-accumulative (Lee et al., 2012; Conder et al., 2008; Martin et al., 2004, 2003). Among the most widely distributed and persistent PFASs are perfluorooctanoic acid (PFOA) (Fig. 1) and perfluorooctane sulfonate (PFOS) (Prevedouros et al., 2006; Lau et al., 2007; Gewurtz et al., 2013).

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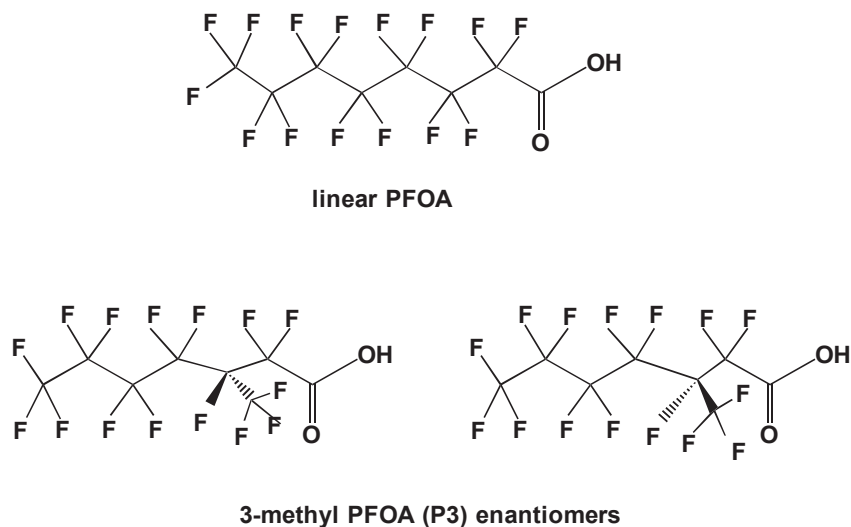


Fig. 1. Structures for linear PFOA and both enantiomers of branched-chain P3 PFOA.

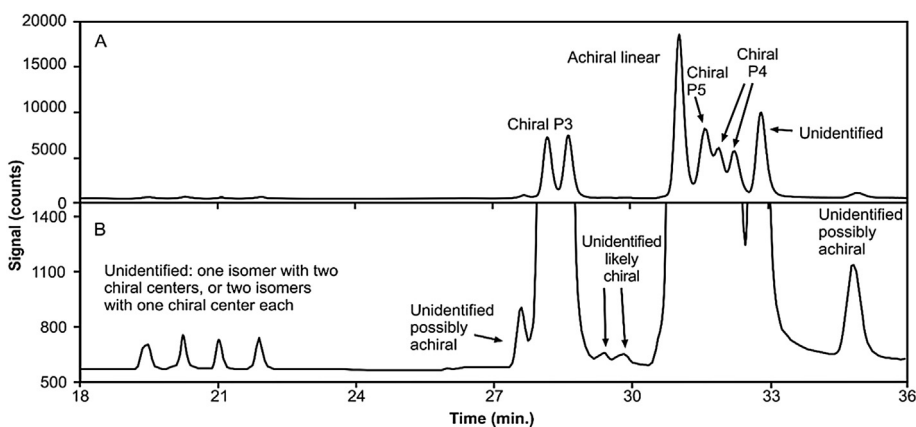


Fig. 2. SIM Chromatogram of technical-grade PFOA standard: Linear PFOA, and chiral P3, P4 and P5 PFOAs, identified with authentic standards, are labeled in 2A. Minor unidentified branched-chain PFOA isomers are labeled in 2B, an expansion of the signal scale in 2A.

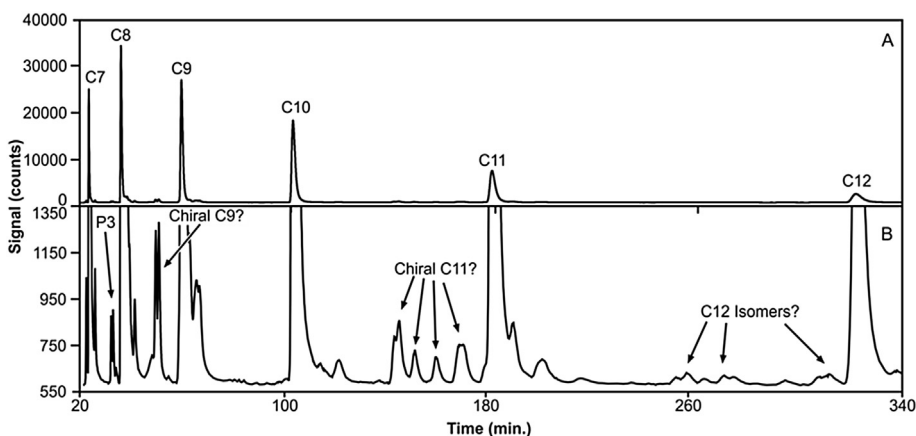


Fig. 3. A) Mixed standards of C7 through C12 PFCAs purchased from Oakwood Products, Inc. in 2005. B) An expansion of the signal field from panel A. Trace levels of chiral and achiral branched-chain isomers evidently are present for several homologs.

PFASs are globally ubiquitous in both remote and urban environments (Paul et al., 2009; Giesy and Kannan, 2001; Yamashita et al., 2005) and PFASs are present in a wide variety of matrices including human blood (whole, plasma and serum), sediments,

water, and wildlife (Higgins et al., 2005; Kannan et al., 2001; Taniyasu et al., 2003; Washington et al., 2007). Due to the widespread use of PFASs, including polymers, in many common products, their degradation products, (Washington et al., 2015) are

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