Differentiation of Important Perfluorooctane Sulfonate Isomers by Tandem Mass Spectrometry

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Introduction

Perfluorooctane sulfonate (PFOS) has become an important environmental contaminant. It is also a model compound concerning the understanding of the environmental distribution of the perfluorinated compounds (PFCs). PFCs have been produced since the 1950ies mainly by 3M company[1]. Due to the specific properties of the strong C-F bond[2], PFOS based compounds are used in a variety of products, such as surface treatments, paper protection and as performance chemicals[3]. Fluorinated compounds are produced via two main routes of synthesis. These are the Simons electrochemical fluorination (ECF), which was employed by 3M, and the telomerisation. Both processes form impurities besides the main linear compound. Therefore, the origin of PFCs in biota can be identified by analysing the impurity pattern. Branched isomers indicate an electrochemical process. Their amount in ECF produced PFCs ranged from 10% to 30%[4]. Previous ^{19}F-NMR data reported the isomeric composition of a PFC solution[5]. Some perfluoromonomethyl and perfluorodimethyl branched isomers were described to be present in ECF based compounds, such as PFOS. Perfluoroisopropyl as well as perfluoromonomethyl substituted isomers were found to be most abundant with a relative abundance of ca. 11% and 17 % respectively. The remaining branched isomers were identified as the *tert*-perfluorobutyl, a-perfluoromethyl and the *gem*-dimethyl isomers[5].

The objective of this study was the mass spectrometric characterisation of some purified PFOS isomers expected to be present as by-products in commercial PFOS solution. This was carried out by high performance liquid chromatography (HPLC) combined with electrospray ionisation (ESI) and triple quadrupole (TQ) mass spectrometry (MS). Seven constitutional isomers previously investigated by ^{19}F-NMR by Wellington Laboratories were studied: Linear PFOS (L-PFOS) and the series of the six possible perfluoromonomethyl substituted structures. These were assigned as iso-PFOS (perfluoroisopropyl), 5m-PFOS (5-perfluoromethyl), 4m-PFOS (4-perfluoromethyl), 3m-PFOS (3-perfluoromethyl), 2m-PFOS (2-perfluoromethyl) and a-PFOS (a-perfluoromethyl) branched isomers.

Materials and Methods

Methanol (≥99.8%) was delivered by SDS (Peypin, France). Water was purified by an Elgastat Maxima HPLC water purification unit (Elga Ltd., Bucks, England).Ammonium acetate (98.0%) was purchased from Merck (Darmstadt, Germany). PFOS isomer fractions were provided by Wellington Laboratories. A commercial sample of PFOS was derivatised and the resulting mixture separated by a combination of crystallisation and preparative-scale HPLC. A set of six fractions was available, each containing a different isomer as the major component accompanied by smaller amounts of up to four further isomers. The compositions of the fractions were checked by ^{19}F-NMR.

The isomer mixtures were analysed as follows: A phenyl perfluorinated phase (PFP) (Fluophase, Thermo Electron, 150 mm column length, 2.1 mm i.d., 5 mm particles size, 100 Å pore size) and a X-Terra C18 phase (Waters, 100 mm length, 3.0 mm i.d., 5 mm particles size, 125 Å pore size) were employed for separation. The following gradient of water and methanol was applied with 4mM ammonium acetate: 30% methanol for 1 min, to 65% within 12 min, kept for 6 min, to 85% within 6 min, isocratic for 6 min. Then, the column was rinsed with 100% methanol for 1 min and returned to the starting conditions within 1 min. The flow rate was 200 ml/min.

Electrospray ionization in the negative ion mode (ESI(-)) was used. The triple quadrupole experiments were conducted with a 1200L mass spectrometer (Varian, USA) and two solvent delivery modules (ProStar 210, Varian, USA). The following instrument parameters were applied: Nitrogen drying gas flow 137 kPa, temperature 200 °C, spray voltage 4.0 kV. Hydrogen was used as nebulizing gas at a flow of 413 kPa. The heated capillary voltage was set to –45 V. Argon was used as collision gas at a collision cell pressure of 0.27 Pa. A degasser (Degassit,

Metachem Technologies, USA) was employed.

Results and Discussion

HPLC-ESI(-)-TQ-MS^2 experiments with a PFP phase allowed the characterisation of six isomers (L-PFOS, iso-PFOS, 5m-PFOS, 4m-PFOS, 3m-PFOS and a-PFOS). Special chromatographic conditions were performed to enable the separation and thus the MS characterisation of 2m-PFOS. A C18 phase employed in the reversed direction was necessary to isolate 2m-PFOS. Figure 1 shows the seven spectra of the pure isomers. Some conclusions concerning the mechanism of fragmentation could be made. Moreover, it will be shortly demonstrated that due to the specific fragmentation behavior of the isomers, PFOS quantification involved systematic error.

The molecular ions (*m/z* 499) common to all the PFOS isomers were selected as precursor ions. In the seven spectra shown in Figure 1, two series of fragmentation were observed typical for PFOS. One was the "9-series" containing *m/z* 119, 169, 219…to *m/z* 419 and one the "0-series" ranged from *m/z* 130, 180…to *m/z* 430. The product ion of each series was separated by 50 mass units (CF_2). Additionally, formation of the fluorosulfonate group *m/z* 99 and the sulfonate group *m/z* 80 was observed. The MS^2 spectra of L-PFOS (Figure 1a) contained mainly these two fragments (*m/z* 80 and 99). The CF_3 branching along the perfluorinated chain caused a specific isomeric pattern (Figure 1b-c-d-e-f-g).

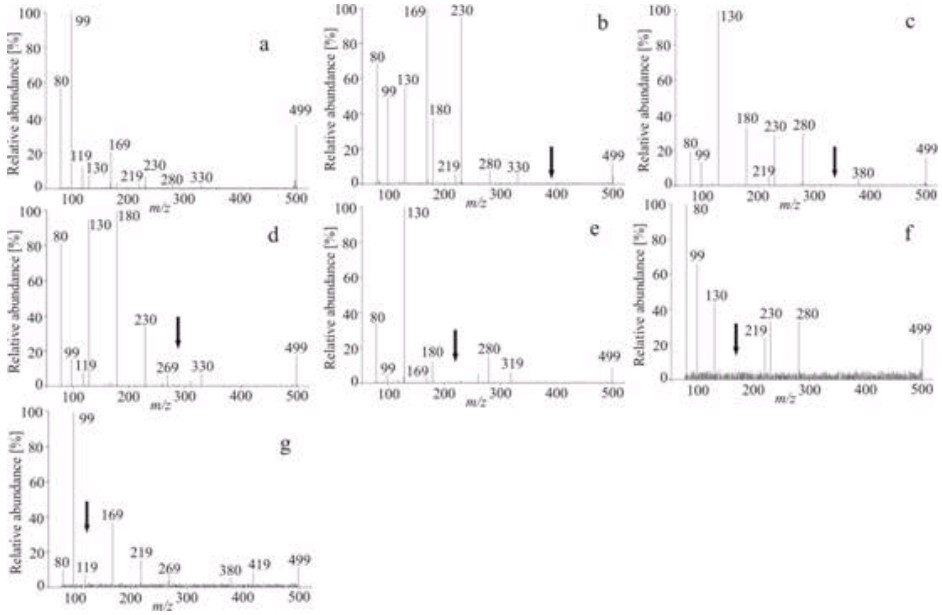

Figure 1: ESI(-)-TQ-MS^2 spectra of L-PFOS (a), iso-PFOS (b), 5m-PFOS (c), 4m-PFOS (d), 3m-PFOS (e), 2m-PFOS (f) and a-PFOS (g) obtained by elution of the isomers on a PFP phase. The molecular ions (*m/z* 499) were under fragmentation (collision energy of 40 V). Missing fragments of the "0-series" are marked with an arrow.

Suppression of the fragmentation at the CF_3 branching point led to a missing fragment in the "0-series". Missing masses were observed at *m/z* 380, 330, 280, 230 and 180 for the iso-PFOS, 5m-PFOS, 4m-PFOS, 3m-PFOS and 2m-PFOS. The MS^2 spectrum of a-PFOS (Figure 1g), did neither show the fragment *m/z* 130 ($[CF_2SO_3]^-$) nor the complete "0-series" of fragmentation. This resulted in an abundant "9-series". Thus, a a-monoperfluoromethyl structure avoided the mechanism of fragmentation which leads to the formation of the "0 series" to occur.

The found fragmentation behavior should allow to identify these PFOS isomers in biota. Moreover, this should also cause a systematic error in the PFOS quantification procedure. First, PFOS determination in biota was based on the 499 ® 99 mass transition[6]. The MS^2 spectra of 5m, 4m and 3m PFOS (Figure 1c-d-e) contain the fragment *m/z* 99 at low relative abundance (< 20%). Thus, final PFOS amount did not take into account these three isomers due to very low limit of detection. Moreover, quantification was verified by quantitative agreement (±30%) between minimum

two additional mass transitions[6]. As shown before, the MS behavior of PFOS isomers was specific with missing masses and preferential formation of fragments. Therefore, a high quantitative agreement value between two mass transitions could result from the predominance in biota of certain isomers.

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References

1. Hekster F., De Voogt P., Pijnenburg A. and Laane, R. (2002) Aquatic Environmental Assessment Report RIKZ/2002.043.

2. Key B., Howell R. and Criddle C. (1997) *Environ. Sci. Technol.* 31: 2445-2454.

3. Organisation for Economic Co-operation and Development. (2002) U.S. Environmental Protection Agency, Docket AR226-1140.

4. De Silva A. and Mabury S. (2004) *Environ. Sci. Technol.* 38: 6538-6545.

5. Kestner T. (1997) U.S. Environmental Protection Agency, Docket AR226-0564.

6. Kannan K., Franson J., Bowerman W., Hansen K., Jones P. and Giesy J. (2001) *Environ. Sci. Technol.* 35: 3065-3070.