

Differentiation of Important PFOS Isomers by Tandem Mass Spectrometry



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Origin of the PFOS isomers

The commercial PFOS solution contains different isomers¹ due to the route of synthesis. Electrochemical fluorination (ECF) is the mostly used process and yields the following composition²:

- Monoperfluoromethyl branched
- Dimethylperfluoromethyl branched
- Linear PFOS (70 %)

Objective

Structure characterisation of seven constitutional PFOS isomers by high performance liquid chromatography (HPLC) coupled with electrospray ionisation in the negative mode (ESI(-)) and tandem MS.

Investigated isomers

- linear PFOS (L-PFOS)
- perfluoroisopropyl (*iso*-PFOS)
- 5-perfluoromethyl (5m-PFOS)
- 4-perfluoromethyl (4m-PFOS)
- 3-perfluoromethyl (3m-PFOS)
- 2-perfluoromethyl (2m-PFOS)
- α -perfluoromethyl (α -PFOS)

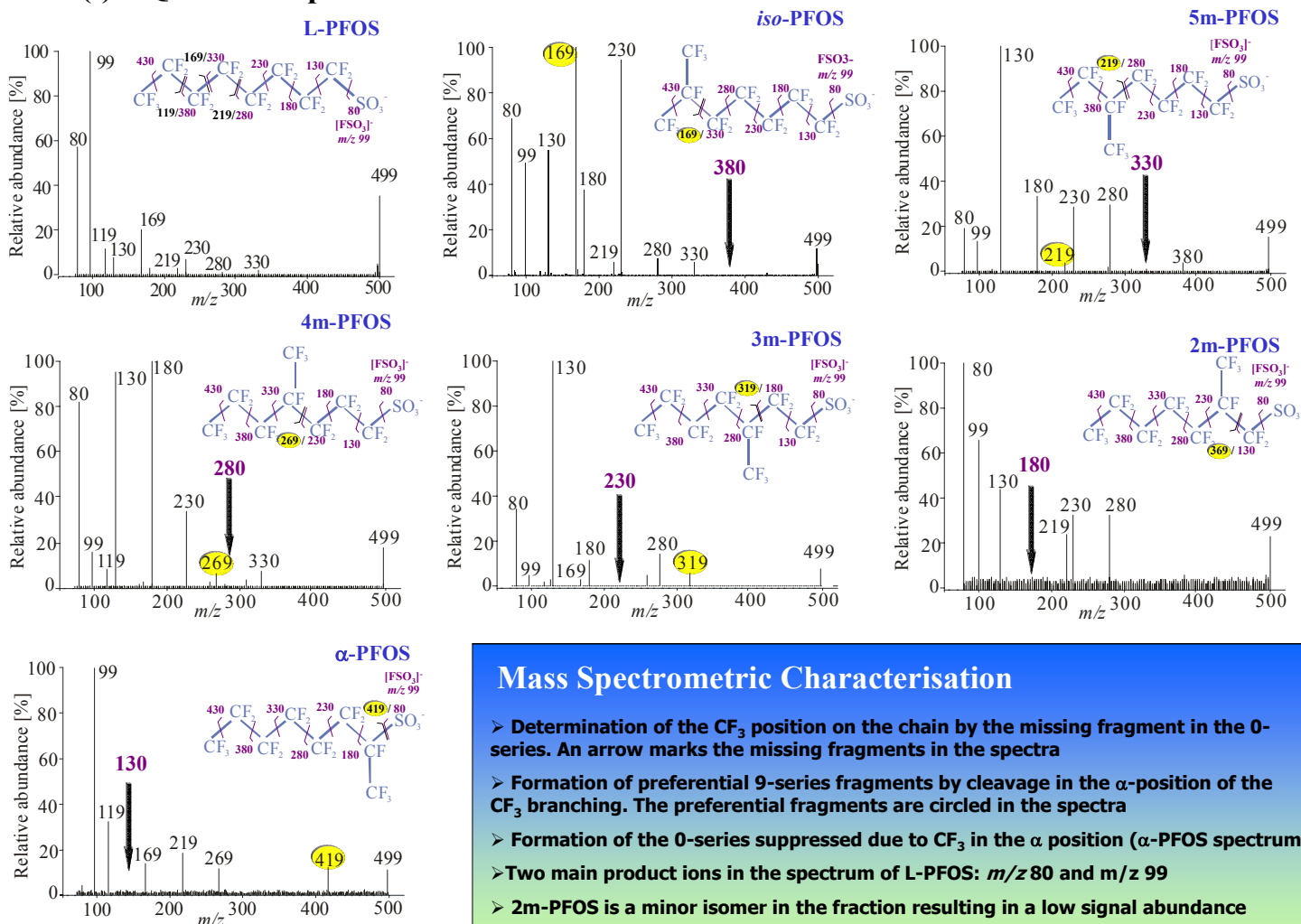
Instrumentation

➤ **PFOS isomer fractions** were obtained after derivatisation, crystallisation and preparative scale HPLC, carried out by Wellington Laboratories Inc.

➤ **Separation:** Fluophase (Thermo Electron, 150 mm * 2.1 mm, 5 μ m) or X-Terra C18 (Waters, 100 mm * 3.0 mm, 5 μ m).

➤ **MS:** 1200L Triple Quadrupole (Varian, USA) with ESI(-), capillary voltage: -45 V, spray voltage: 4 kV, collision gas: Ar. Collision energy: -40 V applied to the molecular ions (m/z 499).

ESI(-)-TQ-MS/MS spectra



Mass Spectrometric Characterisation

- **Determination of the CF_3 position on the chain by the missing fragment in the 0-series.** An arrow marks the missing fragments in the spectra
- **Formation of preferential 9-series fragments by cleavage in the α -position of the CF_3 branching.** The preferential fragments are circled in the spectra
- **Formation of the 0-series suppressed due to CF_3 in the α position (α -PFOS spectrum)**
- **Two main product ions in the spectrum of L-PFOS: m/z 80 and m/z 99**
- **2m-PFOS is a minor isomer in the fraction resulting in a low signal abundance**
- **Reduced isomer detectability when usual mass transition m/z 499 \rightarrow 99 is monitored: only L-PFOS, *iso*-PFOS, 2m-PFOS and α -PFOS give this fragment with a relative abundance >50%**

m/z 499 as precursor ions in all the spectra

References

- 1- Langlois I. and Oehme. M. (2004) *Organohalogen Compd.* 66: 3973-3978.
- 2- Kestner T. (1997) U.S. Environmental Protection Agency. Docket AR 226-0564.

Acknowledgments

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