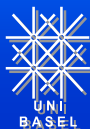


Derivatisation of Perfluorooctane Sulfonate and Perfluorodecanoic acid for the Analysis by Gas Chromatography coupled with Mass Spectrometry



Ingrid Langlois and Michael Oehme
Organic Analytical Chemistry, University of Basel, Switzerland

Objective

- ✗ No GC derivatisation step has been yet reported for perfluorooctane sulfonate (PFOS) although some procedures exist for the perfluorinated carboxylic acids^{1,2}
- ✗ Derivatisation procedure would allow to use GC-MS as an alternative to LC-MS

Derivatisation procedure

- ✗ Conversion of PFOS and PFDcA (perfluorodecanoic acid) to their iso-propyl ester with iso-propanol as derivatisation reagent
- ✗ Identification of the derivatives by electron ionisation-MS
- ✗ Confirmation of the structure of the derivatives by using a labelled derivatisation reagent

Instrumentation

- **Separation:** capillary HP-5MS, 15 m length, 0.25 mm i.d, 0.25 mm film thickness. The temperature program was 40 °C isothermal for 8 min, then 5 °C/min to 130 °C, 30 °C/min to 220 °C and isothermal for 5 min.
- **GC-MS system:** MD800 (Fisons, United Kingdom), electron ionisation (EI) at a collision energy of 70 eV.

Chemicals

PFOS potassium salt from ABCR (Germany), PFDcA from Fluka (Germany), iso-propanol from Biosolve Ltd. (The Netherlands) and iso-propyl-1,1,1,3,3,3-d6 alcohol (99.8 % purity) from CDN Isotopes Inc. (Canada).

Derivatisation procedure

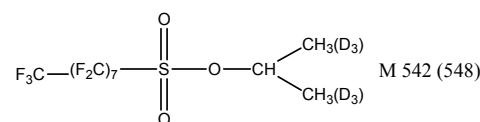
PFOS / PFDcA

+
iso-propanol (or
isopropyl-d6 alcohol)
2 % sulfuric acid

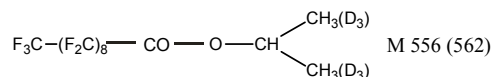
shaken
over night

Extraction with
cyclohexane/water
(800µl/200µl)

deriv-PFOS



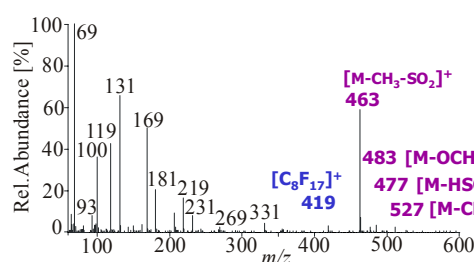
deriv-PFDcA



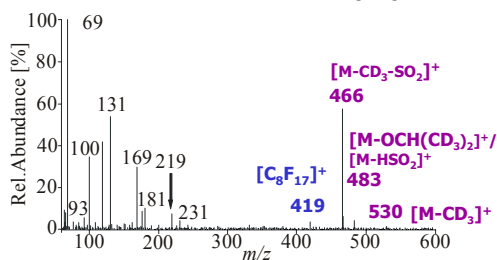
In brackets: molecular weight labelled

EI-MS spectra

Deriv-PFOS



Deriv-PFOS with labelled iso-propanol



Results and discussion

✗ Typically two series of fragmentation of perfluorinated compounds: 9-series (m/z 69, 119, 169...) and 1-series (m/z 131, 181, 231...) and formation of m/z 93 [C_3F_3]⁺ and m/z 100 [C_2F_4]⁺

✗ Confirmation of the perfluorinated chain length by formation of corresponding higher fragment from the 9-series

✗ Fragments of interest in the higher mass range

✗ Similar fragments: [$\text{M}-\text{CH}_3$]⁺ and [$\text{M}-\text{CH}_3-\text{SO}_2$]⁺ (der-PFOS) / [$\text{M}-\text{CH}_3-\text{CO}$]⁺ (der-PFDcA)

✗ Two additional fragments in the EI-MS spectrum of der-PFOS: [$\text{M}-\text{OCH}(\text{CH}_3)_2$]⁺ (m/z 483) and [$\text{M}-\text{HSO}_2$]⁺ (m/z 477)

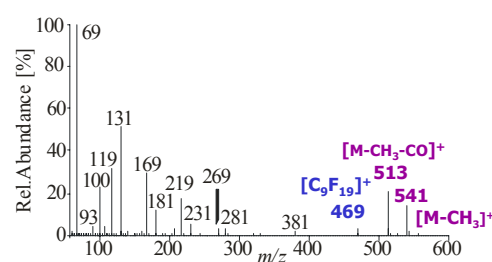
✗ Mass shift of 3/6 units confirmed the structure of the derivatives when labelled iso-propanol was used

✗ m/z 483 involved 2 fragments in the EI-MS spectrum of der-PFOS with labelled iso-propanol

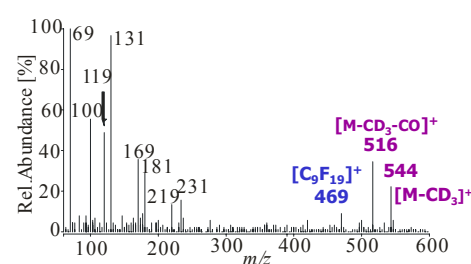
✗ First derivatisation procedure proposed for PFOS

✗ Negative chemical ionisation-MS and EI-high resolution MS were also conducted (results not shown) and confirmed the structure of both derivatives

Deriv-PFDcA



Deriv-PFDcA with labelled iso-propanol



References

- 1- Moody, C. A.; Field, J. A. Environ. Sci. Technol. 1999, 33, 2800-2806.
- 2- Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Analyst 2004, 128, 758-764.

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