



# Analysis and Quantification of the Perfluoroorganic Components Present in the Technical Mixture of Perfluorooctanesulfonate (PFOS)

Nicole Riddell<sup>a</sup>, Gilles Arsenault<sup>a</sup>, Brock Chittim<sup>a</sup>, Alan McAlees<sup>a</sup>, Ingrid Langlois<sup>c</sup>, Robert McCrindle<sup>b</sup>, Michael Oehme<sup>c</sup>.

<sup>a</sup> Wellington Laboratories Inc., Guelph, Ontario, N1G 3M5, Canada  
<sup>b</sup> University of Guelph, Chemistry Dept., Guelph, Ontario, N1G 2W1, Canada  
<sup>c</sup> Organic & Analytical Institute, University of Basel, Switzerland, 4057



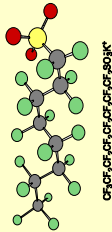
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## Introduction

Perfluorooctanesulfonate (PFOS) has been the subject of recent interest because of its presence as a global pollutant<sup>1</sup> and potential toxicity<sup>2</sup>. The production of PFOS from linear alkyl precursors using electrochemical fluorination is not a clean process, but instead generates complex mixtures. The structures and relative quantities of 11 isomers present in technical PFOS were recently confirmed by <sup>19</sup>F NMR spectroscopy.<sup>3</sup> However, it is unknown at the present time if the individual isomers have different toxicities or varying tendencies to bioaccumulate.

Generally, analysis of the C8 branched isomers by liquid chromatography (LC) has resulted in only partial separation resulting in two broad peaks.<sup>4,5</sup> Recent work has shown the possibility of improved separation of the PFOS isomers using either a pentaffluorophenyl column<sup>6</sup> or an Ultra Performance Liquid Chromatographic (UPLC) system<sup>7</sup>.

The objective of this work was to optimize the separation of the PFOS isomers on an UPLC system. Expanding on work previously performed by Langlois and Oehme<sup>8</sup> on the analysis of fragmentation patterns of some of the individual isomers, we shall summarize results pertinent to the identification and quantification of the various PFOS isomers and some homologues found in technical grade material. It is hoped that this work will eventually lead to the identification and quantification of the individual isomers of PFOS present in environmental samples.



## Experimental

Analysis of the PFOS technical mixture was carried out on a Waters Acquity Ultra Performance LC and Micromass Quattro micro API mass spectrometer in negative ion mode (see below for LC conditions and MS tune parameters). After screening a few different stationary phases, the Acquity UPLC BEH Shield RP<sub>18</sub> column (1.7 µm, 2.1 x 100mm) was chosen for use because the embedded polar functional group appeared to facilitate the separation of the PFOS isomers. Separation of the congeners was carried out in full scan mode while separation of the isomers was completed in SIR mode.

### Gradient for separation of isomers

Start: 55% H<sub>2</sub>O with 10 mM NH<sub>4</sub>OAc  
 47% MeOH/ACN with 10 mM NH<sub>4</sub>OAc  
 Ramp: to 51:49 over 6 min and hold for 17 min  
 Ramp: to 10:90 over 0.5 min to flush and hold for 1 min  
 Return to initial conditions  
 Time: 26 mins  
 Flow: 400 µl/min

### Tune Parameters

Electrospray (negative)  
 Capillary Voltage (kV) = 2.60  
 Cone voltage (V) = 60.00  
 Cone Gas Flow (L/Hr) = 60  
 Desolvation Gas Flow (L/Hr) = 650  
 Collision Gas (mbar) ~ 3.50e-3  
 Collision Voltage (V) = 40

## Results and Discussion

It is important to note that the technical product is comprised of only approximately 85% of the C8 sulfonates (see Figure 2). It has been reported to contain lower homologues such as PFBS, PFPS, PFlHS (10%), as well as small amounts of metals (Ca, Mg, Na, Ni, Fe), inorganic fluoride, hydrocarbon sulfonate salts, and other fluoro-compounds.<sup>9</sup> Indeed, we have found that the technical mixture analyzed also contains higher homologues (C9-C12) and perfluorocarboxylates (C5-C9). Therefore, the technical mixture is not appropriate for use as a quantitative standard. In order to accurately quantify PFOS in environmental samples, it is important to separate the isomers as they have different response factors by LC/MS/MS. The PFOS isomers were successfully separated under UPLC conditions (see Figure 3) and most were identified using <sup>19</sup>F NMR (see Figure 4).

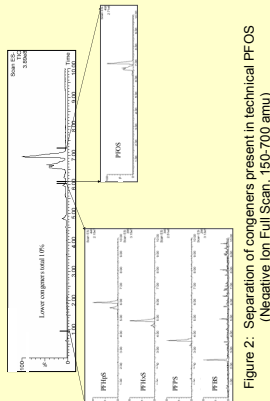


Figure 2: Separation of congeners present in technical PFOS (Negative Ion Full Scan, 150-700 amu)

Results continued....

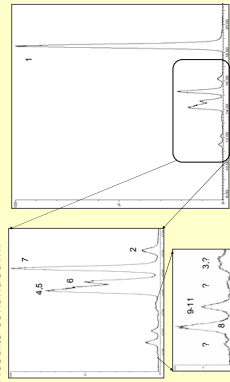


Figure 3: Chromatographic separation of the PFOS isomers (SR, m/z 489)

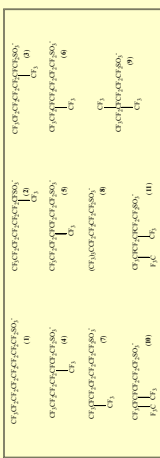


Figure 4: Structures of the branched PFOS isomers determined by <sup>19</sup>F NMR

It may also be possible to identify the isomers through careful analysis of their MS fragmentation patterns. Since charge stabilization at branching points promotes fragmentation and the relative abundance of the parent ion (m/z 499) decreases as the CF<sub>3</sub> substitution gets closer to the sulfonate group, each isomer should have a unique fragmentation pattern. Also, collision cell induced fragmentation produces a major "u-series" (m/z 180 to 430) and a minor "g-series" (m/z 169 to 419), but when a CF<sub>3</sub> group is located on any specific carbon along the chain, the corresponding "o" series fragment is missing. Depending on the degree of branching in any specific isomer, some fragments of both series are either present or absent (see Table 1 and Figure 5).

Table 1: A summary of the expected missing peaks of the branched PFOS isomers

PFOS isomer	Missing peaks
2-CF <sub>2</sub> -PFOS	180
3-CF <sub>2</sub> -PFOS	230
4-CF <sub>2</sub> -PFOS	280
5-CF <sub>2</sub> -PFOS	330
6-CF <sub>2</sub> -PFOS	380
1,1-dimethyl PFOS	130, 369
2,2-dimethyl PFOS	180, 319
3,3-dimethyl PFOS	230, 269
4,4-dimethyl PFOS	280, 219
tert-butyl PFOS	330, 169



Figure 5: Fragmentation patterns and missing peaks of selected PFOS isomers

## Conclusions

- Technical PFOS contains many impurities which can vary from batch to batch. This can lead to inaccurate results if the technical standard is used as a quantification standard.
- It may be possible to identify different isomers of the technical PFOS mixture utilizing their different fragmentation patterns if complete chromatographic resolution of the isomers is not possible.
- Utilizing characteristic "missing peaks" can be a useful tool in identifying PFOS isomers.
- Accurate determination of toxicity can only be achieved if individual PFOS isomers are available.

## References

1. Giesy, J.P. and Kannan K., 2001. Environ Sci Technol. 35, 1339-1342.
2. Yoo, H., Jones, P.D., Bradley, P.W., Guzik, M., Upham, B.L., Trosko, J.E., Newsted, J.L. and Giesy, J.P., 2005. International Symposium On Fluorinated Alkyl Organics in The Environment. Toronto, August 19-20. Abstract# TOX009.
3. Arsenault, G., Chittim, B., McAlees, A. and McCrindle R., 2005. Organohalogen Compd., 57, 818-821. Full paper submitted to Chemosphere for publication.
4. Kikuchi, Y., Vais, N. and Benoit, F.M., 2004. J Environ Monit., 6, 540-545.
5. Kikuchi, Y., Reich, J.A., Tully, J.S., Neebhan, L.L. and Caldwell, A.M., 2004. Environ. Sci. Tech. 38, 3698-3704.
6. Langlois, I. and Oehme, M., 2006. Rapid Commun. Mass Spectrom., 20, 844-850.
7. Jenkins, T., Ellor, N., Twibig, M., Worrall, K. and Kearney, G., 2005. Organohalogen Compd., 67, 244-247.
8. Seacat, A.M., Thorndor, P.J., Hansen, K.J., Clemens, L.A., Eldridge, S.R., Elcombe, C.R., and Buenhoff, J.L., 2003. Toxicology, 183, 117-131.