Aqueous Sample Stability: PFOS, PFOA and Other Fluorinated Compounds

Terry Obal, Ph.D., C.Chem.
ACKNOWLEDGMENTS

Adam Robinson

Sin Chii Chia
‘The most exciting phrase to hear in science, the only one that heralds new discoveries, is not "Eureka!", but rather...

"Hmm... that’s funny...."

- Isaac Asimov
OVERVIEW

- Background
- Objectives
- Experimental Design
- Results
- Conclusions
What are they?

Perfluorooctanoic Acid (PFOA)

Perfluorooctane Sulfonate (PFOS)

Teflon®

Scotchguard®
PFCs and Surfactants

Perfluorooctane Sulfonate (PFOS)

Hydrophilic

Hydrophobic
Why do we care?
## Regulatory Limits – Drinking Water

<table>
<thead>
<tr>
<th>Jurisdiction</th>
<th>PFOA (ug/L)</th>
<th>PFOS (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada – Health Canada</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>U.S.A - EPA</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>U.S.A. – Minnesota</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>U.S.A. – New Jersey</td>
<td>0.04</td>
<td>N/V</td>
</tr>
<tr>
<td>U.S.A. – North Carolina</td>
<td>2</td>
<td>N/V</td>
</tr>
<tr>
<td>Europe – United Kingdom</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>Europe - Germany</td>
<td>0.1 (sum of PFOA and PFOS)</td>
<td></td>
</tr>
</tbody>
</table>
Analytical Challenges

- Sample matrices range from simple to complex
- Adsorption of PFC onto surfaces can be rapid resulting in potential low bias in data
- PFOS data reproducibility of significant concern
Data Impacts

- Data variability
- Lack of confidence in the results
- Inability to make supportable remedial decisions
Study Objectives

- Obtain a “practical” understanding of adsorptive behaviour of PFCs in aqueous samples

- Study adsorption based on:
  - Molecular weight
  - Sample container material
  - Multiple transfers
  - Time
  - Application of matrix modifiers

- Explore the effects of different conditions
PFC Recovery Data: Container Material

Recovery %

PFBA PFBS PFPeA PFHxA PFHxS PFHpA PFOA PFOS PFNA PFDA PFUdA PFDoA PFOSA

Polypropylene Glass HDPE Stainless Steel

> C8
PFOS/PFOA/PFDoA Recovery: Consecutive Sample Transfers
PFOS/PFOA Recovery: Aqueous Matrix Modifiers (pH)

Polypropylene

Glass
PFOS/PFOA/PFDoA Recovery: Organic Matrix Modifiers

**Polypropylene**

**Glass**
PFOS/PFOA/PFDoA Recovery: Time (SA/V Ratio ~ 20; HDPE)
PFOS/PFOA/PFDoA Recovery: Time (SA/V Ratio ~ 20; Glass)
PFOS/PFOA/PFDoA Recovery: Time (SA/V Ratio ~ 0.5; HDPE)
PFOS/PFOA/PFDoA Recovery: Time (SA/V Ratio ~ 0.5; Glass)
Conclusions

- Significant adsorption appears to be independent of sample container material.

- Degree of adsorption appears to be dependent on molecular weight. Significant adsorption can occur for >C8 telomers.

- Adsorption appears to be less significant with perfluorinated carboxylates relative to the perfluorinated sulphonates.
Conclusions

- Addition of an organic matrix modifier/preservative decreases adsorption
  - Field
  - Laboratory

- Surface area to volume ratio is an important consideration in collecting samples
  (i.e. “fill the bottle completely”)
Recommendations

- Adsorption underscores the importance and requirement for isotope dilution in PFC determinations

- Minimize transfer of sample aliquots
  (i.e. as much as is possible, avoid subsampling prior to addressing adsorption)

- Fill bottles completely
Recommendations

- Collect multiple smaller (100mL or less) bottles rather than 1-L

- Consider the addition of an organic preservative (e.g. ACN) to minimize adsorption