Combination of Total organofluorine analysis (TOF) and total oxidizable precursor (TOP) assay for unidentified PFAS

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Photo: Foaming system malfunctions at Pearson airport hangar in 2015 Toronto.ctvnews.ca
Materials and Methods:

Two firefighting foam concentrates available on the Swedish market in 2014:

- **TOP assay**
  - 60 mM $\text{K}_2\text{S}_2\text{O}_8$; 150 mM NaOH in 130 mL bottle; 85°C 6hr

- **Modified SPE**

**Reaction and cleanup**

1. **TOP assay**
   - $\text{S}_2\text{O}_8^{2-} \xrightarrow{\text{heat}} 2\text{SO}_4^{-}$
   - $\text{SO}_4^{-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{OH}$

2. **C8 fluorotelomer precursor**
   - $\text{C}_8\text{F}_{17}$
   - $\text{OH}\bullet$
   - $\text{C}_8\text{F}_{15}$
   - $\text{C}_n\text{F}_{2n+1}\text{COO}^{-}$

**Instrumental Analyses**

- LC-MS/MS
- CIC

### Results and Discussion:

<table>
<thead>
<tr>
<th>Foam</th>
<th>Without Oxidative Reaction</th>
<th>With Oxidative Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng-F/mL after 13,000x dilution</td>
<td></td>
</tr>
<tr>
<td>Foam A</td>
<td>Neutral/cationic</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>Anionic</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Foam B</td>
<td>Neutral/cationic</td>
<td>916</td>
</tr>
<tr>
<td></td>
<td>Anionic</td>
<td>&lt;50</td>
</tr>
</tbody>
</table>

- **Without oxidative reaction:** only neutral or cationic compounds were detected
- **LC-MS/MS → all PFASs unknown**
- **With oxidative conversion:** only anionic compounds were detected
- **Imbalance of fluorine**
Results and Discussion:

NR/OR: Without/With oxidative reaction

- NR: PFHxA
- OR: Eight different PFCAs found (C4 – C11)
- NR: 6:2 FTSA, 4:2 FTSA and 8:2 FTSA
- OR: Thirteen different PFCAs found (C4 – C16)
- C9 – C16 PFCAs indicates presence of other long-chain precursor compounds
Summary and Conclusions:

• PFCA precursors were present in both foams and contributed to the unknown fraction of the TOF concentrations
• The identified unknown precursor compounds were converted from neutral/cationic to anionic after oxidation
• The base of both foam samples might be consisted of 6:2 fluorotelomer compounds
• After TOP assay, PFAS levels detected in Foam A made up for 37 – 45 % and 21 – 44 % in Foam B of the TOF concentrations
• Ultrashort chain PFASs (C2 and C3) are expected to be formed but not measured
• The mass balance after TOP shows that there still is unidentified PFASs present in the foam samples
Comparison of TOF and TOP assay

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