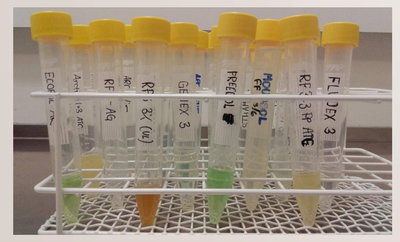
Analysis of firefighting foams on the Swedish market using a non-target analysis approach

Florian Dubocq - Thanh Wang – Anna Kärrman

Man-Technology-Environment (MTM) Research Centre, Örebro University, SE-701 82 Örebro, Sweden

Introduction

Firefighting foams (FFFs) are used as fire extinguishers due to their film-forming properties. These FFFs can contain some organofluorine compounds(1), useful for the physical properties of the foams but also potentially hazardous for environment and human health. The composition of these different FFFs is not always well known and it is important to increase this knowledge to be aware of possible risks for environment or humans. Non-target analysis(2) is a data mining strategy which enables to explore the organic content and identify the main ingredients in 19 different FFFs on the Swedish market avoiding time consuming peak-picking. These FFFs are mainly marketed as foams for flammable and combustible liquid fires (class B fires). Some of the products are marketed as fluorine-free FFF alternatives.



Experiments

❖Extraction

All the FFFs are diluted 10 000 times in a 1:1 MeOH/H_2O mixture prior to direct injection

❖UPLC-qTOF Analysis

Experiments were carried out using a liquid chromatograph hyphenated with a quadrupole-time of flight mass spectrometer (UPLC-qTOF XEVO-G2XS, Waters Corporation, Milford, USA) using an Acquity UPLC BEH C18 column (L 100 mm x ID 2.1 mm, particles of 1.7 µm) with a set temperature of 50°C. The samples has been analysed with an electrospray ionization in both positive and negative mode with an MS^E method. The mobile phase was:

- In positive mode: 70/30 H_2O/MeOH + 0.1% Acetic Acid – MeOH + 0.1% Acetic Acid
- In negative mode: 70/30 H_2O/MeOH + 2mM Ammonium Acetate – MeOH + 2mM Ammonium Acetate

❖Data Analysis

Full scan data has been processed with two softwares, MassLynx (Waters Corporation, Milford, USA) for the acquisition and XCMS network (The Scripps Research Institute, La Jolla, USA) for the statistical tools. For this study, the three main statistical tools used after alignment and grouping tests are :

- Dendogram, to determine groups due to the composition similarities/differences of FFFs.
- Heatmap, where ion signals abundance is converted to Z-scores (rows represent ion features, columns represent different FFFs)
- Principal Component Analysis (PCA), to visualize patterns and emphasize variation among the FFFs

The FFFs has been processed with the non-target analysis in both negative and positive mode. Only the negative ionization results are shown below.

Dendrogram / Heatmap

The dendrogram from 19 FFFs created 5 groups as seen in figure 1. Samples in one group have a more similar composition than samples between different groups. Dendrogram also indicates variation caused by the analytical determination, when replicates are injected, as shown with triplicates (1-3) in figure 1.

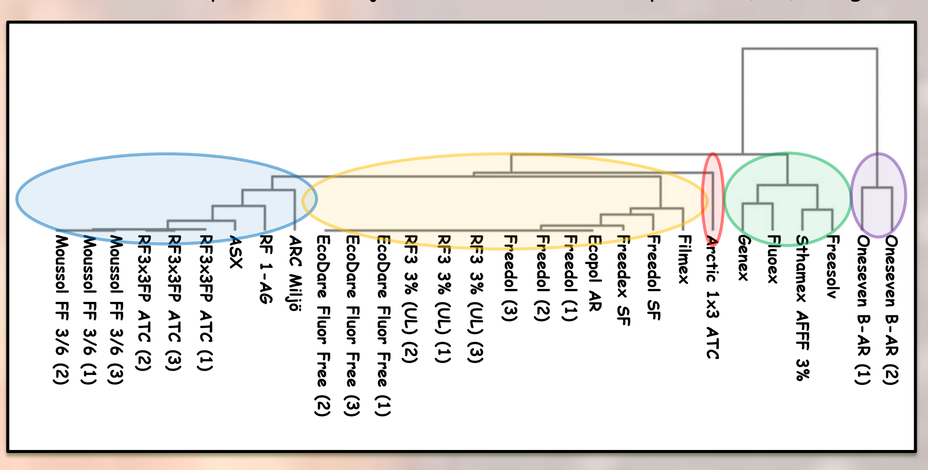


Figure 1: Dendogram for FFFs in negative ionization

The heatmap in figure 2, after the determination of the FFF groups, shows the important markers (rows) for each sample and group (columns).

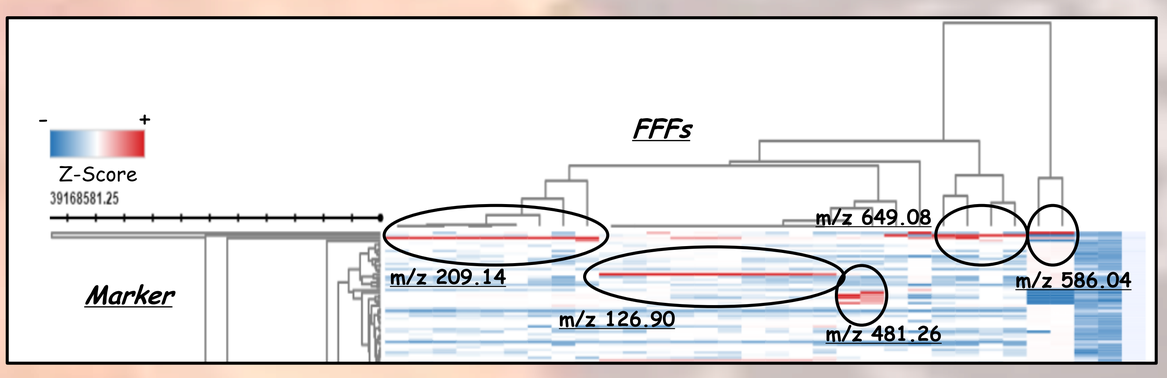
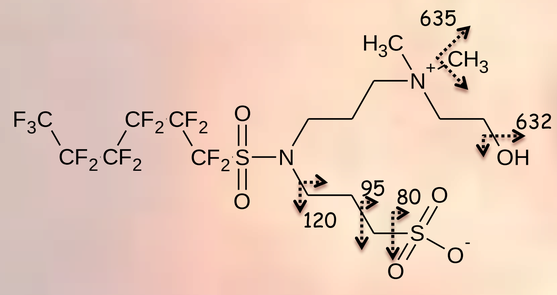


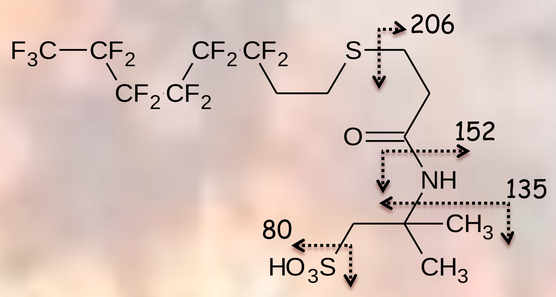
Figure 2: Heatmap for FFFs in negative ionization

Determination of unknowns structure

The last step is to determine the structure of the unknown molecules thanks to the different product ions found in the mass spectra. Below are the proposed structure for the two unknown molecules found in FFFs negative ionization study.



Picture 1: Proposed structure for ion m/z 649.0752



Picture 2: Proposed structure for ion m/z 586.0547

Principal Component Analysis (PCA)

The PCA is an alternative statistical tool to the heatmap and creates an overview of the important markers(3). The PCA in figure 3 provides information about the markers that separate the FFFs. Most of the markers are identical in the heatmap (figure 2) and in the PCA but additional information can be observed using both tools.

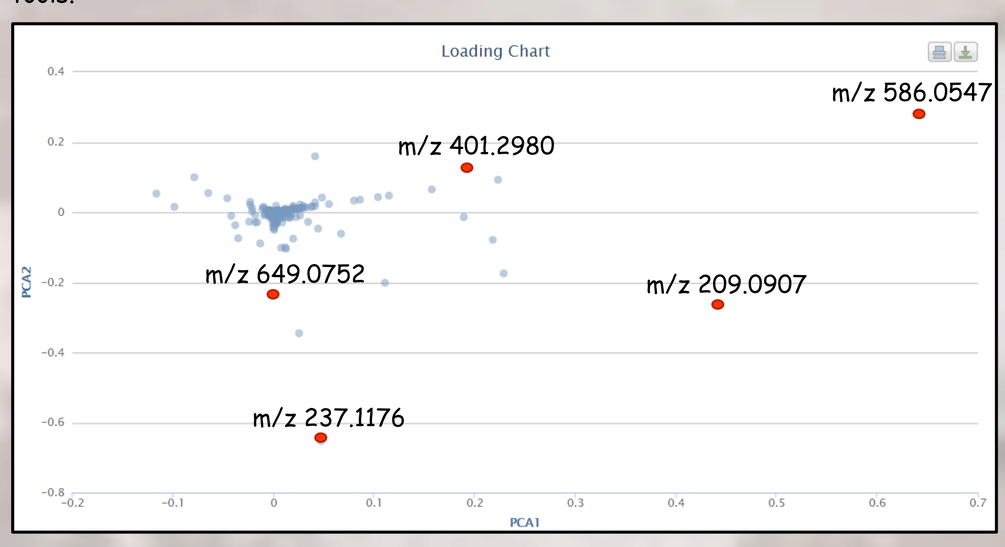


Figure 3: Principal Component Analysis of FFFs in negative ionization

After the determination of the important markers, it is possible to tentatively determine the formula(4) for the different product ions and thus of the molecular ion using exact mass and MS^E spectral information.

Table 1: List of important markers for FFFs negative ionisation analysis

m/z	Rt (min)	Molecular ion	Mass error (ppm)	Product ions → Mass error (ppm)
209.0907	5.27	$[C_8H_{18}O_4S\text{-}H]^-$ Additive to increase boiling point	28.2	96.9603 $[H_2O_4S\text{-}H]^-$ → 7.2 79.9550 $[HO_3S\text{-}H]^-$ → -22.5
237.1176	7.57	$[C_{10}H_{22}O_4S\text{-}H]^-$ Additive to increase boiling point	6.3	96.9596 $[H_2O_4S\text{-}H]^-$ → -13.4 79.9568 $[HO_3S\text{-}H]^-$ → 0.0
586.0547	8.91	$[C_{15}H_{18}F_{13}NO_4S_2\text{-}H]^-$	26.6	566.0323 $[C_{15}H_{17}F_{12}NO_4S_2\text{-}H]^-$ → -1.1 546.0230 $[C_{15}H_{16}F_{11}NO_4S_2\text{-}H]^-$ → -6.8 206.0475 $[C_7H_{13}NO_4S\text{-}H]^-$ → -5.8 152.0388 $[C_4H_{11}NO_3S\text{-}H]^-$ → 4.6 135.0117 $[C_4H_8O_3S\text{-}H]^-$ → 0.7 79.9568 $[HO_3S\text{-}H]^-$ → 0.0
401.2980	9.79	$[C_{21}H_{42}N_2O_5\text{-}H]^-$ Stabilizer	-8.7	387.2851 $[C_{20}H_{40}N_2O_5\text{-}H]^-$ → -2.1 341.2814 $[C_{19}H_{38}N_2O_3\text{-}H]^-$ → 2.9 327.2641 $[C_{18}H_{36}N_2O_3\text{-}H]^-$ → -2.1 102.0540 $[C_4H_9NO_2\text{-}H]^-$ → -14.7
649.0752	8.46	$[C_{16}H_{23}F_{13}N_2O_6S_2\text{-}H]^-$	6.2	635.0568 $[C_{15}H_{20}F_{13}N_2O_6S_2\text{-}H]^-$ → 2.0 632.0687 $[C_{16}H_{22}F_{13}N_2O_5S_2\text{-}H]^-$ → 0.5 629.0671 $[C_{16}H_{22}F_{12}N_2O_6S_2\text{-}H]^-$ → 3.5 491.0678 $[C_{13}H_{16}F_{12}N_2O_2S\text{-}H]^-$ → 3.1 303.0686 $[C_8H_{20}N_2O_6S_2\text{-}H]^-$ → 0.3 182.0492 $[C_5H_{13}NO_4S\text{-}H]^-$ → 2.7 164.0374 $[C_5H_{11}NO_3S\text{-}H]^-$ →-4,3 136.9904 $[C_3H_6O_4S\text{-}H]^-$ → -3.6 119.9889 $[C_3H_5O_3S\text{-}H]^-$ → -6.7 94.9793 $[CH_4O_3S\text{-}H]^-$ → -10.5 79.9568 $[HO_3S\text{-}H]^-$ → 0.0

Conclusion

The non-target data mining used was proven as a suitable method to distinguish different FFFs according to their composition. This method shows that the samples marketed as fluoro-free don't contain fluorine containing molecules. This was also confirmed using a total organic fluorine method (data not shown here). Several surfactants (both with and without fluorine) were tentatively identified as additives or stabilizers. For the two proposed structures, further studies need to be done with standards to confirm the identity.

References

(1) D'Agostino L. *Environ. Sci. Technol. 2014,* ***48****, 121-129* ***(2013)***
(2) *Miljødirektoratet* ***M-27/2013***
(3) Rotander A. et al. *Environ. Sci. Technol. 2015,* ***49****, 2434-2442* ***(2015)***
(4) Schymanski et al. *Anal Bioanal Chem*, 407, 6237-6255 **(2015)**

Contact: florian.dubocq@oru.se