

DETERMINATION OF AFFF COMPONENTS USING A MULTIVARIATE ANALYSIS APPROACH FOLLOWING LC-QTOF MS ACQUISITION

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INTRODUCTION

Aqueous film-forming foams (AFFFs) have been applied to both military and commercial fire-fighting activities to extinguish flammable liquid fuels. However, use of these formulations has resulted, inadvertently, in the release of contaminants into the environment due to migration from the site of application. The various formulations of AFFFs are technical mixtures of numerous fluorocarbon and hydrocarbon compounds¹. Characterizing the unique as well as common components of AFFFs that are currently in use is the starting point to tracking these constituents through various environmental and biological compartments. In this work, seven AFFF mixtures were analyzed using LC-QToF MS in order to obtain full spectral acquisition to which a multivariate analysis approach could be applied to identify unique components within the mixtures.

METHODS

Data was acquired using alternating high and low collision energy states across the full analytical mass range (data independent), such that product and fragment ions were simultaneously generated (MS^F). Samples were diluted in methanol and chromatographic separation performed using an existing liquid chromatography method for the analysis of perfluorinated compounds. Instrument performance with respect to mass accuracy (<5 ppm mass error), retention time conservation and repeatability of analyte response is particularly important in experiments involving non-targeted analysis, and the system was assessed using a solvent standard mixture of compounds. Electrospray positive (ESI⁺) and negative (ESI⁻) modes were acquired separately. Randomized multiple injections of the seven mixtures were subjected to a Principal Component Analysis (PCA). All data was acquired and processed using UNIFI 1.8

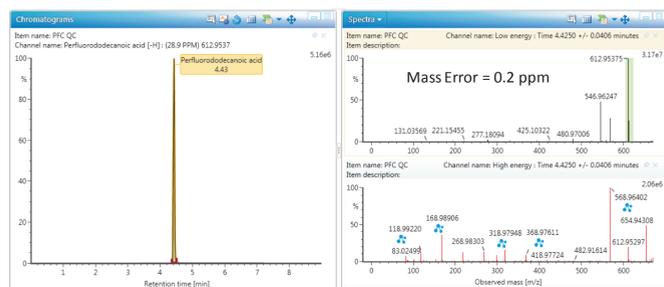


Figure 1. High and low collision energy spectra for perfluorododecanoic acid, one of 13 compounds used as a QC check before and after the randomized samples were analyzed for the ESI⁺ analysis.

LC Conditions

LC System: Waters ACQUITY I-Class
Column: ACQUITY UPLC BEH C18 2.1 x 50 mm, 1.7 μm
Column Temp: 55 °C
Sample Temp: 4 °C

Mobile Phase A: 98:2 water:MeOH 2mM ammonium acetate
Mobile Phase B: MeOH 2mM ammonium acetate

Gradient:	Min.	Flow Rate	%A	%B
Initial	0.650		85	15
	0.5	0.650	85	15
	5	0.650	15	85
	5.10	0.650	0	100
	6.60	0.650	0	100
	6.70	0.650	85	15
	8.50	0.650	85	15

MS Conditions

- MS system: Waters Xevo G2-XS QToF
- Full scan range: 50-1200 m/z
- Source temperature (°C): 120
- Capillary Voltage (μA): 1.0
- Cone voltage (V): 20
- Cone gas flow (L/hr): 50
- Auxiliary gas flow(L/hr): 1000
- Scan Time: 0.2
- Low energy CE (eV): 4
- High energy CE ramp (eV): 40-60
- Lock mass: Leucine enkephalin
- 556.2766 (positive)/554.2610 (negative)

RESULTS AND DISCUSSION

Distinctive groupings from the PCA plot were observed for three AFFFs in both modes with clusters of five of the seven in ESI⁺ and four of the seven in ESI⁻ (Figure 2). Pool samples, which contain all ions used in the multivariate analysis, were clustered appropriately towards the middle. Investigation of exact mass/retention time pairs strongly associated with all groupings (Figures 3 and 4) using molecular formulae calculations and ChemSpider database searching resulted in the identification of multiple sulfate, hydrocarbon and fluorinated compounds. Further interrogation of the markers using trend plots to indicate presence and abundance across all the injections yielded additional identifications that were either unique to specific formulations or in some cases common compounds across multiple AFFFs. For those constituents that had a proposed structure, product ion structures were assigned and used as a means to support a potential identification (Figure 5).

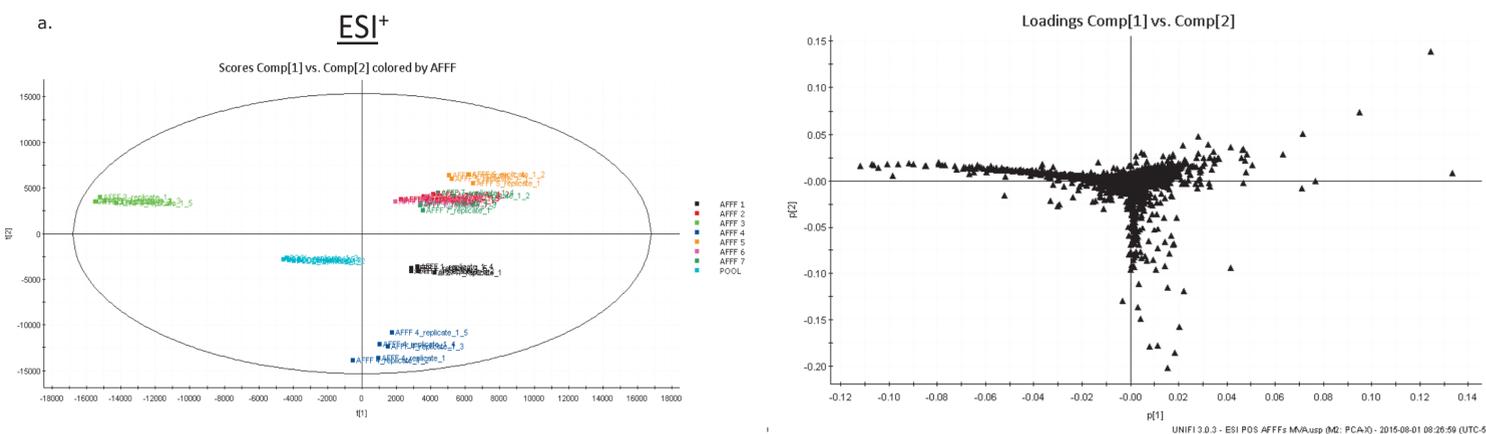


Figure 3. Loadings plot of all exact mass/retention time pairs (markers) identified in the samples, from ESI⁺ analysis. Localization of markers is related to their incidence in an AFFF, as they appear in the PCA plot.

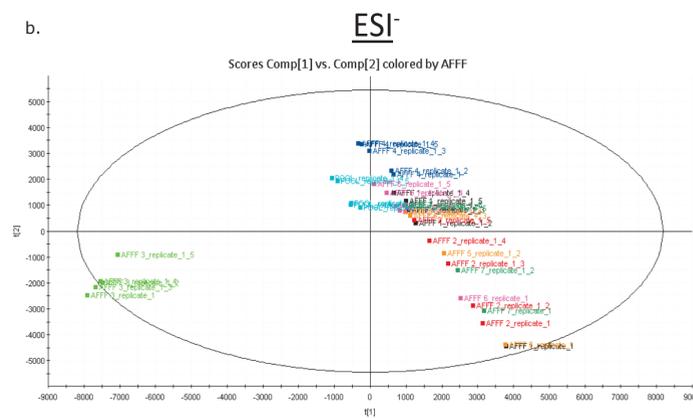


Figure 2. Principal component analysis (PCA) plots for the seven AFFFs analyzed in ESI⁺ (a), and ESI⁻ (b). Both polarities were utilized in order to capture a comprehensive sampling of constituents in the samples.

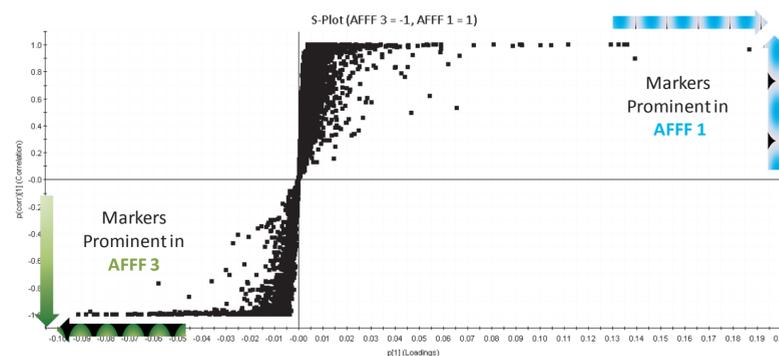


Figure 4. S-plot comparing markers associated with AFFF1 and AFFF 3.

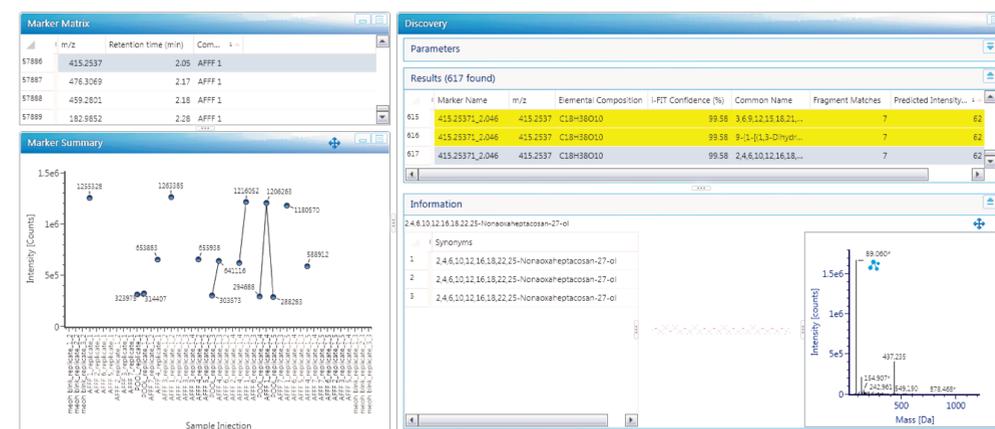


Figure 5. Proposed ID for marker prominent in AFFF 1, and also present in AFFF 4. Pool samples also indicate the presence of the marker, as expected. Discovery Toolset, a feature within UNIFI software, uses a combination of elemental composition proposals, theoretical isotopic distribution comparisons, ChemSpider searching and fragment matching based on proposed structures. Markers were submitted as a batch and searched using this approach. Yellow highlighted hits (as well as the blue hit selected) have over 50% of their spectra explained by the proposed structure and associated fragments.

CONCLUSIONS

•MVA provide facile differentiation between complex chemical mixtures and identification of potential environmental contaminants which comprise AFFFs

•Accurate mass measurements coupled with library searching, molecular formula calculation and fragment ion assignment provide a means for identification of significant markers

•The approach highlighted in this work offers potential for characterization of constituent migration from the point of use of various AFFFs

ACKNOWLEDGEMENTS

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REFERENCES

1. Rotander A., Kärrman A., Toms L.M., Kay M., Mueller J., Ramos M.J.G. *Environ. Sci. Technol. Lett.* 49 (2015) 2434-2442