Hierarchical Analytical Approaches for Unraveling the Composition of Proprietary Mixtures

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INTRODUCTION

Identifying the chemical components of complex, propriety mixtures is the requisite first step towards understanding the occurrence, fate, and transport of the components in the environment. The composition of commercial mixtures including pesticide inert ingredients, aircraft deicers, and aqueous film-forming foam (AFFF) formulations, and by analogy, fracking fluids, are proprietary. Quantitative analytical methodologies can only be developed for mixture components once their identities are known. Because proprietary mixtures may contain volatile and non-volatile components, a hierarchy of analytical methods is often required for the full identification of all proprietary mixture components.

Analytical strategies for identifying non-volatile mixture components are needed to avoid possible bias (artifacts)/sample discrimination. Gas chromatography mass spectrometry (MS) is ideal for identifying volatile chemicals because searchable libraries are well established. While liquid chromatography-tandem mass spectrometric (LC-MS/MS) methods are good for polar compounds, there are no reliable libraries that can be used for screening samples.

Fast-atom bombardment (FAB) MS is a fast, simple method for identifying unknown classes of surfactants in complex mixtures. FAB/MS is a good screening technique to guide LC-MS/MS method development to target masses for identification by high mass accuracy mass spectrometry.

MATERIALS AND METHODS

Complex, proprietary mixtures were analyzed for their polar, non-volatile components with a combination of approaches including FAB/MS, LC-MS/MS, and in the case of AFFF formulations, by high mass accuracy mass spectrometry. Proprietary mixtures investigated:

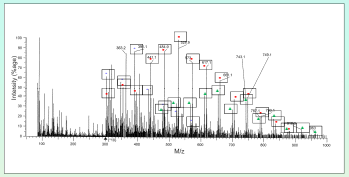
- pesticide inert packages
- aircraft deicers
- AFFF formulations

Major surfactant classes were first identified by FAB/MS analysis and detailed information was obtained on alkyl chain lengths or ethoxylate oligomers. Information on minor components was obtained by infusing standard reference materials and authentic analytical standards into a LC-MS/MS system. In the case of AFFF formulations, target masses of unknowns identified by FAB/MS were then identified by high mass accuracy measurements and confirmed with patent information.

RESULTS AND DISCUSSION

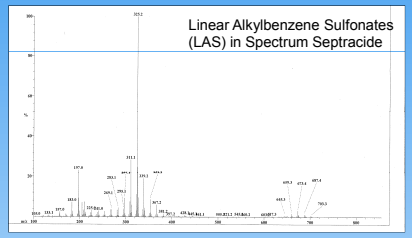
Pesticide Formulations by FAB/MS

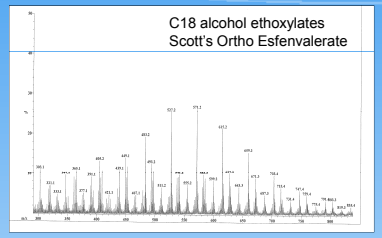
X-77 Spreader 'Inert Ingredient' for Rodeo application



- m/z = 44 characteristic of ethoxylates –[O-CH_2-CH_2]-
- 347, 391….919 of C14 alcohol ethoxylates (n=1-17)
- 353, 397….881 of C16 alcohol ethoxylates (EO_n= 2-14)
- 355, 399…875 nonylphenol polyethoxylates (EO_n=1-14)

✓ **NEXT STEP:** HPLC/fluorescence detection method then developed to determine fate and effects of nonylphenol polyethoxylates when X-77 and Rodeo (glyphosate) applied to control invasive smooth cordgrass, *Spartina Alterniflora*, in an estuary.[1]



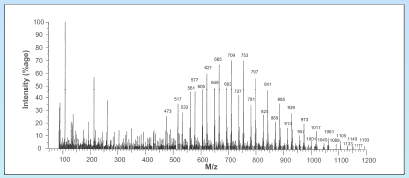


- m/z = 14 corresponds to –CH_2- units
- 256, 283…367 = C_8-C_{15} linear alkylbenzene sulfonates
- no ion series detected in positive ion mode in Spectrum Septracide
- 439, 483, 527, 571….835 = C18 alcohol ethoxylates in Ortho Esfenvalerate

✓ **NEXT STEP**: HPLC/light scatting method was developed to determine effects of LAS on pesticide washoff from hard urban surfaces.[2]

Aircraft Deicer Formulations

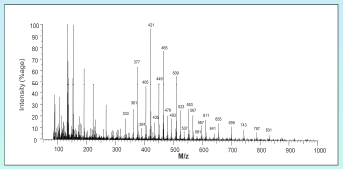
Type I Deicer by Dow



- m/z 44 = ethoxylates
- 473, 517, 561…957 =C_{12} alcohol ethoxylates (EO_n = 6-22)
- 533, 577, 621…1193 =C_{10} alcohol ethoxylates (EO_n= 8-22)

Type IV Anti-Icer by Octagon

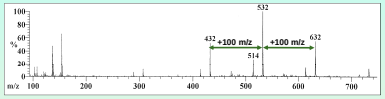
- 317, 361, 405….581 = octylphenol polyethoxylates (EO_n = 2-8)
- 333, 377, 421…641 = C12 alcohol ethoxylates (EO_n = 2-8)
- 391, 435, 479…831 = C14 alcohol ethoxylates (EO_n = 4-14)



✓ **NEXT STEP:** HPLC method developed for quantification of alkylphenols in snow, soil, and runoff from airports.[3,4]

Fluorochemicals in Aqueous Film Forming Foams (AFFF)

FAB/MS of Buckeye AFFF



- *m/z* spacing of 100 indicate C_2F_4 units

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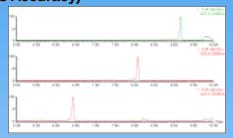
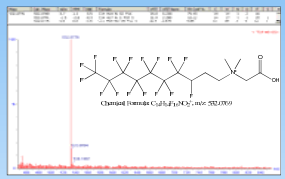
- [2] Jorgenson, B., Young, T. Environ. Sci. Technol., 44 (2010) 4951.
- [3] Corsi, S., Geis, S. Loyo-Rosales, J., Rice, C., Sheesley, R., Failey, G., Cancilla, D. Environ. Sci. Technol., 40 2006) 3195.
- [4] Corsi, S., Zitomer, D. Field, J., Cancilla, D. Environ. Sci. Technol., 37 (2003) 4031.
- [5] Place, B., Field, J. Environ. Sci. Technol., 46 (2012) 7120.
- [6] Backe, W., Field, J. Environ. Sci. Technol. (In Revision).

UPLC-QTOF (High Mass Accuracy)



- extracted ions *m/z* 432, 532, 632 targeted from FAB-MS spectra

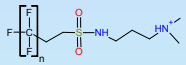
MassLynx Elemental Composition for *m/z* 532



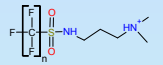
- structure supported by US Patent 5,616,273

Additional Structures Identified[5]

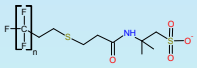
Fluorotelomer Sulfonamido Amines (Nat'l Foam)



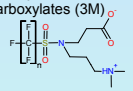
Perfluoroalkyl Sulfonamido Amines



Fluorotelomer Thio Amido Sulfonates (Ansul)



Perfluoroalkyl Sulfonamide Amino Carboxylates (3M)



✓ **NEXT STEP:** HPLC–MS/MS method created to analyze for legacy and newly-identified fluorochemicals in US military site groundwater.[6]

CONCLUSIONS

- FAB/MS is a lesser known, qualitative technique that is well-suited for the characterization of non-volatile surfactants in proprietary mixtures
- FAB/MS most likely can be used to identify surfactant(s) present in fracking fluids
- Once mixture components are identified by FAB/MS, LC-MS/MS methods can be developed for analyte quantification
- FAB/MS also can be used to efficiently target masses of interest for identification by high mass accuracy mass spectrometry
- Patents can be used to further validate the identity of mixture components as well as minor components

ACKNOWLEDGMENTS

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- FAB/MS measurements were performed by Jeff Morre of the Mass Spectrometry Facilities and Services Core of the Environmental Health Sciences Center at Oregon State University, which is funded by grant number P30 ES00210 from the National Institute of Environmental Health Sciences, National Institutes of Health.