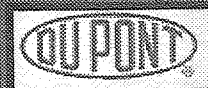


**Development of analytical methodology for  
determination of Telomer B Alcohols, Telomer-derived  
anionic, nonionic fluorosurfactants and polymers.**

**Bogdan Szostek, Keith B. Prickett, Janet C. Maslanka, and  
S. Mark Kennedy**

***<sup>1</sup>DuPont Haskell Laboratory for Health and Environmental  
Sciences, Newark, DE, USA***

SETAC 24<sup>th</sup> Annual Meeting in North America, Austin, TX

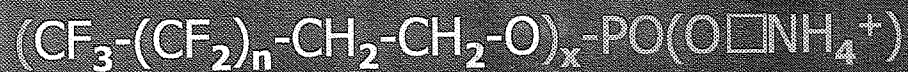


## Telomer B Alcohols and Telomer-derived Surfactants and Polymers

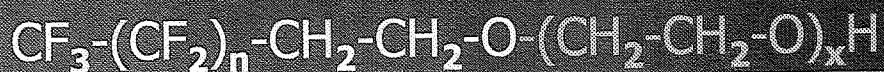
Telomer alcohols:  $\text{CF}_3-(\text{CF}_2)_n-\text{CH}_2-\text{CH}_2-\text{OH}$   $n=3,5,7,9,10, \dots$

8-2 Telomer B Alcohol:  $\text{CF}_3-(\text{CF}_2)_7-\text{CH}_2-\text{CH}_2-\text{OH}$

### Anionic Surfactants:



### Non-ionic Surfactants:



### Polymers:

- urethane: MW ~3500

- acrylate: MW ~35,000

Quantitative analytical methods are needed to support toxicological, environmental fate, and environmental effects studies for these materials.

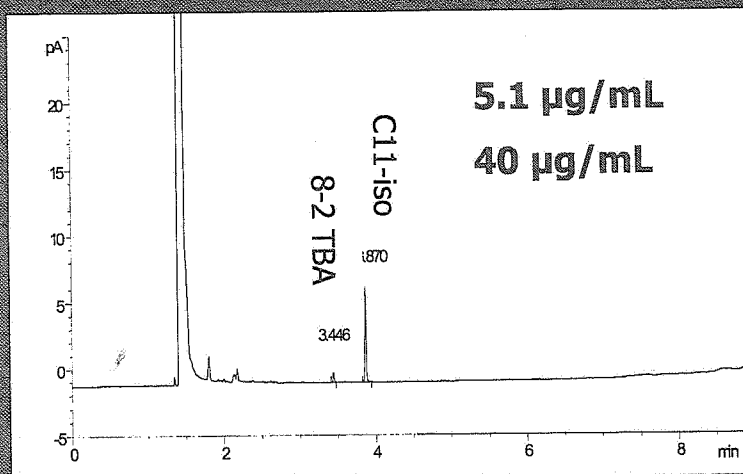


# Analytical options for 8-2 Telomer B Alcohol

## Properties:

- Structure:  $\text{CF}_3-(\text{CF}_2)_7-\text{CH}_2-\text{CH}_2-\text{OH}$
- Water solubility: 150  $\mu\text{g/L}$
- Melting point: 44°C
- Boiling point: 213°C at 760 mm Hg
- Vapor pressure: 3 Pa at 21°C
- UV: none for 225-400 nm

## 1. GC-FID



## 2. GC-MS

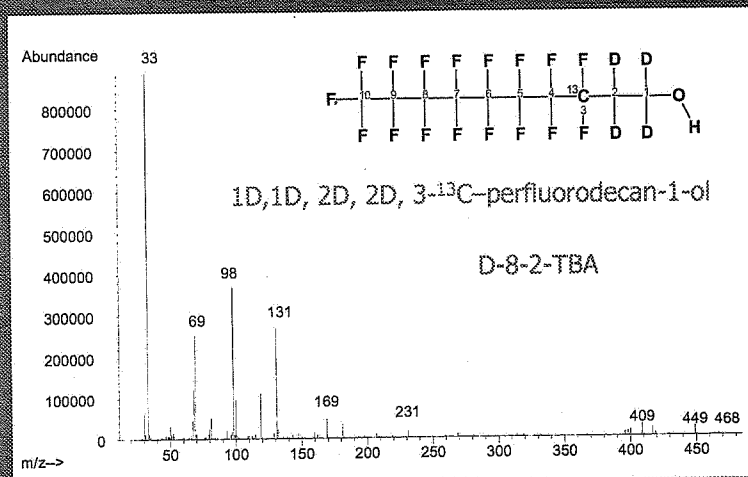
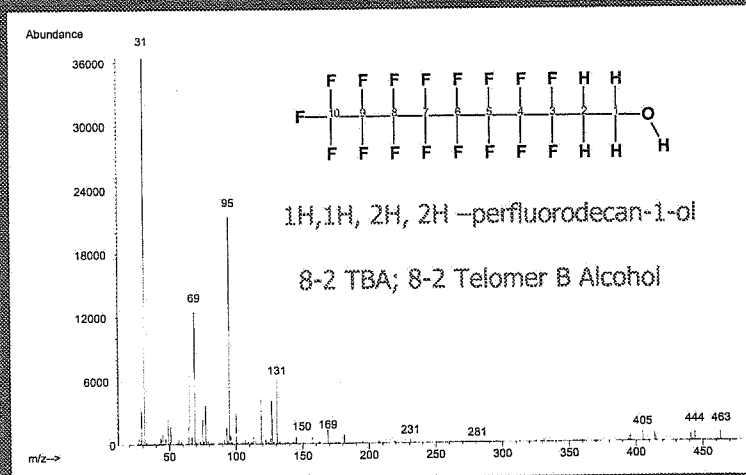
- most often used
- with EI ionization;
- Martin et al., Anal. Chem. 74 (2002) 584;
- PCI and NCI with methane; air sampling

## 3. LC-MS

- desirable for compatibility with acid-type compounds;



# Basics of GC-MS method – EI spectra

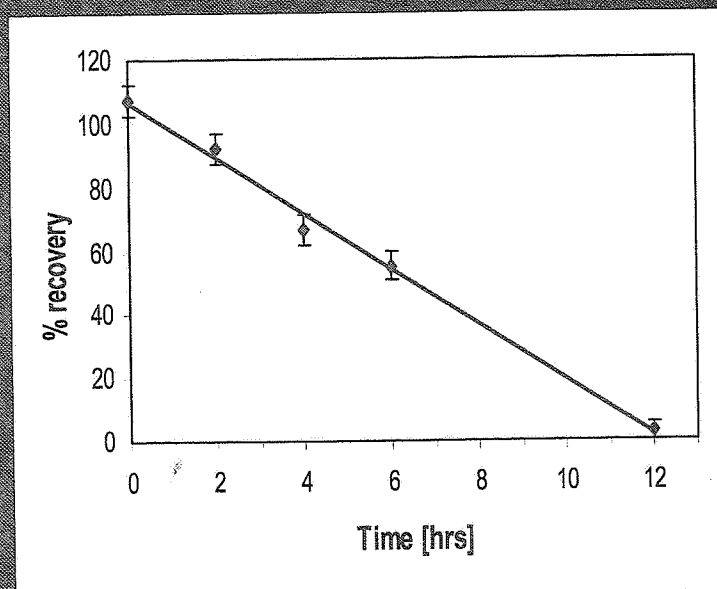


## 8-2 TBA – GC-MS method issues

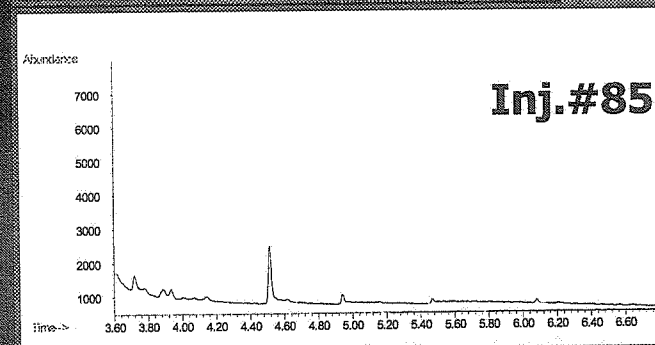
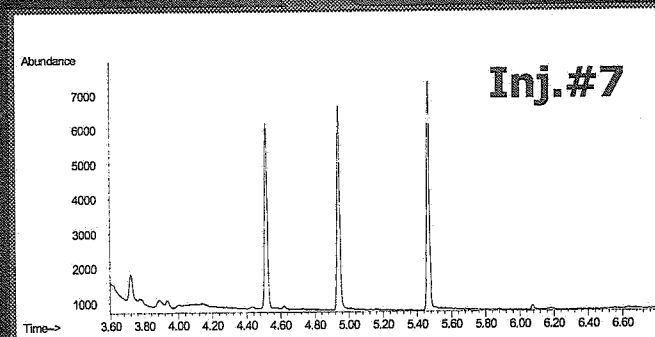
Extraction solvent:

- **MTBE**; Ethyl acetate
- Methanol; **IPA**

Headspace losses



Column performance



## Environmental waters – method validation and sample storage

### Experiment



10 mL glass vial;  
5 mL water;  
8-2 TBA at

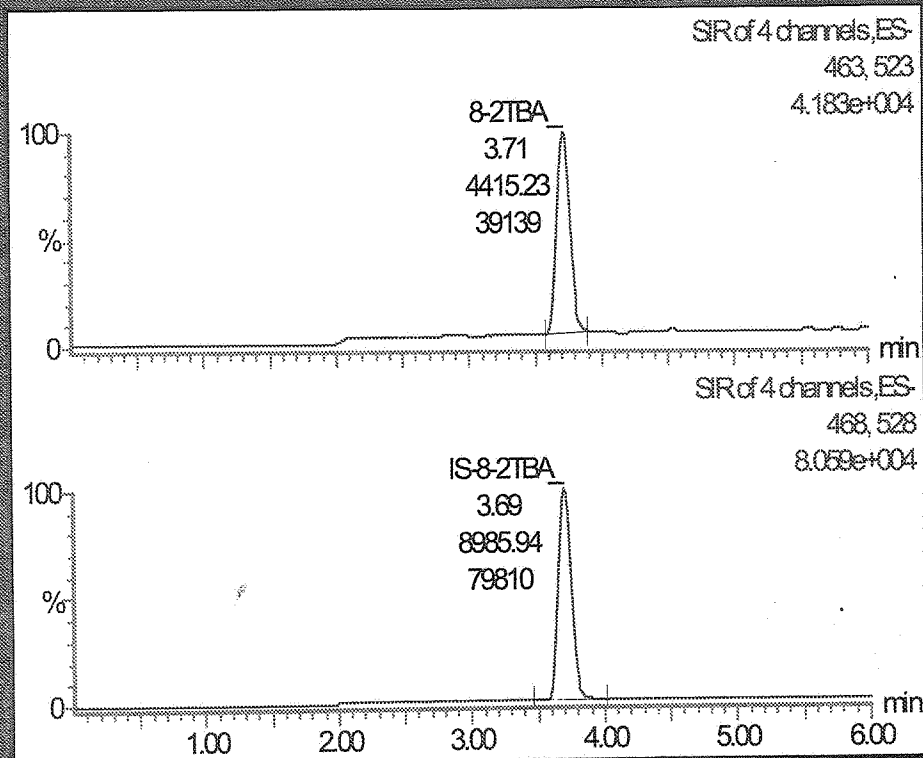
### Results (% recovery $\pm$ st. dev.)

| Water type | 1 hr        | 1 week     | 1 week      | 1 week       | 1 month     | 1 month     |
|------------|-------------|------------|-------------|--------------|-------------|-------------|
|            | RT          | Frozen     | RT          | RT (No foil) | Frozen      | RT          |
| Well       | 102 $\pm$ 6 | 98 $\pm$ 5 | 64 $\pm$ 14 | 35 $\pm$ 4   | 100 $\pm$ 9 | 24 $\pm$ 16 |
| Pond       | 98 $\pm$ 2  | 91 $\pm$ 6 | 57 $\pm$ 12 | 30 $\pm$ 2   | 104 $\pm$ 2 | 26 $\pm$ 15 |
| Creek      | 99 $\pm$ 6  | 86 $\pm$ 5 | 53 $\pm$ 6  | 29 $\pm$ 8   | 100 $\pm$ 2 | 15 $\pm$ 14 |
| Sea        | 96 $\pm$ 2  | 86 $\pm$ 5 | 92 $\pm$ 9  | 29 $\pm$ 8   | 99 $\pm$ 2  | 88 $\pm$ 16 |



## 8-2 TBA – by LC/MS

- 8-2 TBA can be ionized by electrospray;
- forms deprotonated molecular ion (463) and acetate adduct (523);
- gradient of water/methanol is used; aqueous samples in 60% acetonitrile;
- low cone voltage (10 V);
- quantitation down to 3 ng/mL 8-2 TBA



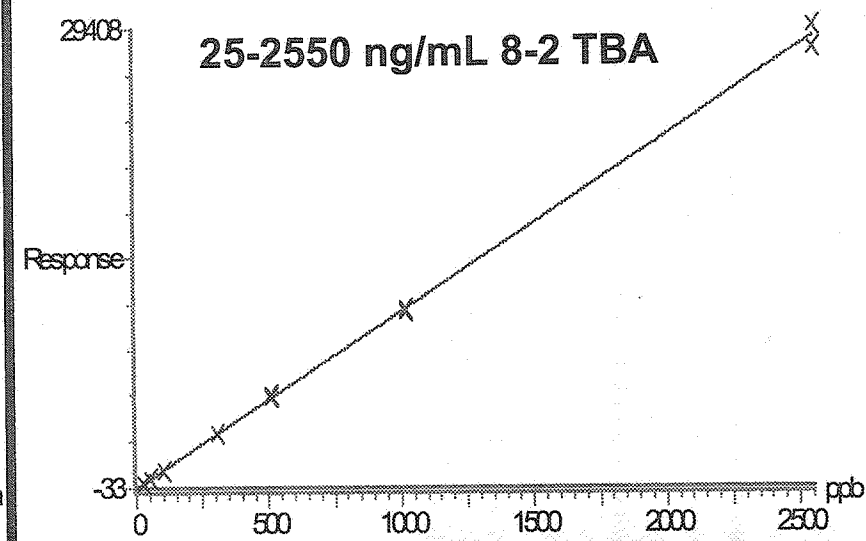
Compound name: 8-2TBA

Correlation coefficient:  $r=0.999698$ ,  $r^2=0.999396$

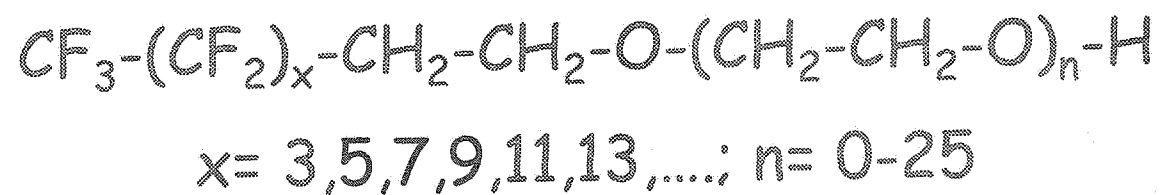
Calibration curve:  $11.2787 \cdot x + -33.2825$

Response type: Internal Std (Ref 2), Area\* (ISConc./ISArea)

Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Ethoxylate nonionic fluorosurfactant



Analytical methods:

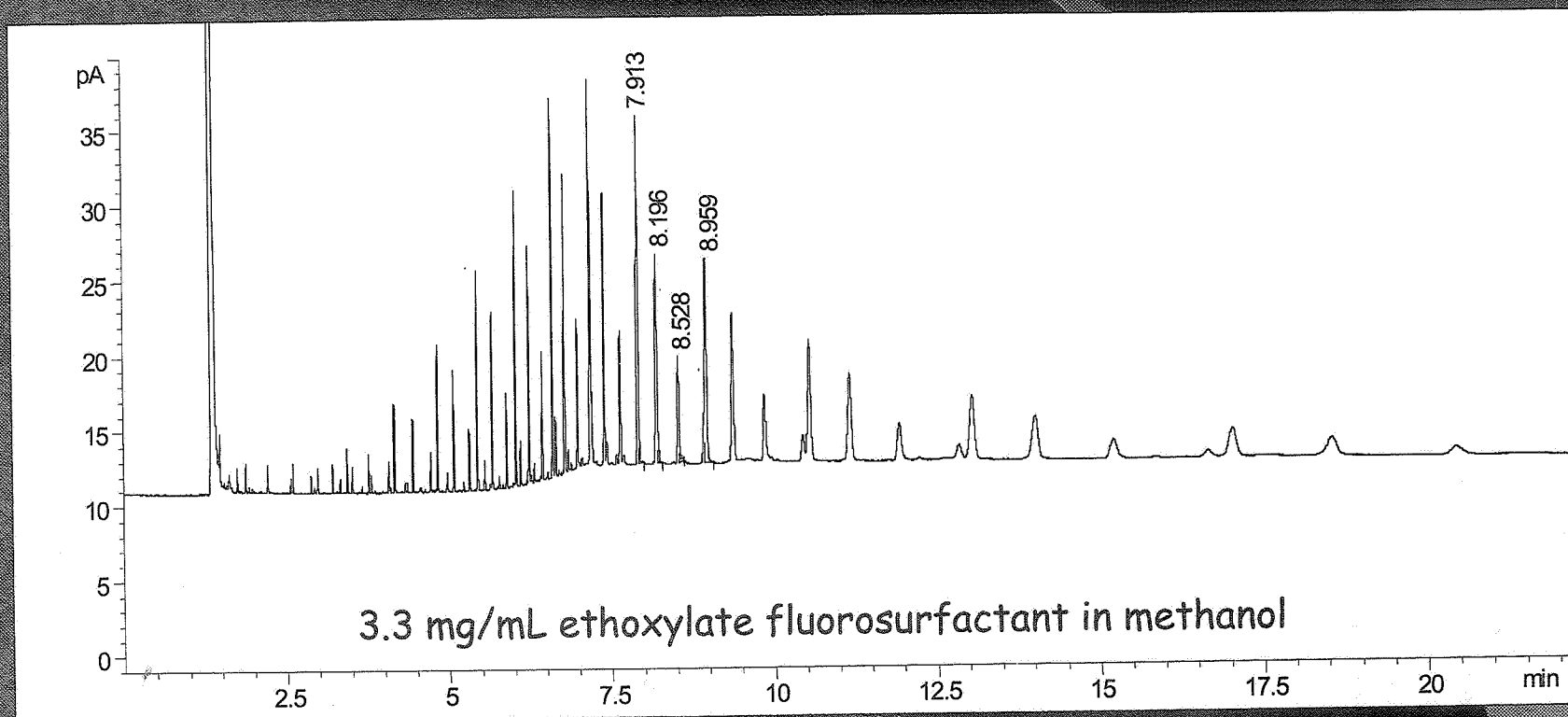
GC-FID

LC-MS



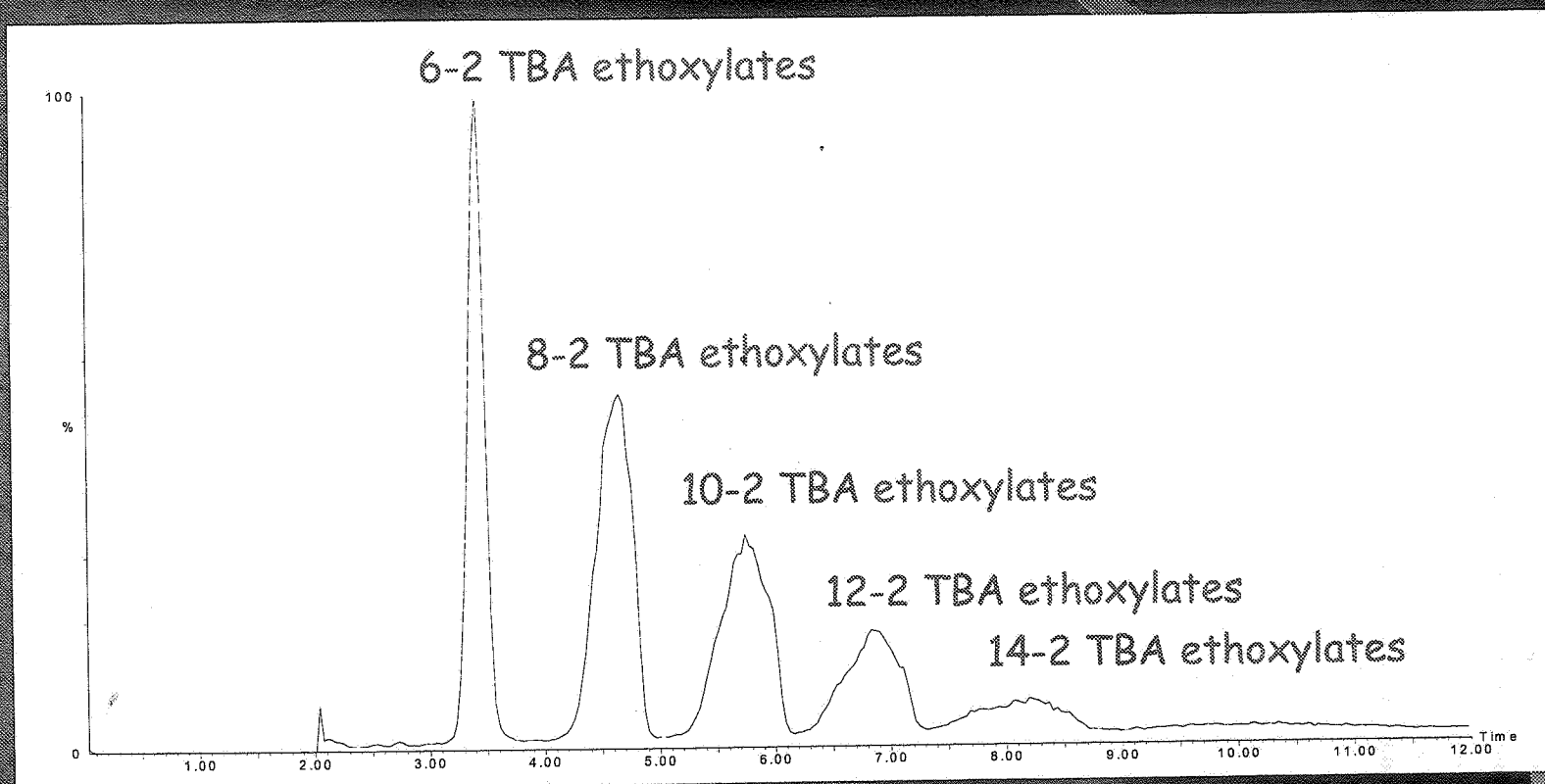
## Ethoxylate nonionic fluorosurfactant by GC-FID

- GC-FID: sensitivity and selectivity problematic
- GC-FID or GC-MS: difficult to assign structure to particular peak

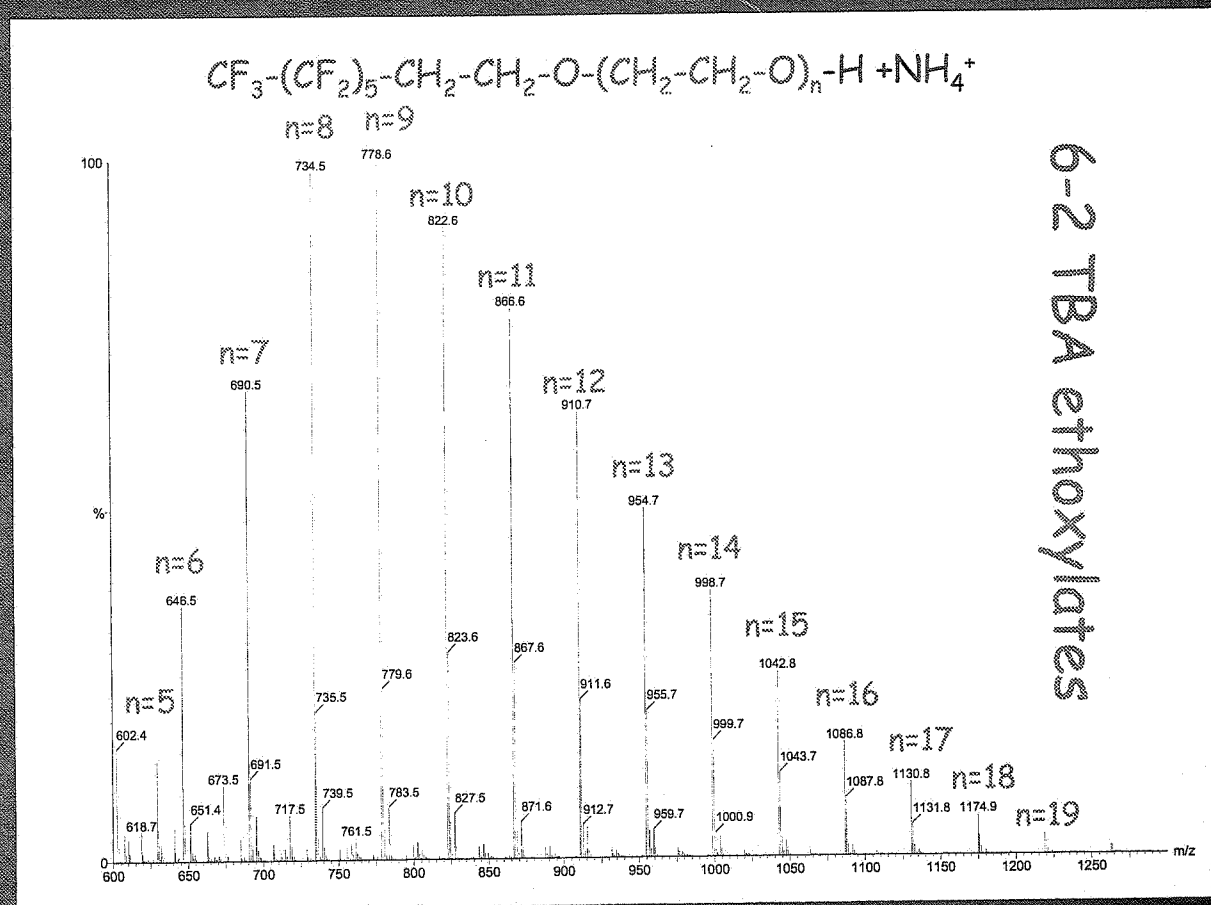


## Ethoxylate nonionic fluorosurfactant by LC-MS

- forms adducts with  $\text{NH}_4^+$  in ESI+
- identification of individual species easy
- baseline separation of TBA ethoxylates



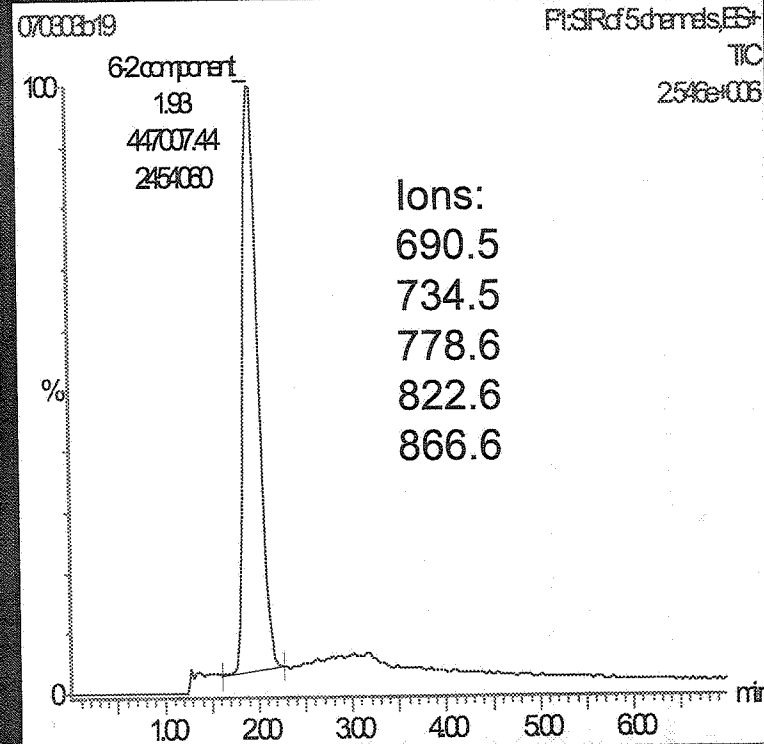
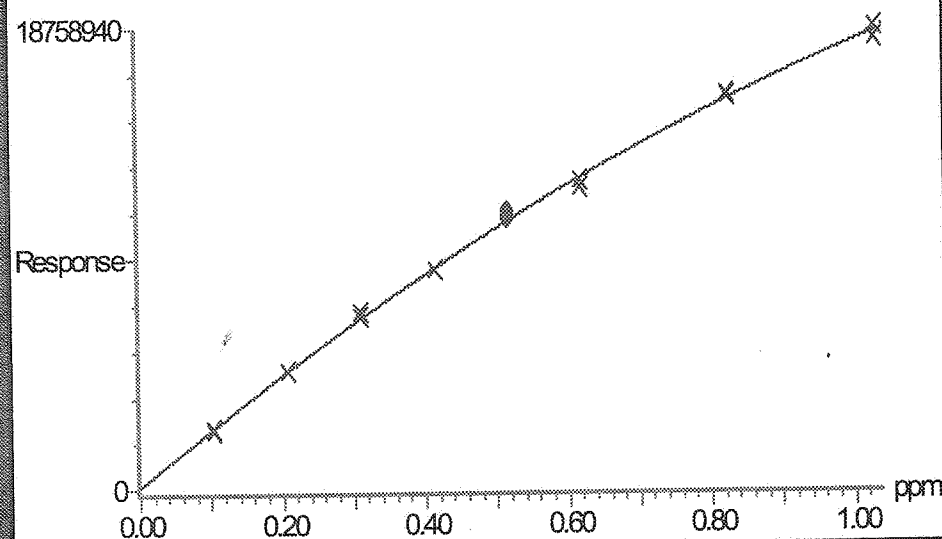
# Ethoxylate nonionic fluorosurfactant by LC-MS



## Ethoxylate nonionic fluorosurfactant by LC-MS

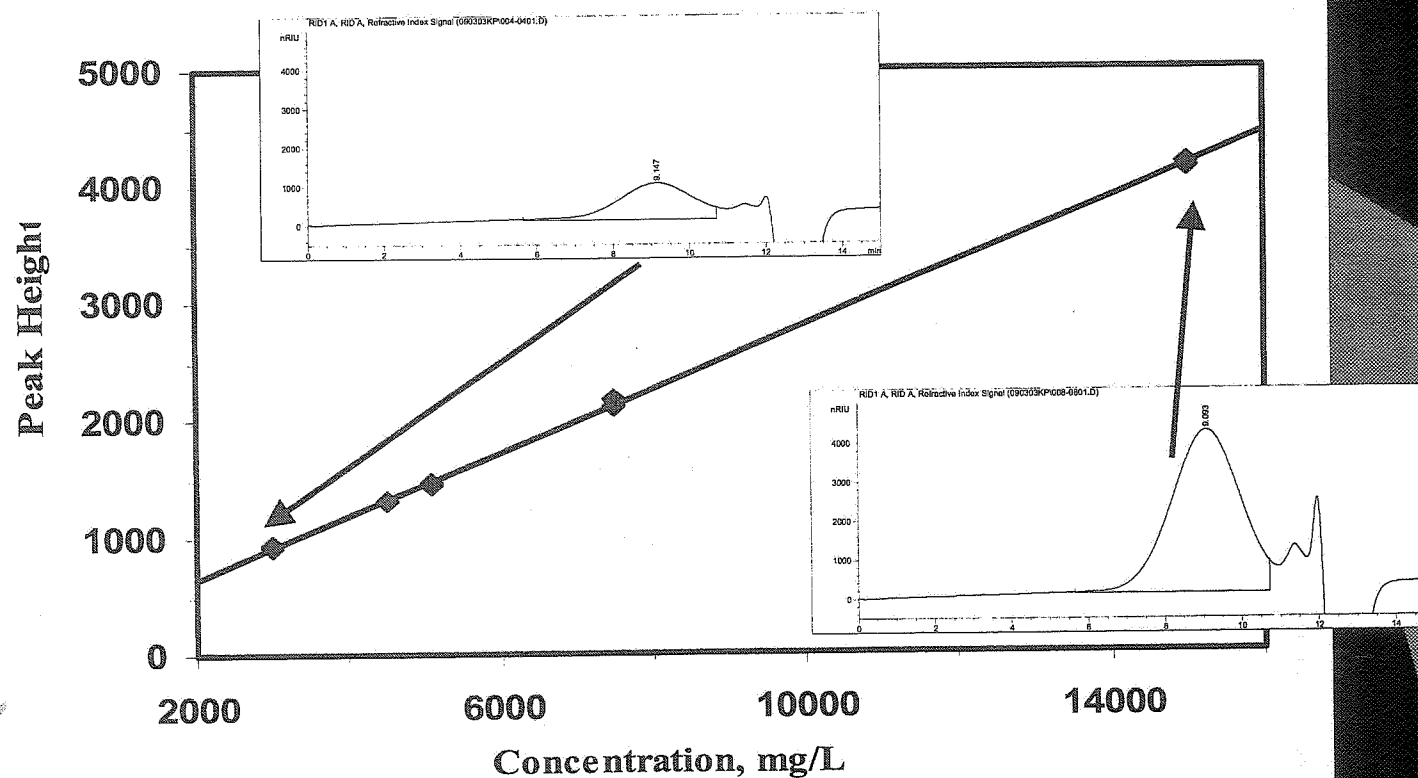
- samples and standards need to contain 50% acetonitrile otherwise are unstable (adsorption to glass)
- quantitation can be achieved by monitoring peak areas for individual TBA ethoxylates (in full scan mode)
- quantitation can also be done by monitoring selected group of ions for each TBA ethoxylates;

Compound name: 6-2 component  
Coefficient of Determination:  $R^2 = 0.999213$   
Calibration curve:  $-5.85091e+006 * x^2 + 2.38974e+007 * x + 116477$   
Response type: External Std, Height  
Curve type: 2nd Order, Origin: Exclude, Weighting: 1/x, Axis trans: None



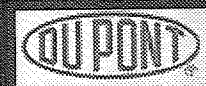
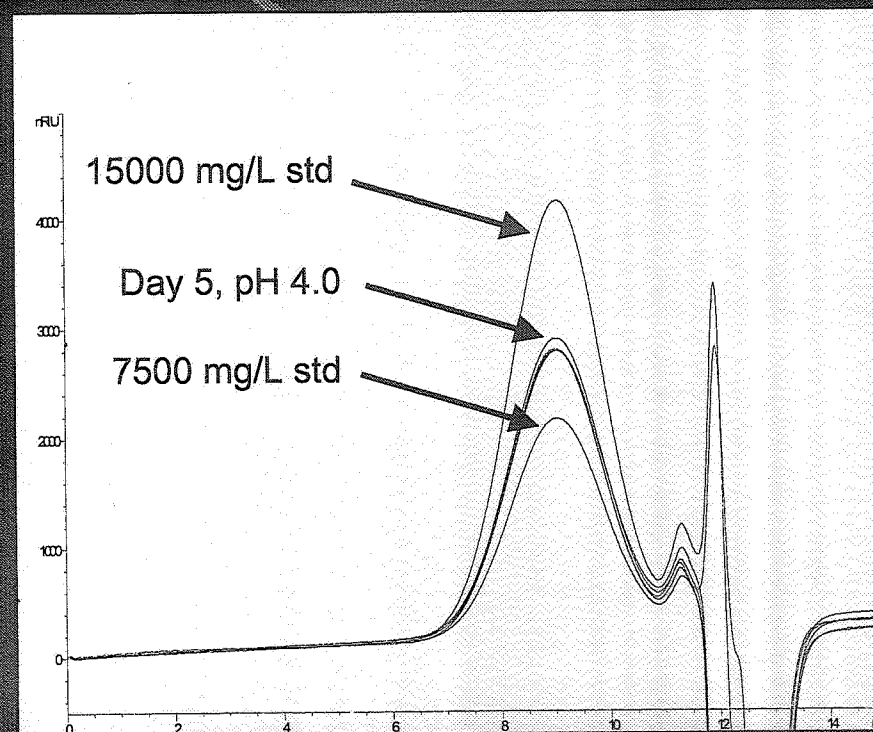
## Acrylate Telomer-based polymer

- co-polymer of vinylidene chloride, Telomer B Acrylate, and stearyl methacrylate
- not soluble in water, methanol, acetonitrile; soluble in THF
- wettable with help of fluorosurfactant
- quantitation using LC-GPC with RI detection



## Acrylate telomer-based polymer – method validation and method application

| Buffer type           | (% recovery<br>± st. dev.) |
|-----------------------|----------------------------|
| pH 1.2,<br>HCl-KCl    | 101±1.2                    |
| pH 4.0,<br>phthalate  | 100±0.5                    |
| pH 7.0,<br>phosphate  | 101±1.3                    |
| pH 9.0, boric<br>acid | 100±1.0                    |



## Summary

### General remarks:

- discussed analytical methodology for analysis of 8-2 TBA, nonionic ethoxylate fluorosurfactant, and acrylate polymer;
- each analyte, even though derived from telomer chemistry, required individual and different approach; Is a single method for all possible?
- analytical methods for many of the fluorinated compounds of interest are being established; rigorous method validation demonstrating proper spike recoveries in the matrix of interest, "clean" blanks, and proper sample storage conditions is critical;

## Summary

Specific recommendations for analytes studied:

- 8-2 TBA:

- can be analyzed either by GC/MS or LC/MS
- volatility losses from water are rapid and significant;
- aqueous samples should be stored frozen;
- GC/MS methods are problematic for trace level analysis in complex matrices;
- aqueous samples can be extracted with 60% MeCN for LC-MS;

- ethoxylate fluorosurfactant:

- LC-MS analysis is advantageous: sensitivity and clear identification of chemical species;
- samples need to be stored in 50 % MeCN;

- acrylate polymer:

- polymer can be isolated from aqueous matrix after wetting with the help of fluorosurfactant;
- quantitative method was established based on LC-GPC analysis with RI detection;