Surfactant Analysis in Hydraulic Fracturing Flowback Waters Using SPE, 2-D UHPLC Followed by Corona CAD, MS/MS and Orbitrap HRAM Detection

Richard Jack, Ph.D.

Director – Vertical Marketing, Environmental and Industrial

Lee Ferguson, Ph.D.

Associate Professor - Pratt School of Engineering &

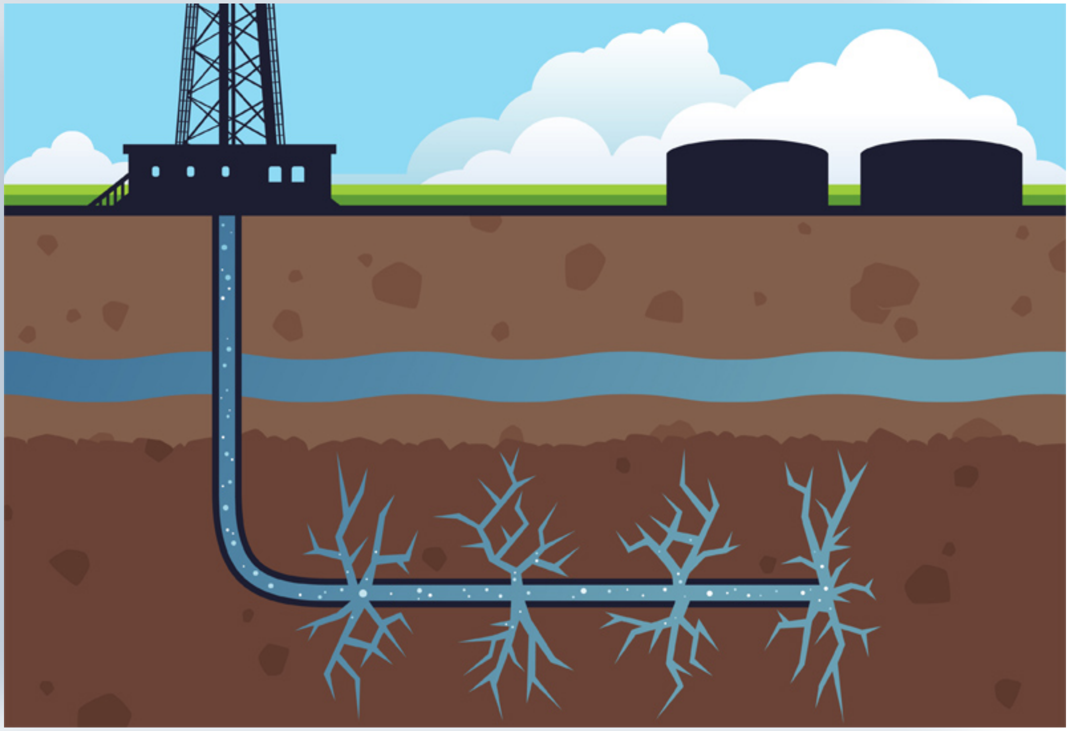
Nicholas School of the Environment

Duke University

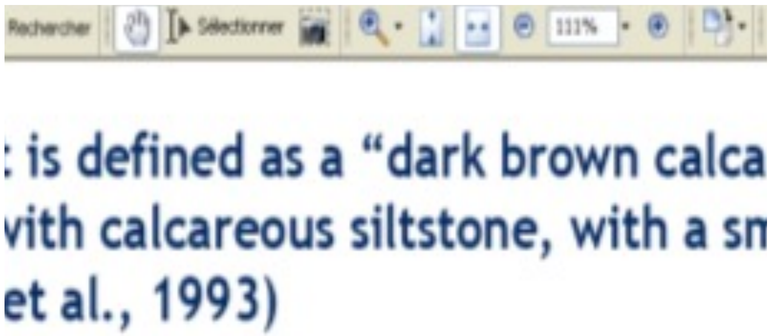
Hydraulic Fracturing Technique

- Hydraulical fracturing or fracking is a technique that consists of pumping water into a wellbore to create small fractures into which fluids can migrate and leave openings to release trapped gas

- Fracking facilitates the extraction of natural gas from shale plays in which it is unreachable with conventional technologies



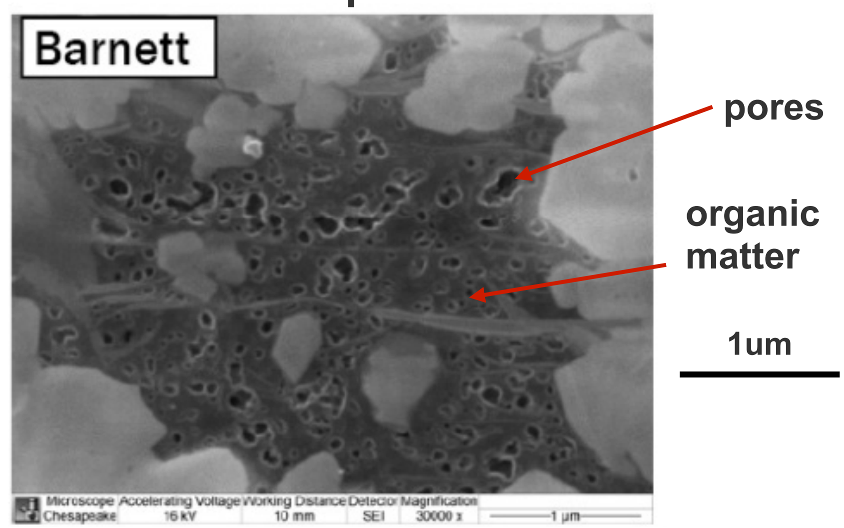
What is Shale Gas?



Typical shale in surface outcrop

- Muddy sediments rich in organic matter are deposited in seas and lakes
- As these rocks are buried, organic matter is converted to gas, and porosity is generated
- These rock layers are often the **source rocks** for conventional oil and gas fields

Microscope view



Hydraulic Fracturing Technique

- With the spreading of fracking, concern is raising about its safety and sustainability for the environment, in particular for air and water quality

- Opponents say there are potential adverse effects on the environment – and perhaps surrounding communities – because of the use of chemicals and large amounts of water that are injected into the subsurface
- Growing concern among the scientific community is that the fracking technology, itself, may result in the leakage of methane into the atmosphere or into water reservoirs

Hydraulic Fracturing Site in WV

Thermo Fisher SCIENTIFIC

Produced Water

High Total Dissolved Solids (60–250,000 mg/L)

Chloride, bromide, strontium, barium

Table A. Typical Composition Data from Several Randomly Selected Flowback Water Streams.

Measurement	--- Randomly Selected Flowback Water Samples ---				
	A	B	C	D	E
pH	5.89	5.83	5.95	5.93	7.0
Sodium, mg/l	54,629	1,477	34,548	43,108	3,310
Calcium, mg/l	15,200	15,680	6,800	3,600	241
Magnesium, mg/l	4,730	1,707	899	6,062	49
Barium, mg/l	98	112	127	547	1
Iron, mg/l	92	60	105	1,274	4
Manganese, mg/l	1.8	1.4	1.7	99.6	na
Bicarbonate, mg/l	195	183	348	415	1,098
Sulfate, mg/l	60	10	20	10	48
Chloride, mg/l	125,000	35,000	68,000	93,000	5,000
Sulfide, mg/l	na	na	na	na	na
Total Dissolved Solids, mg/l	200,006	54,230	110,847	148,016	9,751

Gaudlip et al., 2008. SPE 119898

Thermo Fisher SCIENTIFIC

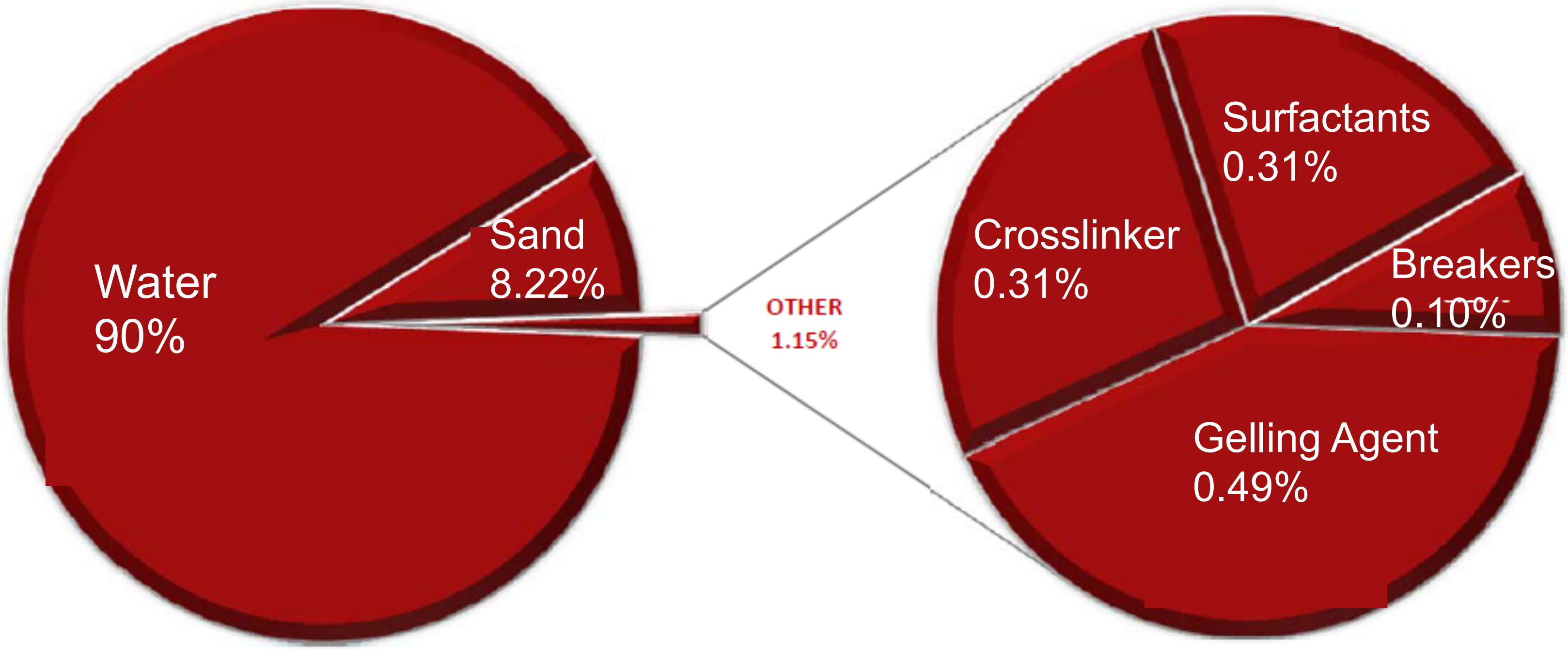
Analysis of Flowback waters – the challenge

- Extremely dirty!
- 20x salt conc. Compared to sea water
- Change over time
- Vary by subsurface
- Additives vary due to cost, personal preference and other factors
- Organics – validated methods are not available

ThermoFisher SCIENTIFIC

Hydraulic Fracturing Fluid Composition

- Mostly Water and Sand
- <2% chemicals



Thermo Fisher SCIENTIFIC

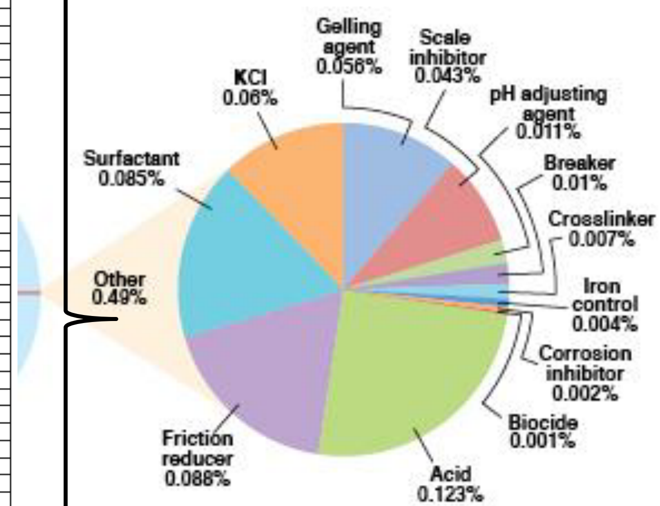
Hundreds of known Chemicals in Fracking solutions

- Hundreds of chemicals in fracking solutions – typically 10-15 used per Fracking operation.
- The EPA has narrowed the list of compounds down to less than 20.
- The EPA is in the process of developing analytical methods

Table continued from previous page

Chemical	Use	Ref.
sodium carboxymethylcellulose	fluid additive	
sodium chloride	brine carrier fluid, breaker	15,16
sodium chlorite	breaker	12,16
sodium chloroacetate		12
sodium citrate		12
sodium dichloro-s-triazinetrione	biocide	
sodium erythorbate		12
sodium glycolate		12
sodium hydroxide	gelling agent	13
sodium hypochlorite		12
sodium ligninsulfonate	surfactant	
sodium mercaptobenzothiazole	corrosion inhibitor	
sodium nitrate	fluid additive	
sodium nitrite	corrosion inhibitor	
sodium metaborate octahydrate		12
sodium perborate tetrahydrate	concentrate	12,16
sodium persulfate		15
sodium polyacrylate		12
sodium sulfate		12
sodium tetraborate decahydrate	crosslinker	13,14
sodium thiosulfate		12
sodium α-olefin sulfonate		12
sorbitan monooleate		12
starch blends	fluid additive	14
styrene	proppant	
sucrose		12
sulfamic acid		12
sulfomethylated tannin		15
talc	fluid additive	14,15
tallow fatty acids sodium salt		12
terpene and terpenoids		12
terpene hydrocarbons		12
tetrachloroethylene		12
tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione		12
tetrakis(hydroxymethyl)phosphonium sulfate		12
tetramethyl ammonium chloride		12
tetrasodium EDTA		12
thioglycolic acid		12
thiourea	acid corrosion inhibitor	13,14
titanium	crosslinker	14
titanium dioxide	proppant	
toluene	gelling agent	13
tributyl phosphate	defoamer	
tributyl tetradecyl phosphonium chloride		12
triethanolamine hydroxyacetate		12
triethanolamine zirconate	crosslinker	16
triethylene glycol		15
trimethylbenzene	fracturing fluid	
trimethyl polyepichlorohydrin		15

Table continued on next page



Compounds found in Hydraulic Fracturing Fluids

Typical Chemical Additives Used in Frac Water

Compound	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Sodium Chloride	Allows a delayed breakdown of the gel polymer chains	Table salt
Polyacrylamide	Minimizes the friction between fluid and pipe	Water treatment, soil conditioner
Ethylene Glycol	Prevents scale deposits in the pipe	Automotive anti-freeze, deicing agent, household cleaners
Borate Salts	Maintains fluid viscosity as temperature increases	Laundry detergent, hand soap, cosmetics
Sodium/Potassium Carbonate	Maintains effectiveness of other components, such as crosslinkers	Washing soda, detergent, soap, water softener, glass, ceramics
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant, sterilization of medical and dental equipment
Guar Gum	Thickens the water to suspend the sand	Thickener in cosmetics, baked goods, ice cream, toothpaste, sauces
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, hair coloring

Source: DOE, GWPC: Modern Gas Shale Development in the United States: A Primer (2009).

Thermo Fisher SCIENTIFIC

5.4. Analytical Method Development

US EPA: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report

Table 45. Chemicals identified for analytical method testing activities. Selection criteria for the chemicals included, but were not limited to, frequency of occurrenc in fracturing fluids and wastewater, toxicity, environmental mobility, and availability of detection systems for the chemical.

Chemical Class	Chemical Name(s)	CASRN	Purpose in Hydraulic Fracturing	Reason Selected
Alcohols	Propargyl alcohol	107-19-7	Corrosion inhibitor	Toxicity, frequency of use
	Methanol	67-56-1		
	Isopropanol	67-63-0		
	t-Butyl alcohol	75-65-0	Byproduct of t-butyl hydroperoxide	
Aldehydes	Glutaraldehyde	111-30-8	Biocide	Toxicity, frequency of use
	Formaldehyde	50-00-0	Biocide	
Alkylphenols	Octylphenol	27193-28-8	Surfactant	Toxicity, frequency of use
	Nonylphenol	84852-15-3		
Alkylphenol ethoxylates	Octylphenol ethoxylate	9036-19-5	Surfactant	Frequency of use
	Nonylphenol ethoxylate	26027-38-3		
Amides	Thiourea	62-56-6	Corrosion inhibitor	Toxicity
	Acrylamide	79-06-1	Friction reducer	Toxicity, frequency of use, requested by EPA researchers
	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	Biocide	
Amines (alcohol)	Diethanolamine	111-42-2	Foaming agent	Frequency of use
Aromatic hydrocarbons	BTEX, naphthalene, benzyl chloride, light petroleum hydrocarbons		Gelling agents, solvents	Toxicity, frequency of use, requested by EPA researchers
Carbohydrates	Polysaccharides		Byproduct	Requested by EPA researchers
Disinfection byproducts	Trihalomethanes, haloacetic acids, N-nitrosamines*		Byproduct	Toxicity
Ethoxylated alcohols	Ethoxylated alcohols, C8–10 and C12–18	68954-94-9	Surfactant	Frequency of use

Table continued on next page

Thermo Fisher SCIENTIFIC

5.4. Analytical Method Development - 2012

Table 46. Existing standard methods for analysis of selected hydraulic fracturing-related chemicals listed in Table 45. The EPA will analyze samples using existing methods to determine if the procedure meets the quality assurance criteria for the current study.

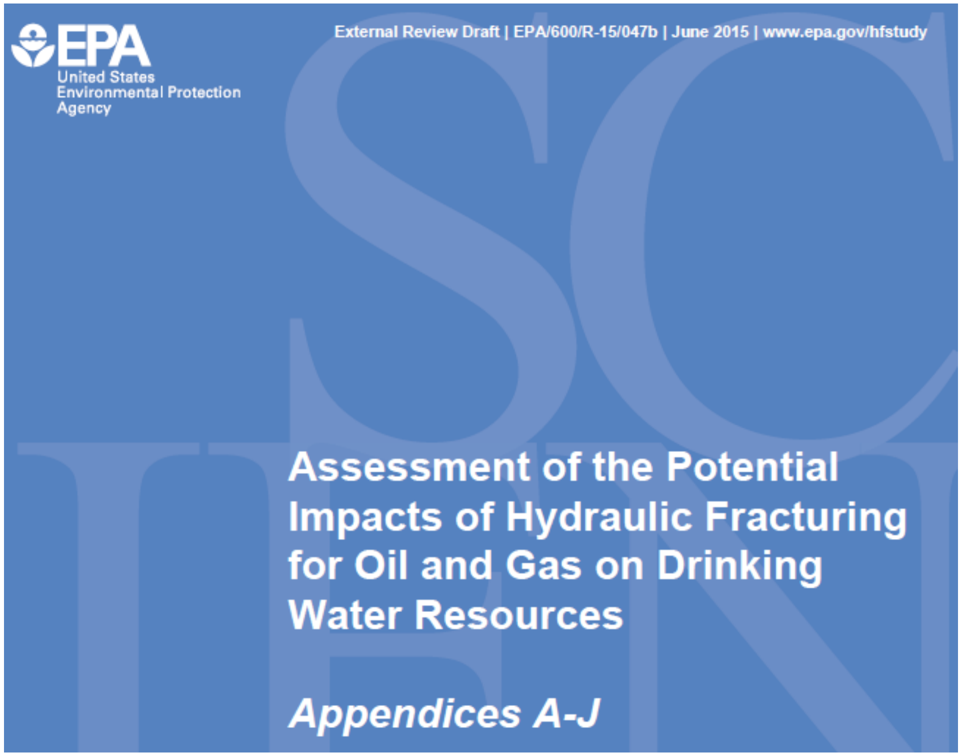
Chemical Class	Standard Method*
Alcohols	SW-846 Methods 5030 and 8260C
Aldehydes	SW-846 Method 8315
Alkylphenols	No standard method
Alkylphenol ethoxylates	No standard method
Amides	SW-846 Methods 8032A
Amines (alcohols)	No standard method
Aromatic hydrocarbons	SW-846 Methods 5030 and 8260C
Carbohydrates	No standard method
Disinfection byproducts	DWA Methods 521, 551, and 552
Ethoxylated alcohols	ASTM D7485-09
Glycols	Region 3 Draft Standard Operating Procedure
Halogens	SW-846 Method 9056A
Inorganic elements	SW-846 Methods 3015A and 6020A
Radionuclides	SW-846 Method 9310

* DWA methods can be found at http://water.epa.gov/scitech/methods/cwa/index.cfm. SW-846 Methods can be found at http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm.

http://www2.epa.gov/hfstudy

Alkylphenol Ethoxylate analysis

- DeArmond P.D., DiGoregorio A.L. Rapid liquid chromatography-tandem mass spectrometry-based method for the analysis of alcohol ethoxylates and alkylphenol ethoxylates in environmental samples. *Journal of Chromatography A, Aug 30; 1305: 154-63 (2013).*
- Assement … 2015 http://www2.epa.gov/hfstudy discusses the prevalence and use of alklyphenols, nonylphenols in the US



Ethoxylates reported in FracFocus

- **Ethoxylation** is an industrial process in which ethylene oxide is added to alcohols and phenols to turn it into a surfactant
- 4-Nonylphenol polyethoxylate
- 2-(2-Butoxyethoxy)ethanol
- 2-(2-Ethoxyethoxy)ethanol
- 2-(2-Ethoxyethoxy)ethyl acetate
- Alcohols, C11-14-iso-, C13-rich, butoxylated ethoxylated
- Alcohols, C11-14-iso-, C13-rich, ethoxylated
- Alcohols, C12-13, ethoxylated
- Alcohols, C12-14, ethoxylated
- Alcohols, C12-14, ethoxylated propoxylated
- Alcohols, C12-14-secondary
- Alcohols, C12-14-secondary, ethoxylated
- Alcohols, C12-15, ethoxylated …..
- ETC

Prevalence in HF – voluntary disclosure in fracfocus.org

Table C-2. Chemicals reported to FracFocus in 10% or more of disclosures for oil-producing wells, with the number of disclosures where chemical is reported, percentage of disclosures, and the median maximum concentration (% by mass) of that chemical in hydraulic fracturing fluid.

Name	Number of disclosures	% of disclosures	Median Maximum concentration in HF fluid
Nonyl phenol ethoxylate	2,829	16.3 %	20%
Ethoxylated propoxylated C12-14 alcohols	2,342	13.5%	2%
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	1668	9.6%	5%

http://www2.epa.gov/hfstudy

Separation

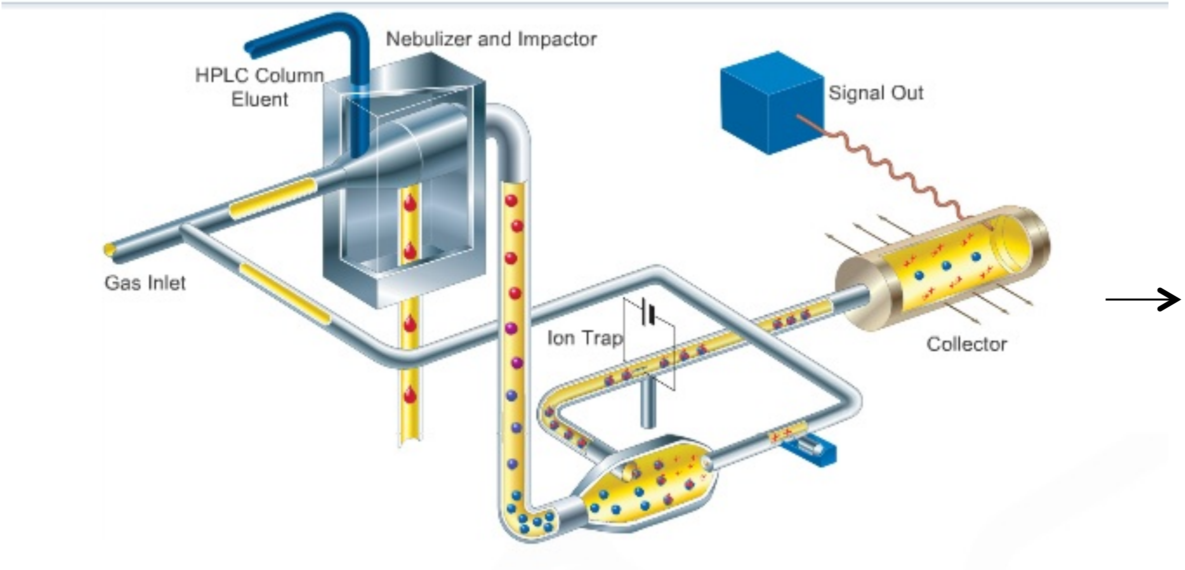
- *Protototype:* SEC 80 Size Exclusion Stationary Phase
- Polymethacrylate-based polymer
- 5-µm diameter
- 80Å pore size

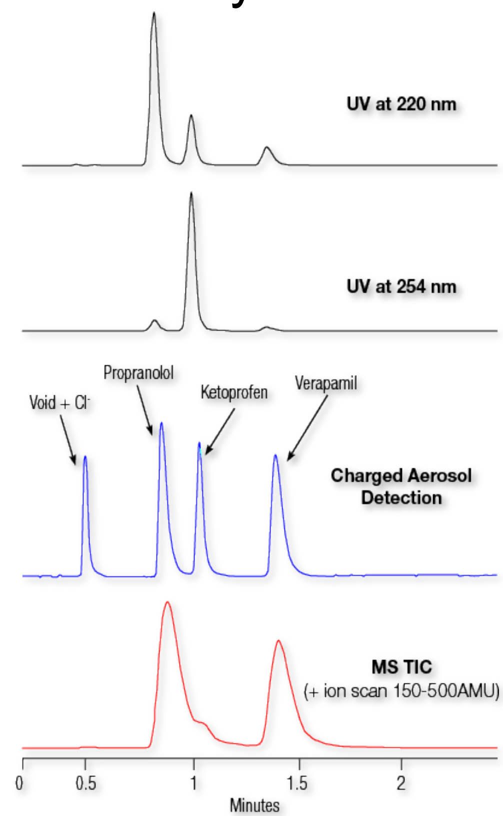
- Thermo Scientific Acclaim™ Surfactant Plus RP
  - anionic surfactants (alkylbenzenesulfonates, alkyl sulfates, alkylether sulfates) and
  - cationic surfactants (alkyl quaternary ammonium salts, benzylalkylammonium salts, pyridinium salts, and quaternary imidazolium compounds)
  - nonionic surfactants, and polyethylene glycols (PEGs).

ThermoFisher SCIENTIFIC

Detection - Charged Aerosol Detection

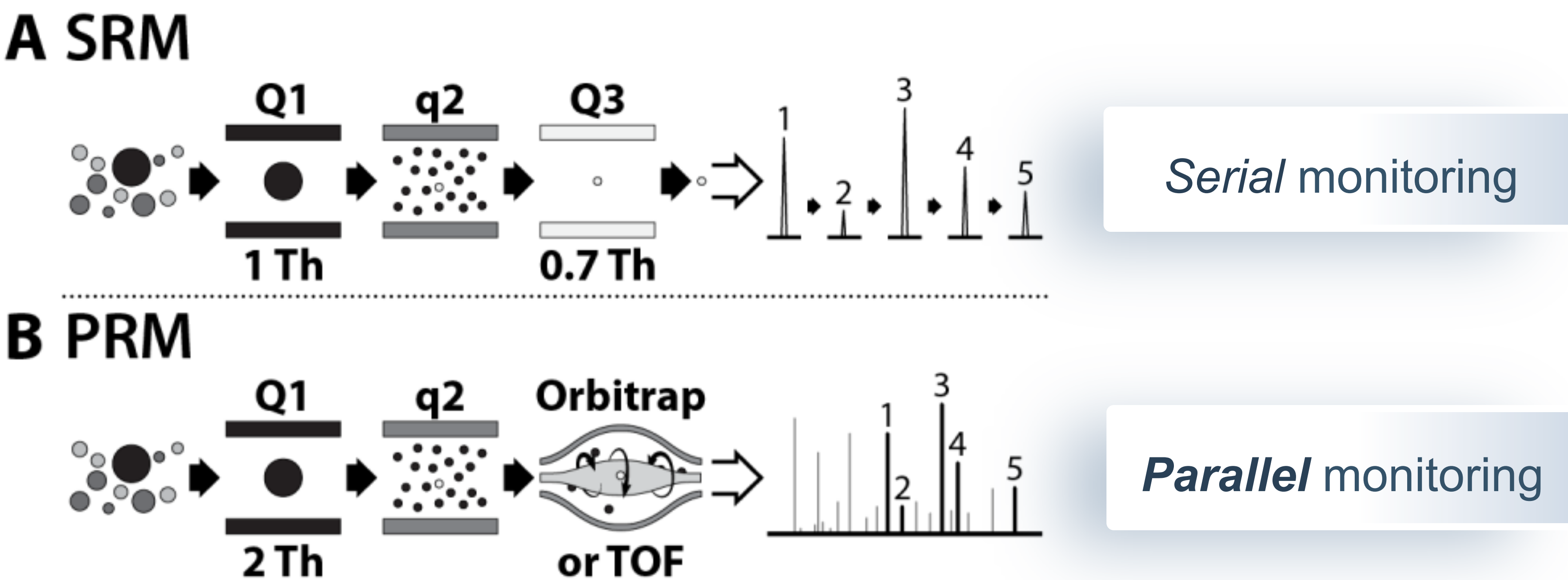
- Detection of non-volatile and many semi-volatile analytes
- Consistent response independent of chemical structure
- Applicable to both HPLC and UHPLC
- Compatible with gradient conditions Sub-nanogram sensitivity





Detection - MS/MS and HRAM

- Quadrupole-equipped HR/AM instruments
- HR/AM analyzer permits parallel detection of all target product ions in one concerted high resolution mass analysis



Identification of Emerging Contaminants

High-resolution mass spectrometry powered by Orbitrap technology helps contaminants "emerge":

Target screening

known contaminants

Target screening

Know contaminants with greater sensitivity

Non-target screening for unknowns

Assign molecular and structural formula to chromatographic features

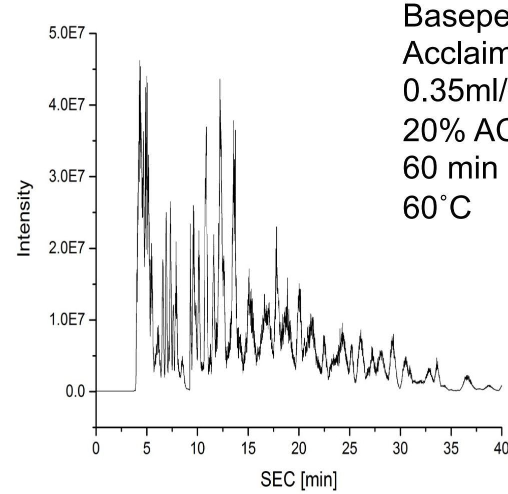
However:

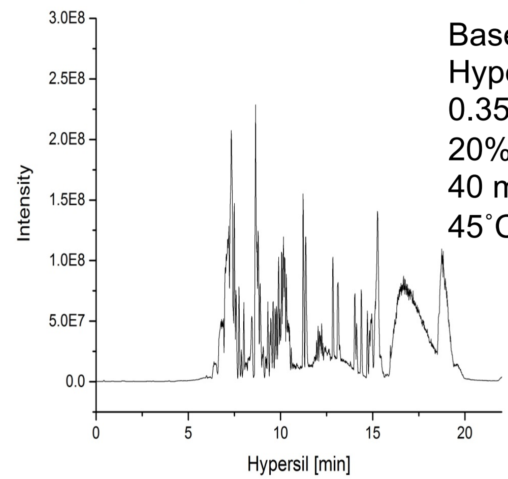
- Environmental samples are highly complex
- Limits on LC-HRMS of complex samples:
  - Poor chromatographic resolution
  - Matrix effects/ion suppression

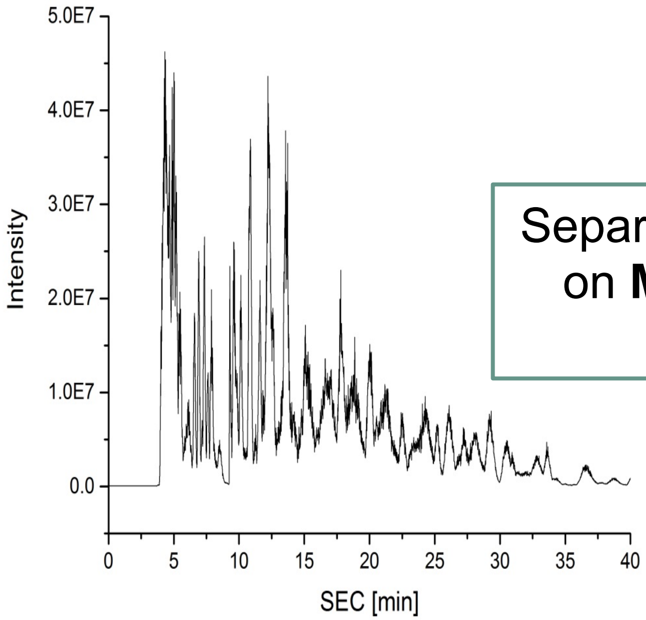
Solution:

- Combine two separation mechanisms into a single analysis

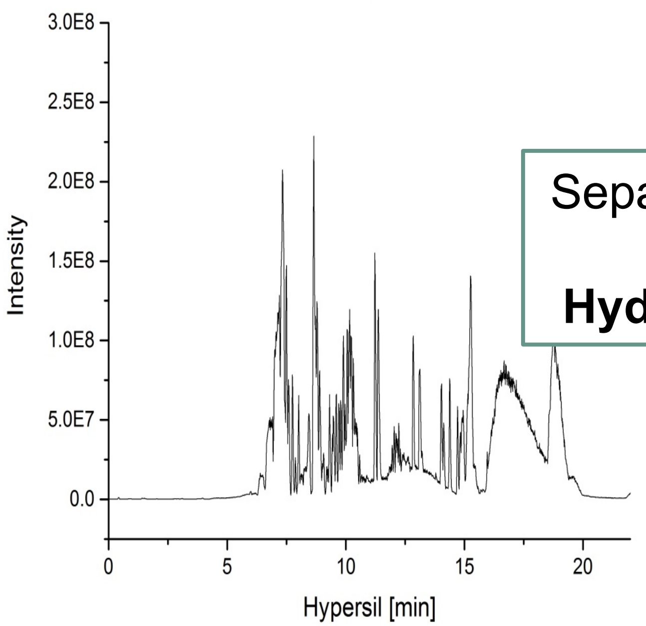
  => 2D HPLC



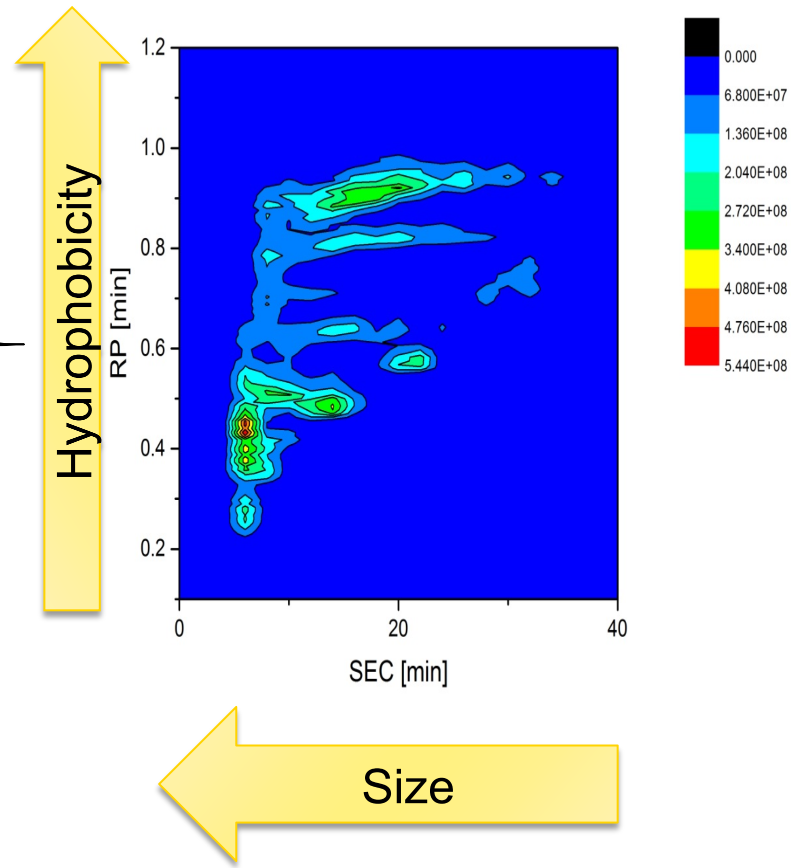




Separation based on **Molecular Size**



Separation based on **Hydrophobicity**

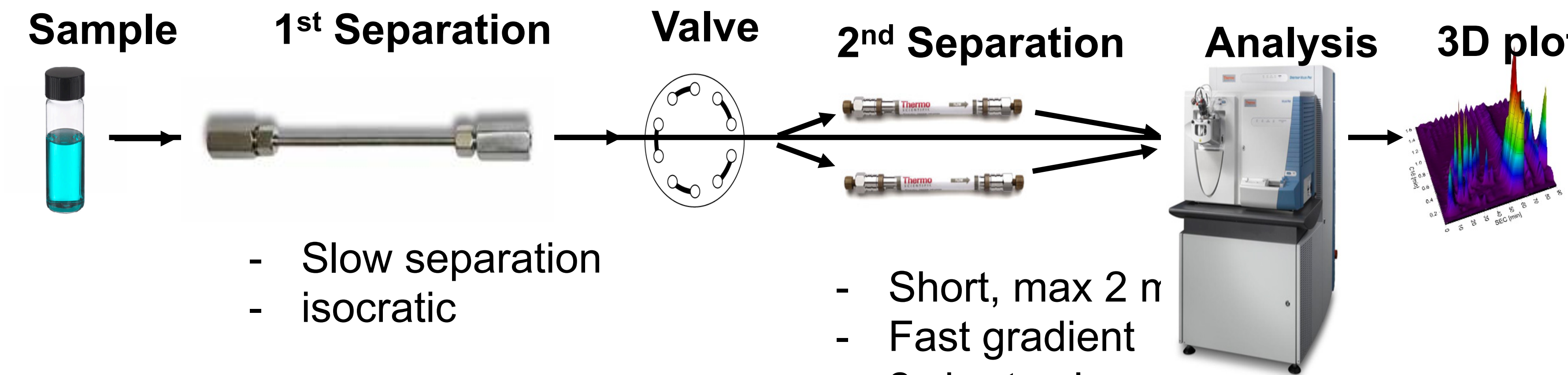


Advantages and Objectives

- Higher resolution in chromatography -> takes full advantage of MS technology
- 2D retention time offers another, complementary source of analyte chemical information
- Matrix reduction due to enhance separation: Gain in signal intensity
- Higher confidence in non target analysis due to reduced co-elution

- Develop a comprehensive 2D HPLC-HRMS approach
- Optimize this technique for analysis of nonionic surfactants
- Test the quantitative ability of this method

How does a 2D HPLC system work?



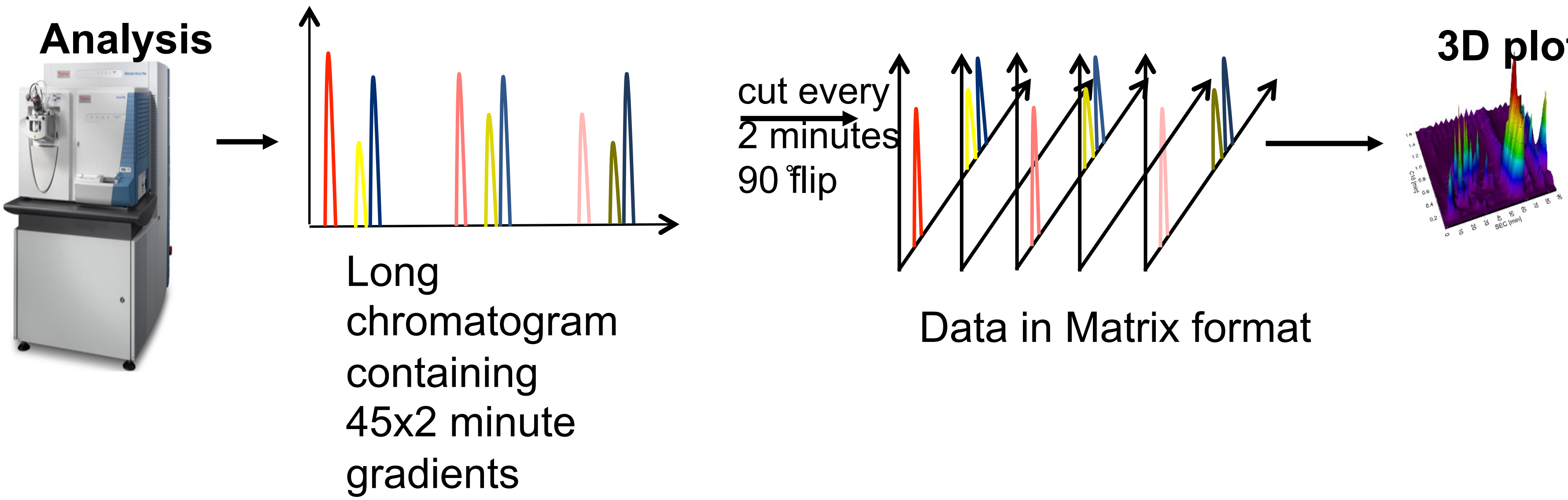
- Slow separation
- isocratic

- Short, max 2 m
- Fast gradient
- 2 short columns
- used alternating

For effective separation:

- Separation mechanisms have to be **orthogonal**.
- Example: Size and Hydrophobicity or Hydrophilic interaction and Hydrophobicity.
- While eluting from the first column – requires strong retention on the second column

How does a 2D HPLC system work?

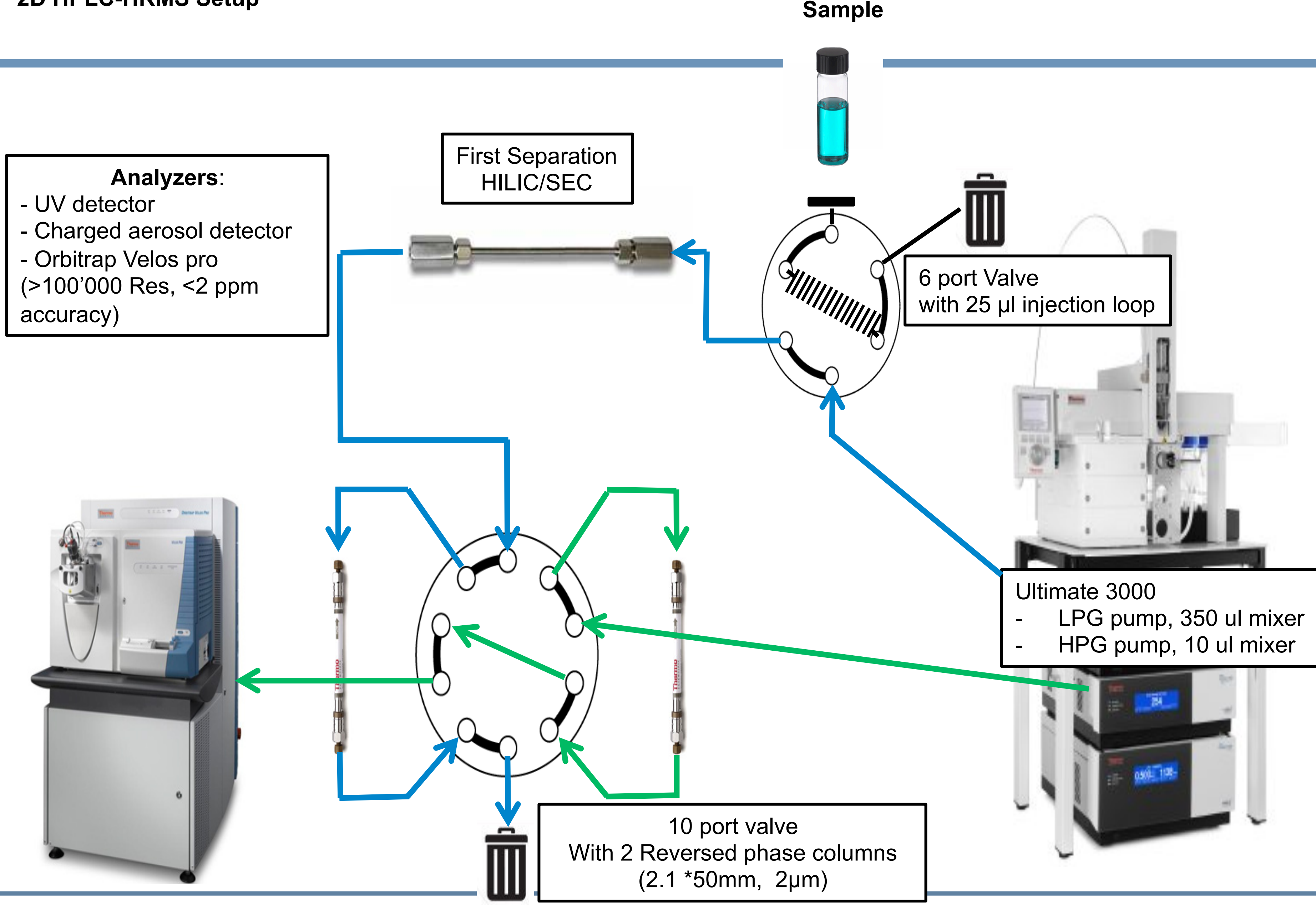


For effective separation:

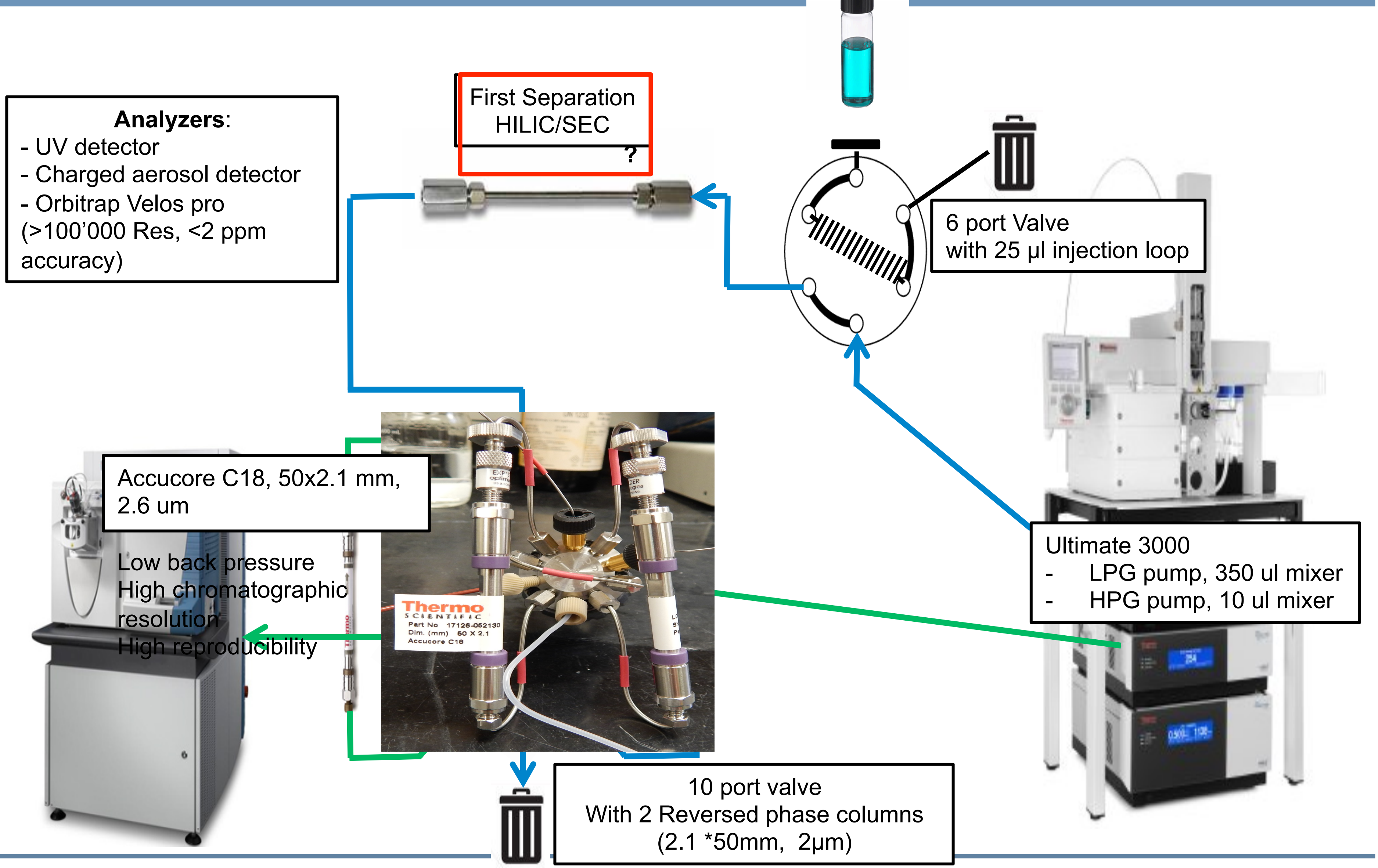
- Separation mechanisms have to be **orthogonal**.
- Example: Size and Hydrophobicity or Hydrophilic interaction and Hydrophobicity.
- While eluting from the first column – requires strong retention on the second column

ThermoFisher SCIENTIFIC

2D HPLC-HRMS Setup



2D HPLC-HRMS Setup



26

ThermoFisher SCIENTIFIC

Two candidates for the first separation

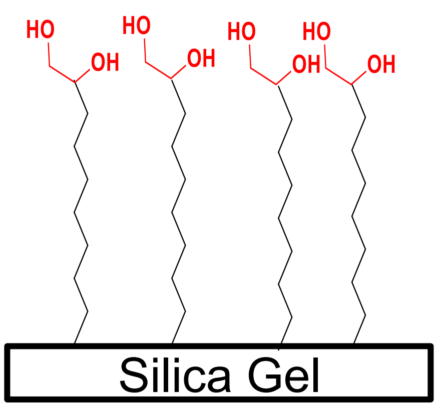
HILIC

Hydrophilic Interaction Chromatography

- Dionex Acclaim HILIC, 1.0 x 15 cm

  Flow rate: 50 µl/min

  99.5 % ACN in H_2O
- Separation based on polarity – apolar elute first
- High organic mobile phase



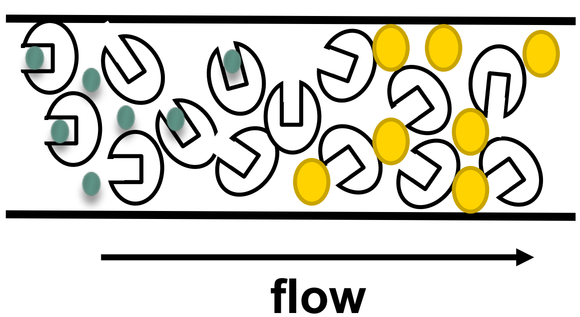
SEC

Size Exclusion

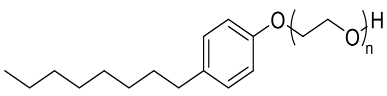
- *prototype* Acclaim SEC80, 4.6 x 300mm

  Flow rate: 350 µl/min

  20% ACN in H_2O
- Separation based on size – large molecules elute first

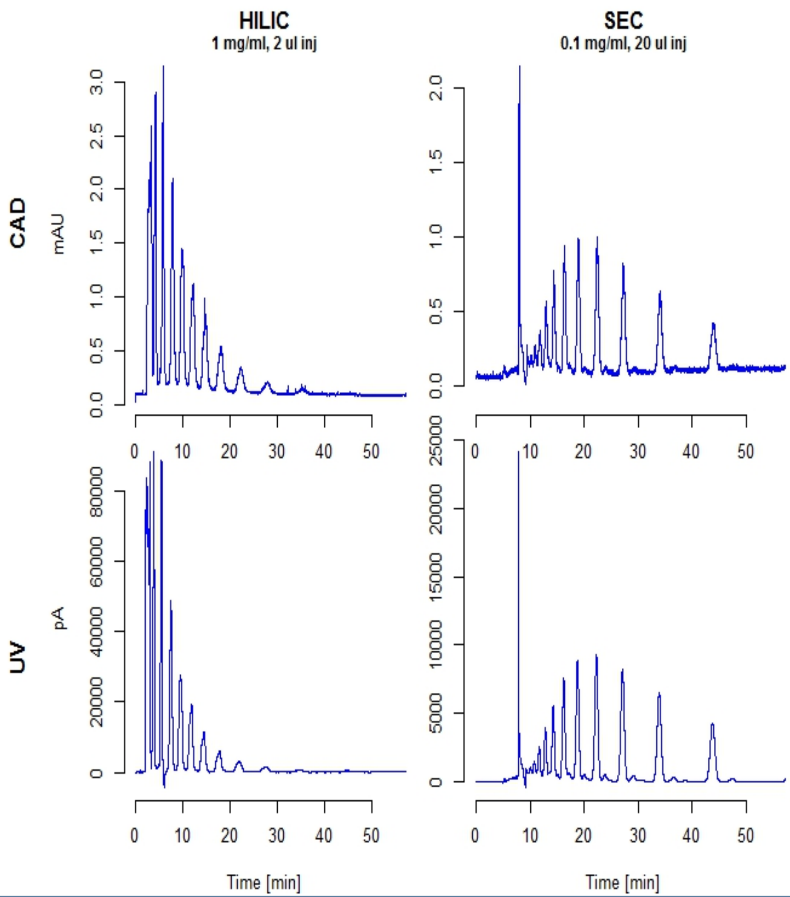


SEC of OPEO



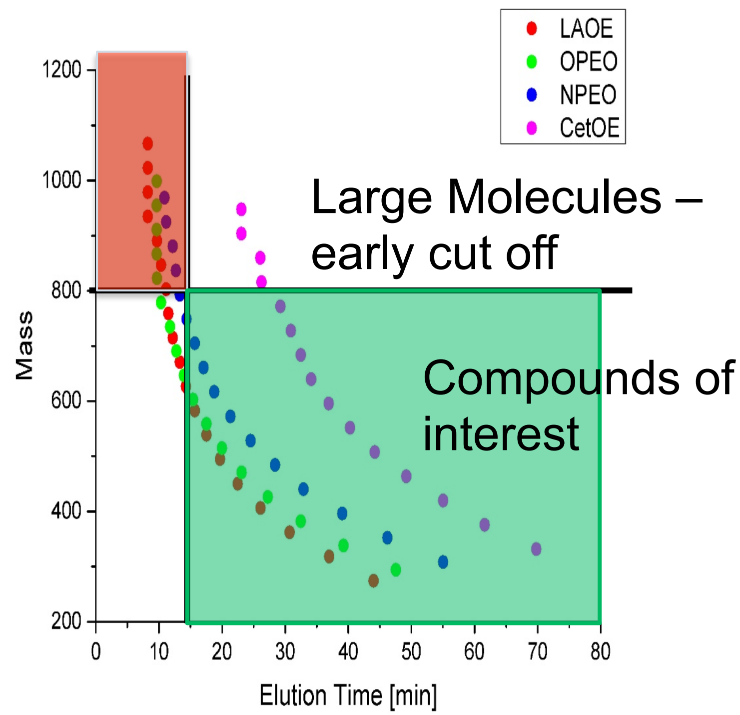
for n=1
$C_{16}H_{26}O_2$
Mass: 250.38
m/z: 268.2271 (NH_4-Adduct)

OPEO



Advantages for SEC

- Longer run => more RP time
- Compatible moble phase: No make-up flow required for RP 2nd dimension
-



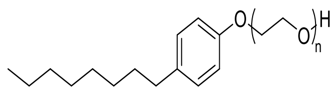
Qualitative and qualitative analysis of nonionic surfactants

- Nonionic surfactants are complex, polymeric series consisting of alcohol- or alkylphenol hydrophobes that are polyethoylated
- They are applied ubiquitously in consumer, industrial, and commercial applications
- Some nonionic surfactants (alkylphenol ethoxylates) are precursors of known endocrine disruptors
- Analysis of these species by HPLC-MS is very challenging due to difficulty in separations, problems with matrix effects

Separating Surfactants by 1D-H

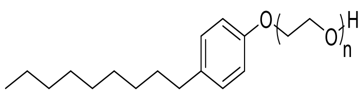
- 4 Surfactant standards for optimization:

Hydrophobicity



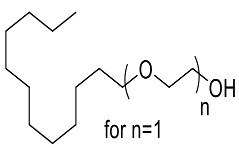
for n=1
$C_{16}H_{26}O_2$
Mass: 250.38

Octylphenol ethoxylate (OPEO)



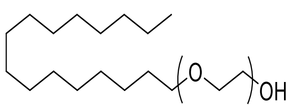
for n=1
$C_{17}H_{28}O_2$
Mass: 264.21

Nonyl phenol ethoxylate (OPEO)



for n=1
$C_{14}H_{30}O_2$
Mass: 230.22

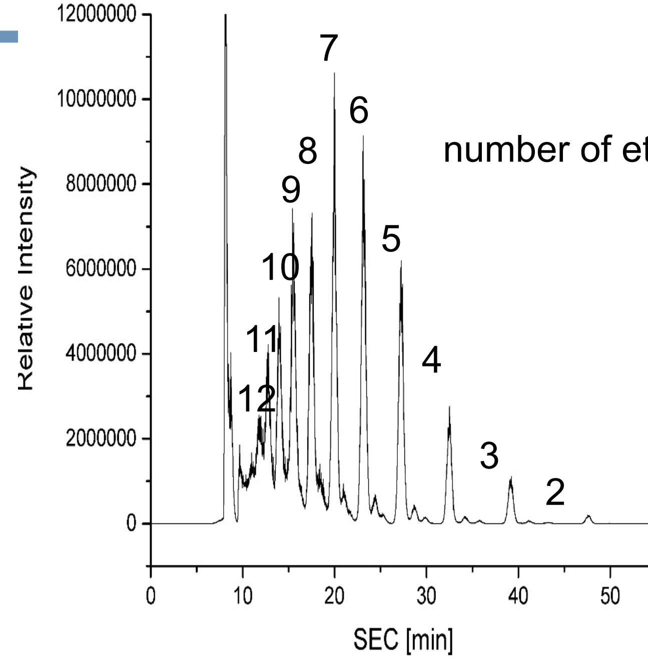
Lauryl alcohol ethoxylate (LaOE)



for n=1
$C_{18}H_{38}O_2$
Mass: 286.29

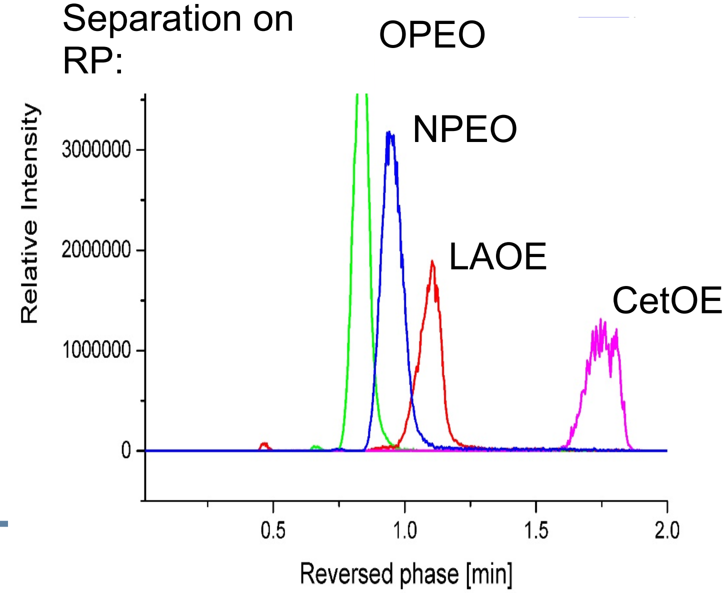
Cetyl alcohol ethoxylate (CetOE)

Separation on SEC:

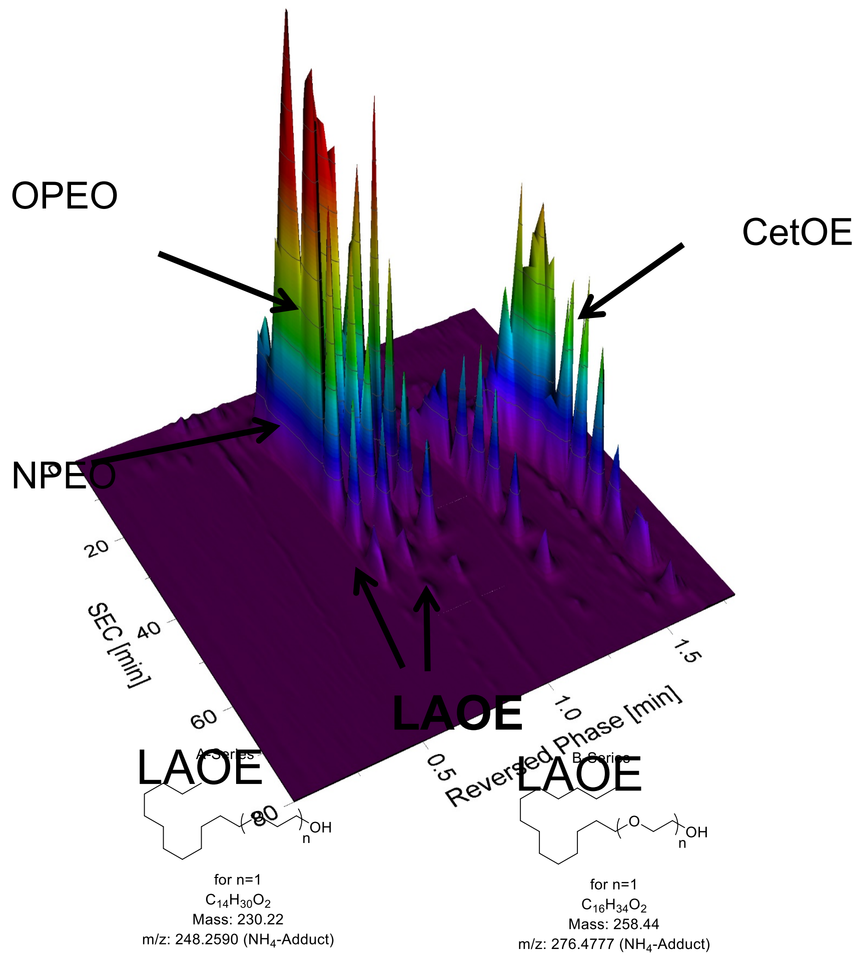


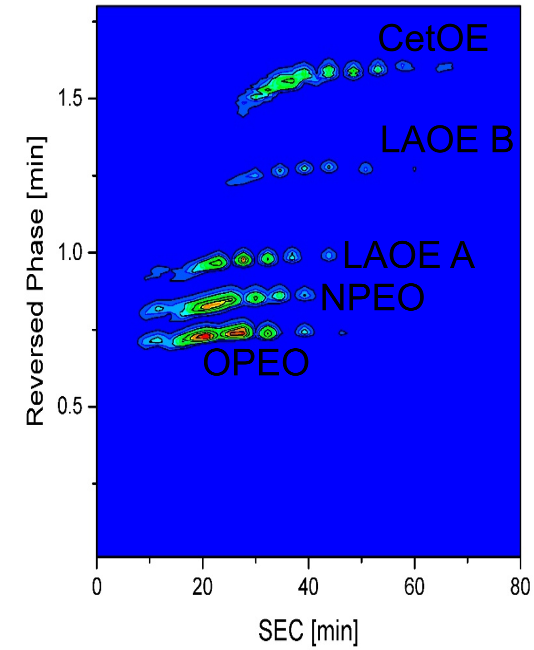
number of ethoxylates (OPEO)

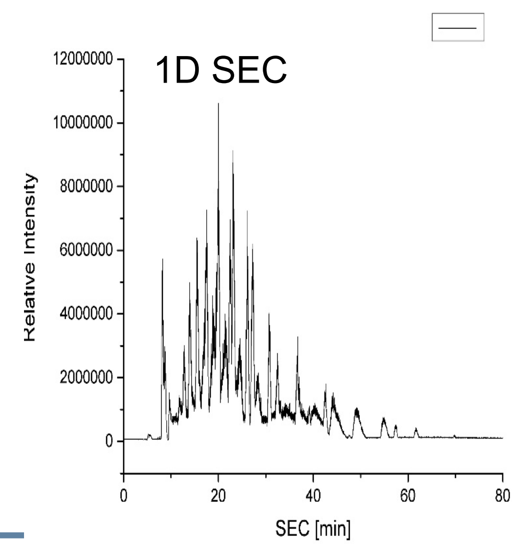
Separation on RP:



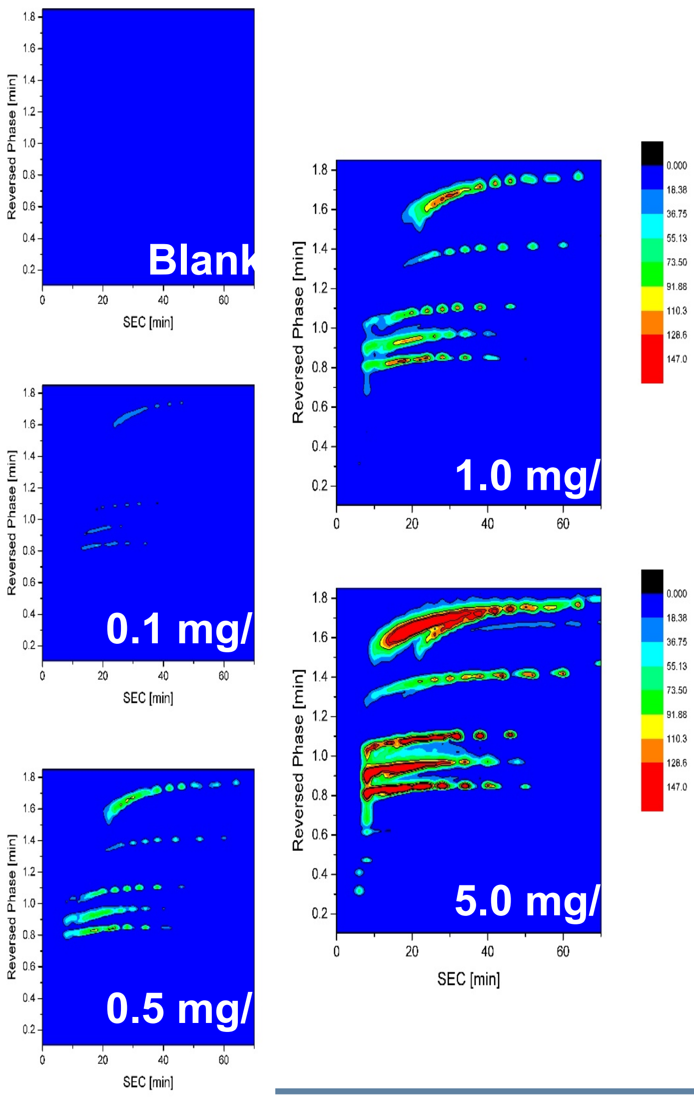
Separating Surfactants by 2D-HPLC

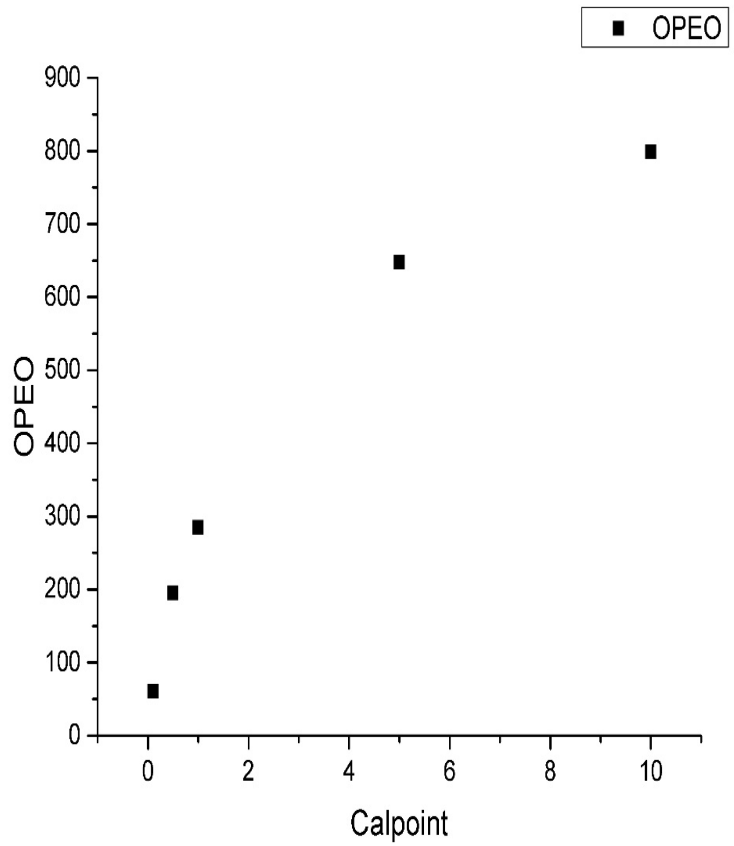






Resolving and quantifying mixtures of nonionic surfactants using the Charged Aerosol Detector





Thermo Fisher SCIENTIFIC

Application to environmental samples

Hydrofracking flowback wastewater sample

- Fracking waters often contain nonionic surfactants as emulsifiers
- To date these surfactants have not been well-characterized in wastewaters discharged from fracking operations

Sample

Wastewater from hydrofracking flowback

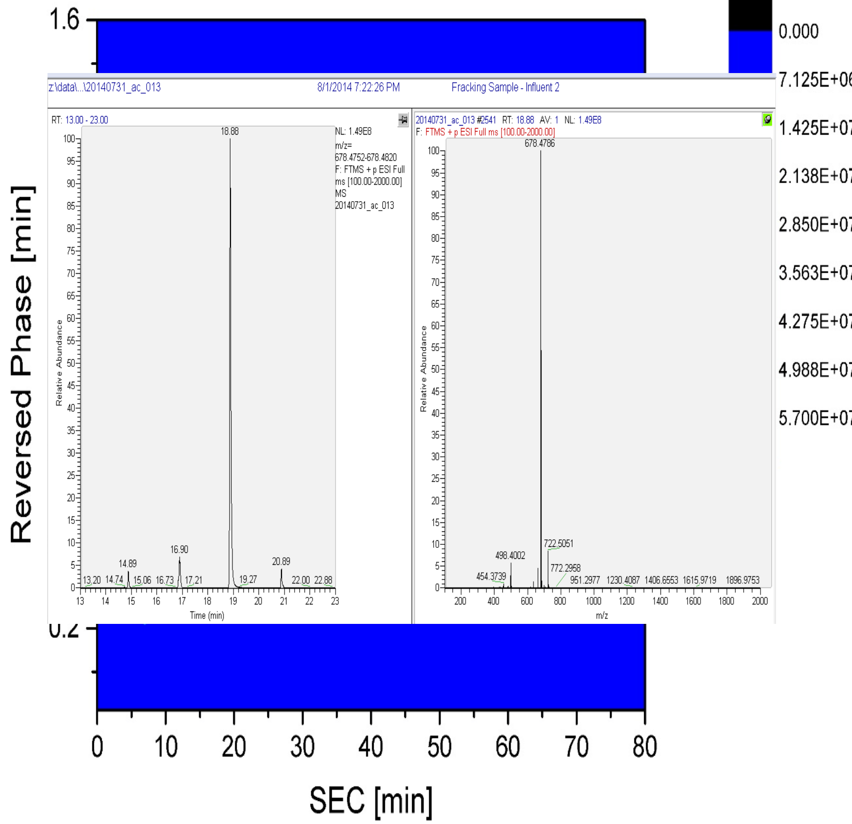
Work up

Extraction with Dionex Autotrace (200 mg HRHPS)

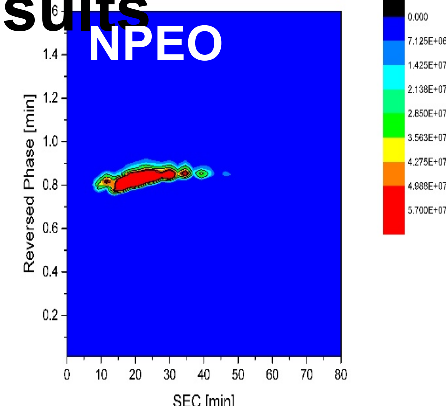
2D Analysis

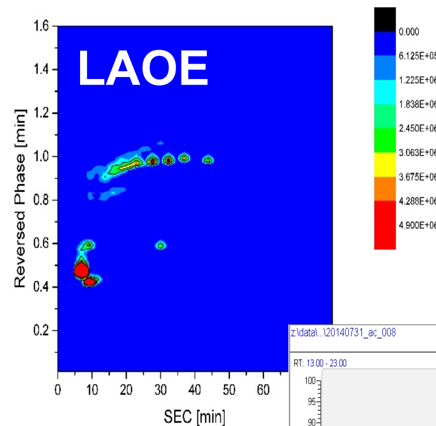
Hydrofracking wastewater- Results

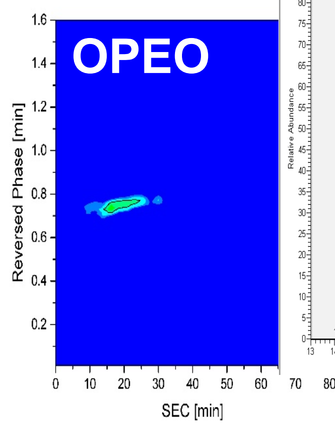
Fracking Fluid Sample - Basepeak



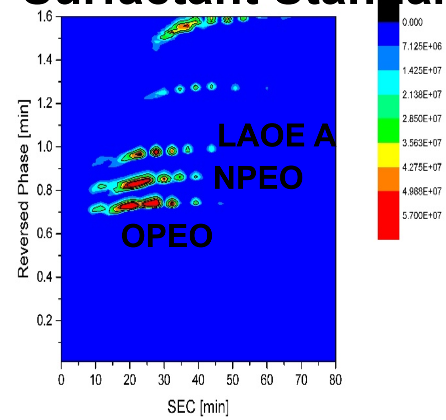
XIC



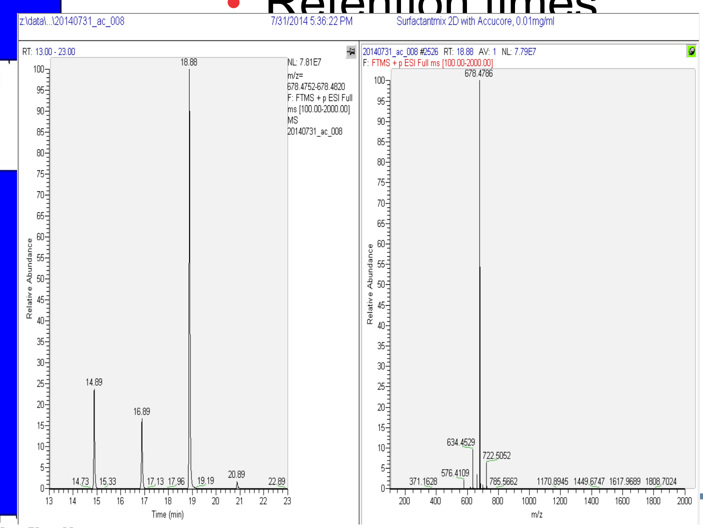




Surfactant Standards



- Environmental sample gives comparable surfactant bands
- Retention times



ThermoFisher SCIENTIFIC

Conclusions

- Two dimensional HPLC combined with HRMS is a powerful tool for resolving micropollutants in complex mixtures
- Size exclusion chromatography combined with reverse phase HPLC provides excellent orthogonality for nonionic surfactant analysis
- Nonionic surfactants can be resolved and identified in hydrofracking wastewaters by 2D-HPLC-HRMS.
- 2D-HPLC-HRMS spectra show lower noise, fewer matrix effects, and less co-elution than 1D HPLC-HRMS analysis
- The developed method can be applied for both target analysis as well as suspect screening of micropollutants in complex environmental samples.

Questions?

The world leader in serving science