BHIMADZU

Simultaneous analysis of cationic, anionic and neutral surfactants from different matrices using LC/MS/MS Rashi Kochhar⁽¹⁾, Shruti Raju⁽¹⁾, Deepti Bhandarkar⁽¹⁾, Bhairavi Saraf⁽¹⁾, Shailendra Rane⁽¹⁾, Ajit Datar⁽¹⁾, Jitendra Kelkar⁽¹⁾, Zhan Zhaoqi⁽²⁾

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I: Introduction

1-1: Surfactants

The term surfactant (short for 'surface active agent') designates a substance which exhibits some superficial or interfacial activity^[1]. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents and dispersants^[1].

In 2008, the worldwide production of synthetic surfactants was estimated to be as high as 13 million metric tons^[2]. Most of these surfactants after use, are sent to sewage treatment plants (STP). Here, (bio)degradation processes and/or adsorption on sludge particles remove these chemicals from waste waters to a greater or lesser extent, depending on the particular nature of the surfactant molecule. After treatment, the STP effluents are discharged into the environment^[3].

Some surfactants are known to be toxic to animals, ecosystems, humans and can increase the diffusion of other environmental contaminants. Some of these surfactants are also potential carcinogens. Despite this, they are routinely deposited in numerous ways on land and in water systems, whether as part of an intended process or as industrial and household waste and therefore, it becomes essential to monitor their levels in environmental effluents.

1-2: Basic structure and classification

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant molecule contains both a water insoluble (or oil soluble) component and a water soluble component. The hydrophobe is usually C8 to C18 hydrocarbon, and can be aliphatic, aromatic or a mixture of both. The hydrophilic groups give the primary classification to surfactants, making them anionic, cationic and nonionic in nature.

Anionic Surfactants dissociate in water to form an amphiphilic anion and a cation, which is in general an alkaline metal (Na⁺, K⁺) or a quaternary ammonium ion.

Nonionic surfactants do not ionize in aqueous solution, because their hydrophilic group is of a nondissociable type such as alcohol, phenol, ether, ester or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics.

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids.

When a single surfactant molecule exhibits both anionic and cationic dissociations it is called <u>amphoteric or zwitterionic.</u>

In this poster, we have presented data for four surfactants namely Perfluorooctanoic Acid (PFOA), Sodium Dodecyl Sulfate (SDS) both of which are anionic surfactants, Cetrimide which is cationic surfactant and Octylphenol Ethoxylates (OPEO) which is nonionic.

2: Method of Analysis

2-1: LC/MS/MS analysis

LC/MS/MS (shown in Figure 1) was used for the analysis of surfactants.

 Column Shim-pack XR ODS II (100mm L x 3mm I.D. x 2.2µm) Mobile phase : A: 20mM Ammonium acetate in water

5 - 7min -> 75%

- B: Methanol
- 0.45mL/min : 55°C
- Oven temperature
- Gradient program (%B)
- MS interface

• Flow rate

- Nitrogen gas flow MS temperature
- Electro Spray Ionization (ESI)
- Nebulizing gas 3L/min; Drying gas 15L/min
 Desolvation line 250°C; Heat Block 400°C

: 0 - 4min -> 75 - 100%; 4 - 5min -> 100 - 75%;





Figure 1. LCMS-8030 triple quadrupole mass spectrometer by Shimadzu

2-2: Standard preparation

A mixture of surfactants standards namely Cetrimide, Perfluorooctanoic Acid (PFOA), Sodium Dodecyl Sulfate (SDS) and Octylphenol Ethoxylates (OPEO) were prepared in methanol for calibration points ranging from 10ppb to 1000ppb.

2-3: Sample preparation

Tap water and sea water samples were collected from Marol area in Andheri and Juhu in Vile Parle respectively in Mumbai, Maharashtra, India.

The tap water sample was spiked with the standard surfactant mixture to obtain a resultant concentration of 100ppb. This sample was filtered through a 0.2µm membrane filter and analyzed by LC/MS/MS.

Similar treatment was given to sea water sample.

3: Results

3-1: LC/MS/MS analysis

The MRM transitions selected for surfactants are given in Table 1 which are based on the probable fragmentation pathway shown in Figure 2. No peak was seen in diluent (methanol) injection at the retention times of the surfactants for selected MRM transitions which confirms the absence of any interference from diluent (shown in Figure 3). Representative MRM chromatogram of 10ppb standard surfactant mixture is shown in Figure 4. Linearity studies were carried out using external standard calibration method and the results of the same are shown in Table 2. For each concentration level %RSD was found to be within the acceptance criteria.

Surfactant	Retention Time (min)	MRM Transition	Mode of Ionization
PFOA	1.59	413 > 369	Negative ESI
SDS	2.49	265 > 97	Negative ESI
Cetrimide	3.39	256 > 60	Positive ESI
OPEO	3.70	664 > 89	Positive ESI

Table 1. MRM transitions selected for surfactants



Figure 2. Probable fragmentation pathway of selected surfactants





Table 2. Calculated values of %RSD for retention time and area for at 100ppb concentration

	Compound Name	% RSD (n=6)		Linearity		
		RT (min)	Area	(10 - 1000ppb)	(ppb)	(ppb)
1	PFOA	0.21	3.41	0.9995	0.55	1.66
2	SDS	0.27	12.68	0.9998	1.63	4.95
3	Cetrimide	0.06	1.70	0.9999	0.04	0.12
4	OPEO	0.19	10.43	0.9999	0.30	0.90

The analytical methodology was tested on water samples from various sources. This exercise was aimed at screening surfactants from different water sources and recoveries were studied from spiked samples.

Tap water and sea water were individually spiked with mix surfactant standards to get a final concentration of 100ppb and subjected to LC/MS/MS.

Recovery percentages for Cetrimide, SDS, OPEO and PFOA were found to be ranging between 50-120% (shown in Table 3). The lower recoveries can be improved by applying extraction procedures to the samples. Blank and spiked sample chromatograms are shown in figures 5-8.



Figure 7. MRM chromatogram of blank sea water

Figure 8. MRM chromatogram of spiked sea water Table 3. Results of the recovery studies

Surfactante	%Recovery			
Sunaciants	Sea water sample	Tap water sample		
PFOA	77	124		
SDS	86	114		
Cetrimide	102	54		
OPEO	73	71		

4: Conclusion

- > The ultrafast polarity switching of 15msec exhibited by LCMS-8030 system along with its compatibility with UHPLC Nexera enabled simultaneous analysis of surfactants with different ionizing tendencies within short analysis time.
- > The analytical method discussed here can be extrapolated to real environmental samples for screening surfactant levels. This method can also be extended to monitor surfactant levels in consumer products.
- > Sensitivity of Nexera coupled with LCMS-8030 has facilitated quantitation of surfactants over the concentration range of 10ppb to 1000ppb with R^2 values greater than 0.9995. Repeatability studies have shown that %RSD for area and retention times are within criteria^[4].

5: References

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