Simultaneous analysis of cationic, anionic and neutral surfactants from different matrices using LC-MS/MS

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Introduction

The term surfactant designates a substance which exhibits some superficial or interfacial activity[1]. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants[1]. Some surfactants are known to be toxic to animals, ecosystems, and 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.

Method of analysis

LC-MS/MS analysis

LCMS-8030 (shown in Fig. 1) was used for the analysis of surfactants.
- Column   Shim-pack XR ODS II
                                     (100 mm L × 3mm I.D. × 2.2 µm)
- Mobile phase   A: 20 mM Ammonium acetate in water
                                     B: Methanol
- Flow rate   0.45 mL/min
- Oven temperature   55ºC
- Gradient program (%B)   0 - 4 min -> 75 - 100%;
                                     4 - 5 min -> 100 - 75%; 5 - 7 min -> 75%
- Interface   Electro Spray Ionization (ESI)
- Gas   Nebulizing gas 3 L/min; Drying gas 15 L/min
- Temperature   Desolvation line 250ºC; Heat Block 400°C

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

Standard preparation

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

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Sample preparation

Tap water, sea water and well water samples were collected from Marol area in Andheri, Juhu in Vile Parle and Vasai area respectively in Mumbai, Maharashtra, India. The tap water sample was spiked with the standard surfactant mixture to obtain a resultant concentration of 100 ppb. This sample was filtered through a 0.2 µm membrane filter and analyzed by LC-MS/MS. Similar treatment was given to sea water and well water samples.

Results

The MRM transitions selected for surfactants are given in Table 1. 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 Fig. 2 and Fig. 3). 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.
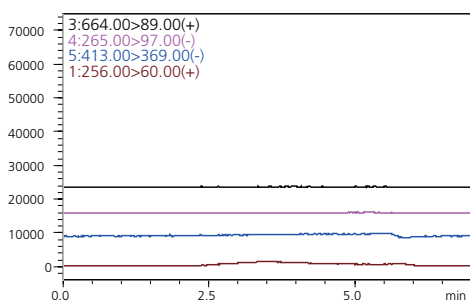

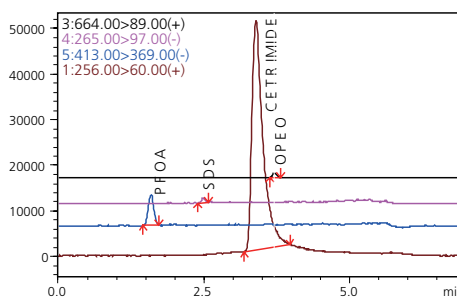Fig. 2 MRM chromatogram of diluent (methanol)

Fig. 3 MRM chromatogram of 10 ppb of standard surfactants mixture in methanol

Table 1 MRM transitions selected for surfactants

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

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.

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

ID	Compound Name	% RSD (n=6)		Linearity	LOD (ppb)	LOQ (ppb)
		RT (min)	Area	(10 - 1000 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

Tap water, sea water and well water were individually spiked with mix surfactant standards to get a final concentration of 100 ppb and subjected to LC-MS/MS. Recovery percentages for Cetrimide, SDS, OPEO and PFOA were found to be ranging between 50-125% (shown in Table 3). The lower recoveries can be improved by applying extraction procedures to the samples

Table 3 Results of the recovery studies

Surfactants	%Recovery		
	Sea water sample	Tap water sample	Well water sample
PFOA	77	124	121
SDS	86	114	117
Cetrimide	102	54	61
OPEO	73	71	70

Conclusions

- The ultrafast polarity switching of 15 msec 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 10 ppb to 1000 ppb with R^2 values greater than 0.9995. Repeatability studies have shown that %RSD for area and retention times are within criteria[2].

References

1 Jean-Louis Salager; Surfactant types and uses, FIRP Booklet # E300-A in english; University of Los Angeles, Chapter 1 (2002) Page 2
2 AOAC guidelines for single laboratory: Validation of chemical methods for dietary supplements and botanicals

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