

Simultaneous analysis of anionic, amphoteric and non-ionic surfactants using ultra-high speed LC-MS/MS

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Introduction

Surfactant chemistry has made a considerable impact on a number of household products including detergents, shampoos and toothpaste. Products are generally classified by the type of each hydrophilic substructure into anionic, cationic, amphoteric and non-ionic surfactants. Either anionic or non-ionic surfactants are typically used as synthetic detergents, however, to better elucidate the

potential risk in environmental samples, mainly in agricultural soils and sediments, methods need to take into account a range of surfactant chemistries. Current surfactant monitoring methodologies tend to focus on a specific surfactant. Here, we have developed the simultaneous analysis method for typical anionic, amphoteric and non-ionic surfactant using LC-MS/MS.

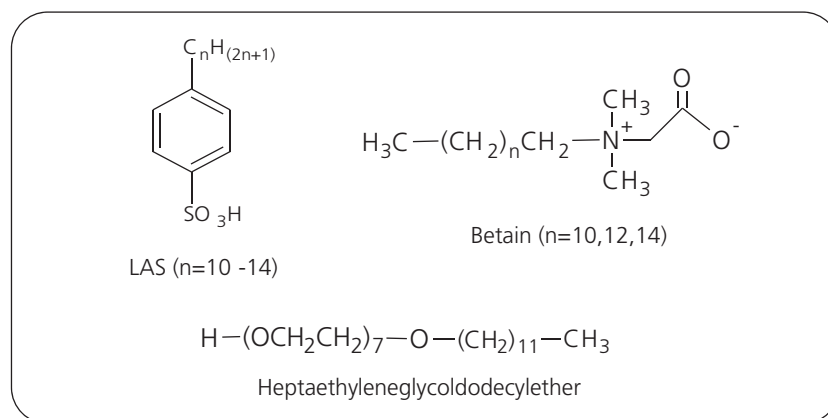


Fig. 1 Structure of anionic, amphoteric and non-ionic surfactant

Methods and Materials

Commercially available surfactants were used for this experiment. Standards of surfactants were diluted with water / acetonitrile =3/7 to an appropriate concentration and then analyzed by LC-MS/MS. As an LC-MS/MS system, UHPLC was coupled to triple quadrupole mass spectrometer (Nexera MP with LCMS-8040, Shimadzu Corporation, Kyoto, Japan). Separation was achieved using a YMC-Triart C8 column (100 mmL., 2.0 mmI.D., 1.9 μ m

particles) and column oven temperature was maintained at 40°C. Samples were eluted at flow rate 300 μ L/min with a binary gradient system; the mobile phase consisted of (A) 10 mM ammonium acetate buffer and (B) mixture of 10 mM ammonium acetate / acetonitrile / isopropanol (1/4/5). LC-MS/MS with electrospray ionization was operated in multiple-reaction-monitoring (MRM) mode with ultra-fast polarity switching.

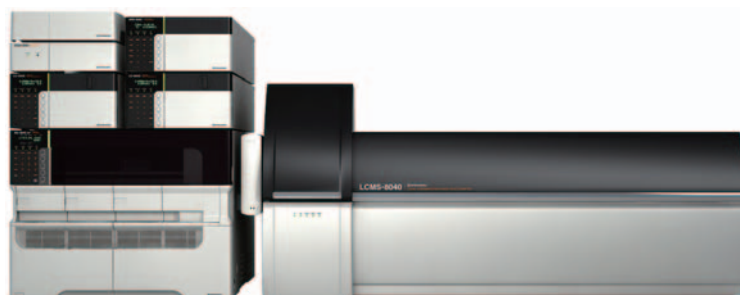


Fig. 2 LCMS-8040 triple quadrupole mass spectrometer

High Speed Mass Spectrometer

- Ultra Fast Polarity Switching
15 msec
- Ultra Fast MRM
Max. 555 transition /sec

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Results

Method development for surfactants

The following standard surfactants were selected and analyzed; anionic surfactant: linear alkylbenzene sulfonate (LAS) C10-C14 mixture, amphoteric surfactant: EMPIGEN BB Detergent (Betaine) C10, C12, C14 mixture (Sigma-Aldrich, St.Louis, MO), and non-ionic surfactant: heptaethyleneglycoldodecylether (HEDE). Full scan measurement by flow injection analysis (FIA) was conducted to determine the optimum ionization polarity of target compounds followed by MRM transition optimization by FIA. As a consequence, all LASs were detected as the de-protonated ions (M-H) in negative ion

mode and m/z 183 was selected as the product ion of MRM transitions for all LASs (C10-C14). All Betaine were detected as protonated ions (M+H) in positive ion and m/z 104 was selected as the product ions of MRM transitions for all Betaines (C10, C12 and C14). HEDE yielded the protonated ion (M+H) in positive ion as the precursor and m/z 133 was selected as product ion for MRM transition. As compounds selected in this experiment formed either positive or negative ion, high-speed polarity switching is an important element to consider in developing an optimized LC-MS/MS method.

UHPLC conditions (Nexera MP system)

Column: YMC TriartC8 100 mm×2.0 mm, 1.9 μ m
 Mobile phase A: 10 mM Ammonium acetate
 B: 10 mM Ammonium acetate / Acetonitrile/ isopropanol (1/4/5)
 Flow rate: 0.3 mL/min
 Time program: B conc.75%(0 min) -95%(1.5-3 min) - 75%(3.01-5 min)
 Injection vol.: 10 μ L
 Column temperature: 40°C

MS conditions (LCMS-8040)

Ionization: ESI, Positive/Negative MRM mode

Table 1 MRM transition of LAS 9 surfactants

Compound	Polarity	MRM transition
LAS C10	-	297.15 > 182.60
LAS C11	-	311.20 > 182.60
LAS C12	-	325.20 > 182.70
LAS C13	-	339.20 > 182.60
LAS C14	-	353.40 > 182.60
Betain C10	+	271.95 > 103.80
Betain C12	+	300.00 > 103.70
Betain C14	+	328.20 > 103.70
HEDE	+	495.30 > 133.15

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Fig. 3 shows MRM chromatograms of the nine surfactants. It took 5 minutes per one LC-MS/MS analysis, including column rinsing, and excellent separation and high sensitive detection were obtained.

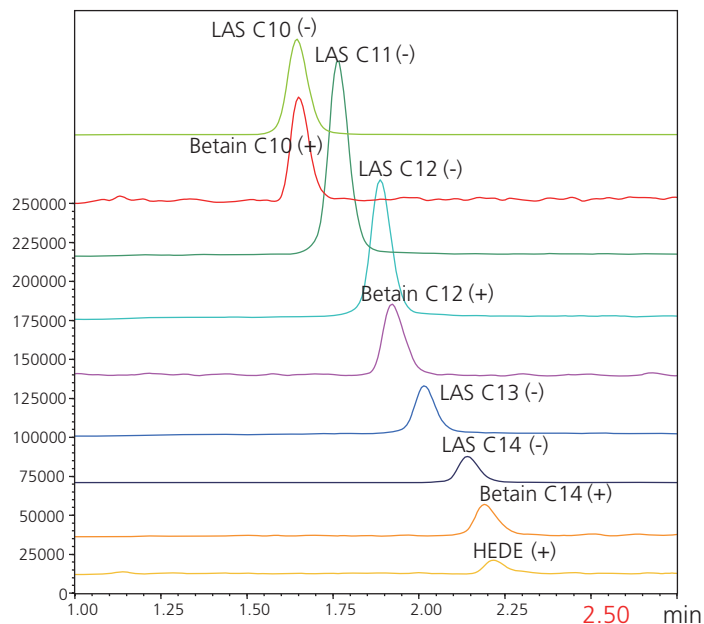


Fig. 3 Mass Chromatograms of typical anionic, amphoteric and non-ionic surfactant (concentration of each compound : 5 ppb)

The dilution series of these compounds were analyzed. All compounds were detected at ppb level with excellent linearity (Table 2, Fig. 4).

Table 2 Linearity 9 surfactants

Compound	Polarity	Coefficient (r ²) 0.998
LAS C10	1-500 ppb	0.999
LAS C11	1-500 ppb	0.997
LAS C12	1-500 ppb	0.999
LAS C13	1-500 ppb	0.998
LAS C14	0.5-100 ppb	0.999
Betain C10	1-100 ppb	0.999
Betain C12	1-100 ppb	0.999
Betain C14	1-100 ppb	0.999
HEDE	1-100 ppb	

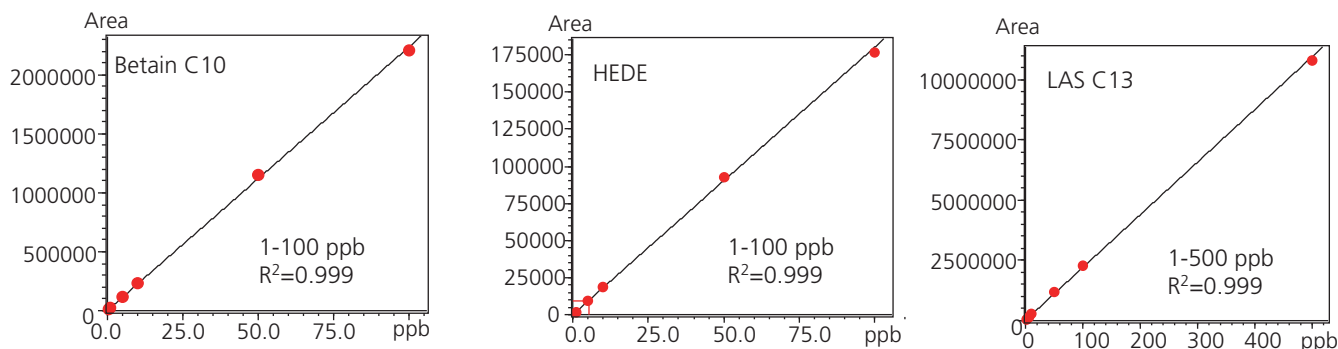


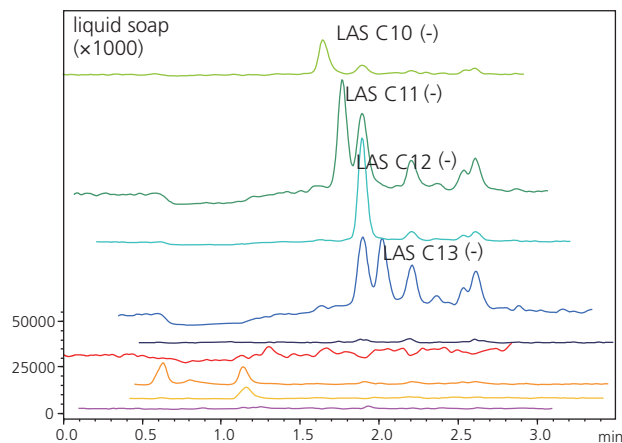
Fig. 4 Representative calibration curve (Betain C10, HEDE, LAS C13)

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Quantitative Analysis of real world sample

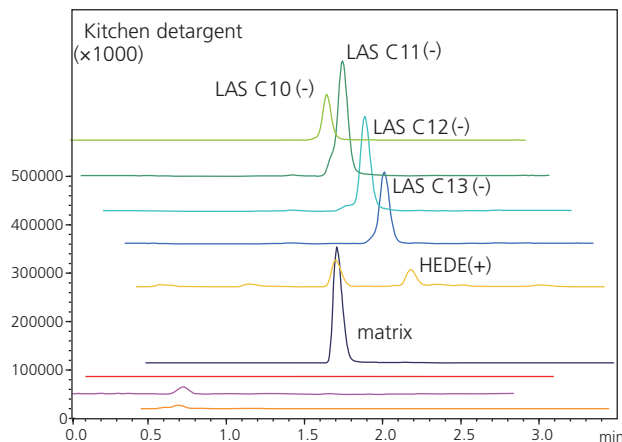
The quantitative analysis of real world sample using the kitchen detergents and liquid soap was achieved using this method. Kitchen detergents and liquid soap was diluted 1000 to 1 with water / acetonitrile= 3/7. Finally, it was filtered through a 0.2 um filter and analyzed by LC-MS/MS. MRM chromatograms of each surfactants in the kitchen detergents and liquid soap is shown Fig. 5,6.

The 1000 to 1 dilution of liquid soap contained approximately 5 to 6 ppb LAS C12 and C13. Therefore, it was determined that undiluted liquid soap contains 5 to 6 ppm LAS C12 and C13. On the other hand, undiluted kitchen detergent contains approximately 40 ppm LAS C10, C11, C12 and C13, and approximately 75 ppm HEDE.



	Concentration (ppb)
LAS C10	< 1 ppb
LAS C11	< 1 ppb
LAS C12	4.9 ppb
LAS C13	6.1 ppb
LAS C14	no detection
HEDE	no detection
Betain C10	no detection
Betain C12	no detection
BetainC14	no detection

Fig. 5 Measurement results of liquid soap (dilution 1000 times)



	Concentration (ppb)
LAS C10	75.2 ppb
LAS C11	no detection
LAS C12	no detection
LAS C13	no detection
LAS C14	no detection
HEDE	35.7 ppb
Betain C10	31.0 ppb
Betain C12	40.4 ppb
BetainC14	44.3 ppb

Fig. 6 Measurement results of Kitchen detergent (dilution 1000 times)

Conclusions

- Typical anionic, amphoteric and non-ionic surfactant were separated with high resolution within 2.5 minute. Even though selected compounds formed either positive or negative ion, all surfactants were detected with high sensitivity. High-speed polarity switching is an important element for simultaneous analysis of various surfactants.
- This method was able to be applied to the quantification of surfactants in kitchen detergents and liquid soap.



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