

Analysis of linear alkylbenzene sulfonate in environmental water using online SPE LC system coupled with LC-MS/MS

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1. Introduction

Surfactant chemistry makes affect to a number of household products including detergents, shampoos and toothpaste. Anionic surfactants have been widely distributed throughout the water environment via household effluent. LAS (linear alkylbenzene sulfonate) is the commonest in various kinds of anionic surfactants. As the presence of LAS in environmental water can seriously affect aquatic organism, it is necessary to monitor the

concentration of LAS in environmental water. In case that it may be present at trace level, sample preparation have generally been conducted such as the solid phase extract (SPE) and concentration. In this study, automation of the sample preparation using online SPE LC system coupled with LC-MS/MS was developed for the determination of LAS concentration in environmental water.

2. Methods and Materials

Standards of 6 linear alkylbenzene sulfonates (LAS, C8, C10-C14), anion surfactants, including various isomers, were optimized on each compound-dependent parameter and MRM transition (Q1/Q3). As a consequence, all LASs were detected as M-H ions at negative polarity and m/z 183 was selected as the product ion of MRM transitions regardless of linear carbon chain length (Fig. 1).

Standards of surfactants were diluted with water / acetonitrile =50/50 to an appropriate concentration. LAS (C8) was used as internal standard. Then they were analyzed on LC-MS/MS condition as follows. Samples were measured by LCMS-8040 triple quadrupole mass spectrometer coupled to online-SPE LC system.

Chromatographic separations were carried out using Shim-pack XR-ODSII column (2.0 mmI.D., 100 mmL/150 mmL., 2.2 μ m). The column temperature was maintained at 40°C. Samples were eluted at flow rate 0.2 mL/min with a

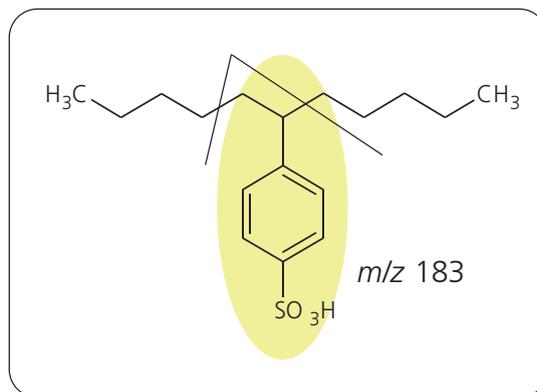


Fig. 1 Structure of LAS (C11)

binary gradient system; the mobile phase consisted of (A) 50 mM ammonium formate + 0.1% formic acid buffer and (B) acetonitrile.



High Speed Mass Spectrometer
• Polarity Switching : 15 msec
• Scanning Speed : Max. 15000 u/sec

Fig. 2 LCMS-8040 triple quadrupole mass spectrometer

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3. Results

3-1. Method development for surfactants

First, the dilution series of LASs were analyzed without online SPE preparation. It was confirmed that the linearity of calibration curve and repeatability for each LAS was excellent and all LASs can be detected from 0.1 ppb. In the case of analyzing river water without sample preparation such as SPE, LASs were subjected to effect from some hydrophilic matrices. Fig. 3 shows mass chromatograms

and recoveries (Area%, river water area count / standard solution area count) of LASs, when the river water sample spiked each LAS (10 ppb) was analyzed without preparation. The recovery of LAS C8 especially was low, because it was assumed that LAS C8 and hydrophilic matrices were eluted nearly at same time.

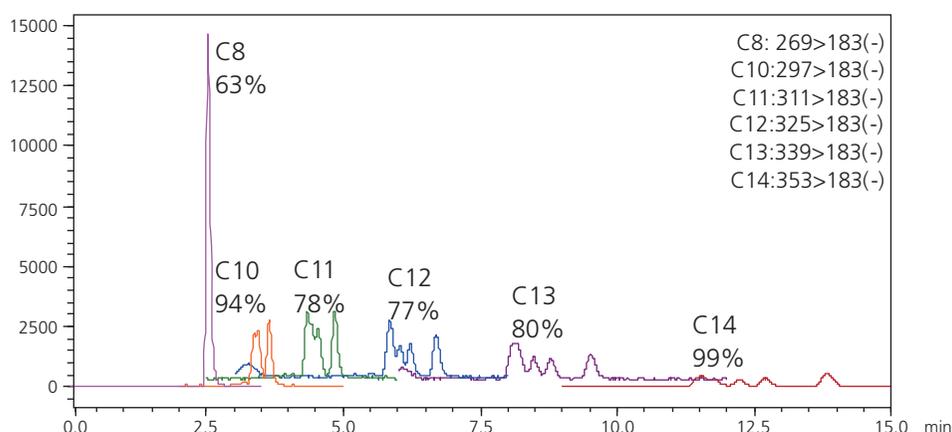


Fig. 3 Mass Chromatograms and recoveries of the river water sample spiked LAS (each LAS :10 ppb)

Table 1 Analytical condition of LAS

Column	: Shim-pack XR-ODSII (150 mmL. × 2.0 mmI.D.,2.2 um)
Mobile Phases	: A:0.1%Formic acid-50 mM Ammonium formate water B: Acetonitrile
Flow Rate	: 0.2 mL/min
Time program	: B conc.65% (0-15 min) -95% (15.01-20 min) - 65% (20.01-25 min)
Column Temperature	: 40°C
Injection Volume	: 5 uL
MRM Transition (ESI, Negative mode)	: C8 :m/z 269>183, C10:m/z 297>183, C11:m/z 311>183, C12:m/z 325>183, C13:m/z 339>183, C14:m/z 353>183

Then, online SPE LC System was constructed. The sample injected from the autosampler was introduced into the preparation column (Fig. 4 (1)). The flow channel was then switched to introduce the analytical mobile phase. And it guided LASs from the preparation column to the analytical column (Fig. 4 (2)).

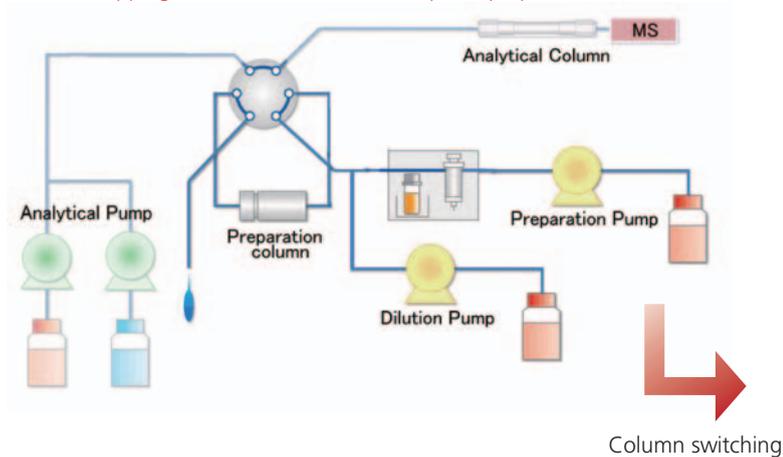
Preparation mobile phase, flow rate and preparation time were optimized. At first, LAS could not be trapped in the preparation column even with water-only mobile phase. The reason was that the sample solution contained 50% acetonitrile to prevent adsorption of LASs on glass vials.

Acetonitrile weakened retention of LAS in the preparation column than expected. Therefore, a dilution pump was added to lower the concentration of acetonitrile in front of the preparation column. In this preparation, LAS was concentrated by water-rich mobile phase flow. At the same time, it was expected that some hydrophilic matrices were eliminated.

Otherwise, it was found that optimum preparation time was 4.5 min. Fig. 5 shows MRM chromatograms of 6 LAS (1 ppb). High sensitive detection were obtained.

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(1) Trapping LAS of environmental sample in preparation column



(2) Eluting LAS from preparation column to analysis column

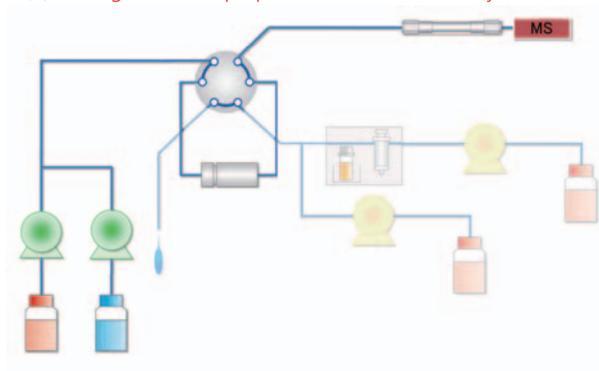


Fig. 4 The flow path of online SPE LC

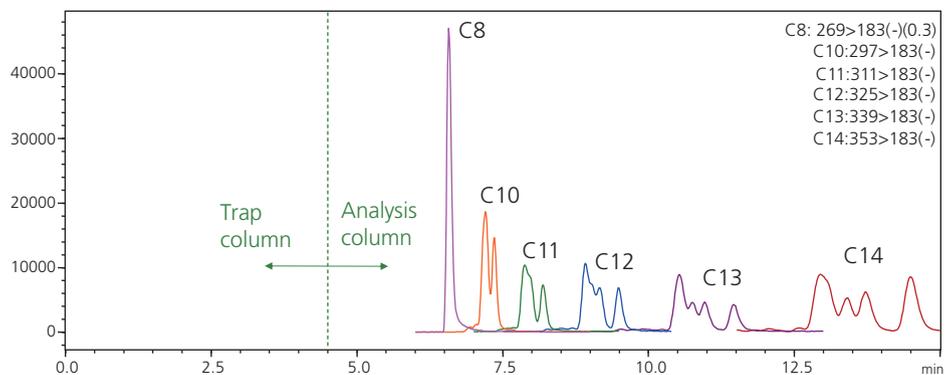


Fig. 5 Mass Chromatograms of 6 LASs (concentration of each LAS: 1 ppb)

Table 2 Analytical condition of LAS with online SPE LC system

Preparation column	: CHEMCO MASK-ENV (10 mL. × 2.0 mL.D.)
Preparation mobile phase	: 0.1%Formic acid-50mM Ammonium formate water
Preparation flow rate	: 0.5 mL/min (containing pump dilution 0.4 mL/min)
Analysis column	: Shim-pack XR-ODSII (100 mL. × 2.0 mL.D., 2.2 μm)
Mobile Phases	: A: 0.1%Formic acid-50 mM Ammonium formate water B: Acetonitrile
Flow Rate	: 0.2mL/min
Time program	: B conc.65% (0-20 min) -95% (20.01-28 min) - 65% (28.01-30 min)
Column Temperature	: 40°C
Injection Volume	: 50 μL
MRM Transition (ESI, Negative mode)	: C8 :m/z 269>183, C10:m/z 297>183, C11:m/z 311>183, C12:m/z 325>183, C13:m/z 339>183, C14:m/z 353>183

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3-2. Quantitative Analysis of LAS in river water

The dilution series of these compounds were analyzed. All LASs were detected at ppb level with excellent linearity and repeatability (Fig. 6, Table3).

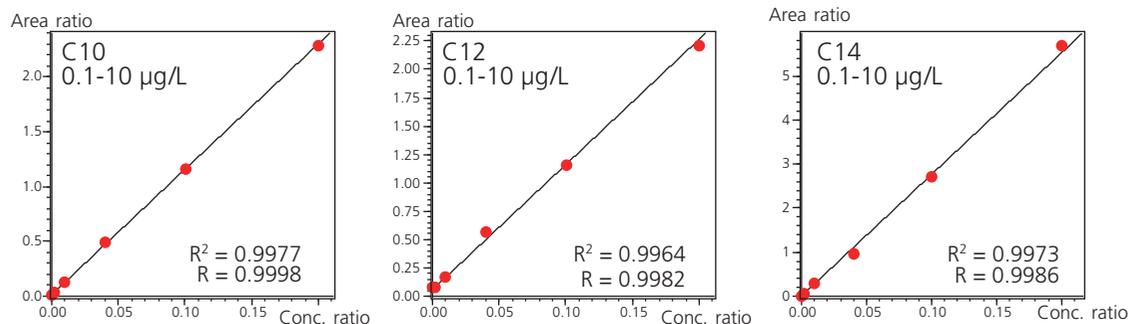


Fig. 6 Representative calibration curve (LAS C10, C12, C14)

Table 3 Area repeatability of 0.5 ppb (n=5)

	C10	C11	C12	C13	C14
Repeatability (RSD%)	0.7	0.9	1.2	0.8	0.9

Recovery rate was evaluated using the river water spiked LASs. The river water sample spiked each LAS (4 ppb) was diluted to twice with water. Next, It was diluted to twice with acetonitrile in order to prevent from being absorbed on the surface of glass vials. Recovery was calculated, taking blank of river water sample (no spiked) and system blank in consideration. The river water sample spiked each LAS (final

concentration 1 ppb) showed good recoveries with almost 100% (Table 4). By connecting an online SPE LC system to LC-MS/MS, the determination of LAS concentration in environmental water could be automated and simplified. It indicates that this LC-MS/MS method was not influenced by sample matrix in river water.

Table 4 Recovery data spiked in river water sample at 1 ppb (n=3)

	C10	C11	C12	C13	C14
Recovery (%)	99.7	102.7	94.6	102.9	99.5

Determination was performed by internal standard.

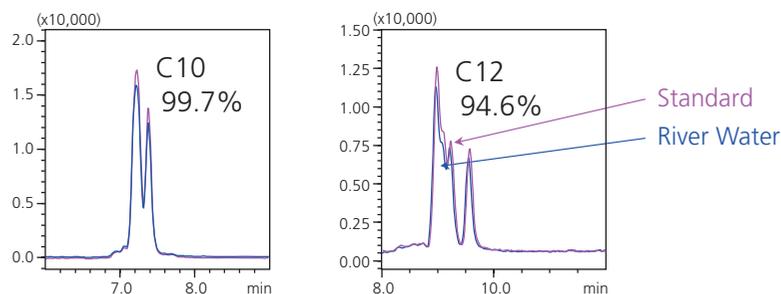


Fig. 7 MRM Chromatograms of river water spiked LASs (each 1 ppb)

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4. Conclusions

- Automation of the sample preparation using online SPE LC system coupled with LC-MS/MS was developed for the determination of LAS concentration in environmental water.
- Determination performed using this system produced good linearity and recovery due to elimination of some hydrophilic matrices.