

## Application News

High Performance Liquid Chromatograph Mass Spectrometer LCMS-8050RX

### Analysis of Anionic Surfactants Using Triple Quadrupole Mass Spectrometry Based on Water Quality Standards

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#### User Benefits

- ◆ Anionic surfactants stipulated in Japan's Drinking Water Quality Standards (DWQS) can be analyzed in 9 minutes per cycle.
- ◆ Anionic surfactant compounds can be detected at concentrations of 2 % or less of the DWQS standard value (0.2 mg/L).
- ◆ Analysis of anionic surfactants in tap water can be performed with good repeatability and recovery rates that meet the MHLW's Guidelines for the Validation of Drinking Water Quality Test Methods.

#### ■ Introduction

Anionic surfactants are substances that dissociate ions in aqueous solutions, with the anionic part exhibiting surface activity. Among anionic surfactants, linear alkylbenzene sulfonates (LAS) with 10 to 14 carbon atoms (C10–C14) are listed in the Ministry of Health, Labour and Welfare's (MHLW) ministerial ordinance on drinking water quality standards,<sup>1)</sup> which stipulates a standard value of  $\leq 0.2$  mg/L for 5 constituent compounds.

Following an amendment to the DWQS in April 2023 that added LC-MS to the list of LAS assay methods, a study analyzing LAS (C10–C14) using a triple quadrupole mass spectrometer was presented in the Application News No. 01-00519-JP. In this study anionic surfactants were analyzed using LCMS-8050RX. It successfully detected compounds at concentrations of 2 % or less of the DWQS standard value for anionic surfactants (0.2 mg/L), which complies with the methods stipulated in the MHLW's ministerial ordinance on drinking water quality standards.



Fig. 1 LCMS-8050RX and CoreSpray

#### ■ Sample Preparation

The calibration standards were prepared using equal parts water and acetonitrile. The tap water samples were prepared using equal parts tap water and acetonitrile. Internal standards were prepared by spiking each sample with <sup>13</sup>C-labeled LAS (C12-LAS-<sup>13</sup>C) to obtain a final concentration of 5 µg/L.

#### ■ Analytical Conditions and Mass Chromatograms

The analytical conditions and the MRM conditions are shown in Tables 1 and 2, respectively. In this study, analyses were performed using the LCMS-8050RX (Fig. 1). The LCMS-8050RX is equipped with the new CoreSpray technology, which enables more consistent nebulizer flow than previous systems. In consecutive analyses, the LCMS-8050RX enabled longer and more robust measurements.

Standard mixture samples containing LAS (C10–C14) 2 µg/L (equivalent to a test water concentration of 4 µg/L) and internal standard (C12-LAS-<sup>13</sup>C) 5 µg/L were analyzed using LC-MS/MS.

The results demonstrated that all 5 anionic surfactant compounds could be detected at concentrations of 2 % or less of the standard value (0.2 mg/L) (Fig. 2).

Table 1 LC-MS/MS Analytical Conditions

[HPLC Conditions] (Nexera™ X3)	
Column:	Shim-pack™ GIS-HP C8-L*1 (150 mm × 2.1 mm I.D., 3 µm)
Mobile Phase:	A) 0.1 % Formic Acid in Water B) Acetonitrile A/B = 35/65 (0 - 9 min)
Flowrate:	0.2 mL/min
Column Temp.:	40 °C
Injection Volume:	1 µL
[MS Conditions] (LCMS-8050RX)	
Ionization:	ESI
Interface Voltage:	-3 kV
Nebulizing Gas Flow:	2 L/min
Drying Gas Flow:	15 L/min
Heating Gas Flow:	5 L/min
Interface Temp.:	200 °C
DL Temp.:	200 °C
Heat Block Temp.:	400 °C
Probe Position:	+2 mm

\*1 P/N: 227-30956-04

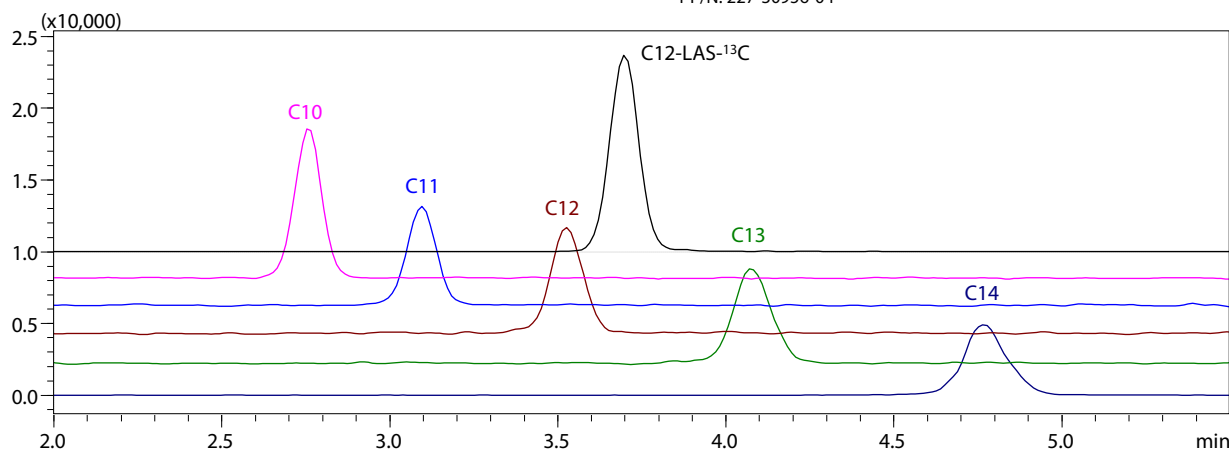


Fig. 2 Mass Chromatograms of Each Compound (2 µg/L is Equivalent to Test Water Concentration of 4 µg/L)

Table 2 Transitions of Each Compound

Compound	Polarity	MRM Transition
C10-LAS	(-)	297 > 183
C11-LAS	(-)	311 > 183
C12-LAS	(-)	325 > 183
C13-LAS	(-)	339 > 183
C14-LAS	(-)	353 > 183
C12-LAS- <sup>13</sup> C	(-)	331 > 176

### ■ Compound Calibration Curves

In Fig. 3, calibration curves using the internal standard method ( $n = 3$ ) are made for each compound at concentrations ranging from 2  $\mu\text{g/L}$  to 100  $\mu\text{g/L}$  (6 calibration points).

The coefficient of determination ( $r^2$ ) of each of the five compound calibration curves was  $r^2 > 0.998$ , demonstrating good linearity across each calibration range.

At the lowest point on the calibration curve (2  $\mu\text{g/L}$ ), good results were obtained that met a mean concentration precision of 90 – 110 % and intra-assay precision value (concentration %RSD) of < 10 for each compound (Table 3).

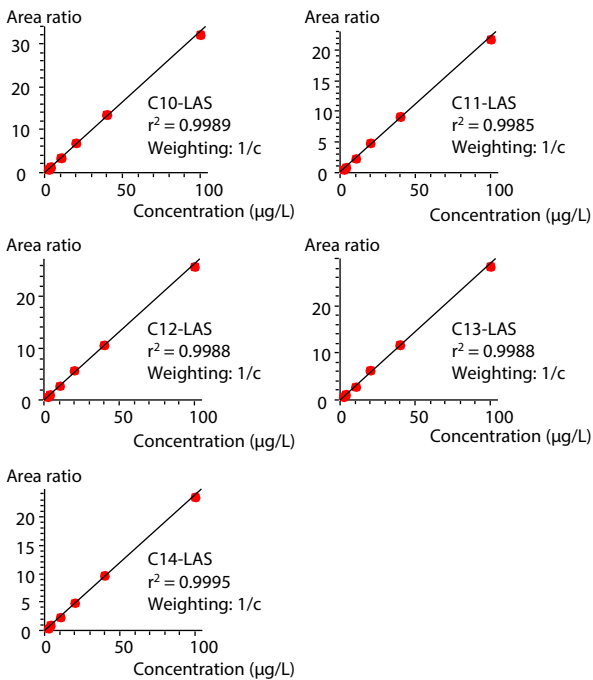


Fig. 3 Compound Calibration Curves

Table 3 Results of Replicate Analysis of Standard Samples (2  $\mu\text{g/L}$ ,  $n = 3$ )

Compound	Mean Accuracy (%)	Intra-Assay Precision (Concentration %RSD)
C10-LAS	94.9	2.9
C11-LAS	94.1	1.5
C12-LAS	94.4	0.4
C13-LAS	96.6	5.9
C14-LAS	96.8	4.2

### ■ Tap Water Spike-and-Recovery Tests

Spike-and-recovery tests were performed using tap water samples from Kanagawa Prefecture in Japan. The spiked tap water samples contained each LAS compound at concentrations of 2  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$ , which is equivalent to test water concentrations of 4  $\mu\text{g/L}$  and 20  $\mu\text{g/L}$ , respectively.

At concentrations of 10 % of each target compound's DWQS standard value (10  $\mu\text{g/L}$  is equivalent to a test water concentration of 20  $\mu\text{g/L}$ ), good results were obtained that met the recovery rate of 100 – 102 % and an intra-assay precision value (concentration %RSD) of < 3 for all the compounds (Table 4).

Moreover, at concentrations of 2 % of each target compound's DWQS standard value (2  $\mu\text{g/L}$  is equivalent to a test water concentration of 4  $\mu\text{g/L}$ ), good results were obtained that met the above-mentioned Guidelines for the Validation of Drinking Water Quality Test Methods (Table 5).

Table 4 Results of Tap Water Spike-and-Recovery Tests ( $n = 5$ )  
(10  $\mu\text{g/L}$  is Equivalent to Test Water Concentration of 20  $\mu\text{g/L}$ )

Compound	Recovery Rate (%)	Intra-Assay Precision (Concentration %RSD)
C10-LAS	101.5	0.5
C11-LAS	100.1	1.6
C12-LAS	101.9	2.1
C13-LAS	100.6	2.1
C14-LAS	100.9	1.9

Table 5 Results of Tap Water Spike-and-Recovery Tests ( $n = 5$ )  
(2  $\mu\text{g/L}$  is Equivalent to Test Water Concentration of 4  $\mu\text{g/L}$ )

Compound	Recovery Rate (%)	Intra-Assay Precision (Concentration %RSD)
C10-LAS	91.3	3.1
C11-LAS	87.9	2.2
C12-LAS	92.3	1.6
C13-LAS	91.4	3.4
C14-LAS	100.2	1.2

### ■ Conclusion

In this study, analyses performed with the LCMS-8050RX using the methods stipulated by the MHLW's ministerial ordinance on drinking water quality standards yielded good sensitivity at concentrations of 2 % or less of the DWQS standard value (0.2  $\text{mg/L}$ ).

Spike-and-recovery testing of tap water samples yielded good recovery rates and repeatability at 20  $\mu\text{g/L}$  and 4  $\mu\text{g/L}$  test water equivalent concentrations, thereby demonstrating that LC-MS can be used to analyze anion surfactant compounds in tap water samples with good precision and which meet the MHLW's Guidelines for the Validation of Drinking Water Quality Test Methods. The LCMS-8050RX enabled robust analysis of all the samples.

### References

- 1) The methods stipulated by MHLW's ministerial ordinance on drinking water quality standards (MHLW Notice No. 261 issued in 2003)

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Triple Quadrupole LC-MS/MS

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