

Application News

Analysis of Surfactants Using Quadrupole Time-of-Flight LC-MS

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User Benefits

- ◆ With its accurate mass data acquisition capability, the LCMS-9030 enables extensive screening of surfactants registered in the surfactant compound list.
- ◆ Continuous detection of surfactants—with their varying degrees of polymerization—enables prediction and identification of the surfactant's structural information, such as alkyl chains and polyoxyethylene groups.
- ◆ The system produces chromatograms with low noise and minimally contaminated peaks using extracted ion chromatogram (XIC) with a narrow m/z window.

Introduction

Surfactants have a unique chemical structure with both hydrophilic and hydrophobic moieties in the same polymer molecule. Due to these useful properties, surfactants are used in a diverse range of products, from household goods such as kitchen and laundry detergents to foods, pharmaceuticals, cosmetics, pesticides, adhesives, and concrete admixtures.

Despite their benefits in a wide range of applications, products containing surfactants are also involved in numerous accidents and incidents, such as contamination or accidental ingestion of foods and beverages and contamination of intravenous fluids administered by healthcare professionals. When determining the causes of these incidents, surfactant analysis can be an effective tool for identifying the cause of contamination. However, this analysis inherently requires an extensive & comprehensive analysis technique given the various surfactants in existence. Moreover, even the same type of surfactant can take the form of numerous compounds with different chain lengths, making continuous detection essential. Within this context, targeted screening using high-resolution LC-MS is very well suited to surfactant analysis.

This edition of Application News describes a case study of comprehensive analysis using the LCMS-9030 Quadrupole Time-of-Flight (QTOF) LC-MS system (Fig. 1) by presenting the results of analysis of tea beverages spiked with surfactants.



Fig. 1 Nexera™ X3 and LCMS-9030

Samples

Samples were prepared by spiking commercially marketed tea beverages with 2 mg commercial detergent and 2 mL ultrapure water per 0.5 mL tea. Two types of dishwashing detergent (A and B) and one type of laundry detergent were used.

The samples underwent solid-phase extraction followed by evaporation in accordance with the procedure described in the references.^{1,2)} Next, the samples were reconstituted in 60 % methanol and filtered using a membrane filter with 0.45 μ m pore size, with the resulting filtrate used as the LC/MS samples. The sample pretreatment procedure is shown in Fig. 2. Styrene-divinylbenzene copolymer was used in the solid-phase column.

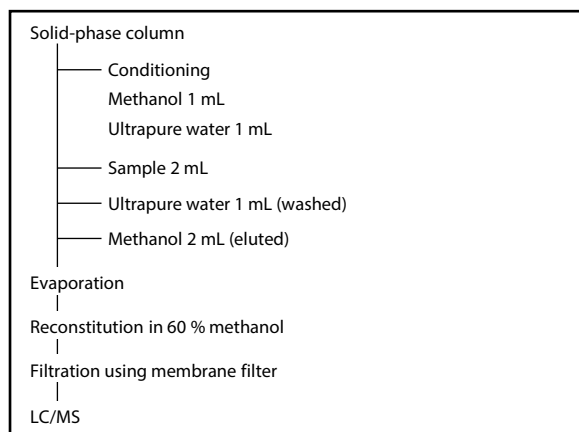


Fig. 2 Sample Pretreatment Procedure

Analytical Conditions

The HPLC and MS conditions are shown in Table 1.

Table 1 Analytical Conditions

UHPLC (Nexera™ X3 system)	
Column:	L-column2 ODS (150 mmL × 1.5 mmI.D., 5.0 μ m, Chemicals Evaluation and Research Institute)
Mobile Phase A:	Methanol: 10 mM Ammonium acetate-Water (50:50, v/v)
Mobile Phase B:	Methanol: 10 mM Ammonium acetate-Water (95:5, v/v)
Gradient Program:	B conc. 40 % (0 min)-100 % (20 min)-100 % (40 min)-40 % (40.01-50 min)
Flowrate:	0.1 mL/min
Column Temp.:	25 °C
Injection Volume:	3 μ L
MS (LCMS-9030)	
Ionization:	ESI (Positive and Negative)
TOF-MS:	m/z 100-1000
Nebulizing Gas Flow:	3.0 L/min
Drying Gas Flow:	10.0 L/min
Heating Gas Flow:	10.0 L/min
DL Temp.:	250 °C
Block Heater Temp.:	400 °C
Interface Temp.:	300 °C

■ Surfactant Compound List

Most surfactants have various hydrophobic alkyl chains, because such alkyl chains come from higher alcohols, fatty acids, and oils derived from animals, plants and petroleum. Polyoxyethylene alkyl ether (POEAE) surfactants, which are commonly used in household detergents, are produced by addition polymerization (polyaddition) of higher alcohols with ethylene oxide. Polyoxyethylene and other polymer groups with a hydrophilic moiety are therefore known to develop a wide range of polymerization levels in the polymer synthesis process. Fig. 3 shows the structures of typical surfactants POEAE, alkylamine oxide (AO), alkyl ethoxylated sulfate (AES), and alkyl sulfate (AS). Numerous surfactants with different alkyl chains and polymerization levels are currently in circulation.

A partial list of the surfactant compounds used in this experiment is presented according to positive ion mode analysis in Table 2 and negative ion mode analysis in Table 3. The surfactant compound list used for analysis in positive ion mode (POEAE, AO, etc.) and negative ion mode (AES, AS, etc.) was prepared from a total of more than 800 database-registered compounds. The compound nomenclature used in the tables indicates the number of alkyl chain carbons and the number of polyoxyethylene groups. For example, in "Polyoxyethylene alkyl ether (POEAE.C10 EO6)," C10 denotes 10 alkyl chain carbons, and EO6 denotes 6 polyoxyethylene groups.

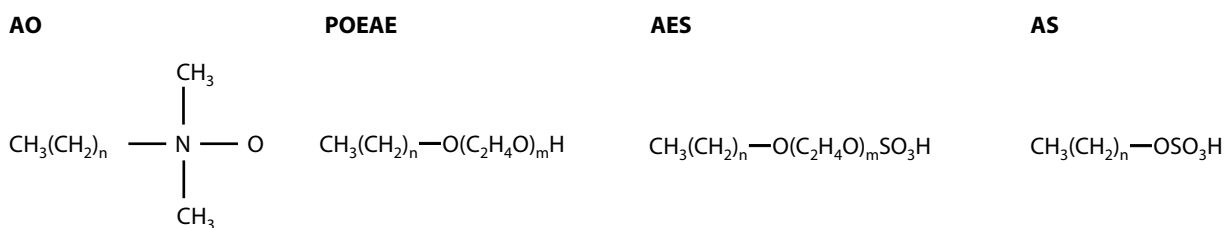


Fig. 3 Surfactant Structures

Table 2 Partial List of Surfactant Compounds for Positive Ion Mode Analysis

Compound	Molecular formula	Selected ion	m/z
Alkyldimethylamine oxide (C8)	C ₁₀ H ₂₃ NO	[M+H] ⁺ /[M+NH ₄] ⁺	174.1852/191.2118
Alkyldimethylamine oxide (C9)	C ₁₁ H ₂₅ NO	[M+H] ⁺ /[M+NH ₄] ⁺	188.2009/205.2274
Alkyldimethylamine oxide (C10)	C ₁₂ H ₂₇ NO	[M+H] ⁺ /[M+NH ₄] ⁺	202.2165/219.2431
Alkyldimethylamine oxide (C11)	C ₁₃ H ₂₉ NO	[M+H] ⁺ /[M+NH ₄] ⁺	216.2322/233.2587
Alkyldimethylamine oxide (C12)	C ₁₄ H ₃₁ NO	[M+H] ⁺ /[M+NH ₄] ⁺	230.2478/247.2744
Alkyldimethylamine oxide (C13)	C ₁₅ H ₃₃ NO	[M+H] ⁺ /[M+NH ₄] ⁺	244.2635/261.2900
Alkyldimethylamine oxide (C14)	C ₁₆ H ₃₅ NO	[M+H] ⁺ /[M+NH ₄] ⁺	258.2791/275.3057
Polyoxyethylene alkyl ether (POEAE.C10 EO6)	C ₂₂ H ₄₆ O ₇	[M+H] ⁺ /[M+NH ₄] ⁺	423.3316/440.3582
Polyoxyethylene alkyl ether (POEAE.C10 EO7)	C ₂₄ H ₅₀ O ₈	[M+H] ⁺ /[M+NH ₄] ⁺	467.3579/484.3844
Polyoxyethylene alkyl ether (POEAE.C10 EO8)	C ₂₆ H ₅₄ O ₉	[M+H] ⁺ /[M+NH ₄] ⁺	511.3841/528.4106
Polyoxyethylene alkyl ether (POEAE.C10 EO9)	C ₂₈ H ₅₈ O ₁₀	[M+H] ⁺ /[M+NH ₄] ⁺	555.4103/572.4368
Polyoxyethylene alkyl ether (POEAE.C10 EO10)	C ₃₀ H ₆₂ O ₁₁	[M+H] ⁺ /[M+NH ₄] ⁺	599.4365/616.4630
Polyoxyethylene alkyl ether (POEAE.C10 EO11)	C ₃₂ H ₆₆ O ₁₂	[M+H] ⁺ /[M+NH ₄] ⁺	643.4627/660.4893
Polyoxyethylene alkyl ether (POEAE.C10 EO12)	C ₃₄ H ₇₀ O ₁₃	[M+H] ⁺ /[M+NH ₄] ⁺	687.4889/704.5155

Table 3 Partial List of Surfactant Compounds for Negative Ion Mode Analysis

Compound	Molecular formula	Selected ion	m/z
Polyoxyethylene alkyl ether sulfate (AES.C12 EO1)	C ₁₄ H ₃₀ O ₅ S	[M-H] ⁻	309.1741
Polyoxyethylene alkyl ether sulfate (AES.C12 EO2)	C ₁₆ H ₃₄ O ₆ S	[M-H] ⁻	353.2033
Polyoxyethylene alkyl ether sulfate (AES.C12 EO3)	C ₁₈ H ₃₈ O ₇ S	[M-H] ⁻	397.2266
Polyoxyethylene alkyl ether sulfate (AES.C12 EO4)	C ₂₀ H ₄₂ O ₈ S	[M-H] ⁻	441.2528
Polyoxyethylene alkyl ether sulfate (AES.C12 EO5)	C ₂₂ H ₄₆ O ₉ S	[M-H] ⁻	485.2790
Polyoxyethylene alkyl ether sulfate (AES.C12 EO6)	C ₂₄ H ₅₀ O ₁₀ S	[M-H] ⁻	529.3052
Polyoxyethylene alkyl ether sulfate (AES.C12 EO7)	C ₂₆ H ₅₄ O ₁₁ S	[M-H] ⁻	573.3314
Polyoxyethylene alkyl ether sulfate (AES.C12 EO8)	C ₂₈ H ₅₈ O ₁₂ S	[M-H] ⁻	617.3576
Polyoxyethylene alkyl ether sulfate (AES.C12 EO9)	C ₃₀ H ₆₂ O ₁₃ S	[M-H] ⁻	661.3838
Polyoxyethylene alkyl ether sulfate (AES.C12 EO10)	C ₃₂ H ₆₆ O ₁₄ S	[M-H] ⁻	705.4101
Polyoxyethylene alkyl ether sulfate (AES.C12 EO11)	C ₃₄ H ₇₀ O ₁₅ S	[M-H] ⁻	749.4363
Polyoxyethylene alkyl ether sulfate (AES.C12 EO12)	C ₃₆ H ₇₄ O ₁₆ S	[M-H] ⁻	793.4625
Polyoxyethylene alkyl ether sulfate (AES.C12 EO13)	C ₃₈ H ₇₈ O ₁₇ S	[M-H] ⁻	837.4887
Polyoxyethylene alkyl ether sulfate (AES.C12 EO14)	C ₄₀ H ₈₂ O ₁₈ S	[M-H] ⁻	881.5149

■ Surfactant Analysis Using LCMS-9030

The pretreated tea samples spiked with detergent were analyzed using LCMS-9030. Next, screening analysis was performed using the LabSolutions Insight Explore™ software and the prepared compound list, resulting in the successful detection of various surfactants including POEAE, AO, and AES. Illustrative results are presented below for positive ion mode analysis of POEAE.C10 EOm (with 10 alkyl chain carbons and *m* polyoxyethylene groups) in tea samples spiked with dishwashing detergent A, and for negative ion mode analysis of AES.C12 EOm (with 12 alkyl chain carbons and *m* polyoxyethylene groups) in tea samples spiked with dishwashing detergent B. Fig. 4 (A) shows the total ion current chromatogram (TICC) and the POEAE.C10 EOm extraction ion chromatogram (XIC) obtained from positive ion mode analysis of pretreated tea samples unspiked or spiked with dishwashing detergent A. Fig. 4 (B) shows the mass spectrum for the dishwashing detergent A-spiked sample's Peak (a) at a retention time of 14–15 minutes. The XIC extraction range is ± 5 ppm. Fig. 4 (A) shows that the POEAE.C10 EOm peak was successfully detected in the samples spiked with dishwashing detergent A but was not detected in the unspiked sample.

The expanded chromatogram obtained by repeated XIC shows that the POEAE.C10 EOm peaks are continuously detected. The mass spectrum in Fig. 4 (B) shows 15 spectra with *m/z* 44 intervals originating from polyoxyethylene groups. The results demonstrate that dishwashing detergent A contains POEAE.C10 EOm and that the number of polyoxyethylene groups is distributed throughout the alkyl chain region.

Similarly, Fig. 5 shows the negative ion mode TICC of samples spiked with dishwashing detergent B and laundry detergent, and the XIC of AES.C12 EOm. Fig. 5 indicates that the AES.C12 EOm peak was successfully detected in the samples spiked with dishwashing detergent B but was not detected in the sample spiked with laundry detergent. The expanded chromatogram in Fig. 5 obtained by repeated XIC shows that the AES.C12 EOm peaks were continuously detected. Table 4 summarizes the different types of surfactants that were detected in each detergent. The analysis results are consistent with the surfactants listed on the respective detergent product labels, suggesting that this technique is capable of analyzing different types of surfactants.

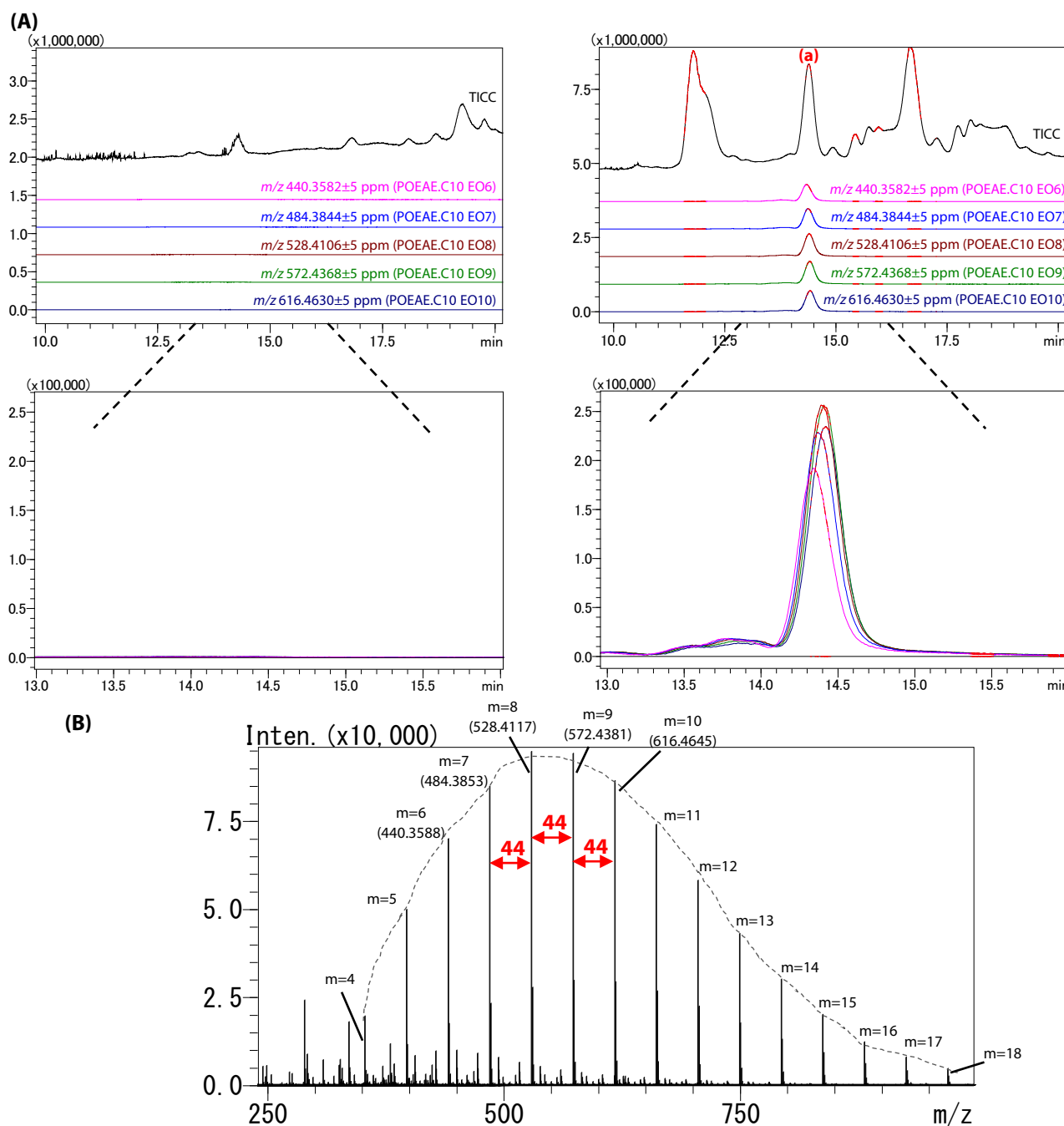


Fig. 4 (A) TICC and XIC of POEAE.C10 EOm for Samples Unspiked (Left) and Spiked (Right) with Dishwashing Detergent A, and (B) Mass Spectrum of Peak (a)

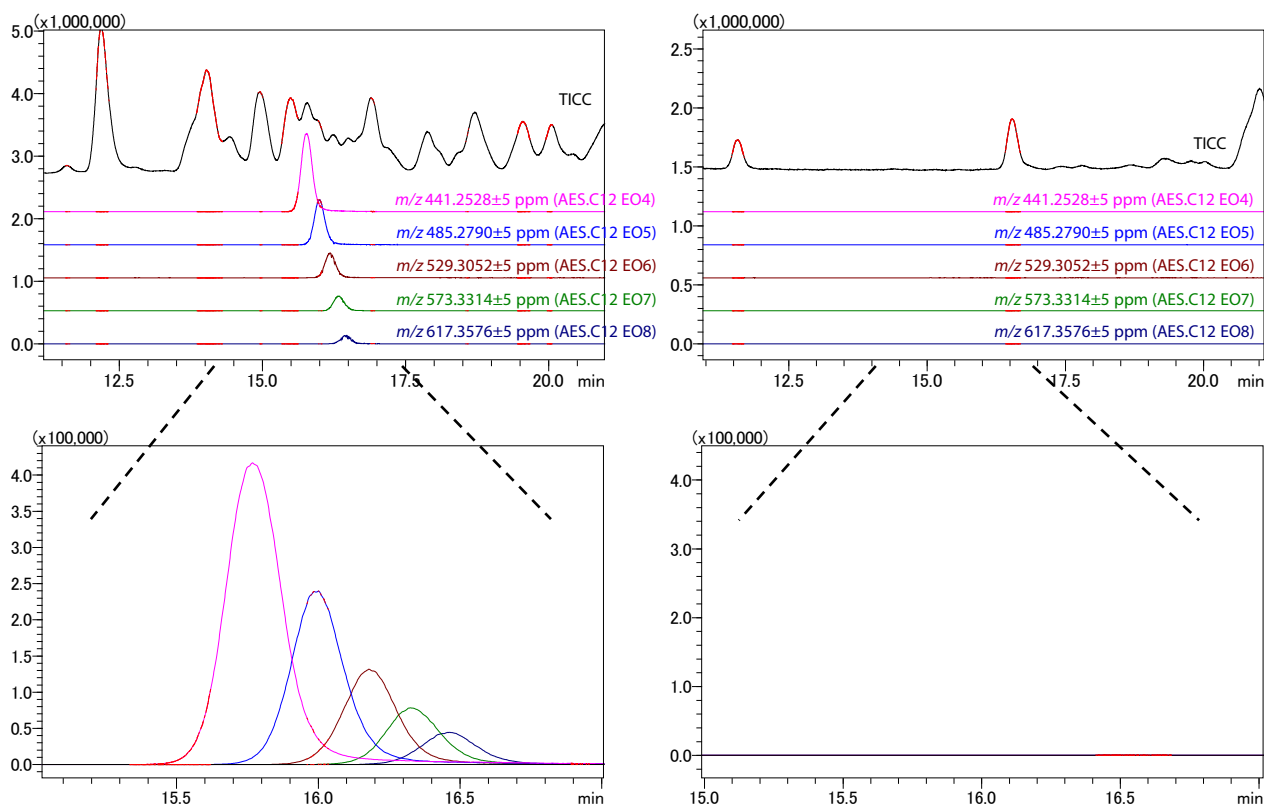


Fig. 5 TICC of Samples Spiked with Dishwashing Detergent B (Left) and Laundry Detergent (Right) and XIC of AES.C12 EOm

Table 4 Surfactants Detected in Each Detergent

Spiking detergent	Surfactant			
	POEAE	AO	AES	AS
Dishwashing detergent A	○	○	○	
Dishwashing detergent B	○	○	○	○
Laundry detergent	○	○		

Note: The black and red circles indicate the surfactants detected using positive and negative ion modes, respectively.

Conclusion

This case study describes how the LCMS-9030 system can analyze surfactants in tea spiked with detergents. Using positive ion mode or negative ion mode analysis, the system enables continuous detection of surfactants with different chain lengths due to differences in the polymerization level of their polyoxyethylene groups. The findings also suggest that the LCMS-9030 system can be used to analyze different types of surfactants. The analysis technique described in this case study simplified the prediction and identification of surfactant types contained in samples.

References

- 1) Nakano S, Kamata H, Sasaki K, Shima N, Kamata T, Matsuta S, Kakehashi H, Nishioka H, Miki A, Tsuchihashi H, Katagi M. Development of the Exact Mass Database of Surfactants and Its Forensic Application. J. Mass Spectrom. Soc. Jpn., 67, 2 (2019).
- 2) Adachi Y, Takahashi T. Simultaneous Extraction of Surfactants for Product Tampering Case involving Dishwashing Detergents. Jpn J Forensic Sci Technol., 12 45 (2007).

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