

Application News

No. L535

High Performance Liquid Chromatography

High Speed Analysis of Anionic Surfactants

In the quantification of anionic surfactants in tap water, standard solution containing various branched types of C10 to C14 are analyzed and about twenty peaks obtained are classified by carbon number. Each sum of peak areas from identical carbon chain number is then used for quantification. Separation columns for anionic surfactants can be categorized into (1) columns that afford multiple peaks by the recognition of the branched chains for each carbon number and (2) columns that do not recognize branched chains by carbon number and thus afford only a single peak for each carbon number.

According to the Ministerial Ordinance on Water Quality Standards⁽¹⁾, solid phase extraction-high performance liquid chromatography has been adopted as the test method for anionic surfactants and the reference value is 0.2 mg/L as the total for 5 classified carbon chain groups. For this test method, a Ministerial Ordinance specifies "a stainless steel column having an internal diameter of 4.6 mm and a length of 15 to 25 cm, packed with silica gel having a particle size of 3 to 5 μm chemically bonding an octadecyl silyl base, or a column having separation performance equal or superior thereto"⁽²⁾. The column specified in this Ordinance is classified as the above-mentioned (1) type of column.

In Application News No. L477B, a Shim-pack™ VP-ODS (internal diameter: 4.6 mm, length: 25 cm, particle size: 5 μm) was used. The present article introduces an application using a Shim-pack FC-ODS (internal diameter: 4.6 mm, length: 15 cm, particle size: 3 μm). High speed analysis using a Shim-pack XR-ODS II (internal diameter: 3.0 mm, length: 10 cm, particle size: 2.2 μm) is also introduced.

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■ Analysis of Anionic Surfactants

The analytical system used here was Prominence™-i integrated high-performance liquid chromatograph. Fig.1 shows the chromatogram for the standard mixture of anionic surfactants (total of 50 mg/L for 5 classified groups, 10 mg/L each). Table 1 shows the analytical conditions. This concentration corresponds to the reference concentration through the pretreatment procedure assigned in the water quality inspection method, which includes the 250 times concentration of the test water by solid phase extraction.

Using the previously-reported VP-ODS, elution required approximately 20 min. However, with the FC-ODS having a particle size of 3 μm, all components could be eluted in about 10 min while maintaining separation by each carbon number.

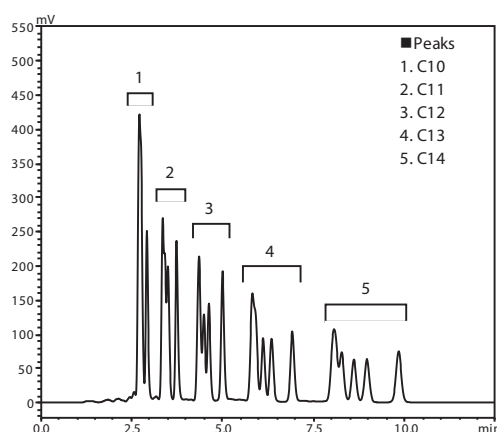


Fig. 1 Chromatogram of Standard Mixture of 5 Anionic Surfactants (FC-ODS)

■ High Speed Analysis of Anionic Surfactants

The analytical system, piping and mobile phase were the same as those used in the previous section, and only the analytical column was changed to a UHPLC column. Fig.2 shows the chromatogram for the standard mixture of anionic surfactants (total of 50 mg/L for 5 classified groups, 10 mg/L each). Table 2 shows the analytical conditions.

Using the XR-ODS II having a particle size of 2.2 μm, it was possible to elute all components in approximately 5 min while maintaining separation by each carbon number.

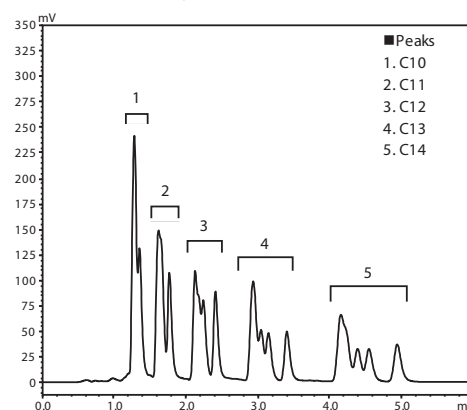


Fig. 2 Chromatogram of Standard Mixture of 5 Anionic Surfactants (XR-ODS II)

Table 1 Analytical Conditions (FC-ODS)

System	: Prominence-i
Column	: Shim-pack FC-ODS (150 mm L. × 4.6 mm I.D., 3 μm)
Flow rate	: 1.0 mL/min
Mobile phase	: Water/Acetonitrile=35/65 (v/v) containing 0.1 mol/L Sodium perchlorate
Column temp.	: 40 °C
Injection volume	: 20 μL
Detection	: RF-20A, Ex at 221 nm, Em at 284 nm

Table 2 Analytical Conditions (XR-ODS II)

System	: Prominence-i
Column	: Shim-pack XR-ODS II (100 mm L. × 3.0 mm I.D., 2.2 μm)
Flow rate	: 0.7 mL/min
Mobile phase	: Water/Acetonitrile=35/65 (v/v) containing 0.1 mol/L Sodium perchlorate
Column temp.	: 40 °C
Injection volume	: 5 μL
Detection	: RF-20A, Ex at 221 nm, Em at 284 nm

■ Calibration Curves

The standard solution for creating the calibration curve was prepared by diluting a commercially-available standard mixture of anionic surfactants (containing 1 mg/mL each of C10 to C14) with methanol. Fig. 3 shows the calibration curves for 0.5 to 10 mg/L of each carbon number (as concentration of sample water, 0.002 to 0.04 mg/L) on the Shim-pack FC-ODS and the Shim-pack XR-ODS II. Table 3 shows the relative errors at the prepared concentrations. The results showed accuracy of the contribution rate of 0.9999 or more for all carbon numbers and the relative error of 10 % or less for all concentrations.

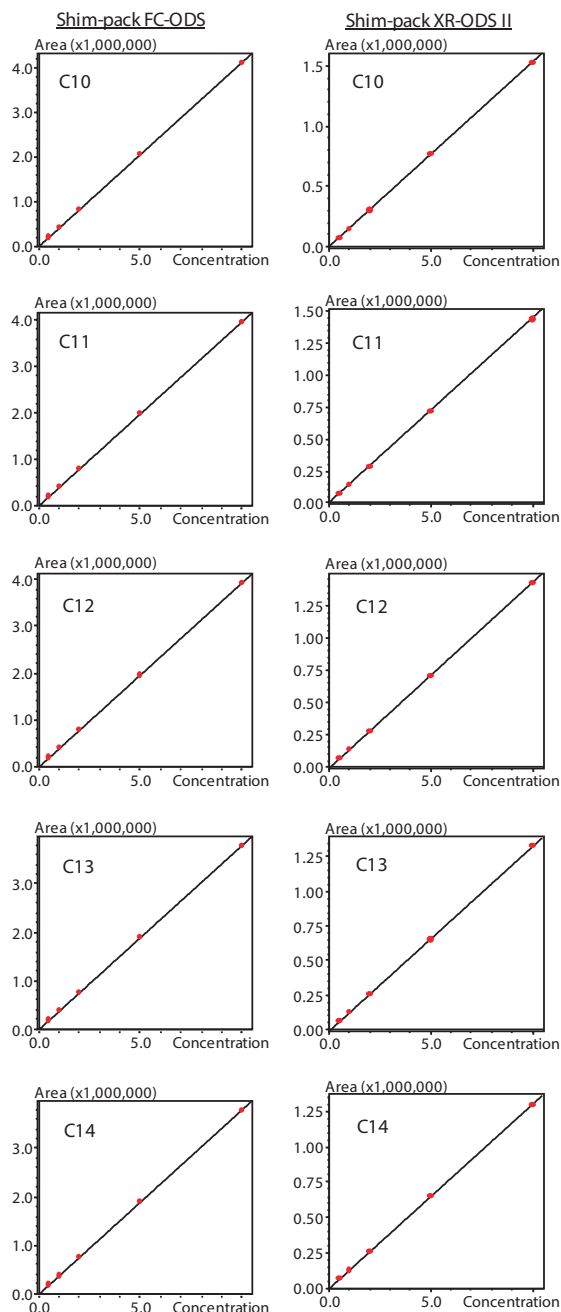


Fig. 3 Calibration Curves
(Left: Shim-pack FC-ODS, Right: Shim-pack XR-ODS II)

Table 3 Relative Errors of the Prepared Concentrations (%)

Shim-pack FC-ODS					
	C10	C11	C12	C13	C14
0.5 mg/L	4.95	2.53	1.04	2.73	3.52
1.0 mg/L	0.97	0.49	0.22	1.51	1.29
2.0 mg/L	1.40	1.04	0.6	1.58	0.99
5.0 mg/L	0.40	0.01	0.27	0.05	0.50
10 mg/L	0.13	0.03	0.04	0.05	0.14

Shim-pack XR-ODS II					
	C10	C11	C12	C13	C14
0.5 mg/L	2.93	0.53	1.89	4.89	1.67
1.0 mg/L	0.42	0.78	2.40	0.68	0.15
2.0 mg/L	0.15	0.13	0.80	0.56	0.40
5.0 mg/L	0.61	0.30	0.01	0.82	0.11
10 mg/L	0.15	0.07	0.01	0.21	0.04

■ Repeatability of Peak Areas

Table 4 shows the relative standard deviation (%RSD) of the peak areas based on 6 repeated analyses of standard solutions containing 0.5 mg/L each and 1.0 mg/L each of the surfactants on the two columns, which have different particle sizes. Both of the 0.5 mg/L solution (one-twentieth of the reference concentration as the test water) and 1.0 mg/L solution (one-tenth concentration), %RSD were 1 % or less.

Table 4 Relative Standard Deviation (%RSD) of the Peak Areas based on 6 Repeated Analyses

Shim-pack FC-ODS					
	C10	C11	C12	C13	C14
0.5 mg/L	0.30	0.48	0.55	0.60	0.81
1.0 mg/L	0.21	0.24	0.21	0.38	0.51

Shim-pack XR-ODS II					
	C10	C11	C12	C13	C14
0.5 mg/L	0.52	0.59	0.54	0.56	0.84
1.0 mg/L	0.41	0.24	0.50	0.52	0.38

■ Conclusion

An RF-20A fluorescence detector was connected to a Prominence-*i* integrated high-performance liquid chromatograph to study the applicability of high speed analysis without changing the standard specifications of the piping and detector cell.

FC-ODS provided approximately a half of elution time for target components compared to that of VP-ODS while complying with the water quality standard.

XR-ODS II provided a quarter of elution time as well.

The linearities, relative errors of the prepared concentrations and the repeatabilities on the peak areas of both analytical columns were satisfactory.

[References]

- (1) Ordinance No. 101 of the Ministry of Health, Labour and Welfare, Japan (MHLW), May 30, 2003 (Partially revised by MHLW Ordinance 29, March 2, 2015)
- (2) Ordinance No. 261 of the Ministry of Health, Labour and Welfare, Japan (MHLW), July 22, 2003 (Partially revised by MHLW Ordinance 138, March 28, 2018)

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