

## Application News

# No. L527

### High Performance Liquid Chromatography

## Analysis of Non-Ionic Surfactant by Solid Phase Extraction-HPLC Conforming to Water Quality Standard

A standard value of 0.02 mg/L or less was established for non-ionic surfactants (NIS) by enforcement of a ministerial ordinance concerning water quality standards (ordinance of the Ministry of Health, Labour and Welfare No. 101, May 30, 2003). Although a notice had specified solid phase extraction-absorptiometry as the analytical method, solid phase extraction-high performance liquid chromatography (HPLC) (2 of Attached Table 28) was added in a partial revision in FY 2012. This article introduces an example of analysis of NIS in tap water by using Shimadzu HPLC.

### ■ Analysis of Standard Solution

In this test method, the sample water is concentrated 100 times by solid phase extraction and reacted with various reagents, and the complex (Co-Par) of cobalt and 4-(2-pyridylazo)-resorcinol (PAR), which is the final product, is detected at wavelengths around 510 nm by using a UV-VIS detector. High sensitivity analysis is possible by using a tungsten lamp in detection.

Fig. 1 shows the chromatograms of the standard solution, and Table 1 shows the analytical conditions. Because the 10 mmol/L sodium tetraborate aqueous solution used in the mobile phase has a pH of approximately 9, use of an alkali-resistant analysis column and analytical instrument is recommended.

In some cases a Co-PAR peak may be detected in the blank sample (concentration: 0 mg/L). This is considered to be due to the impossibility of completely eliminating cobalt that has not formed a complex and metals contained as impurities in the sample preparation process.

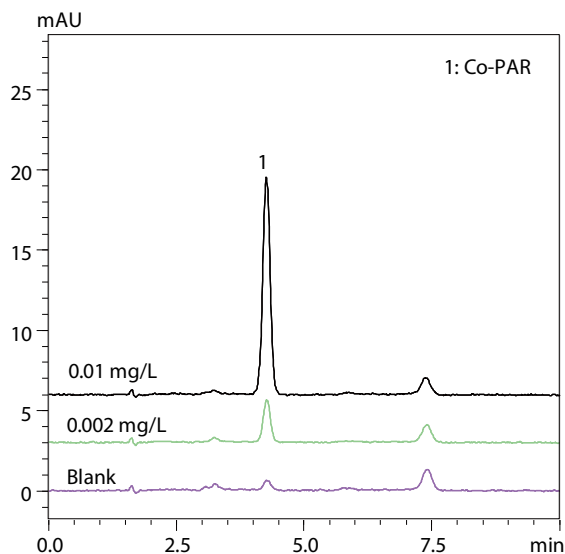


Fig. 1 Chromatograms of Standard Solution

Table 1 Analytical Conditions

Instrument	: Prominence™ HPLC system
Column	: Shim-pack™ GIST C18 (150 mm L × 4.6 mm I.D., 5 μm)
Mobile phase	: Methanol / 10 mmol/L Sodium tetraborate = 38 / 62 (v/v)
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detection	: SPD-20AV (W Lamp) 510 nm
Sample Vol.	: 10 μL

### ■ Linearity

Fig. 2 shows the calibration curve for the concentration range of 0.002-0.01 mg/L specified in the test method. The correlation coefficient ( $R^2$ ) was 0.998.

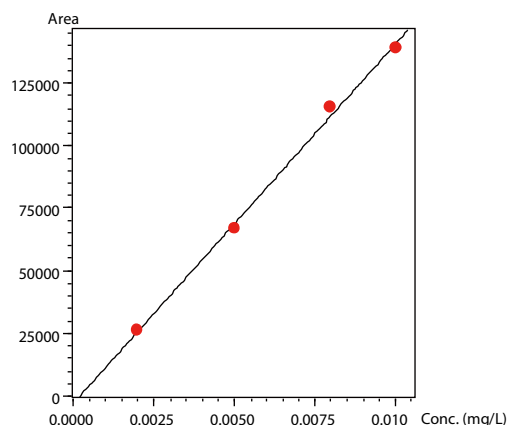


Fig. 2 Calibration Curve

### ■ Repeatability

Six consecutive analyses were performed with a standard solution of 0.002 mg/L, which is the smallest value of the calibration curve and is equivalent to 1/10 of the standard value. Satisfactory results were obtained, as the relative standard deviation (RSD) of the peak area was 1.2 % and the RSD of the retention time was 0.16 %. The chromatograms are shown in Fig. 3.

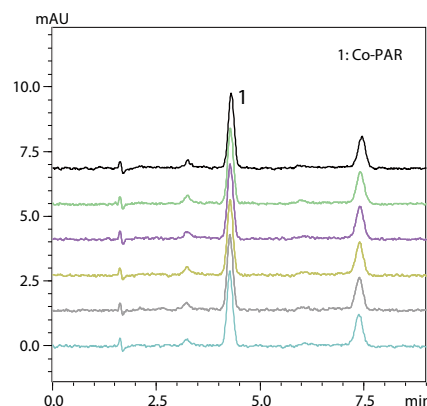
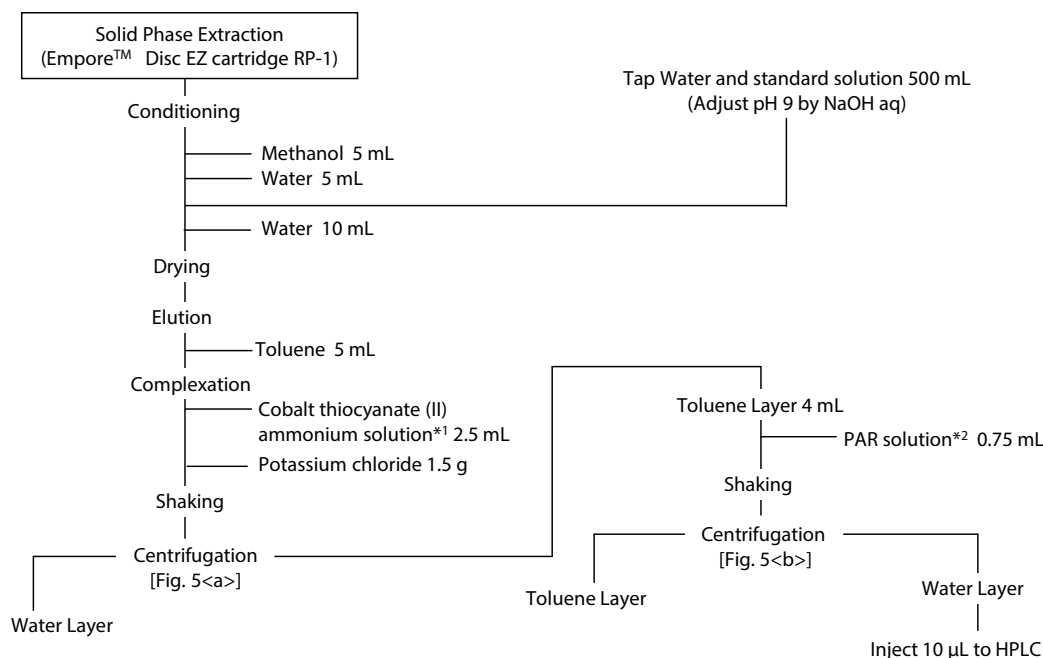


Fig. 3 Chromatograms of 6 Consecutive Analyses with 0.002 mg/L Standard Solution

## Sample Preparation Method

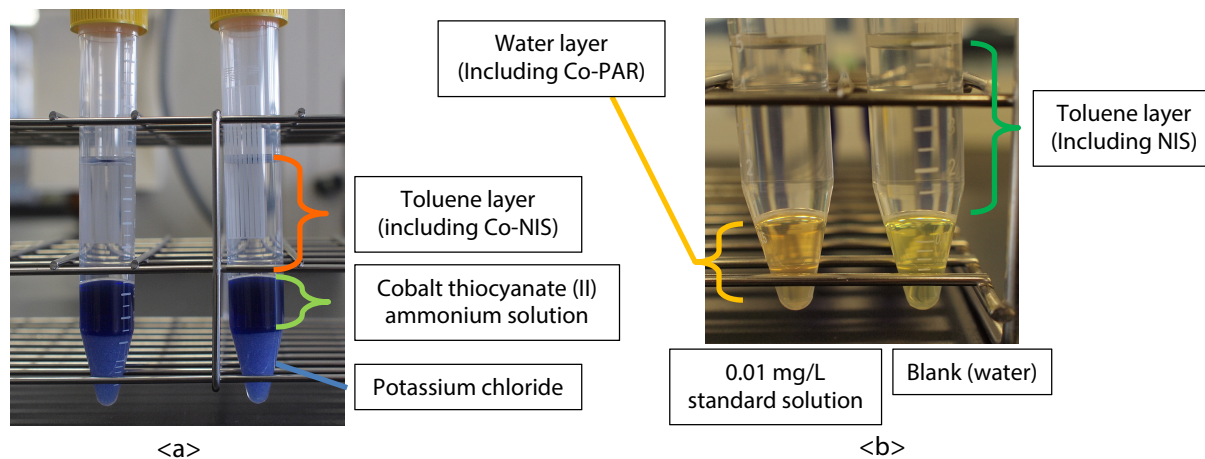
The sample preparation method is shown in Fig. 4. Use of resin equipment is recommended because non-ionic surfactants are readily adsorbed on glass, and the PAR reagent forms undesired complexes with metals other than cobalt. Fig. 5<a> shows a photograph of the solution after adding a cobalt thiocyanate (II) ammonium solution and potassium chloride to a solution in which NIS was eluted from the solid phase extraction cartridge by toluene, shaking and centrifugal separation. If centrifugal separation is performed normally, only the fraction of cobalt proportional to the NIS content will

move to the toluene layer. However, if centrifugal separation is inadequate, excess cobalt will remain in the toluene layer. In cases where the correlation coefficient of the calibration curve decreases, this may be caused by preparation process such as poor centrifugal separation or other problems. Fig. 5<b> shows a photograph of the solution after addition of a PAR solution and the toluene layer in Fig. 5<a>, shaking and centrifugal separation. After the color reaction, the water layer containing the PAR solution shows a strong reddish color that increases in strength with the concentration of NIS.



**Fig. 4 Sample Preparation Method**

- \*1 Solution prepared by mixing ammonium thiocyanate aqueous solution (456 g/L) and cobalt nitrate hexahydrate aqueous solution (46.6 g/L) at 1/1 (v/v) immediately before use.  
 \*2 Solution prepared by 10 × dilution of PAR solution (0.1 g/L; adjusted to pH 11 with 4 w/v% NaOH aqueous solution) with ultrapure water.



**Fig. 5 <a> Complexation and <b> Color Reaction**

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