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Application News

No.L508

High Performance Liquid Chromatography

Analysis of Formaldehyde by the Derivatization-High Performance Liquid Chromatography Method, in Compliance with Water Quality Standards

Revisions to the ministerial ordinance related to water quality standards were announced on March 30 2016 (Japan's Ministry of Health, Labour and Welfare Ordinance No. 115; enacted April 1 2016), and Ordinance No. 261 was partially revised. The derivatization-high performance liquid chromatography method was added therein as a formaldehyde inspection method. The standard value remains unchanged at 0.08 mg/L max.
This article introduces an example of the analysis of formaldehyde in compliance with the derivatization-high performance liquid chromatography method (hereinafter the official method), using a Shimadzu Prominence-i high performance liquid chromatograph.

Analytical Method

In the official method, phosphoric acid and a solution of 2,4-dinitrophenylhydrazine (hereinafter DNPH solution) are added to the sample as derivatization reagents. If the water sample contains residual chlorine, 0.1 to 0.5 mL of an ammonium chloride solution (1 w/v%) is added per 100 mL of the sample, after which derivatization is performed. The pretreatment procedure from the official method is shown in Fig. 1.

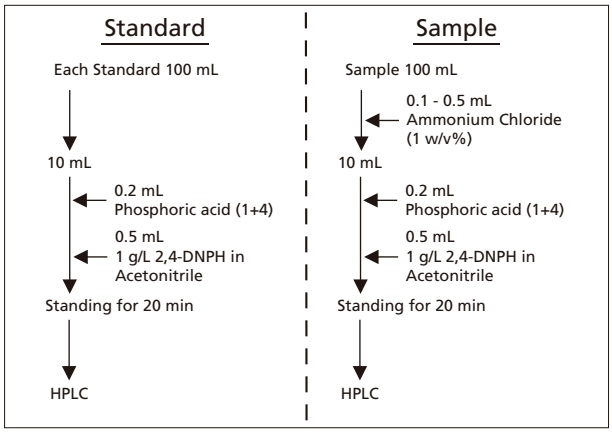

Fig. 1 Pretreatment

Analysis of Standard Solution

The analysis result for a standard formaldehyde solution (0.005 mg/L) at a concentration of 1/10 the standard value or less is shown in Fig. 2. The analytical conditions are shown in Table 1. When the same derivatization was performed with respect to ultrapure water, trace formaldehyde was detected. However, it was confirmed that the value was less than that prescribed in the validity evaluation guidelines* for tap water quality inspection procedures.

* In the "Validity Evaluation Guidelines for Tap Water Quality Inspection Procedures" from the Japan's Ministry of Health, Labour and Welfare, if an interference peak is evident, you must check that the area of the interference peak is less than 1/3 the area of the peak obtained from a standard solution at 1/10 the concentration of the standard value.

Table 1 Analytical Conditions

Column	: Shim-pack VP-ODS (150 mm L. × 4.6 mm I.D.)
Mobile Phase	: Water/Acetonitrile = 50/50(v/v)
Flowrate	: 1.0 mL/min
Column Temp.	: 40 ˚C
Injection	: 50 µL
Detection	: UV 360 nm (Cell temp. 40 ˚C)

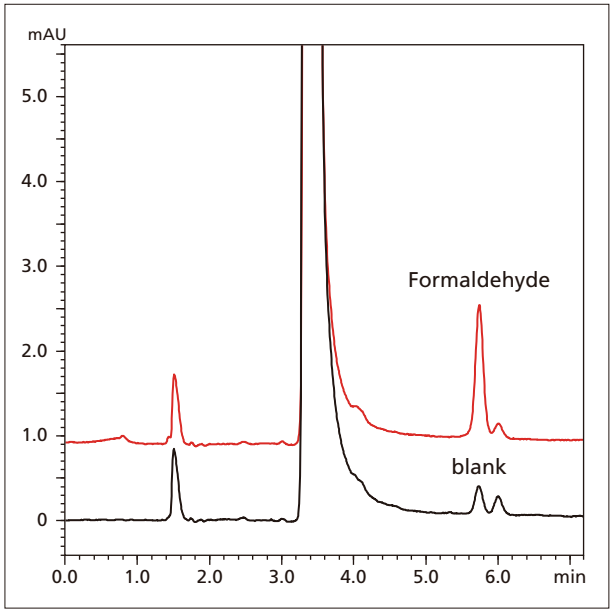

Fig. 2 Chromatograms for a Standard Formaldehyde Solution (Upper: Formaldehyde at 0.005 mg/L; Lower: Blank)

Linearity

A calibration curve for the standard formaldehyde solution is shown in Fig. 3. It was created for a concentration range of 0.005 to 0.1 mg/L, as prescribed in the official method. Favorable linearity is indicated, with a coefficient of correlation (R^2) of 0.999 or higher.

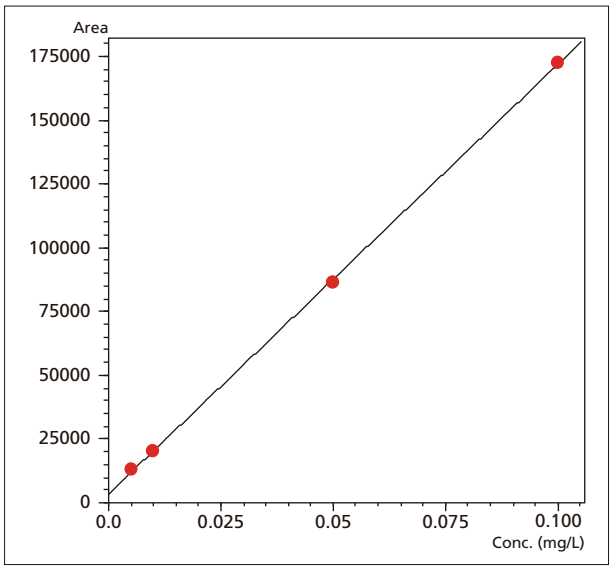

Fig. 3 Calibration Curve

Repeatability

The chromatograms, retention times, and relative standard deviations (%RDS) for area are shown in Fig. 4 for a standard formaldehyde solution (0.005 mg/L), at a concentration of 1/10 the standard value or less, analyzed six times.

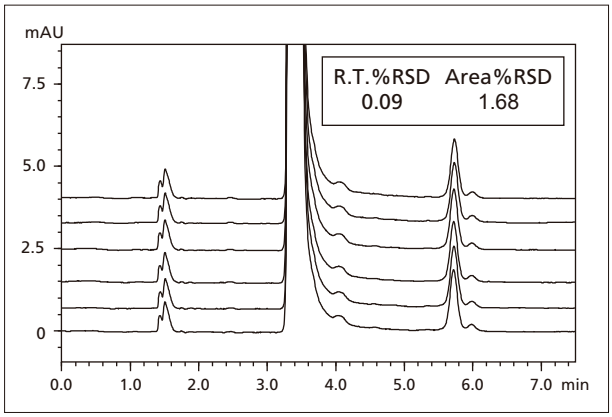

Fig. 4 Chromatograms for a Standard Formaldehyde Solution (0.005 mg/L, n = 6)

Analysis of Tap Water

The analysis result for a standard formaldehyde solution at 0.008 mg/L, a concentration of 1/10 the standard value, added to tap water are shown in Fig. 5. The tap water used in this instance contained formaldehyde at the standard concentration or less, but this did not have an impact on the quantitative results. The additive recovery ratio was 109 %.

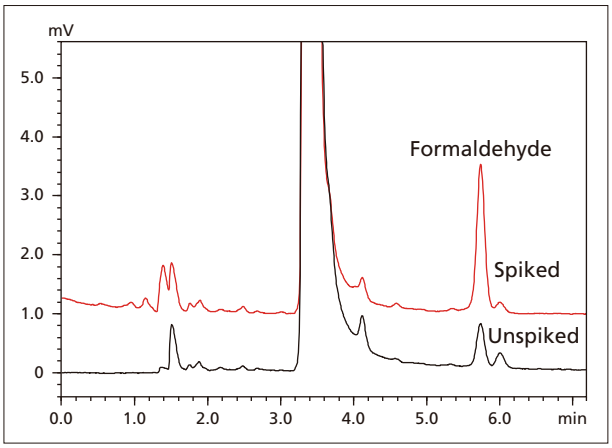

Fig. 5 Chromatograms for Tap Water (Upper: Spiked with 0.008 mg/L Formaldehyde; Lower: Unspiked)

First Edition: Aug. 2016

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