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Application News

No.C128

Liquid Chromatography Mass Spectrometry

Analysis of Formaldehyde in Drinking Water Using Triple Quadrupole LC/MS/MS [LCMS-8050]

Formaldehyde is highly toxic and the levels are regulated in many products, including cosmetics, textiles, household products, and indoor (work) environments since it is also one of the causes of sick house syndrome.
Japan has a water quality standard in place for formaldehyde levels in drinking water (0.08 mg/L), and a test method is specified in appended table 19, solvent extraction-derivatization-gas chromatography-mass spectrometry method, of the methods determined by the Minister of Health, Labour and Welfare based on prescriptions of ministerial ordinance concerning water standards (Health, Labour and Welfare Ministry notification No. 261 of July 22, 2003).
Revisions to the ministerial ordinance concerning water standards were promulgated on March 30, 2016 (Health, Labour and Welfare Ministry notification No. 115 effective April 1, 2016), adding two new formaldehyde test methods, appended table 19-2 derivatization-high performance liquid chromatography method and appended table 19-3 derivatization-liquid chromatography-mass spectrometry method, to the methods determined by the Minister of Health, Labour and Welfare based on prescriptions of ministerial ordinance concerning water standards. We describe an example of simultaneous analysis of formaldehyde and another compound that requires examination, acetaldehyde, according to the derivatization-liquid chromatography-mass spectrometry method that was added to the ministerial ordinance.

Sample Pretreatment

The pretreatment described by the new derivatization-liquid chromatography-mass spectrometry test method shown in appended table 19-3 removes the need for solvent extraction with hexane and iodometric titration, which are both performed in the current method shown in appended table 19 solvent extraction-derivatization-gas chromatography-mass spectrometry method.
The new test method also reduces standing time after derivatization to around one-sixth of the current method, and overall is expected to provide substantial improvements in pretreatment efficiency.
The work flows of pretreatment by each test method are shown in Fig. 1.

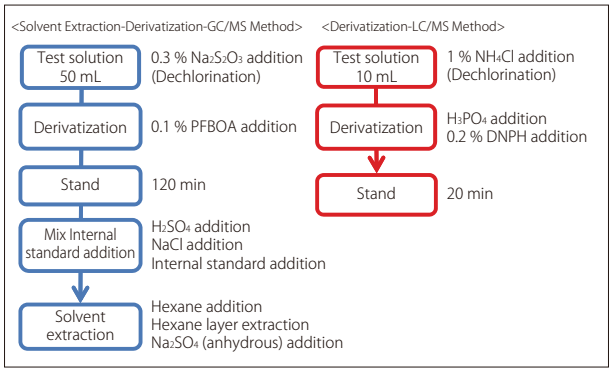

Fig. 1 Pretreatment Work Flows

Analysis of Formaldehyde-Acetaldehyde Reference Standard Mixture

A formaldehyde-acetaldehyde reference standard mixture at 0,005 mg/L, which is less than 1/10th the water standards level for formaldehyde (0.08 mg/L), was derivatized with DNPH and analyzed. MRM chromatograms of this analysis are shown in Fig. 2.
Good results were obtained, with peak area repeatability (n=6) that met the condition of %RSD < 20 % for both DNPH derivatized formaldehyde and acetaldehyde.
Analytical conditions are shown in Table 2.

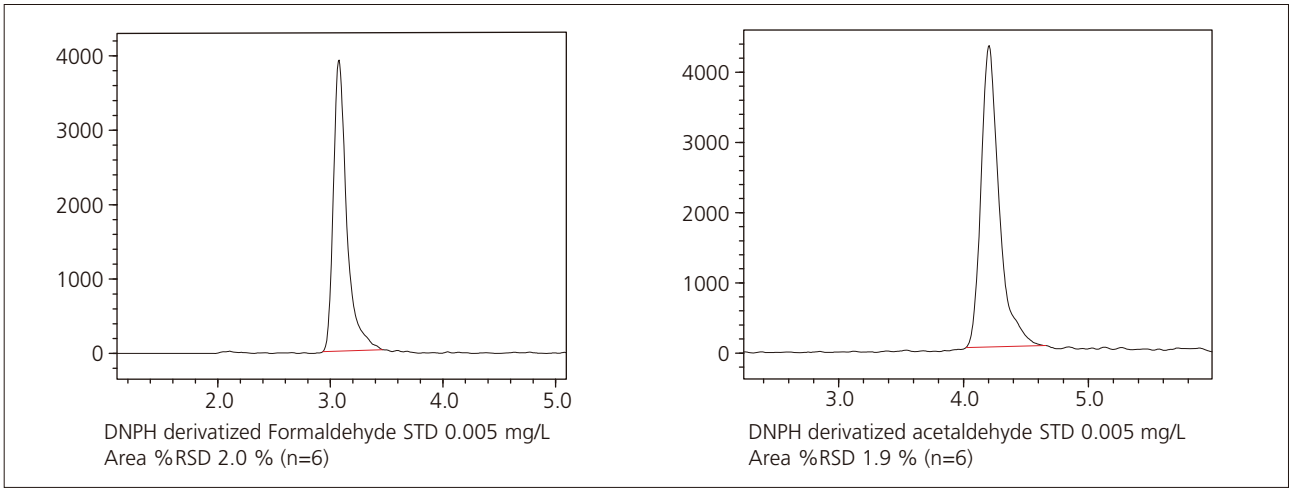

Fig. 2 MRM Chromatograms of DNPH Derivatized Formaldehyde and Acetaldehyde Reference Standards

Fig. 3 shows calibration curves (n=6) created for DNPH derivatized formaldehyde and acetaldehyde based on five points in the concentration range of 0.005 to 0.100 mg/L, which includes 0.008 mg/L that is 1/10th the water standards level for formaldehyde. Good linearity was obtained, with a coefficient of determination (R^2) > 0.999 for both calibration curves.

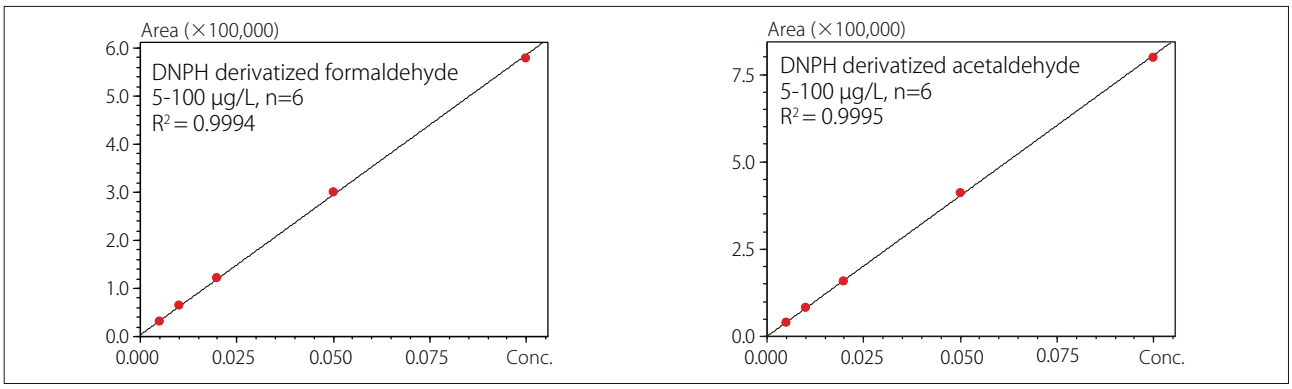

Fig. 3 Absolute Calibration Curves on Five Points

Spike Recovery Test in Drinking Water

A spike recovery test was performed for formaldehyde and acetaldehyde using actual drinking water. Drinking water was spiked with formaldehyde and acetaldehyde at the water standards level of formaldehyde (0.08 mg/L) and one-tenth this concentration (0.008 mg/L), after which DPNH derivatization was performed.
MRM chromatograms obtained from drinking water spiked with the two compounds at 0.008 mg/L are shown in Fig. 4. Selectivity was confirmed since the peak areas for the two compounds in blank drinking water samples were one-third or below peak areas in the spiked drinking water samples.
Good recovery of 101 % to 105 % was obtained for both compounds at both the water standards level of formaldehyde and one-tenth this concentration.

Table 1 Spike Recovery Test Results (n=6)

Recovery	0.08 mg/L spike	0.008 mg/L spike
(DNPH derivatized) Formaldehyde	103.0 %	101.4 %
(DNPH derivatized) Acetaldehyde	104.3 %	101.1 %

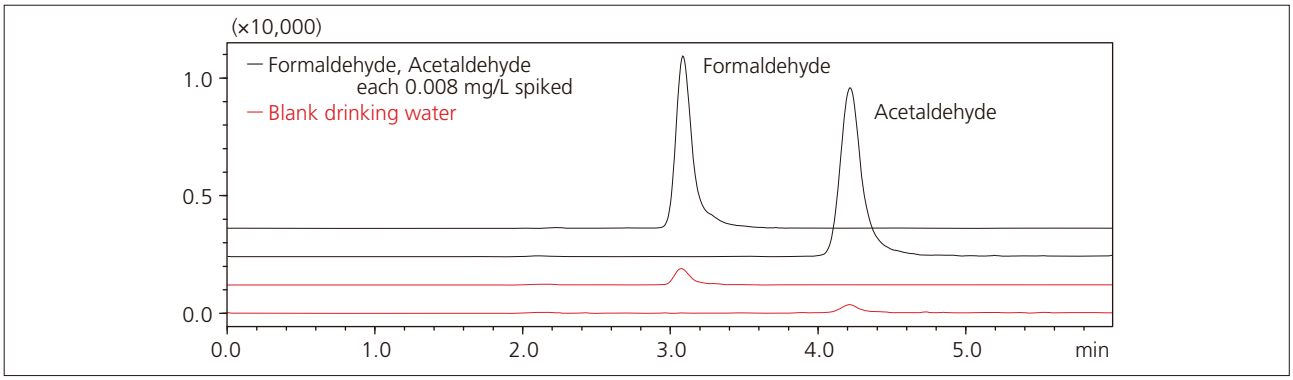

Fig. 4 MRM Chromatograms of Drinking Water Blank and Drinking Water Spiked with Formaldehyde and Acetaldehyde by DNPH Derivatization

Table 2 Analytical Conditions

Column	: Shim-pack FC-ODS (75 mm L. × 2.0 mm I.D., 3 µm, Shimadzu)	DL Temperature	: 150 °C
Mobile Phases	: Water / Acetonitrile = 50 / 50 (v/v)	Block Heater Temperature	: 300 °C
Flow Rate	: 0.20 mL/min	Interface Temperature	: 200 °C
Column Temperature	: 30 °C	Nebulizing Gas Flow	: 2 L/min
MS program	: FCV2 = 1 (0.001 min) → FCV2 = 0 (2.000 min)	Drying Gas Flow	: 10 L/min
Injection Volume	: 1.0 µL	Heating Gas Flow	: 10 L/min
Probe Voltage	: -3 kV (ESI-Negaitive)	MRM Transition	: Formaldehyde *m/z* 209.00 > 151.00
			Acetaldehyde *m/z* 223.00 > 163.00

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