

Application News

No. C96

Liquid Chromatography Mass Spectrometry

Analysis of Phenols in Drinking Water Using Triple Quadrupole LC/MS/MS (LCMS-8040)

Phenols can be formed as wastewater purification and disinfectant by-products, and Japan's Ministry of Health, Labour and Welfare have designated six phenols, including phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol as subject to water quality standards requirements. The method designated (by the ministry notification) for analysis of these six phenol components is solid-phase extraction – derivatization – GC/MS.

Here, we introduce an example of phenol analysis by UHPLC/MS/MS. Unlike the use of GC/MS for this analysis, LC/MS/MS does not require derivatization, and therefore simplifies the analysis process^{1), 2)}.

■ UHPLC/MS/MS Analysis

Sample pretreatment was conducted using the same solid phase extraction procedure as that designated in the notification (solid-phase extraction – derivatization – GC/MS) (Fig. 2). For the solid phase column, an N-containing poly (styrene-divinylbenzene-methacrylic acid) copolymer was used.

Fig. 1 shows the results obtained from measurement of a standard solution containing 0.4 µg/L of each of the six analytical target substances. Since the test water sample concentration is increased 50-fold using solid phase extraction, the equivalent concentration in the test water becomes 0.008 µg/L. Table 1 shows the linearity of the calibration curves over a concentration range equivalent to 0.008 to 1 µg/L in the test water sample, and the repeatability using a concentration of 0.008 µg/L. Excellent linearity and repeatability were obtained with respect to all of the components.

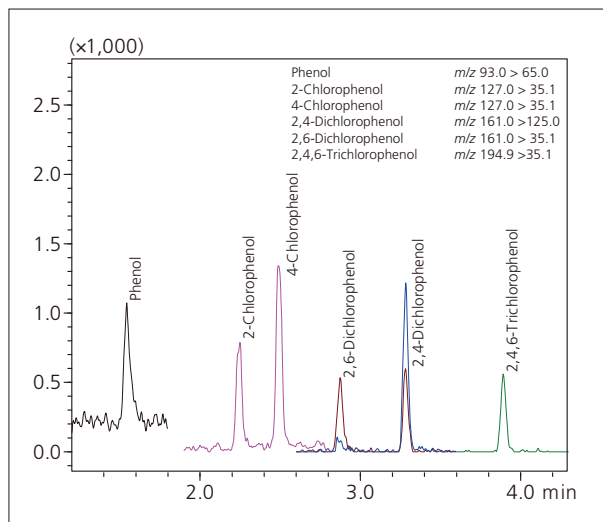


Fig. 1 Mass Chromatograms (MRM) of Phenols

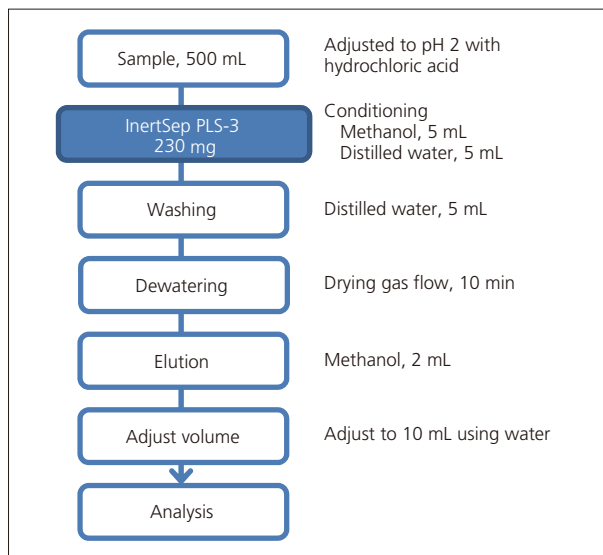


Fig. 2 Pretreatment Flow

Table 1 Calibration Curves and Repeatability

	Injection Sample Concentration (µg/L)	Test Water Sample Concentration (µg/L)	Coefficient of Determination R ²	Area Repeatability %RSD (Calibration point minimum concentration)
Phenol	0.4 – 50	0.008 – 1	0.99938	7.4
2-Chlorophenol	0.4 – 50	0.008 – 1	0.99967	4.5
4-Chlorophenol	0.4 – 50	0.008 – 1	0.99960	5.0
2,4-Dichlorophenol	0.4 – 50	0.008 – 1	0.99966	3.9
2,6-Dichlorophenol	0.4 – 50	0.008 – 1	0.99960	7.0
2,4,6-Trichlorophenol	0.4 – 50	0.008 – 1	0.99960	7.8

■ Spike and Recovery Test for Drinking Water

Using this analytical method, we conducted spike and recovery testing of the phenols in tap water. Fig. 3 shows mass chromatograms (MRM) of a blank tap water sample subjected to pretreatment, and a test water sample spiked with six different phenol compounds, each at a concentration equivalent to 0.08 µg/L in the test sample. These spike concentrations

were approximately equivalent to 1/10 the reference values of the phenols (in terms of the amount of phenol, 0.005 mg/L or less). Regarding the tap water samples analyzed here, there was no indication of significant interference due to contaminating components (Fig. 3). In addition, good recoveries were obtained, ranging between and 90 to 110 % (Table 2).

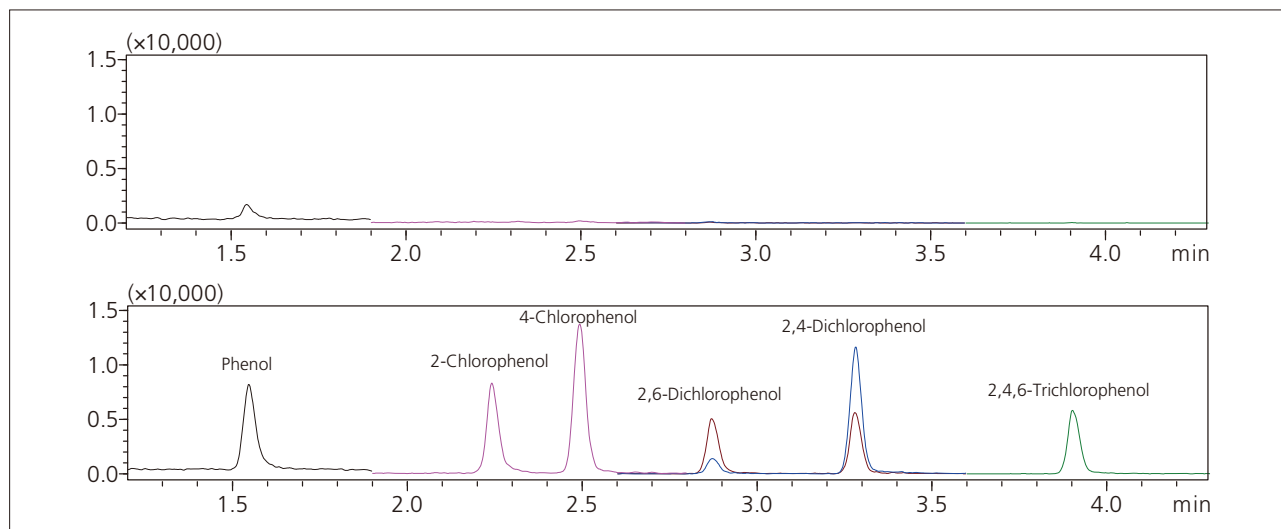


Fig. 3 Mass Chromatograms (MRM) of Drinking Water (Upper: Blank, Lower: 0.08 µg/L spiked)

Table 2 Results of Spike and Recovery Test (n=5)

	Recovery % (Corresponding to 0.08 µg/L)	Recovery % (Corresponding to 0.4 µg/L)
Phenol	103.7	99.6
2-Chlorophenol	104.8	100.1
4-Chlorophenol	104.1	100.2
2,4-Dichlorophenol	104.6	100.4
2,6-Dichlorophenol	102.0	100.3
2,4,6-Trichlorophenol	105.6	99.3

Table 3 Analytical Conditions

Column	: InertSustain C18 HP (100 mm L. × 2.1 mm I.D., 3 µm)
Mobile Phases	: A) Water : B) Methanol
Flowrate	: 0.5 mL/min
Time Program	: B conc. 40 % (0 min) – 95 % (4.8 – 5.4 min) – 40 % (5.41 – 7.5 min)
Column Temperature	: 40 °C
Injection Volume	: 50 µL
Probe Voltage	: -3.5 kV (APCI-negative mode)
DL Temperature	: 200 °C
Block Heater Temperature	: 200 °C
Interface Temperature	: 350 °C
Nebulizing Gas Flow	: 3 L/min (Air)
Drying Gas Flow	: 5 L/min (N ₂)
MRM Transition	: Phenol: <i>m/z</i> 93.0 > 65.0, 2-Chlorophenol: <i>m/z</i> 127.0 > 35.1, 4-Chlorophenol: <i>m/z</i> 127.0 > 35.1, 2,4-Dichlorophenol: <i>m/z</i> 161.0 > 125.0, 2,6-Dichlorophenol: <i>m/z</i> 161.0 > 35.1, 2,4,6-Trichlorophenol: <i>m/z</i> 194.9 > 35.1

[References]

- 1) Reiji Kubota, Norihiro Kobayashi, Maiko Tahara, Naoki Sugimoto, Yoshiaki Ikarashi: Investigation of the Analytical Method for Phenols and Chlorophenols in Tap Water by Solid-Phase Extraction - LC/MS; The 22nd Annual Conference and Symposium of Japan Society for Environmental Chemistry (JEC), p.586-587 (2013)
- 2) Reiji Kubota, Norihiro Kobayashi, Kaori Saito, Nobuhiro Saito, Toshiya Suzuki, Yuki Kosugi, Minako Tanaka, Taku Tsukamoto, Hiroshi Hayashida, Tatsuya Hirabayashi, Isoaki Yamamoto, Yoshiaki Ikarashi: Validity Assessment of Phenols Investigation Method by Solid-Phase Extraction - LC/MS; The 23rd Annual Conference and Symposium of Japan Society for Environmental Chemistry (JEC), p.126-127 (2014)