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Application News

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LC/MS

Simultaneous Analysis of Chlorate, Bromate, Perchlorate and Chlorite in Tap Water Using a Triple Quadrupole LC/MS/MS

Chlorate is derived from impurities in sodium hypochlorite, which is used as a disinfectant in the process of water purification or is generated in the same process. Bromate is also known to be derived from impurities or generated in the water purification process, especially when ozone disinfection is used.

Chlorate and bromate, which may have an adverse effect on human health, have been added to the water quality standards of Japan for tap water. The analytical method has been designated in "Method Determined by the Minister of Health, Labour and Welfare on the Basis of the Ordinance Provisions Relating to Water Quality Standards (Notification No. 261 issued by the Ministry of Health, Labour and Welfare of Japan (MHLW) in 2003)".

In addition to bromate, specified as an item contained in annex table 18-2 "Liquid Chromatography – Mass Spectrometry", chlorate, which had been specified as a component to be contained in Annex table 13 of "Simultaneous Analysis by Ion Chromatography", was added to the above annex table in response to the 2020 amendment, meaning that these components can now be analyzed simultaneously (Notification No. 95 issued by the MHLW in March 2020).

Using LCMS™-8060, this article introduces an example of simultaneous analysis of four components, consisting of perchlorate (as a tentative item under consideration) and chlorite (as a complementary item with a target value), in addition to chlorate and bromate for which the water quality control standards are already established, based on the method specified in "the annex table 18-2".

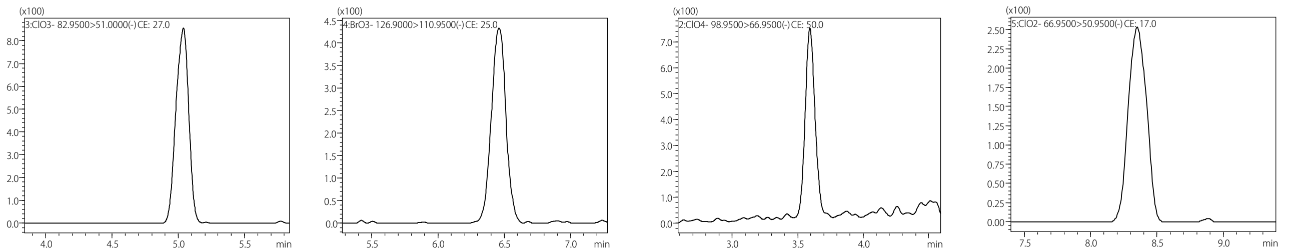
H. Niwa, H. Horiike

MRM Chromatograms of Chlorate, Bromate, Perchlorate and Chlorite (Analysis of Standard Mixture)

Fig. 1 shows the MRM chromatograms obtained from a standard mixture of chlorate, bromate, perchlorate and chlorite at concentrations of 0.005 mg/L (standard value: 0.6 mg/L), 0.0005 mg/L (standard value: 0.01 mg/L), 0.0005 mg/L (target value: 0.025 mg/L) and 0.03 mg/L (target value: 0.6 mg/L), respectively. The chromatograms indicate that analysis of these components is possible at concentrations of 1/10 or lower of these standard or target values.

The analytical conditions are shown in Table 1.

LCMS™-8060



(a) 0.005 mg/L Chlorate **(b) 0.0005 mg/L Bromate** **(c) 0.0005 mg/L Perchlorate** **(d) 0.03 mg /L Chlorite**

Fig. 1 MRM Chromatograms of (a) Chlorate, (b) Bromate, (c) Perchlorate and (d) Chlorite

Table 1 Analytical Conditions

Column	:	Acclaim® Trinity™ P1 (100 mm × 3.0 mm I.D., 3 µm)			
Mobile phases	:	A 200 mmol/L ammonium acetate - water containing 0.5 % acetic acid			
		B Acetonitrile			
Time program	:	B.conc 95 % (0 min) → 90 % (3-10 min) → 5 % (10.5–15.5 min) → 95 % (16–22 min)			
Flow rate	:	0.4 mL/min			
Column temperature	:	35 °C			
Injection volume	:	1 µL			
Ionization	:	ESI - Negative			
Probe voltage	:	-1.0 kV			
DL temperature	:	150 °C			
Block heater temperature	:	400 °C			
Interface temperature	:	400 °C			
Nebulizing gas flow	:	2 L/min			
Drying gas flow	:	5 L/min			
Heating gas flow	:	20 L/min			
MRM transition	:	Chlorate ion	*m/z*	82.95 > 51.00 (Quantifier ion)	82.95 > 66.95 (Qualifier ion)
		Bromate ion	*m/z*	126.90 >110.95 (Quantifier ion)	128.90 > 113.00 (Qualifier ion)
		Chlorite ion	*m/z*	66.95 > 50.95 (Quantifier ion)	66.95 > 34.95 (Qualifier ion)
		Perchlorate ion	*m/z*	98.95 > 66.95 (Quantifier ion)	98.95 > 82.95 (Qualifier ion)

Linearity of Calibration Curves for Chlorate, Bromate, Perchlorate and Chlorite (Analysis of Standard Mixture)

Fig. 2 shows calibration curves created by an external standard method for chlorate, bromate, perchlorate and chlorite in the concentration ranges of 0.005 - 0.05 mg/L (4 points), 0.0005 - 0.005 mg/L (4 points), 0.0005 - 0.005 mg/L (4 points) and 0.03 - 0.6 mg/L (5 points), respectively.
Good linearity was obtained with correlation coefficients R of > 0.999 for all calibration curves.

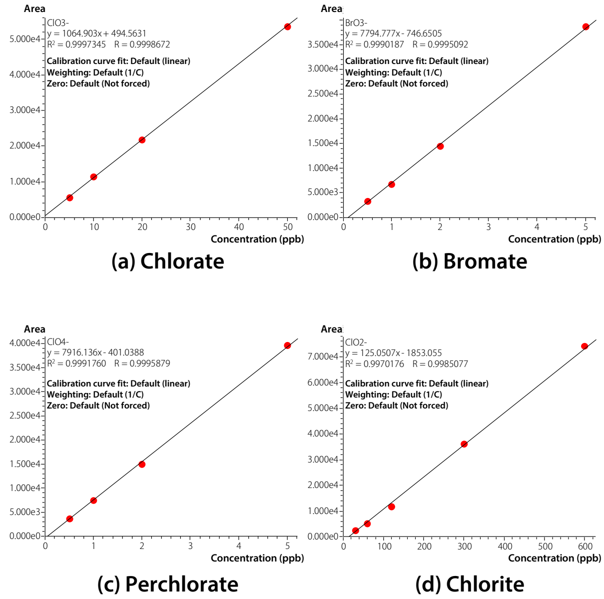


Fig. 2 Calibration Curves of (a) Chlorate, (b) Bromate, (c) Perchlorate and (d) Chlorite

Analysis of Tap Water

A spike-and-recovery test was performed using tap water (from Kanagawa Prefecture). Collected tap water, which was dechlorinated by adding ethylenediamine, was spiked with chlorate, bromate, perchlorate and chlorite to prepare standard solutions with volumes of 10 µg/L, 1 µg/L, 1 µg/L and 60 µg/L, respectively. Fig. 3 shows MRM chromatograms of blank tap water and spiked test solutions obtained from analysis of these samples. Additionally, Table 2 shows the quantitative results and the recoveries and peak area reproducibilities (%RSDs) for the samples.

Conclusion

The use of LCMS in accordance with the method specified in "annex table 18-2" enabled a precise analysis of chlorate and bromate that have been added to the water quality standards, and perchlorate (a tentative item under consideration) and chlorite (a complementary item for water quality control with a target value).

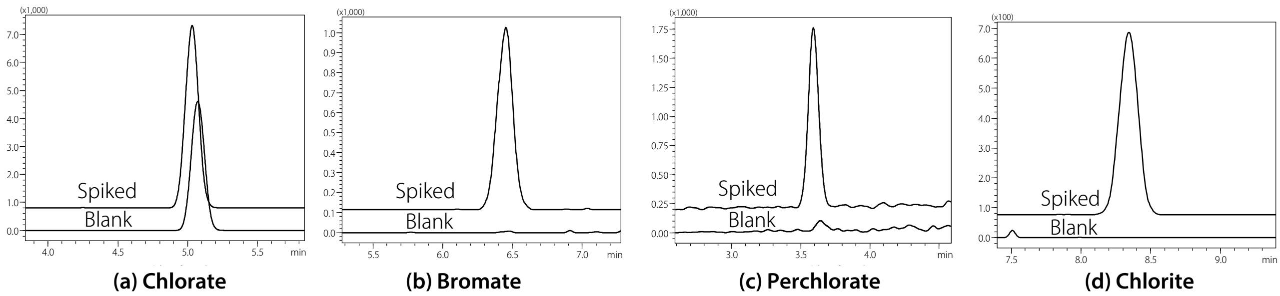


Fig. 3 MRM Chromatograms of Tap Water (Blank) and Spiked Samples

Table 2 Spike-and-Recovery Test Results Using Tap Water

Component	Spiked conc. (µg/L)	Quantitative conc. of tap water (blank) (µg/L)	Quantitative conc. of spiked samples (N=5, µg/L)	Recovery (N=5)	%RSD (N=5)
Chlorate	10	29.16	41.19	120 %	2.12
Bromate	1	0.10	1.06	96 %	6.32
Perchlorate	1	0.10	1.18	108 %	3.77
Chlorite	60	N.D.	63.06	105 %	2.85

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