

Detection of oxyhalides using a compact ion chromatography system coupled with mass spectrometry

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Keywords

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Introduction

Disinfection treatment is used to protect municipal water from potentially dangerous microbes. The most common chemical disinfectants are chlorine, chlorine dioxide, chloramine, and ozone.^{1,2} These chemical disinfectants can react with natural organic and inorganic matter in the source water to produce disinfection byproducts (DBPs), including oxyhalides (e.g., bromate, chlorate, etc.), that are potentially harmful to humans.

This application brief demonstrates a method for detecting trace concentrations of oxyhalides using a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system with a Thermo Scientific™ Dionex™ IonPac™ AS19-4 μ m column set for separation, coupled to a Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer. The combination of ion chromatography and mass spectrometry (IC-MS) for oxyhalide detection can maximize the benefits of both chromatography and mass confirmation.

Figure 1 shows chromatograms of a 0.5 mg/L fluoride, 0.4 mg/L iodate, 0.1 mg/L bromate, chlorite, and chlorate standard using suppressed conductivity detection and a MS detector in selected ion monitoring (SIM) mode. The conductivity detector responds to all charged species regardless of their molecular mass. The Dionex IonPac AS19-4 μ m column is recommended to separate low concentrations of oxyhalides from the significantly higher concentrations of inorganic anions in drinking water.

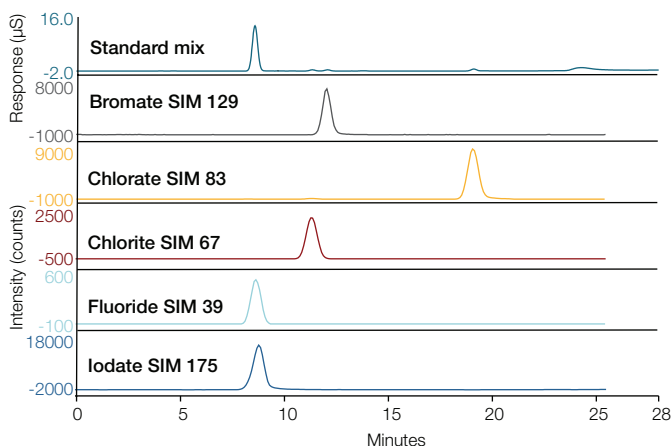


Figure 1. Conductivity and SIM chromatograms of a 0.5 mg/L fluoride, 0.4 mg/L iodate, 0.1 mg/L bromate, chlorite, and chlorate standard.

The column's selectivity and high capacity allow the determination of low $\mu\text{g/L}$ concentrations of bromate in drinking water. However, fluoride and iodate coelute on the Dionex IonPac AS19-4 μm column and, therefore, cannot be identified and quantified with suppressed conductivity detection. Mass detection, on the other hand, can resolve co-eluting peaks if those peaks differ in their mass-to-charge ratio (m/z). With the use of very specific MS selected ion monitoring (SIM) detection, m/z 39 for fluoride, which appears to form $[\text{F}(\text{HF})]$, and m/z 175 for iodate respectively, they are fully resolved in different SIM channels. Mass detection also adds confidence to chromatographic peak mass confirmation with the corresponding m/z 129 for bromate, m/z 83 for chlorate, m/z 67 for chlorite.

In the Figure 2, three oxyhalides (iodate, chlorite, and chlorate) and fluoride were identified in drinking water on the basis of chromatographic peak and mass confirmation. Bromate was not detected by either detector. Although one peak showed in the SIM channel for bromate, it was at approximately 17 min and the retention time of bromate is 12.07 min.

The selectivity of IC-MS allows peak confirmation, reduces the likelihood of false negatives and false positives, and can often resolve co-eluting peaks using their mass-to-charge ratio.

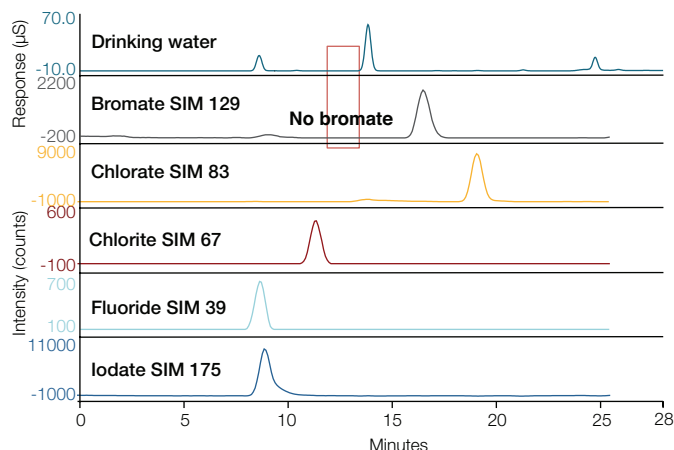


Figure 2. The identification of four compounds in drinking water by the comparison of retention time and m/z . No bromate was detected in drinking water.

Method

IC system:	Dionex Integriion HPIC system
MS detector:	ISQ EC single quadrupole mass spectrometer
Columns:	Dionex IonPac AS19-4 μm Guard, 2 \times 50 mm Dionex IonPac AS19-4 μm Analytical, 2 \times 250 mm
Eluent source:	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge with Thermo Scientific™ Dionex™ CR-ATC 600
Gradient:	8 mM KOH (0-10 min), 8-30 mM KOH (10-18 min), 30-100 mM KOH (18-24 min), 100-8 mM (24-25 min), 8 mM (25-28 min)
Flow rate:	0.25 mL/min
Injection volume:	250 μL
Temperature:	30 $^{\circ}\text{C}$ (column compartment), 20 $^{\circ}\text{C}$ (detector compartment)
System backpressure:	~2200 psi
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500e Electrolytically Regenerated Suppressor (2 mm), AutoSuppression, 62 mA, external water mode via Thermo Scientific™ AXP™ Pump, external water flow rate (0.5 mL/min)
Background conductance:	~ 0.3 μS
Run time:	28 min

Mass spectrometric detection

Ionization interface: Electrospray ionization (ESI), negative mode

Gas control: Sheath gas pressure: 40 psi
Aux gas pressure: 6 psi
Sweep gas pressure: 0.0 psi

Source voltage: 3000 v

Vaporizer temperature: 250 °C

Ion transfer tube temperature: 300 °C

Advanced scan mode:

Scan Name	Mass list (amu)	Dwell or Scan Times (sec)	SIM Widths (amu)	Ion Polarity	SourceCl DVoltage
Bromate	129	0.6	0.5	Negative	0
Chlorite	67	1	0.5	Negative	0
Iodate	175	1.2	0.5	Negative	0
Chlorate	83	1.2	0.5	Negative	0
Fluoride [F(HF)] ⁻	39	1.2	0.5	Negative	0

Groups: Chrom. Filter Peak Width (sec): 3.0

References

1. Drinking Water Treatment; Document No. 810-F-99-013; U.S. Environmental Protection Agency: Cincinnati, OH, 1999.
2. Disinfectants and Disinfection By-Products; International Programme on Chemical Safety–Environmental Health Criteria 216; World Health Organization: Geneva, Switzerland, 2000.

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