

Detection of common inorganic anions using a compact ion chromatography system coupled with a single quadrupole mass spectrometer

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Introduction

This application brief describes a method for detecting seven common anions using a Thermo Scientific™ Dionex™ Integriion™ HPIC™ system coupled to a Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer. The determination of common inorganic anions in drinking water is one of the most important ion chromatography (IC) applications worldwide. In the U.S., the Environmental Protection Agency (EPA) defines the Maximum Contaminant Levels (MCLs) of toxic contaminants, such as fluoride, nitrite, and nitrate in the National Primary Drinking Water Regulations (NPDWR).¹ EPA Methods 300.0² and 300.1³ are IC methods approved by the U.S. EPA for analysis of common anions in the U.S.

As demonstrated in this brief, IC offers the analyst the advantage of selectivity for common low-mass anions. Mass detection adds confidence to inorganic anion identity and sometimes greater sensitivity than provided by conductivity detection. Samples were separated with a Thermo Scientific™ Dionex™ IonPac™ AS20 column set using a Dionex Integriion HPIC system, and an ISQ EC Single Quadrupole Mass Spectrometer. Figure 1 shows chromatograms of a 0.2 mg/L fluoride, 0.3 mg/L chloride, 1 mg/L nitrite, bromide, and nitrate, and 1.5 mg/L phosphate and sulfate standard using suppressed conductivity detection followed by an MS detector in selected ion monitoring (SIM) mode. It is important to note that the SIM ion selected for fluoride is 39.1 *m/z*, which is associated with the fluoride adduct [F(HF)]⁻. The

deprotonated sulfate [HSO_4^-] and phosphate [H_2PO_4^-] ions which have the same mass-to-charge ratio (m/z) at 97.1 are shown as two peaks in SIM channel 97.1, and can also be accurately quantified because they are chromatographically separated. The differentiation of sulfate from phosphate can be confirmed by the isotope peak 99.1 ($[\text{H}^{34}\text{SO}_4^-]$) at ~5% relative peak intensity of peak 97.1. A smaller peak in SIM channel 97.1, which may be a single water complex of bromide, $[\text{Br}(\text{H}_2\text{O})^-]$, appears at the same retention time as bromide.

Representative municipal drinking water and bottled water samples were analyzed by IC-MS (Figures 2 and 3). Using IC, the anionic components in water samples can be identified by comparing their retention times to those of the standards. To confirm these identifications, a mass selective detector can record SIM channels at the appropriate mass-to-charge ratios. In Figure 2, six anions (fluoride, chloride, nitrite, nitrate, sulfate, and phosphate) were identified in municipal drinking water on the basis of peak retention time and mass confirmation. Bromide was not detected by either detector. Although two peaks showed in the SIM channel for bromide, they did not match the retention time of bromide. Figure 3 shows the conductivity and SIM chromatogram of a bottled water sample. Neither nitrite nor bromide was detected in this sample. With the use of very specific MS SIM detection, ppb-level analyte identification can be achieved with greater confidence on a wide range of samples, such as bottled drinking water.

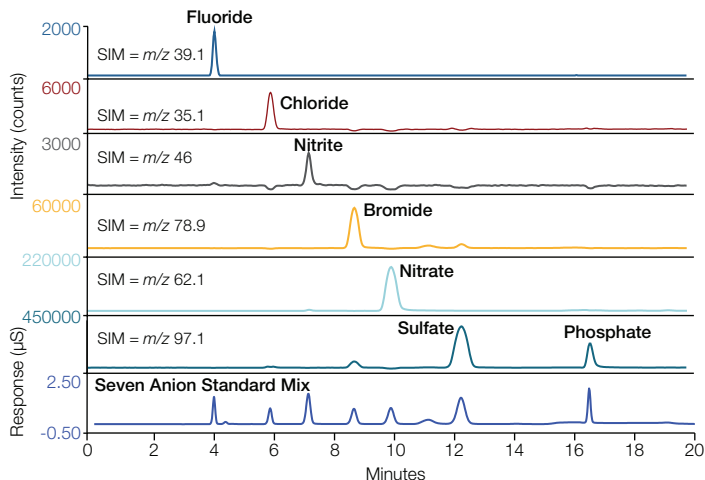


Figure 1. Conductivity and SIM chromatograms of a 0.2 mg/L fluoride, 0.3 mg/L chloride, 1 mg/L nitrite, bromide, nitrate and 1.5 mg/L phosphate and sulfate standard.

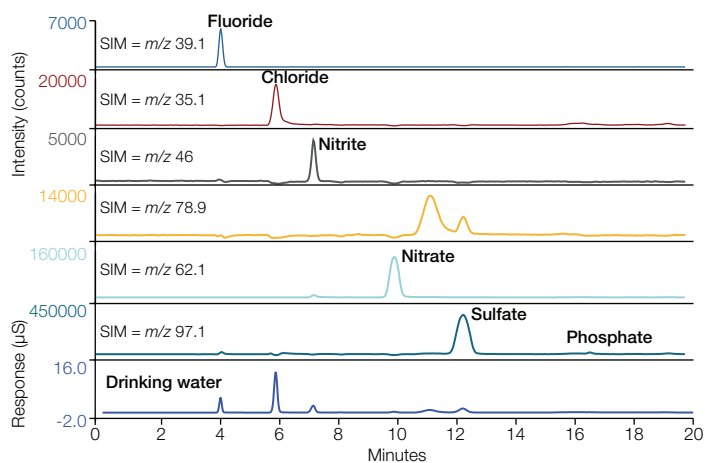


Figure 2. The identification of seven anions in municipal drinking water by the comparison of retention time and m/z . Bromide was not detected in municipal drinking water.

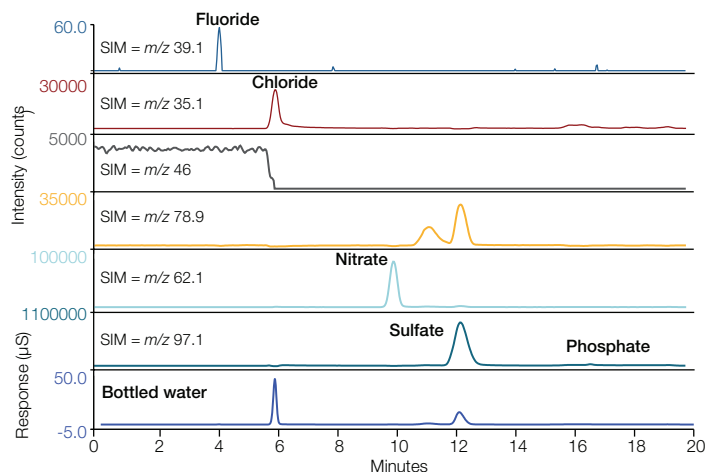


Figure 3. The identification of seven anions in bottled water by the comparison of retention time and m/z . Nitrite and bromide were not detected in this bottled water sample.

