

# Determination of Common Anions and Organic Acids Using Ion Chromatography-Mass Spectrometry

## **INTRODUCTION**

Mass spectrometry (MS) as a detector for ion chromatography (IC) has gained popularity recently due to the increasing demand for sensitivity, selectivity, confirmation of identity, and structural interpretation.<sup>1-8</sup> Compared to other commercially available MS detectors, the MSQ Plus™ detector offers substantially improved performance for low-molecular weight analytes, which covers most analytes for small-molecule IC applications.

This application note (AN) demonstrates the IC-MS method using the MSQ Plus detector for the determination of five common anions and selected organic acids. Method performance with respect to calibration range, reproducibility, and method detection limits are also presented.

## **EXPERIMENTAL**

### **Instrumentation**

System:	Dionex ICS-2000 RFIC™ system
Columns:	IonPac® AS20 (2.1 × 250 mm) with AG20 (2.1 × 50 mm) CR-ATC Continuously Regenerated Anion-Trap Column
Mobile Phase:	28 mM hydroxide generated from EGC II KOH cartridge
Flow Rate:	0.25 mL/min
Injection Volume:	5 µL
Detection:	Suppressed conductivity (external water at 0.50 mL/min) MSQ Plus single quadrupole mass spectrometer
Ionization Interface:	Electrospray ionization (ESI)
Desolvation Solvent:	0.22 mL/min acetonitrile delivered by an AXP-MS auxiliary pump
MS Detection Mode:	Negative Selected Ion Monitoring (SIM) Scan details shown in Table 1.
Needle Voltage:	1.5 kV
Nebulizer Gas:	Nitrogen at 85 psi
Probe Temperature:	450 °C

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## Software

Instrument control, data acquisition, processing, and report generation were accomplished through the Chromeleon® Chromatography Data System (version 6.8 SR6).

## Reagents and Standards

All stock standard solutions for individual analytes were prepared in deionized water (D.I. water, 18.2 MΩ·cm<sup>-1</sup>, Millipore). Fluoride and nitrate standards were prepared by diluting standard solutions obtained from Ultra Scientific (P/N ICC-003) and Dionex (P/N 060254) respectively. Chloride, sulfate, and phosphate standards were prepared by dissolving potassium salts in D.I. water (pure chemicals obtained from Mallinckrodt and Fisher). Standard solutions of organic acids were prepared by dissolving each chemical (in organic or salt form) in D.I. water: pyruvic acid, sodium salt (Sigma, P2256), α-ketoglutaric acid, monopotassium salt (Sigma, K2000), and tartaric acid (Aldrich, T400). Methanol (CH<sub>3</sub>OH) and acetonitrile (CH<sub>3</sub>CN) were purchased from Burdick & Jackson (HPLC/UV grade, Honeywell, Muskegon, MI).

The mixed standard solution, including each of the listed analytes at 5.0 ppm, was prepared by diluting each of the stock standard solutions in D.I. water. Calibration standards were prepared by series dilution to 1000 ppb, 500 ppb, 200 ppb, 100 ppb, 50 ppb, 20 ppb, 10 ppb, 5 ppb, and 2 ppb.

## RESULTS AND DISCUSSION

The optimization of the acquisition parameters of the MSQ Plus spectrometer for IC analysis of common anions and selected organic acids is discussed in detail elsewhere.<sup>9</sup> MSQ parameters, including probe temperature, nebulizer gas flow, assistant makeup flow rate, needle voltage, and cone voltage were optimized using Response Surface Methodology (RSM) with Central Composite Design (CCD). Compared to the one-parameter-at-a-time approach for optimization, RSM with CCD includes the effects from interactions between parameters (ignored by a single parameter approach) and also minimizes the numbers of experiments required to reach the optimum system performance. The optimum conditions determined for the MSQ Plus spectrometer in these experiments are listed in the instrumentation section

**Table 1. MS SIM Scans\***

Analyte	Adduct	Observed ( <i>m/z</i> )	Cone Voltage (V)
Fluoride	[F(HF)] <sup>-</sup>	39.1	88
Chloride	[Cl] <sup>-</sup>	35.1	26
Nitrate	[NO <sub>3</sub> ] <sup>-</sup>	62.1	73
Sulfate	[HSO <sub>4</sub> ] <sup>-</sup>	97.1	45
Phosphate	[H <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	97.1	69
Pyruvate	[CH <sub>3</sub> COCOO] <sup>-</sup>	87.1	52
α-Ketoglutarate	[HOCCO(CH <sub>2</sub> ) <sub>2</sub> COO] <sup>-</sup>	145.2	50
Tartrate	[HOOC(CH <sub>2</sub> OH) <sub>2</sub> COO] <sup>-</sup>	149.2	37

\* Use 0.5 span and 0.1 s dwell time for all SIM scans.

and the analyte individualized cone voltages for SIM scans are listed in Table 1.

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)]<sup>-</sup>. Representative conductivity and SIM chromatograms are shown in Figure 1 (1 ppm with 5 μL). Compared to nonspeciating conductivity detection, each analyte can be quantified very specifically using MS SIM detection, shown as one peak in SIM channel for each target analyte. The deprotonated sulfate [HSO<sub>4</sub>]<sup>-</sup> and phosphate [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> ions which have the same mass-to-charge ratio (*m/z*) at 97 are shown as two peaks in SIM channel 97, 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 ([H<sup>34</sup>SO<sub>4</sub>]<sup>-</sup>) at ~5% relative peak intensity of peak 97.

Calibration curves were generated using concentrations from low ppb to 1.0 ppm, and method detection limits (MDL) were calculated by  $MDL = S \times t_{99\%, n=7}$  where *S* is the standard deviation and *t* is the Student's *t* at 99% confidence interval. Seven replicate injections of a calibration standard at 20 ppb were performed to calculate the MDL (100 ppb was used to calculate MDL for fluoride). Calibration range, coefficient of determination, and MDL values are summarized in Table 2. Figure 2 shows the calibration curve for tartrate from 2 ppb to 1000 ppb and the graphic insert shows the linear curve at the lower levels.

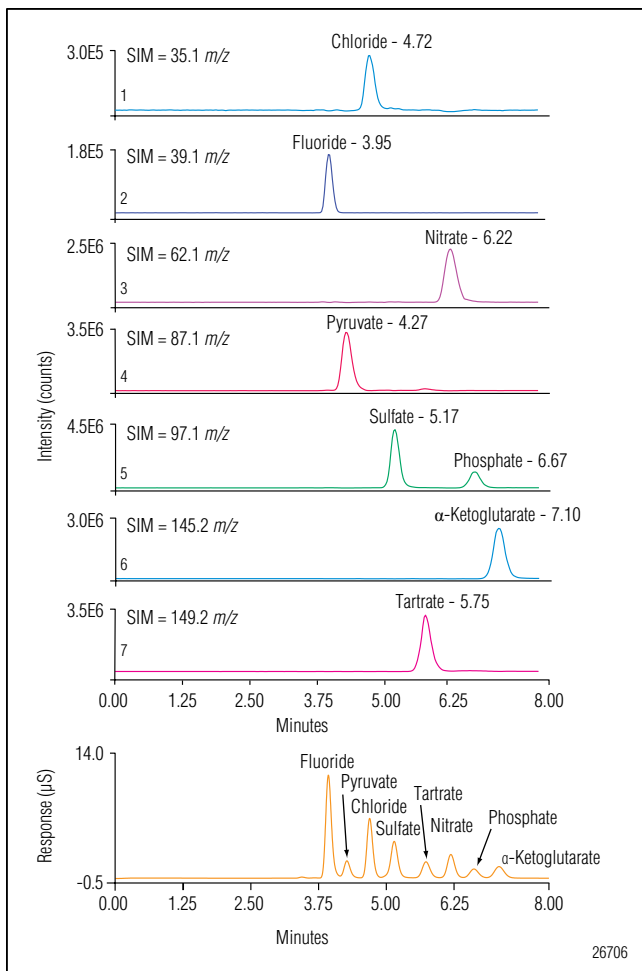


Figure 1. Conductivity and SIM chromatograms of five common anions and three selected organic acids.

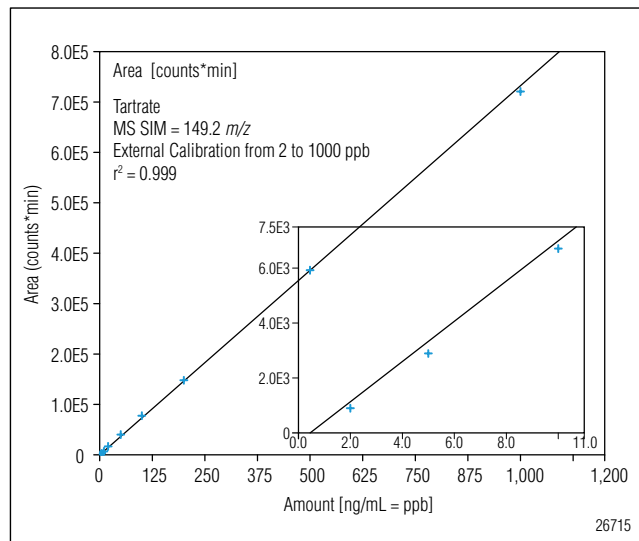


Figure 2. Calibration curve of tartrate at concentrations from 2 ppb to 1000 ppb.

Table 2. Calibration Range, Coefficient of Determination, and MDLs

Analyte	Calibration Range (ppb)		Calibration Type	Weighting	r <sup>2</sup>	%RSD*	MDL (ppb)
Fluoride	100	1000	Linear	1/X	0.997	9.35	29.4
Chloride	2	1000	Cubic	1/X	0.980	5.16	3.2
Nitrate	2	1000	Cubic	1/X	0.992	4.05	2.5
Sulfate	2	1000	Linear	1/X	0.998	5.75	3.6
Phosphate	5	1000	Linear	1/X	1.000	7.78	4.9
Pyruvate	2	1000	Quadratic	1/X	0.999	5.06	3.2
α-Ketoglutarate	5	1000	Linear	1/X	0.998	4.98	3.1
Tartrate	2	1000	Linear	1/X	0.999	5.20	3.3

\* %RSD was calculated from 7 replicate injections of a calibration standard at 20 ppb except for fluoride (100 ppb).

After calibration, this method was used for quantification of the target analytes in commercially bottled drinking water. A bottled water sample was injected directly without sample preparation. Figure 3 shows the overlay of SIM chromatograms. Four anions were detected in the bottled water sample: 713 ppb chloride, 496 ppb sulfate, 143 ppb nitrate, and 181 ppb phosphate.

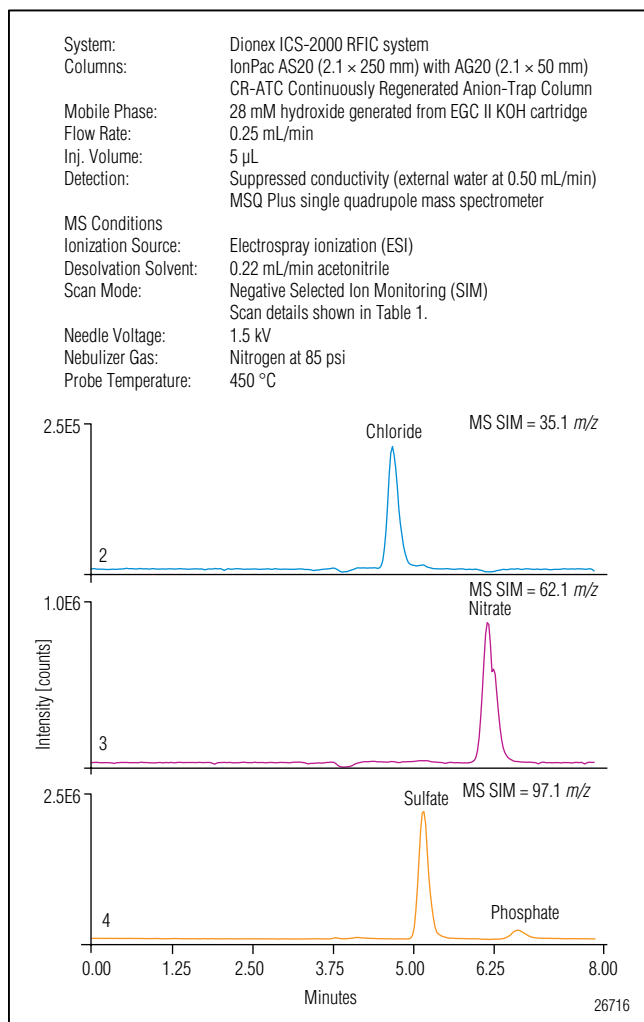


Figure 3. Anions in a bottled water sample.

## CONCLUSION

This application note demonstrates the use of the IC-MS method for the determination of five common anions and three organic acids at parts per billion levels. With the use of very specific MS SIM detection, ppb level quantification can be performed with greater confidence on real world samples, such as bottled drinking water. The quantification results from MS were without prior sample preparation or employing preconcentration, which may be required with other detection methods.

Note that the optimum settings and responses may vary on different instruments; optimization of MSQ Plus source conditions and acquisition parameters is highly recommended for best results.

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LPN 2374 PDF 12/09  
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