Ion Chromatography Determination of Inorganic Anions Coupled With the Advion Compact Mass Spectrometer (CMS)

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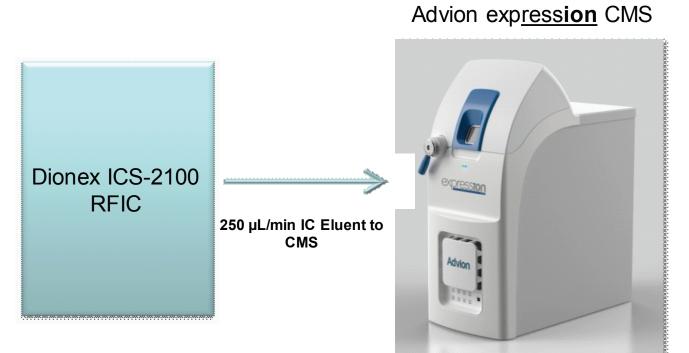
Advion

Overview:

- The Advion single quadrupole compact mass spectrometer (CMS) was coupled to ion chromatography for the analysis of 7 common inorganic anions (fluoride [F^- m/z 19], chloride [Cl^- m/z 35], nitrite [NO_2^- m/z 46], nitrate [NO_3^- m/z 62], bromide [Br^- m/z 79], sulphate [HSO_4^- m/z 97] and phosphate [$H_2PO_4^-$ m/z 97]).
- Performance of the CMS was optimized for low molecular mass. A new detector configuration for low mass optimization was evaluated – flat conversion dynode vs. curved conversion dynode
- [19]Fluoride was detected and not the commonly observed adduct of [$F(HF)^-$ m/z 39]. The eluent from the ion chromatograph was coupled to the CMS without the need for an organic modifier (such as methanol, acetonitrile or isopropanol) as is commonly reported in literature.
- Analysis of a 10 ppb fluoride standard, 100 ppb seven anion standard mix, tap and spring water was performed.
- Limit of detection (LOD) of perchlorate as well as flow injection analysis (FIA) and infusion experiments of cations was also performed.
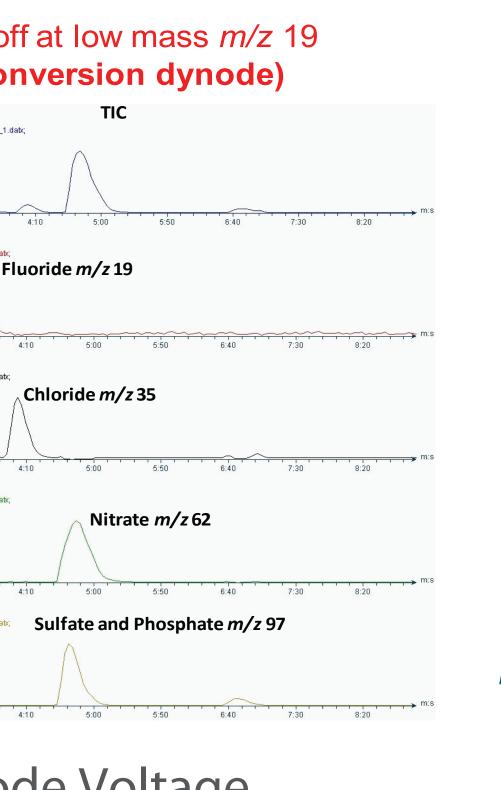
Introduction:

- There is a concerted effort by regulatory bodies, such as the EPA to reduce the exposure of environmental contaminants, such as inorganic anions to humans and the environment.
- Achieving lower analytical detection limits of hazardous compounds in environmental matrices such as water, soils and sediments allows regulatory bodies to make better informed decisions on the degree of contamination of an environmental system as well as the remedial actions required to limit adverse health and environmental effects.
- Mass spectrometry provides the tool to achieve lower detection limits and greater selectivity when compared to conductivity and UV detectors.
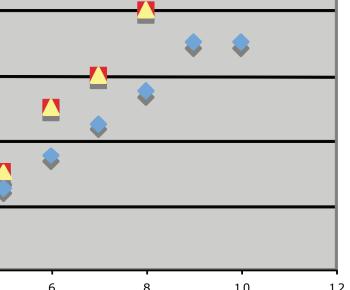
Advion **expression** CMS

Dionex ICS-2100 RFIC → 250 μL/min IC Eluent to CMS

Methods and Materials:

Advion CMS Specifications & Method

Parameter	Advion CMS
Mass filter	Quadrupole
Mass range	m/z 10 – m/z 1200
Mass accuracy	0.1 m/z units
Mass stability	0.1 m/z units over 12 hours
Resolution	0.5 - 0.7 FWHM
Selected Ion Monitoring (SIM) Masses for IC/MS experiments	Fluoride – m/z 18.99
	Chloride (I) – m/z 34.97
	Chloride (II) – m/z 36.97
	Nitrite – m/z 46.10
	Nitrate – m/z 62.10
	Bromide (I) – m/z 78.92
	Bromide (II) – m/z 80.92
	Sulfate (I) – m/z 96.96
	Sulfate (II) – m/z 98.96
	Phosphate – m/z 96.97

Dionex ICS-2100 RFIC Method

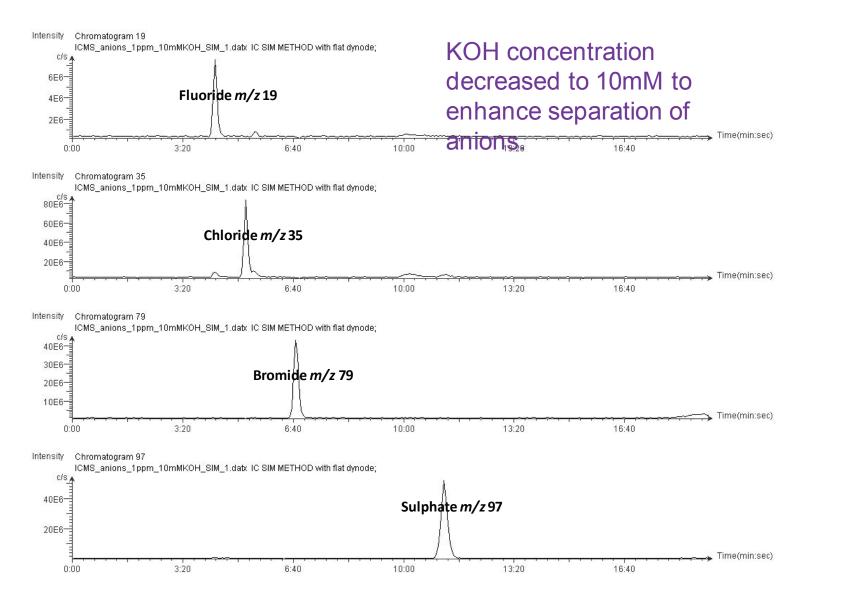| System	Dionex ICS-2100 RFIC system
Columns	Ion Pac AS16 (2.0 X 250 mm) with AG16 (2.0 X 50 mm)
Mobile Phase	0.25mL/min
	35 mM hydroxide generated from EGC II KOH Cartridge
Injection volume	75 uL
Detection	Suppressed conductivity (external water at 0.5 mL/min, Compact Mass Spectrometer
Ionization Interface	Electrospray Ionization
Desolvation Solvent	None
MS Detection Mode	Negative Selected ion monitoring

Curved Conversion Dynode

Dramatic signal drop-off at low mass m/z 19 (standard 'curved' conversion dynode)

TIC
Fluoride m/z 19
Chloride m/z 35
Nitrate m/z 62
Sulfate and Phosphate m/z 97

Curved vs. Flat Dynode

Standard 'curved' dynode
F^- ion intensity of 80,000 c/s

New experimental 'flat' dynode
F^- ion intensity of >800,000 c/s

Signal intensity of m/z 19 was >10X using the new 'flat' dynode

Optimal Dynode Voltage

Plot of intensity versus dynode voltage

Signal intensity was optimal at a voltage of 10kV for new 'flat' dynode

Signal intensity (for fluoride) was optimal at a gain/voltage of 1750V using the new 'flat' dynode detector

Optimal Detector Gain (Voltage)
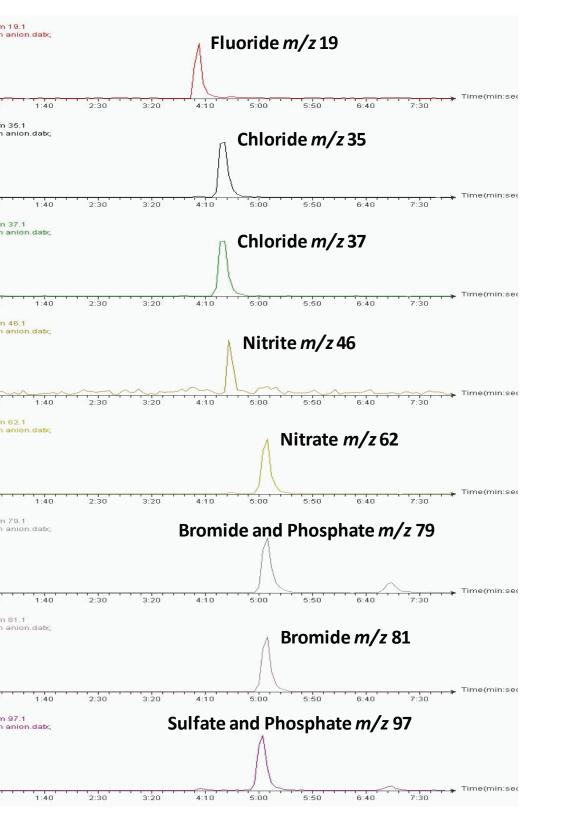
Fluoride Intensity versus Gain

Results:

SIM IC/MS Determination of Seven Anion Mix – 100ppb levels

Fluoride m/z 19
Chloride m/z 35
Chloride m/z 37
Nitrite m/z 46
Nitrate m/z 62
Bromide and Phosphate m/z 79
Bromide m/z 81
Sulfate and Phosphate m/z 97
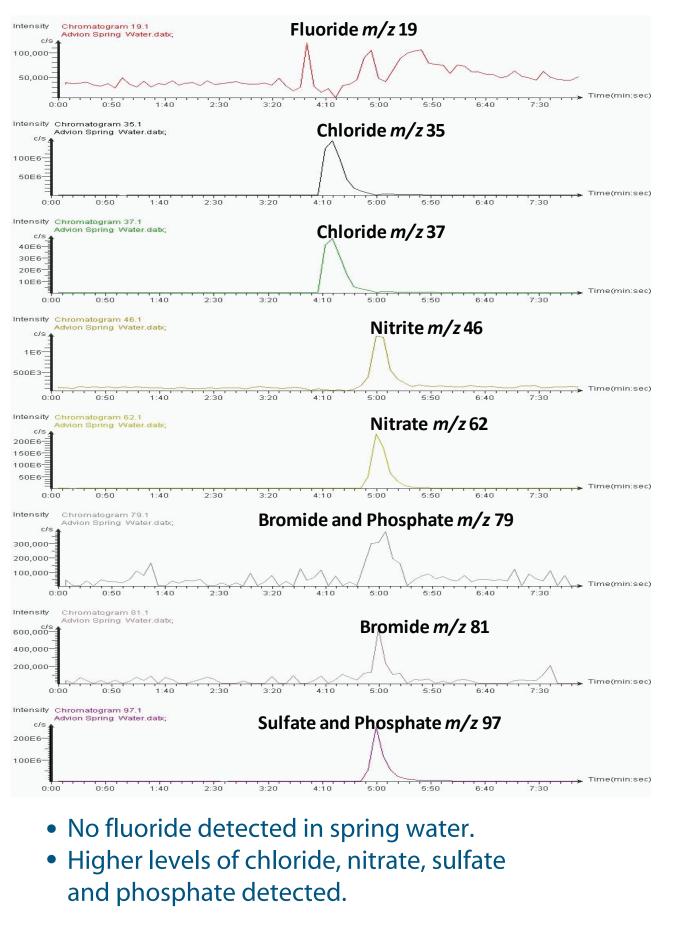
SIM IC/MS Analysis of Household Tap Water from Clay, NY

Fluoride m/z 19
Chloride m/z 35
Chloride m/z 37
Nitrite m/z 46
Nitrate m/z 62
Bromide and Phosphate m/z 79
Bromide m/z 81
Sulfate and Phosphate m/z 97

- Fluoride detected in water sampled from Clay, NY
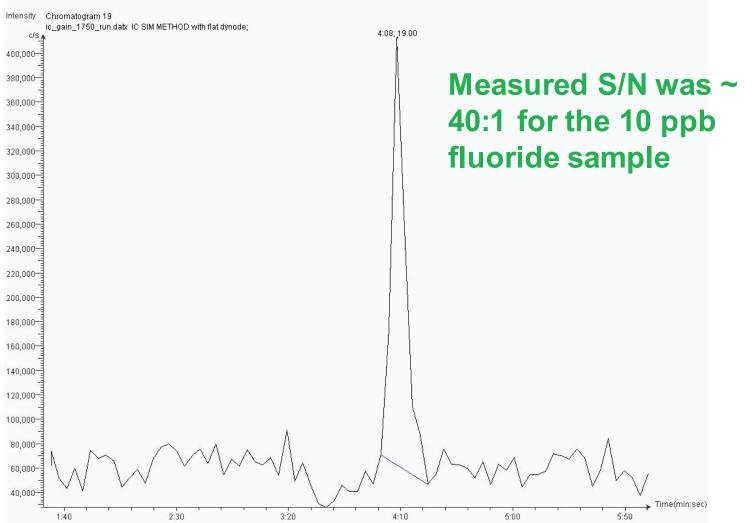
SIM IC/MS Analysis of Spring Water

Fluoride m/z 19
Chloride m/z 35
Chloride m/z 37
Nitrite m/z 46
Nitrate m/z 62
Bromide and Phosphate m/z 79
Bromide m/z 81
Sulfate and Phosphate m/z 97

- No fluoride detected in spring water.
- Higher levels of chloride, nitrate, sulfate and phosphate detected.

Infusion of Cations

$[Li(IPA)]^+$ m/z 67.07
$[Li(IPA)_2]^+$ m/z 127.13
$[Li(IPA)_3]^+$ m/z 187.19
Na^+ m/z 22.99
K^+ m/z 38.96
Cs^+ m/z 132.91

Flow Injection Analysis of Cations

200ppb Standard
K^+ m/z 38.96
Cs^+ m/z 132.91

100ppb Standard
$[Li(IPA)]^+$ m/z 67.07
$[Li(IPA)_2]^+$ m/z 127.13
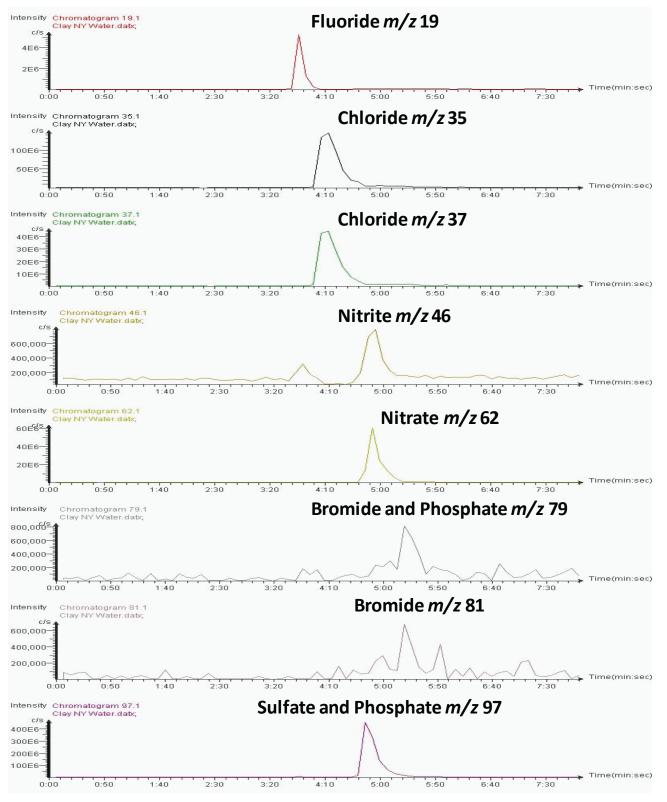$[Li(IPA)_3]^+$ m/z 187.19

CMS IC/MS Results from a 100 ppb Solution in SIM Mode

Analyte	Observed Ion (m/z)	% Natural Abundance	Species Detected	S/N of 100 ppb solution in SIM mode (25 uL injected)
Fluoride	18.99	100	F^-	110
Chloride (I)	34.97	75.77	Cl^-	257
Chloride (II)	36.97	24.23	Cl^-	118
Nitrite	46.1	>99	NO_2^-	50
Nitrate	62.1	>99.6	NO_3^-	435
Bromide (I)	78.9	50.5	Br^-	297
Bromide (II)	80.9	49.5	Br^-	261
Sulfate (I)	96.96	95.02	HSO_4^-	90
Sulfate (II)	98.96	4.22	HSO_4^-	ND
Phosphate	96.97	100	$H_2PO_4^-$	42

Anions 1ppm SIM – 10mM KOH

KOH concentration decreased to 10mM to enhance separation of anions.

Fluoride m/z 19
Chloride m/z 35
Bromide m/z 79
Sulphate m/z 97

10ppb Fluoride via Selected Ion Monitoring (SIM) IC/MS

Measured S/N was ~ 40:1 for the 10 ppb fluoride sample
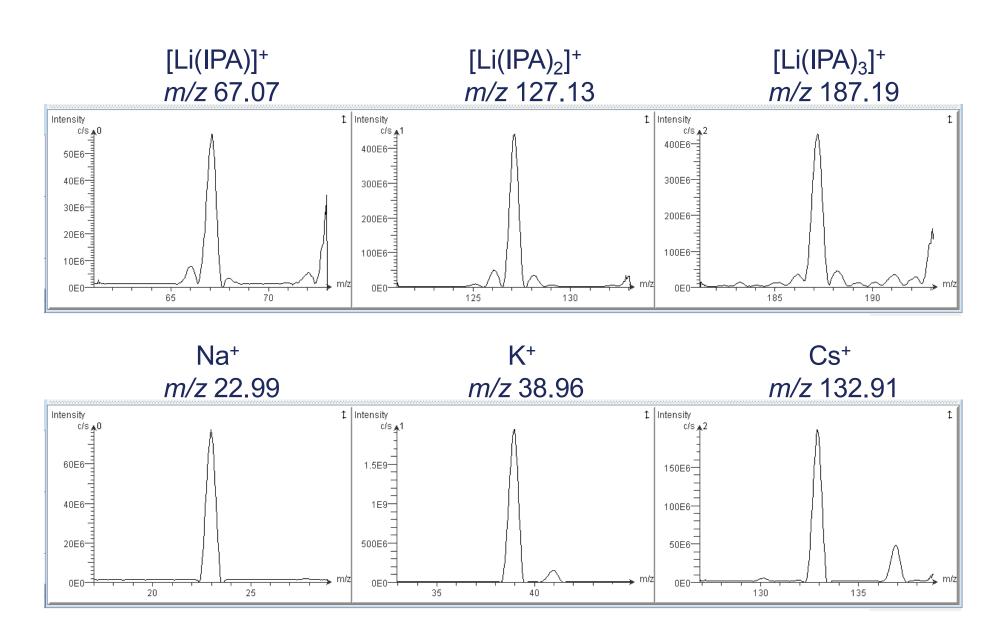
Perchlorate
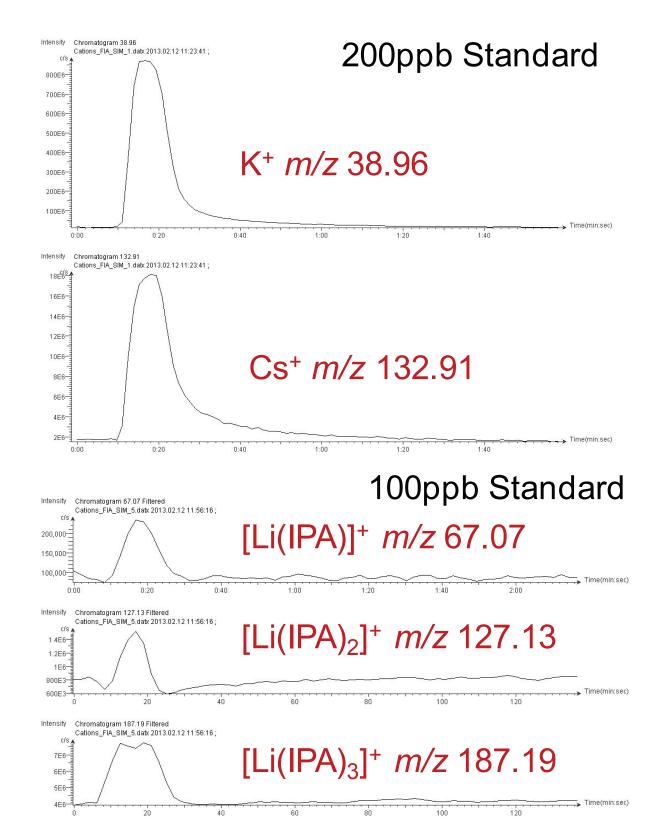
Limit of detection (LOD) was performed for perchlorate (m/z 99)

20ppt - S/N: 20:1
100ppt - S/N: 100:1

Summary:

- The signal intensity of fluoride m/z 19 was at least an order of magnitude greater when using the new 'flat' conversion dynode detector
- A 10 ppb (750 pg total injected) fluoride standard analyzed by IC/MS (in SIM mode for m/z 19) using the flat dynode observed a S/N of about 40:1
- A limit-of-detection of 20ppt was achieved for perchlorate
- The Advion CMS was also optimized for the analysis of lithium-IPA adducts, sodium, potassium and cesium by infusion and flow injection analysis