

Determination of Perchlorate in Environmental Waters by Ion Chromatography Coupled with Electrospray Mass Spectrometry (IC-MS)

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Introduction

Perchlorate has been used as an oxidizer in rockets, munitions, and fireworks since the 1950s, and has been found to cause thyroid dysfunction in humans. The California Department of Health Services first reported the determination of perchlorate in drinking water in 1997.¹ The EPA has stated that defense facilities from Los Angeles to Cape Cod have discharged large amounts of perchlorate onto the ground, contaminating groundwater in many places. In 2001, it was reported that perchlorate (ClO_4^-) was migrating into groundwater in California from a landfill site for civilian and military explosives. In 2002, the EPA recommended a maximum containment level (MCL) for perchlorate of 1 ppb in drinking water. Some states have set their own limits ranging from 4–18 ppb. For example, California's current "action level" is 6 ppb.¹

The ion chromatography (IC) method with conductivity detection for the determination of perchlorate can quantify perchlorate at 2 $\mu\text{g/L}$ (ppb) using the 4 mm i.d. Thermo Scientific™ Dionex™ IonPac™ AS16 column, large-loop injection, eluent generator and suppressor.^{2–4} The IC-MS method uses a similar method, substituting a 2 mm column format, a stable-labeled internal standard, a matrix diversion valve to eliminate the need for off-line sample pretreatment, and a mass spectrometer with an electrospray interface as the detector. The mass spectrometer is a more selective detector than conductivity in that it monitors the mass/charge ratio (m/z) of the analyte.⁵ The m/z ratio provides peak identification information for perchlorate at both 99 and 101 m/z due to the relative isotopic abundance of ^{35}Cl and ^{37}Cl .

Mass spectrometry (MS) can provide lower detection limits in high-ionic-strength matrices than conductivity. The selectivity of the mass spectrometer allows the

quantification of perchlorate at 99/101 m/z in high-ionic-strength matrices at well below the California 6 ppb action level. Recoveries must be determined in the appropriate matrices.

This application note describes the use of IC-MS to determine perchlorate in environmental waters. The described method includes in-line diversion of the sample matrix to waste and the use of an internal standard. Quantification using 99 m/z as compared to the perchlorate isotope (101 m/z) is also shown.

Equipment

- Thermo Scientific Dionex ICS-2500 Ion Chromatography System:
 - GS50 Gradient Pump
 - EG50 Eluent Generator
 - CD25A Conductivity Detector, cell with shield or DS3
 - LC30 Chromatography Oven or equivalent
 - AS50 Autosampler, with or without injection valve, 100 μL or 250 μL loop
- Rear-loading PEEK™ valve (Rheodyne® 9126, for matrix diversion)
- Grounding adaptor (P/N 059066)
- Thermo Scientific MSQ™ Enhanced Low-mass Option Mass Spectrometer (P/N 060045)
- Thermo Scientific Dionex AXP-MS Auxiliary Pump (P/N 060684)
- External water kit (P/N 038018)
- Static mixing tee
- Thermo Scientific Dionex Chromeleon™ 6.5 or higher Chromatography Management Software

Consumables

- Nitrogen source, 70–80 psi regulated
- Dionex IonPac AS16 column, 250 × 2 mm i.d. (P/N 055378)
- Dionex IonPac AG16 column, 50 × 2 mm i.d. (P/N 055379)
- Thermo Scientific Dionex ASRS™ ULTRA II Suppressor, 2 mm (P/N 061562)
- Thermo Scientific Dionex EluGen™ EGC II KOH cartridge (P/N 058900)
- Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)

Reagents and Standards

- Deionized water (DI H₂O), Type I reagent grade, 17.8 megohm-cm resistance or better
- Sodium perchlorate, 99% A.C.S. reagent grade or better
- Sodium perchlorate, Internal Standard (ISTD), 1 mg/L (P/N 062923)
- A.C.S. reagent-grade sodium salts for interference studies

Conditions

Column:	Dionex IonPac AS16, 250 × 2 mm i.d.
Suppressor:	Dionex ASRS ULTRA II, 2 mm, external water, 70 mA
GS50 Eluent:	45 mM KOH
AXP-MS Eluent:	50/50 v/v acetonitrile/water
Flow Rate:	0.3 mL/min, GS50 Gradient Pump and Dionex AXP-MS Auxiliary Pump
Temperature:	28 °C
Matrix Diversion Time:	2–9 min
Injection Volume:	100 µL
Detection:	1. Suppressed Conductivity 2. MS
MS Conditions:	Mode, –ESI Cone voltage, 70 V Probe voltage, –3 kV Probe temp., 450 °C SIM channels, 99, 101, and 107 <i>m/z</i> SIM parameters, span 0.3 amu, dwell time 1 s
Run Time:	13 min
Expected System Backpressure:	2100–2350 psi
Expected Background Conductance:	<1.5 µS

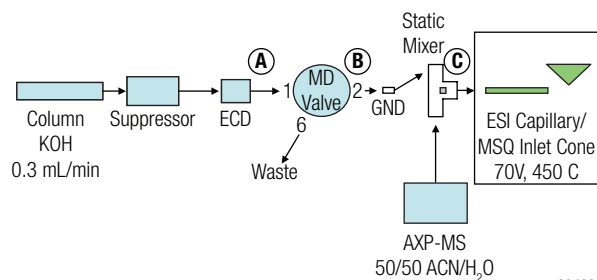


Figure 1. Flow diagram showing IC-MS with matrix diversion.

Setup

The information in this section is provided as a general discussion of the main connections required for this method. See Figure 1. The individual modules have their own installation guides available on the reference CD-ROM.⁶

The ion chromatograph is set up in the standard configuration, from left to right, of pump/detector, eluent generator, chromatography module, and mass spectrometer. The MSQ mass spectrometer is installed according to the installation guide (P/N 031869). It is assumed that the MSQ mass spectrometer has pumped down and reached vacuum for several hours or overnight. The Dionex CR-ATC column is installed between the pump and the eluent generator according to the Dionex Continuously Regenerated Anion Trap Column manual. The eluent generator and cartridge are purged and operated according to the eluent generator installation guide for low-flow rate operation. The backpressure through the system should be about 2200 psi for optimal performance of the eluent generator. See the EG50 Eluent Generator manual (P/N 031908) for complete instructions. The column and suppressor are plumbed in the normal configuration, with pressurized external water used for the suppressor, Dionex CR-ATC column, and EG50 Eluent Generator. The air pressure provided to the external water bottle is normally about 10–15 psi. Chemical regeneration of the suppressor is not recommended because higher background signal is seen in the MS. For example, sulfate from sulfuric acid regenerant has an isotopic peak at 99 *m/z*, the selected ion monitoring (SIM) mass for perchlorate.³ Note that the backpressure downstream of the suppressor must be <100 psi. The tubing A, B, and C in Figure 1 can be black PEEK (0.010 in. i.d.) to obtain the necessary low backpressure.

The “Matrix Diversion” valve is plumbed as shown and kept in the divert position, with flow from the Dionex AXP-MS Auxiliary Pump flowing to the MSQ mass spectrometer, until the background conductivity is below 1.5 µS. The Dionex AXP-MS Auxiliary Pump delivers 50/50 acetonitrile water to the MSQ mass spectrometer throughout the method. The addition of solvent through the static mixer improves the electrospray process and provides higher area counts than a 100% water-based method.

The connection to the mass spectrometer is not made until the background conductivity is below 1.5 µS.

Trigger for the MSQ Mass Spectrometer Start

A connection is made between the user I/O of the MSQ mass spectrometer (rear panel, large green connector) and Relay 1 on the pump or detector module. This relay connection is necessary to supply the trigger that synchronizes the detector start times with the MSQ mass spectrometer. See the MSQ Mass Spectrometer Installation Guide for complete instructions.

Grounding the Detectors

The grounding adaptor is placed as shown in Figure 1.

Nitrogen Nebulization Gas

The nitrogen can be supplied by a nitrogen generator, cylinders of compressed gas, or liquid nitrogen Dewar cylinders. In standard 10 h operation, a 180 L liquid nitrogen Dewar will replace about 11–13 nitrogen cylinders and last about two weeks.

How to Set Up an Internal Standard Method Using Sodium Perchlorate Oxygen-18 ISTD

Use of a stable-labeled internal standard is a well-accepted methodology for accurate, long-term quantification in chromatography mass spectrometry methods. Because the internal standard and analyte are chemically indistinguishable, the two species have the same behavior in the analytical method and are affected in the same way by chemical and instrumental variations. Because the analyte and the internal standard coelute, two SIM channels are used in the mass spectrometer for selective detection. A ratio of the response for the internal standard and the analyte can give very accurate and sensitive quantification. In this method, 99 or 101 m/z is used to detect the indigenous perchlorate and 107 m/z is used as the unique mass for the internal standard.

The sodium perchlorate ISTD is enriched with ^{18}O and the base mass peak is 107 m/z . The relative abundance of 99 and 101 m/z in the ISTD is less than 0.1%. For the quantification of trace-level perchlorate, the recommended concentration in each standard and sample is 1 $\mu\text{g/L}$, as indicated below.

Chromeleon software can provide the quantification using separate SIM channels for the analyte perchlorate and the internal standard. Quantification can be performed using 99 or 101 m/z , as desired. Figure 4 shows the QNT page from the Chromeleon software that can be set up to perform this calculation.

Standards

- Perchlorate ISTD: Stable Label Sodium Perchlorate, 107/109 m/z , 1 mg/L in water
- Perchlorate STD: NaClO_4 , 99%, A.C.S. reagent, Sigma-Aldrich cat. no. 41,024-1 (Aldrich)

Method of Use

1. Prepare 10 mL each of:

- Water blank (deionized or suitable ionic composition)
- 1 ppb perchlorate STD in water (no ISTD)
- 125 ng/L, 250 ng/L, 500 ng/L, 1000 ng/L, 2500 ppt ng/L, and 5000 ng/L perchlorate STD in water

2. Add 10 μL 1 mg/L perchlorate ISTD to each 10-mL standard and a water blank

Chromeleon PGM for Manual Injection

The PGM in Figure 2 controls a pump, AS50 Autosampler, conductivity detector, eluent generator, Dionex ASRS ULTRA II suppressor, and MSQ mass spectrometer. A moderate amount of smoothing is performed on the MS data for on-line viewing of the data during acquisition. The injection valve is kept in the inject position throughout the run for better reproducibility. Note that the Chromeleon software configuration has four items: pump, conductivity detector, MS, and autosampler.

```

Pressure.LowerLimit = 200
Pressure.UpperLimit = 3000
%A.Equate = "%A"
%B.Equate = "%B"
%C.Equate = "%C"
%D.Equate = "%D"
FlushVolume = 100
Wait FlushState
NeedleHeight = 2
CutSegmentVolume = 0
SyringeSpeed = 5
CycleTime = 0
Data_Collection_Rate = 5.0
Temperature_Compensation = 1.7
DS3_Temperature = Off
Suppressor_Type = ASRS_2mm
Suppressor_Current = 70
Range = 6
Smoothing = boxcar
SmoothingPoints = 3

```

;Matrix Diversion Valve: Sample to MSQ

```

Pump_ColumnValve.State Col_B
Sampler_InjectValve.State LoadPosition
Concentration = 45.00
EluentGenerator.Curve = 5
Flow = 0.3
%B = 0.0
%C = 100.0
%D = 0.0
Pump.Curve = 5
WaitForTemperature = False
Wait SampleReady
Run = 1
AuxFlow = 0.30

```

-0.100 ; this negative step is for command traffic.

```

0.000 ECD.Autozero
ECD_1.AcqOn
Sampler.Load
Wait Sampler.CycleTimeState
Sampler.Inject
Wait InjectState
;MSQ Start
Pump_Relay_1.Closed Duration = 2.00
Sampler_InjectValve.Inject PositionDuration
= 2.00

```

;Matrix Diversion Valve: Sample Matrix to Waste for 7 minutes

```

2.000 Pump_ColumnValve.State = Col_A
Col_A Duration=420.00
11.700 Log ECD_1.Signal.Value
13.0 ECD_1.AcqOff
Pump_ColumnValve.State = Col_A
Wait EluentGenerator.Ready
End

```

20470

Figure 2. Chromeleon PGM command page for perchlorate method using matrix diversion and the AS50 Autosampler with internal injection valve.

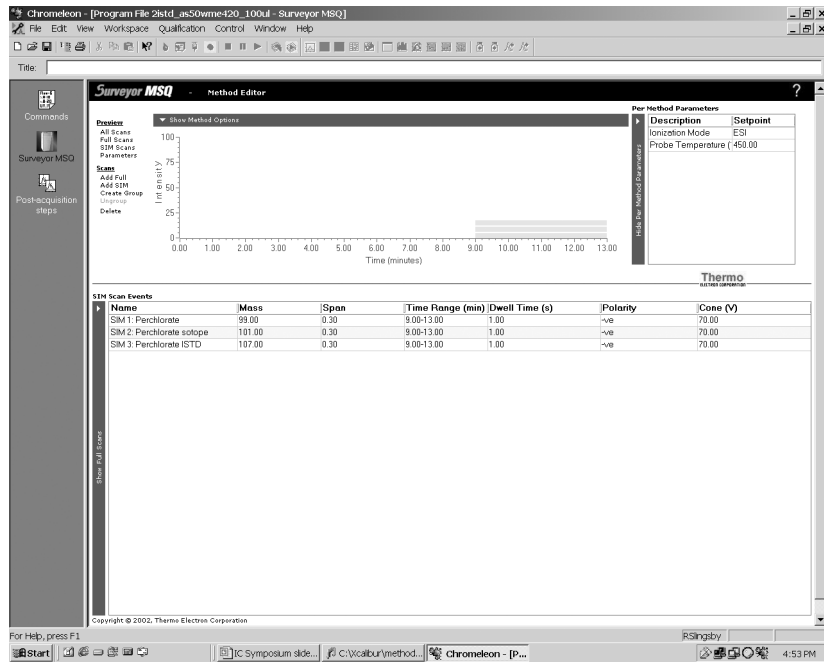


Figure 3. Chromeleon MS page.

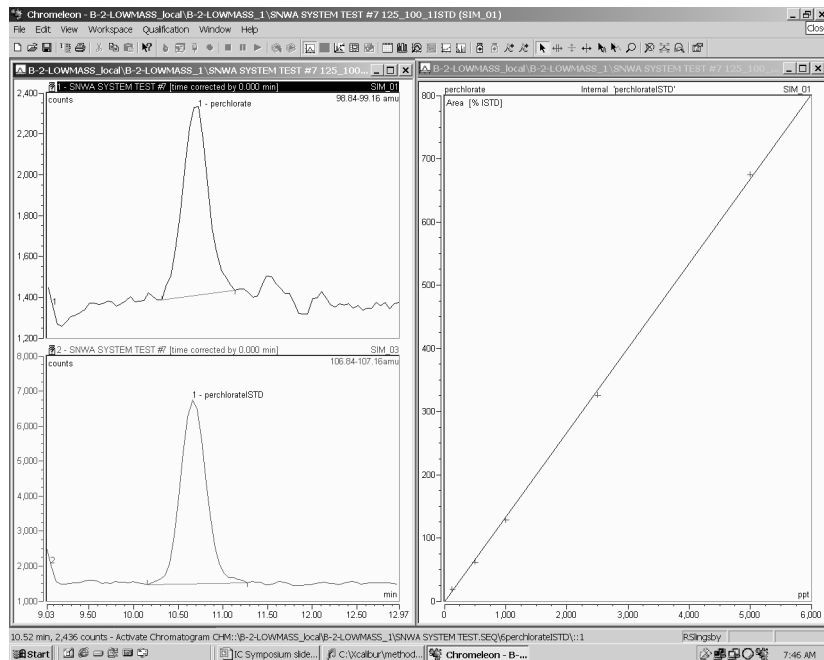


Figure 4. Quantification of perchlorate with stable-labeled internal standard.

Figure 3 is a screen capture of the Chromeleon software MSQ mass spectrometer detector page in the PGM. The electrospray probe is set to 450 °C. Three SIM channels are set at 99, 101, and 107 m/z . The ionization mode is electrospray (ESI) and the polarity is negative (-ve) with a source voltage of 70 V. MS data is collected over the time range of 9–13 min during the 13-min run. The span as shown is set for 0.3 m/z . Data is collected for SIM 1 in the range of 98.85–99.15 m/z , SIM 2 in the range of 100.85–101.15 m/z , and SIM 3 in the range of 106.85–107.15 m/z . This range can be narrowed for better signal-to-noise, if necessary.

Common matrix ions elute in the 0–5 min time range. The data file size is kept to a minimum by only collecting data as shown. But if desired, data can be collected over the entire run by changing the time range for MS data collection to 0–12 min. Also, a full scan can be run simultaneously with the SIM mode by opening the full-scan section of the setup screen and filling in the information. For a full scan, the mass range is usually set to cover from 15 m/z up to several hundred m/z . The “Additional Information Section” at the end of this document provides masses for some commonly occurring anions.

Daily Start-up for an IC-MS System

The following section can be used as a checklist for daily start-up of the IC-MS system. *The matrix diversion valve is set to divert the analytical stream to waste.* The end of the PEEK tube from port 6 of the matrix diversion valve can be placed into a waste container.

1. Add fresh deionized water to the instrument reservoir and turn on the external water to the suppressor and eluent generator.
2. Turn on the heater/voltage and nitrogen for the MS from the TUNE page of the MSQ mass spectrometer software, making sure that the probe temperature is as expected at 450 °C.
3. Check the nitrogen source and confirm that the pressure is at 70–80 psi for electrospray operation.
4. Turn on the water in the analytical pump to start flow through the system to waste.
5. Turn on the Dionex AXP-MS Auxiliary Pump to start flow to the MS.
6. Set the eluent generator concentration and suppressor current manually from the Chromeleon panel for IC-MS. Observe that the conductivity will begin high but drop rapidly to below 3 μ S.
7. When the conductivity is below 1.5 μ S, switch the matrix diversion valve to send the analytical flow to the MS. This operation can be accomplished from the panel.
8. Observe the MS background in –ESI mode on the TUNE page of the MSQ mass spectrometer software.
9. Equilibrate this system for at least 30 min. If working near the detection limit, at least an hour is needed for reproducible results.
10. Faster morning start-up can be accomplished by recycling the conductivity cell effluent back through the suppressor “Regen In” port overnight with the eluent concentration set to 5 mM and the suppressor current set to 10 mA.

Daily Shutdown of the IC-MS (Without Recycle)

1. Disconnect the PEEK tube and fitting from the inlet of the MSQ mass spectrometer and place in a waste container.
2. Turn off the eluent flow (which also turns off the eluent generator and the suppressor current).
3. Turn off the external water source.
4. Turn off the heater and voltages from the TUNE page of the MSQ mass spectrometer software or from the Chromeleon software panel.
5. Turn off the nitrogen once the temperature shown on the TUNE page is below 200 °C.

Note: If a salty or otherwise dirty liquid was flowing through the ESI probe at the time of shutdown, the probe should be flushed with water or 50/50 acetonitrile/water prior to shutdown. This flushing is conveniently accomplished by using the Dionex AXP-MS Auxiliary Pump. Be careful not to flow solvent through the analytical column and suppressor if solvent was not part of the method. A clogged ESI probe will cause poor signal.

Results

Figure 5 shows an expected result from the injection of 1000 CCS high salt matrix (1000 mg/L each chloride, carbonate, and sulfate) spiked with 125 ng/L perchlorate in an IC-MS system. The system was configured as described in this application note, including the use of matrix diversion and the internal standard.

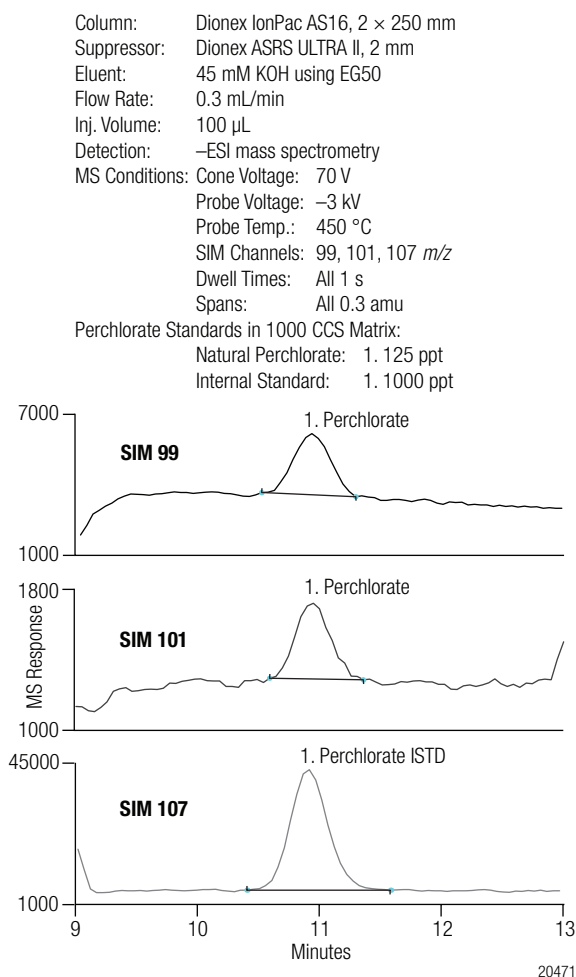


Figure 5. High ionic matrix spiked with 125 ppt perchlorate and internal standard.

Table 1 shows the results from seven replicate injections of 500 ng/L perchlorate in the 1000 CCS matrix. The amount values were calculated from an internal standard calibration curve. Method detection limit (MDL) values in deionized water matrix are 15–30 ng/L.

Table 1. MDL Calculation using 500 ng/L perchlorate and 1000 ng/L internal standard in 1000 CCS matrix.

Replicate	Amount 99 <i>m/z</i> (ng/L)	Amount 101 <i>m/z</i> (ng/L)
1	511	527
2	472	507
3	466	529
4	500	421
5	511	481
6	528	461
7	463	570
Average	493	499
Standard Deviation	25.7	49.3
% RSD	5.2	9.9
MDL (3.14 × s.d.)	80	155

Figure 6 shows the linear calibration curves for perchlorate in 1000 CCS matrix at 99 *m/z* and 101 *m/z* over the range of 125–5000 ng/L, using the internal standard method. The sodium chloride used to prepare the matrix contributed a small perchlorate peak to the matrix, as seen in the y-intercept. These data show that quantification can be performed at either mass with good linearity and sensitivity.

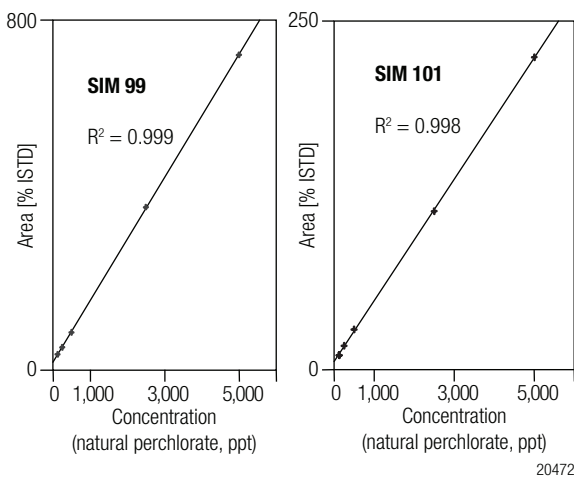


Figure 6. Linear calibration of perchlorate spiked into 1000 CCS matrix using $-ESI/MS$ and internal standard $Cl^{18}O_4^-$.

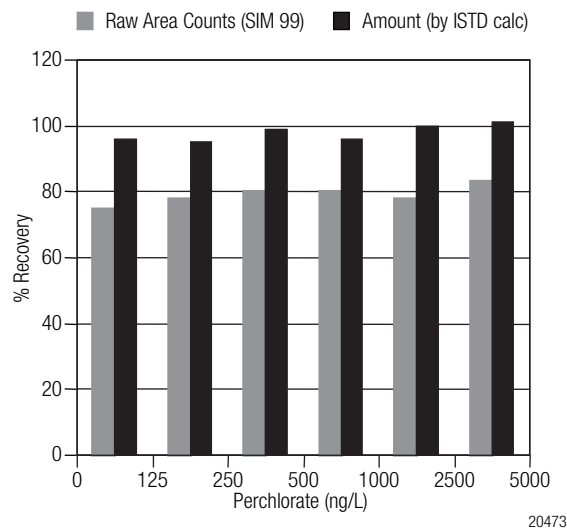


Figure 7. IC-MS determination of perchlorate in a 1000 CCS matrix-%recovery for 100 injections.

Figure 7 shows the recoveries in raw area counts and amount calculated by internal standard method over a sequence of 100 injections. The raw area counts have recoveries at all concentrations greater than 75%. The amount values calculated with the internal standard have recoveries in excess of 95% at all levels. The peak integrations were uncorrected in the Chromeleon software.

References

1. www.dhs.ca.gov/ps/ddwem/chemicals/perchl/actionlevel.htm
2. Dionex Corporation (now part of Thermo Scientific). *Determination of Low Concentrations of Perchlorate in Drinking and Ground Waters Using Ion Chromatography*; Application Note 134; Sunnyvale, CA.
3. Dionex Corporation (now part of Thermo Scientific). *Determination of Perchlorate in Drinking Water by Ion Chromatography*; Application Update 145; Sunnyvale, CA.
4. Dionex Corporation (now part of Thermo Scientific). *Determination of Perchlorate in Drinking Water Using Reagent-Free Ion Chromatography*; Application Update 148; Sunnyvale, CA.
5. Roehl, R.; Slingsby, R.; Avdalovic, N.; Jackson, P. E. J. *Chromatogr. A* 2002, 956, 245–254.
6. Dionex (now part of Thermo Scientific) Reference Library CD-ROM, August 2002 or later.

Additional Information

Table 2 on the next page provides a listing of other anions that are detectable by IC-MS, with the appropriate SIM masses for each. The last column in this table gives the isotopes, which most commonly are derived from the presence of S, Cl, and Br. The isotopic peaks provide confirmatory evidence for the presence of these elements in the analyte. Reference 2 provides retention time data for many of these anions for the Dionex IonPac AS16 column.

Table 2. Anion SIM masses for IC-MS.

SIM Mass	Anion	Formula	Major Isotopes	SIM Mass	Anion	Formula	Major Isotopes
19	fluoride	F ⁻		113	thiosulfate	HS ₂ O ₃ ⁻	113/115
35	chloride	Cl ⁻		113	trifluoroacetate	F ₃ CCO ₂ ⁻	
45	formate	HCO ₂ ⁻		115	maleate	HOOCCHCHCO ₂ ⁻	
46	nitrite	NO ₂ ⁻		115	fumarate	HOOCCHCHCO ₂ ⁻	
58	thiocyanate	SCN ⁻	58/60	117	chromate	HCrO ₄ ⁻	
59	acetate	CH ₃ CO ₂ ⁻		117	succinate	HOOCCH ₂ CH ₂ CO ₂ ⁻	
61	bicarbonate	HCO ₃ ⁻		122.9	arsenate	ASO ₃ ⁻	
62	nitrate	NO ₃ ⁻		127	bromate	BrO ₃ ⁻	127/129
67	chlorite	ClO ₂ ⁻	67/69	127	dichloroacetate	Cl ₂ CHCO ₂ ⁻	127/129
73	glyoxylate	CHOCOO ⁻		127	iodide	I ⁻	
73	propionate	CH ₃ CH ₂ CO ₂ ⁻		128.9	selenite	SeO ₃ ⁻	128/126
75	glycolate	HOCH ₂ CO ₂ ⁻		129	bromate	BrO ₃ ⁻	127/129
79	bromide	Br ⁻	79/81	131	glutarate	HOOC(CH ₂) ₃ CO ₂ ⁻	
83	chlorate	ClO ₃ ⁻	83/85	133	malate	HOOCCH ₂ CHOHCO ₂ ⁻	
87	butyrate	CH ₃ CH ₂ CH ₂ CO ₂ ⁻		133	tartrate	HOOC(CHOH) ₂ CO ₂ ⁻	
87	pyruvate	CH ₃ COCO ₂ ⁻		139	bromoacetate	BrCH ₂ CO ₂ ⁻	
89	methoxyacetate	CH ₃ OCH ₂ CO ₂ ⁻		141	arsenate	ASO ₃ •H ₂ O	
89	lactate	CH ₃ CHOHCO ₂ ⁻		144.9	selenate	SeO ₄ ⁻	144/142
89	oxalate	CO ₂ HCO ₂ ⁻		145	adipate	HOOC(CH ₂) ₄ CO ₂ ⁻	
93	chloroacetate	ClCH ₂ CO ₂ ⁻	93/95	173	bromochloroacetate	BrClCHCO ₂ ⁻	mixed
95	methanesulfonate	CH ₃ SO ₃ ⁻	95/97	183	styrenesulfonate	CH ₂ CHC ₆ H ₄ SO ₃ ⁻	
96	sulfamate	NH ₂ SO ₃ ⁻	96/98	191	citrate	HOOCCH ₂ COHCO ₂ HCH ₂ CO ₂ ⁻	
97	sulfate	HSO ₄ ⁻	97/99	191	quininate	C ₇ H ₁₂ O ₆ ⁻	
97	phosphate	H ₂ PO ₄		191	isocitrate	HOOCCH ₂ COHCO ₂ HCH ₂ CO ₂ ⁻	
99	perchlorate	ClO ₄ ⁻	99/101	207	dichlorobromoacetate	Cl ₂ BrCCO ₂ ⁻	mixed
101	valerate	CH ₃ CH ₂ CH ₂ CH ₂ CO ₂ ⁻		207	dibromochloroacetate	Br ₂ ClCCO ₂ ⁻	mixed
103	hydroxybutyrate	CH ₃ CHOHCH ₂ CO ₂ ⁻		217	dibromoacetate	Br ₂ CHCO ₂ ⁻	mixed
103	malonate	HOOCCH ₂ CO ₂ ⁻		248.8	tungstate	HWO ₄ ⁻	mixed
				251	tribromoacetate	Br ₃ CCO ₂ ⁻	mixed

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