

Determination of perchlorate in environmental waters using a compact ion chromatography system coupled with a single quadrupole mass spectrometer

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Keywords

Integrion HPIC, Dionex IonPac AS20 column, ISQ EC Single Quadrupole Mass Spectrometer, IC-MS, drinking water analysis, perchlorate analysis, anion analysis

Goal

To accurately determine trace concentrations of perchlorate in environmental waters and provide a reference method for perchlorate analysts using a compact, high-pressure ion chromatography (HPIC) system coupled with a single quadrupole mass spectrometer

Introduction

Perchlorate has been used as an oxidizer in rockets, munitions, and fireworks since the 1950s. It has been found to cause thyroid dysfunction and has been linked to tumors in humans. Perchlorate is regulated under the Safe Drinking Water Act (2011), although the Maximum Contaminant Level Goal (MCLG) and Maximum Contaminant Level (MCL) have not yet been established. Additionally, numerous U.S. states have promulgated enforceable standards for the levels of perchlorate in drinking water. Massachusetts and California have established standards for drinking water of 2 $\mu\text{g/L}$ and 6 $\mu\text{g/L}$, respectively. More than 10 other states have also set advisory levels or health-based goals for perchlorate in drinking water ranging from 1 to 18 $\mu\text{g/L}$.

Determination of perchlorate in environmental samples has also gained the attention of the International Standards Organization (ISO). ISO 19340 specifies a method for the determination of dissolved perchlorate in water (e.g. drinking water, mineral water, raw water, surface water, partially treated water or swimming pool water, waste water from drinking/swimming pool water treatment plants).¹ Another ISO method, ISO/DIS 20295, specifies a method for the determination of perchlorate in soil and soil materials.²

Ion chromatography (IC) with suppressed conductivity detection and electrospray ionization/mass spectrometry is one of the most sensitive and robust characterization methods available for perchlorate. Thermo Scientific Application Note 151³ (AN151) describes a method for perchlorate determination in environmental waters using a Thermo Scientific™ Dionex™ IonPac™ AS16 2 mm column with a Thermo Scientific™ Dionex™ ICS-2500 ion chromatography system, and a Thermo Scientific™ MSQ™ enhanced low-mass option mass spectrometer. Mass spectrometry (MS) provides lower detection limits in high-ionic-strength matrices than conductivity detection alone. MS also provides peak identification information for perchlorate by monitoring the appropriate mass/charge ratio (m/z). The two predominant perchlorate ions that occur naturally at a ratio of 3.086:1 are $^{35}\text{Cl}^{16}\text{O}_4^-$, m/z 99, and $^{37}\text{Cl}^{16}\text{O}_4^-$, m/z 101, respectively.⁴ The m/z 99/101 area count ratio and relative retention time are used for confirmation of perchlorate in samples.

This Application Update revises AN151 using a Thermo Scientific™ Dionex™ IonPac™ AS20 column set, on a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, coupled with a recently introduced Thermo Scientific™ ISQ™ EC single-quadrupole mass spectrometer. The Dionex IonPac AS20 column simplifies trace analysis of perchlorate in drinking water, surface water, and groundwater samples, even in the presence of very high concentrations of chloride, carbonate, and sulfate. The Dionex Integrion HPIC system is a robust, easy-to-use system that includes features such as eluent generation, temperature control, easy access to consumables (e.g., columns and suppressors), high-pressure capability, consumables tracking, and low-void-volume Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings. The selectivity of the ISQ EC MS allows the quantification of perchlorate in high-ionic strength matrices at well below currently enforced action levels. For peak confirmation, the ISQ EC MS provides mass-to-charge (m/z) confirmation for perchlorate to give confidence in the results. The HESI-II electrospray improves ionization efficiency, eliminating the need to add organic solvents to enhance ionization. The ISQ EC mass spectrometer also offers full integration with the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, allowing novice and advanced users to easily master MS.

Experimental

Equipment and consumables

- Dionex Integrion HPIC system including:
 - Eluent generator
 - Pump
 - Degasser
 - Conductivity detector
 - Column oven temperature control
 - Detector-suppressor compartment temperature control
 - Tablet control
- Thermo Scientific™ Dionex™ AS-AP Autosampler with Sample Syringe, 250 μL (P/N 074306) and Buffer line, 1.2 mL (P/N 074989)
- Thermo Scientific™ Dionex™ 6-port high-pressure valve (P/N 22153-60014)
- Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer (P/N ISQEC000IC)
- Thermo Scientific™ Dionex™ AXP Auxiliary Pump (P/N 063973)
- Peak Scientific Genius 1022 nitrogen generator (P/N 10-6022 (230v))
- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ AERS 500e Anion Electrolytically Regenerated Suppressor for External Water Mode (Dionex AERS 500e (2 mm), P/N 302662)
- Dionex IC PEEK Viper Fitting Tubing Assembly Kits (P/N 088798)
- Dionex AS-AP Autosampler Vials 10 mL (P/N 074228)
- Chromeleon Chromatography Data System software version 7.2 SR6
- Thermo Scientific™ Nalgene™ Syringe Filters, PES, 0.2 μm (Fisher Scientific P/N 09-740-61A)
- AirTite™ All-Plastic Norm-Ject™ Syringes, 5 mL, Sterile (Fisher Scientific P/N 14-817-28)
- Thermo Scientific™ Nalgene™ 1000 mL, 0.2 μm Nylon Filter Units (Fisher Scientific P/N 09-740-46)

Reagents and standards

Reagents

- Deionized (DI) water, Type I reagent grade, 18 M Ω -cm resistivity or better filtered through a 0.2 μ m filter immediately before use.

Standards

- Sodium perchlorate, Acros Organics (Fisher Scientific P/N AC447421000)
- Thermo Scientific™ Dionex™ Perchlorate-ISTD (¹⁸O-enriched Internal Standard, P/N 062923)
- Sodium Chloride, (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N S271-500)
- Sodium Sulfate Anhydrous, (Granular/Certified ACS), Fisher Chemical (Fisher Scientific P/N S421-500)
- Sodium Carbonate Anhydrous, (Powder/Certified ACS), Fisher Chemical (Fisher Scientific P/N S263-500)

System configuration

The information in this section is provided as a general discussion of the main connections required for this method. See Figure 1 for a schematic of the setup used for this study. In this method, the auxiliary six-port valve was placed between the conductivity detector and the mass spectrometer.

Please follow the flow diagram shown in Figure 1 to plumb the consumables and modules of the Dionex Integriion HPIC system in external water mode. Install and condition/hydrate the Dionex EGC 500 KOH Eluent Generator cartridge, Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column, and Dionex AERS 500e Anion Electrolytically Regenerated Suppressor according to the product manual instructions.⁵⁻⁷ The ISQ EC mass spectrometer is installed according to the ISQ EC MS Operating Manual.⁷ Note: The system pressure should be above 2000 psi for optimal performance.

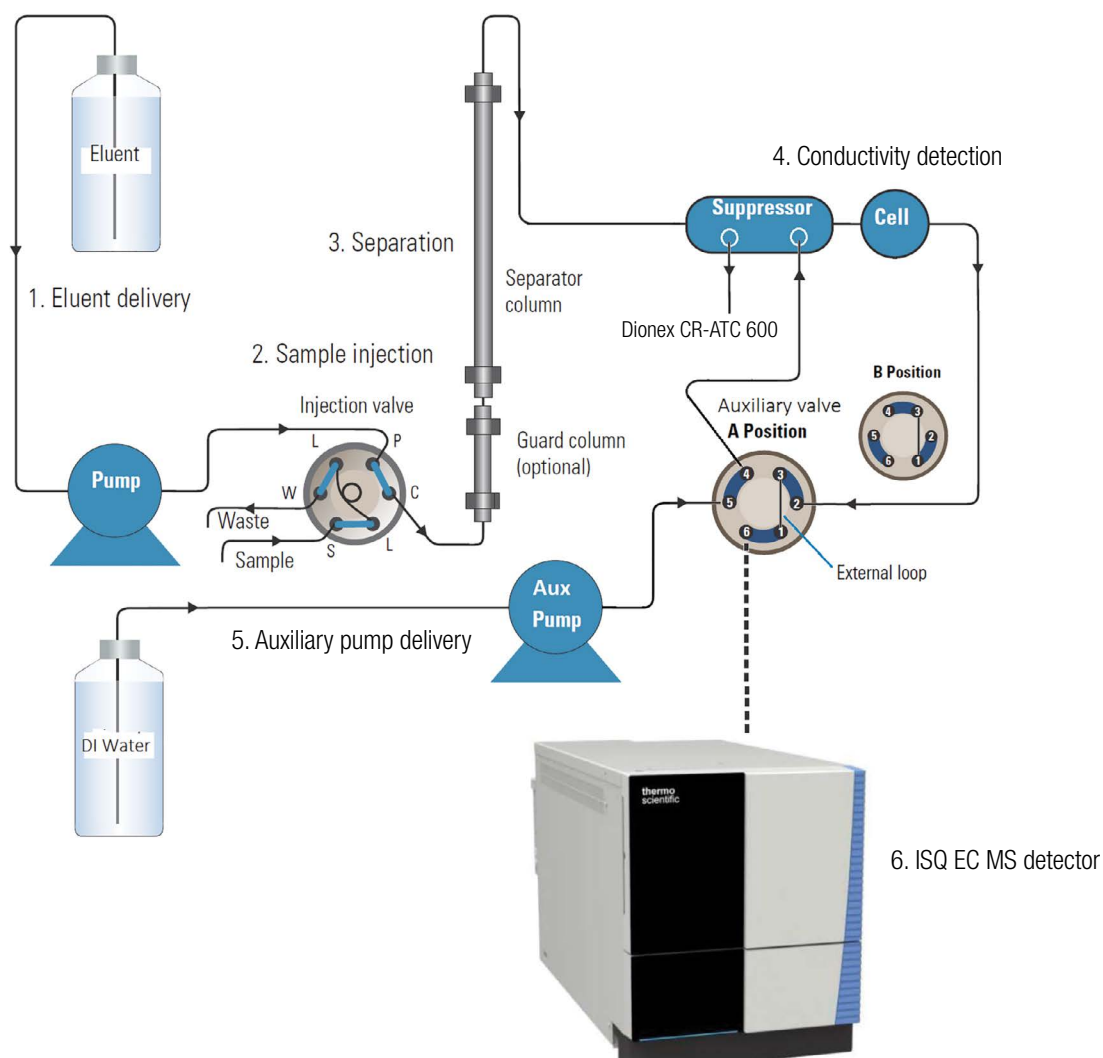


Figure 1. IC-MS configuration with matrix diversion.

IC Conditions	
IC System:	Dionex Integrion HPIC system
MS Detector:	ISQ EC single quadrupole mass spectrometer
Columns:	Dionex IonPac AG20 Guard, 2 × 50 mm Dionex IonPac AS20 Analytical, 2 × 250 mm
Eluent Source:	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge with Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column
Eluent:	55 mM KOH
Flow Rate:	0.3 mL/min
Injection Volume:	100 µL
Temperature:	30 °C (column compartment), 20 °C (detector compartment)
System Backpressure:	~2350 psi
Detection:	Suppressed Conductivity, Dionex AERS 500e Anion Electrolytically Regenerated Suppressor (2 mm), AutoSuppression, 41 mA, external water mode via Thermo Scientific™ Dionex™ AXP Auxiliary Pump, external water flow rate (0.6 mL/min)
Background Conductance:	~ 0.3 µS
Run Time:	14 min

MS Detection Conditions	
Ionization	Electrospray ionization
Interface:	(ESI), negative mode
Divert Valve Switch Time:	6.0–14.0 min (0.0–6.0 min to waste, 6.0–14.0 min to ISQ EC MS)
Gas Control:	Sheath gas pressure: 50 psi Aux gas pressure: 5 psi Sweep gas pressure: 0.0 psi
Source Voltage:	-2500 v
Vaporizer Temperature:	450 °C
Ion Transfer Tube Temperature:	200 °C
Advanced Scan Mode	See Table 1
Groups:	Chrom. Filter Peak Width (s): 25

Table 1. Advanced scan mode parameters.

Scan Name	Mass List (amu)	Dwell or Scan Times (s)	SIM Widths (amu)	Ion Polarity	Source CID Voltage
Perchlorate 99	99	1.2	0.3	Negative	0
Perchlorate 101	101	1.2	0.3	Negative	0
Perchlorate ISTD	107	1.2	0.3	Negative	0

The Dionex AERS 500e Anion Electrolytically Regenerated Suppressor is recommended for all applications where external water mode is employed, in particular IC-MS applications.

The “Matrix Diversion” valve is plumbed as shown in Figure 1, with flow from the Dionex AXP-MS Auxiliary Pump flowing to the ISQ EC mass spectrometer, until the background conductivity is below 1.5 $\mu\text{S}/\text{cm}$. The “Matrix Diversion” valve can be configured in the A position or the B position. Figure 1 shows the liquid flow paths through the valve ports at each valve position. When it is in B position, the suppressor actually runs in recycle mode that uses the suppressed conductivity cell effluent as the source of water for the regenerant. The Dionex MSQ mass spectrometer used the addition of acetonitrile/water (50/50) throughout the method to enhance detection by assisting with desolvation of the eluent and the formation of a stable electrospray. Ionization improvements to the ISQ EC mass spectrometer’s electrospray source have been made to eliminate the need for additional organic solvents, and thus simplify operation.

The connection to the mass spectrometer is not made until the background conductivity is below 1.5 $\mu\text{S}/\text{cm}$.

Trigger for the ISQ EC mass spectrometer start

The ISQ EC MS instrument is controlled directly by the Chromeleon 7.2 Chromatography Data System (CDS) software. Unlike other MS instruments, there is no auxiliary software required to directly control the MS. Please follow the steps as described in Section 3.3: Software Operation of the ISQ EC MS Operating Manual for complete instructions.⁸

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 separation 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 responses 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 endogenous 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 internal standard concentration in each standard and sample is 1 $\mu\text{g}/\text{L}$, as indicated below.

Chromeleon CDS software can provide 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. Calibration curves can be constructed using the internal standard and external methods, respectively.

Method of use

1. Prepare 10 mL each of:
 - Water blank (DI or suitable ionic composition)
 - 1 ppb perchlorate standard in water blank (no ISTD)
 - 125 ng/L, 250 ng/L, 400 ng/L, 800 ng/L, 1000 ng/L, 2000 ng/L, and 5000 ng/L perchlorate standard in water blank
2. Add 10 μL 1 mg/L perchlorate ISTD to each 10 mL standard and water blank

The script for the matrix diversion method in Chromeleon CDS 7.2 software

Analytes, such as chloride and sulfate, become acidic ($\text{KCl} \rightarrow \text{HCl}$, $\text{K}_2\text{SO}_4 \rightarrow \text{H}_2\text{SO}_4$) after they flow through the suppressor. As a consequence, at high concentrations, they can cause corrosion or inlet fouling in the MS instrument at high concentrations. In anion chromatography, the anions are separated by charge, size, and polarizability. As a large polarizable molecule, ClO_4^- elutes later than the common inorganic anions (Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^-). Having the eluent flow from the column diverted to waste prior to the perchlorate elution can minimize interferences by the matrix ions.

A high purity water sample is unlikely to need the eluent diverted prior to MS detection, but we still recommend diverting it to waste to ensure IC background falls to a reasonable level and to reduce the risk of sending KOH eluent into the mass spectrometer. Any crystallization on the entrance cone and optics requires frequent cleaning to maintain performance. Therefore, we always recommend a conductivity detector and a diverter valve.

The ISQ EC MS method editor follows the same rules and logic as other IC modules and detectors. After the MS instrument is properly connected and controlled by the Chromeleon CDS software, the user may create an

instrument method. Select “create instrument method” in the Chromeleon CDS 7.2.6 software and follow the automated prompts. Once done, the software will automatically generate the method script. Due to the need for matrix diversion, some commands should be manually inserted to make the method complete. These commands include keeping the diverter valve in the B position before the run, switching from B position to A position at the appropriate running time, and eventually switching back to B position after the run. The script of this method is presented in Table 2. The inserted commands are highlighted with boxes.

Table 2A. Method script.

Time	Command	Value
{Initial Time}	Instrument Setup	
	Wait	Sampler.Ready, Run=Hold, Timeout=Infinite
	Sampler.TempCtrl	Off
	Sampler.CycleTime	0 [min]
	Sampler.LoopOverfill	5
	Sampler.InjectMode	PushFull
	Sampler.BufferWashFactor	2
	Sampler.WashDispSpeed	20.0 [µl/s]
	Sampler.InjectWash	AfterInj
	Sampler.SyncWithPump	On
	Sampler.WashSpeed	20.0 [µl/s]
	Sampler.WashVolume	250.0 [µl]
	Sampler.SampleHeight	2.000 [mm]
	Sampler.WasteSpeed	20.0 [µl/s]
	Sampler.DispenseDelay	2.0 [s]
	Sampler.DispSpeed	10.0 [µl/s]
	Sampler.DrawSpeed	10.0 [µl/s]
	Sampler.DrawDelay	2.0 [s]
	Sampler.DilutionMixDispenseSpeed	60.0 [µl/s]
	Sampler.DilutionMixIterations	3
	Sampler.DilutionMixSpeed	30.0 [µl/s]
	Pump_ECD.Pressure.UpperLimit	5000.00 [psi]
	Pump_ECD.%A.Equate	%A
	Pump_ECD.Pressure.LowerLimit	200.00 [psi]
	Pump_ECD.Compartment_TC.Mode	On
	Pump_ECD.Compartment_TC.TemperatureSet	20.0 [°C]
	Pump_ECD.Column_TC.Mode	On
	Pump_ECD.Column_TC.TemperatureSet	30.0 [°C]
	Electrolytics.Suppressor.Type	AERS_2mm

Table 2B. Method script.

Time	Command	Value
	Electrolytics.Suppressor.Carbonate	0.0 [mM]
	Electrolytics.Suppressor.Bicarbonate	0.0 [mM]
	Electrolytics.Suppressor.Hydroxide	55.0 [mM]
	Electrolytics.Suppressor.Tetraborate	0.0 [mM]
	Electrolytics.Suppressor.OtherEluent	0.0 [mM]
	Electrolytics.Suppressor.RecommendedCurrent	41 [mA]
	Electrolytics.Suppressor.CurrentSet	41 [mA]
	Electrolytics.EluentGenerator.Concentration	55.00 [mM]
	CDet.Rise_Time	0.5 [s]
	CDet.Data_Collection_Rate	5.0 [Hz]
	CDet.CellHeater.Mode	On
	CDet.CellHeater.TemperatureSet	35.0 [°C]
	CDet.Temperature_Compensation	1.7 [%]
	Pump_ECD.Flow.Nominal	0.3 [ml/min]
	ISQEC.ISQEC_MethodSettings.UseThisDetector	Yes
	ISQEC.ISQEC_MethodSettings.SourceSettingsView	Advanced
	ISQEC.ISQEC_MethodSettings.Robustness	3
	ISQEC.ISQEC_MethodSettings.MobilePhaseVolatility	3
	ISQEC.ISQEC_MethodSettings.AnalyteStability	3
	ISQEC.ISQEC_MethodSettings.MethodType	ScanMode
	ISQEC.ISQEC_MethodSettings.IonTransferTubeTemperature	200 [°C]
	ISQEC.ISQEC_MethodSettings.VaporizerTemperature	450 [°C]
	ISQEC.ISQEC_MethodSettings.SourceType	ESI
	ISQEC.ISQEC_MethodSettings.SourceVoltagePositive	3000 [V]

Table 2C. Method script.

Time	Command	Value
	ISQEC.ISQEC_MethodSettings.SourceVoltageNegative	-2500
	ISQEC.ISQEC_MethodSettings.SourceCurrentPositive	50 [µA]
	ISQEC.ISQEC_MethodSettings.SourceCurrentNegative	50 [µA]
	ISQEC.ISQEC_MethodSettings.AuxGasPressure	5 [psig]
	ISQEC.ISQEC_MethodSettings.SheathGasPressure	50 [psig]
	ISQEC.ISQEC_MethodSettings.SweepGasPressure	0 [psig]
	ISQEC.ISQEC_MethodSettings.ManualPumpFlowRate	0.2 [ml/min]
	Electrolytics.CR_TC.CR_TC	On
	Sampler.PunctureOffset	0 [mm]
	Pump_ECD.HP_Valve.B	
	Wait	Pump_ECD.Ready
0.000	Inject Preparation	
	Wait	ISQEC.Ready
0.000	Inject	
	Wait	Sampler.CycleTimeState, Run=Hold, Timeout=Infinite
	Sampler.Inject	
0.000	Start Run	
	Pump_1.Pump_1_Pressure.AcqOn	
	CDet.CD.AcqOn	
	CDet.CD_Total.AcqOn	
	CDet.Autozero	

Table 2D. Method script.

Time	Command	Value
0.000	Run	Duration = 14.000 [min]
	ISQEC.ISQEC_MethodSettings.StartSegment	25.000, "LastTune"
	ISQEC.ISQEC_MethodSettings.DoSIMScan	Masses="99", ScanTimes="1.2", ScanWidths="0.3", Polarity=Negative, SourceCIDVolt-age=0.0, TubeLensVolt-age="LastTune"
	ISQEC.ISQEC_MethodSettings.DoSIMScan	Masses="101", ScanTimes="1.2", ScanWidths="0.3", Polarity=Negative, SourceCIDVolt-age=0.0, TubeLensVolt-age="LastTune"
	ISQEC.ISQEC_MethodSettings.DoSIMScan	Masses="107", ScanTimes="1.2", ScanWidths="0.3", Polarity=Negative, SourceCIDVolt-age=0.0, TubeLensVolt-age="LastTune"
6.000	Pump_ECD.HP_Valve.A	
14.000	Stop Run	
	Pump_1.Pump_1_Pressure.AcqOff	
	CDet.CD.AcqOff	
	CDet.CD_Total.AcqOff	
	Pump_ECD.HP_Valve.B	
	ISQEC.ISQEC_MethodSettings.StopAcquisition	
End		

The ion transfer tube temperature and vaporizer temperature are set to 200 °C and 450 °C, respectively. The ionization mode is electrospray (ESI) and the polarity is negative (–ve) with a source voltage of 2500 V. Three SIM channels are set at 99, 101, and 107 *m/z*. The span as shown is set for 0.3 *m/z*. Data is collected for SIM 99 in the range of 98.85–99.15 *m/z*, SIM 101 in the range of 100.85–101.15 *m/z*, and SIM 107 in the range of 106.85–107.15 *m/z*. If needed, this range can be narrowed for a better signal-to-noise value. High dwell or scan times for selected ions will increase the amount of time that the MS scans the SIM ion mass. This can improve the limit of quantitation (LOQ). In this application, common matrix ions elute from 0 to 5 min. The data can be collected over the entire run or after elution of common matrix ions.

Results and discussion

Separation

The Dionex IonPac AS20 column is a high capacity, hydroxide selective anion-exchange column designed for the isocratic separation of polarizable anions including iodide, thiocyanate, thiosulfate, and perchlorate in a variety of sample types. The key application for this column is the determination of low concentrations (single digit µg/L) of perchlorate in drinking water and other environmental samples.

Figure 2 shows the separation of perchlorate in DI water and Laboratory Synthetic Sample Matrix (LSSM, 1000 mg/L each of chloride, carbonate, and sulfate) on a Dionex IonPac AS20 column set. Perchlorate is fully resolved from the common anions. The system was configured as described in this application note, including the use of matrix diversion and the internal standard. The MS detector is a more powerful tool to detect perchlorate in high-ionic-strength samples compared to suppressed conductivity detection. Of the common anions found in drinking waters (Cl⁻, SO₄²⁻, CO₃²⁻, and HCO₃⁻), sulfate can be the most problematic. Sulfate elutes before perchlorate on most of the anion chromatography columns currently being used for perchlorate analysis; however, at high concentrations it has a tendency to elute broadly, tailing into the retention time of perchlorate. There is typically no visible perchlorate peak by conductivity detection when concentrations are 2 µg/L or

less and there is a high (1000 mg/L) sulfate concentration in the sample. Formation of H³²SO₄⁻ (*m/z* 97) and H³⁴SO₄⁻ (*m/z* 99) are favored in the suppressor. They are also formed in the electrospray ionization interface. In general, the result of high sulfate concentrations was observed to be an inability to detect the *m/z* 99 ion, whereas the *m/z* 101 ion was still detected at low concentration (Figure 2B). However, an area count ratio (*m/z* 99/101) 3.38 detected by the ISQ EC MS can easily meet the requirement that the measured ratio must fall within ±25% (2.31–3.85) if the concentration of perchlorate is 1 µg/L or higher regardless of 1000 mg/L sulfate concentrations (Figure 2C).

Calibration, limit of detection, and limit of quantitation

An ¹⁸O-enriched perchlorate (³⁵Cl¹⁸O₄⁻) internal standard (*m/z* 107) is recommended for quantitation to improve accuracy and ruggedness of the method in U.S. EPA Method 332.⁹ In our study, calibration curves with seven concentration levels ranging from 125 to 5000 ng/L were constructed for perchlorate in DI water and LSSM matrix using the internal standard and external standard methods respectively (Table 3). The calibration curves for perchlorate in the high-ionic-strength matrix at 101 *m/z* over the range of 125–5000 ng/L using the internal standard and external standard methods showed good linearity with the coefficients of determination being 0.9993 and 0.9999, respectively (Figure 3). All results showed the ISQ EC MS can perform ppb-level perchlorate quantification using either internal or external standard methods with great confidence.

Determination of the signal-to-noise ratio is performed by comparing measured signals from samples with known low concentrations of analyte with those of blank samples and by establishing the minimum concentration at which the analyte can be reliably detected. A signal-to-noise ratio of 3:1 is generally considered acceptable for estimating the limit of detection (LOD). The LOD was then calculated from the peak height of seven injections of 125 ng/L perchlorate spiked into DI water or LSSM. The results of the calibration and LOD are summarized in Table 3.

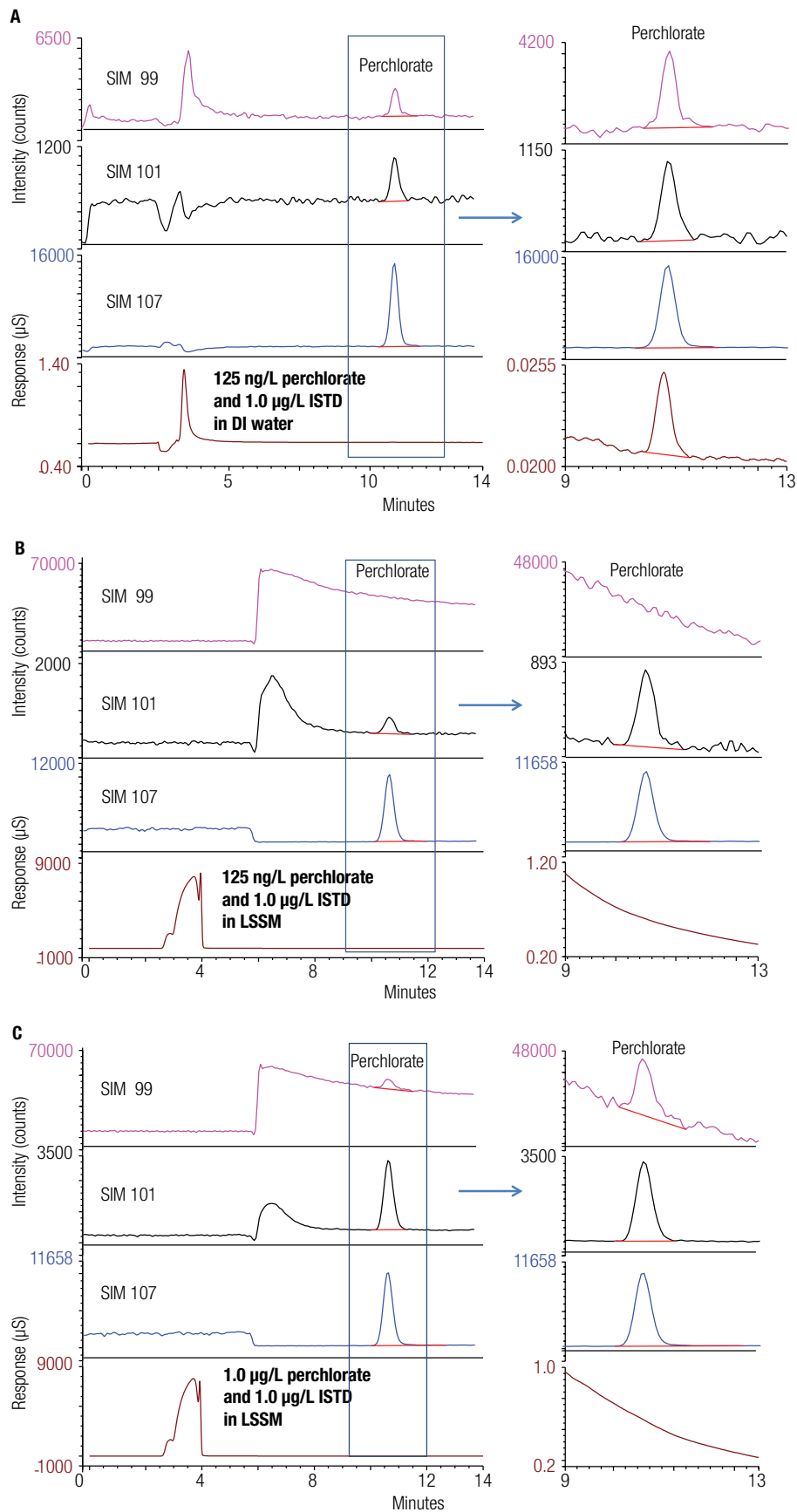


Figure 2. The separation of perchlorate in deionized water and Laboratory Synthetic Sample Matrix (LSSM, 1000 mg/L each chloride, carbonate, and sulfate) using a Dionex IonPac AS20 column set. (A) 125 ng/L perchlorate in deionized water with enlarged box section (B) 125 ng/L perchlorate in LSSM with enlarged box section (C) 1.0 $\mu\text{g/L}$ perchlorate in LSSM with enlarged box section.

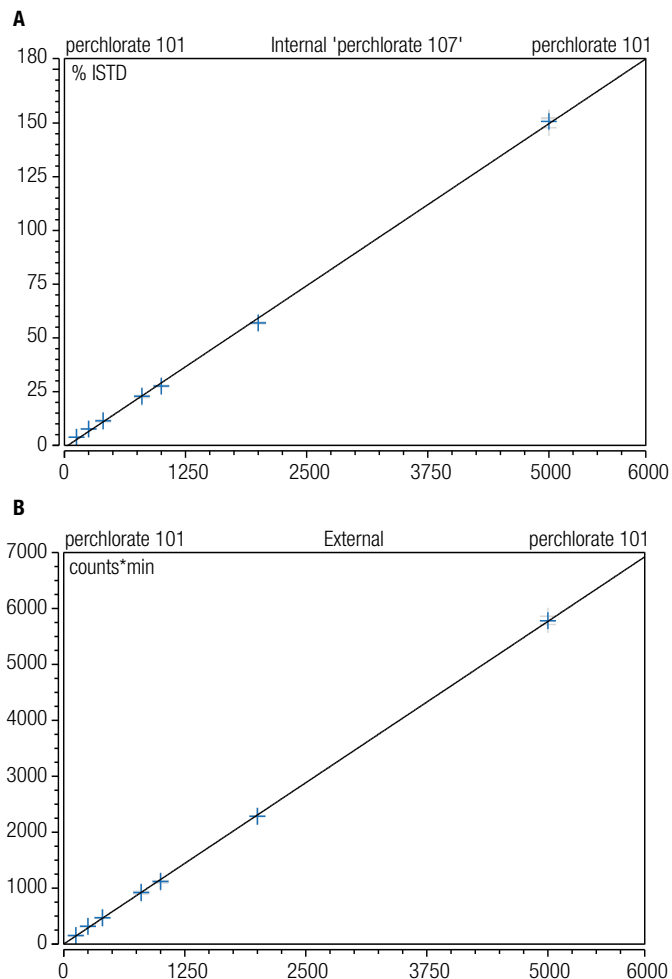


Figure 3. Calibration plot for perchlorate in LSSM at 101 *m/z* over the range of 125–5000 ng/L using the internal standard (A) and external standard methods (B).

Recovery

Figure 4 shows the recoveries in raw area counts and amount calculated by the internal standard method over a sequence of 100 injections. The raw area counts have recoveries at all concentrations between 98% and 106%. The amount values calculated with the internal standard have recoveries between 96% and 120%.

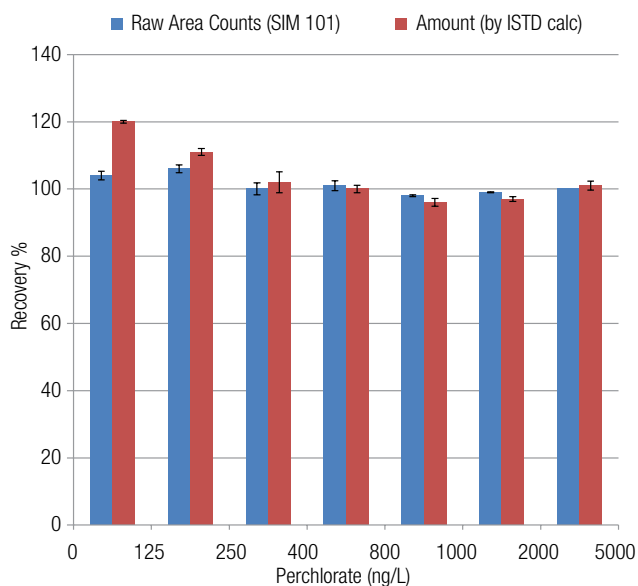


Figure 4. IC-MS determination of perchlorate in LSSM recovery for 100 injections.

Table 3. Method calibration and LOD for IC-MS of perchlorate.

Name	Quantitation Ion	Calibration Method	Coefficient of Determination (r^2)	LOD ^a (ng/L)
Perchlorate in deionized water over the range of 125–5000 ng/L	<i>m/z</i> 99	Internal standard	0.9994	20–60
		External standard	1.000	
Perchlorate in LSSM over the range of 400–5000 ng/L	<i>m/z</i> 101	Internal standard	0.9997	30–60
		External standard	0.9999	
Perchlorate in LSSM over the range of 125–5000 ng/L	<i>m/z</i> 99	Internal standard	0.9995	n.a.
		External standard	0.9996	
Perchlorate in LSSM over the range of 125–5000 ng/L	<i>m/z</i> 101	Internal standard	0.9993	30–60
		External standard	0.9999	

^aLOD=3×S/N

Conclusion

This application update demonstrates an improved approach for the determination of perchlorate in environmental waters using IC-MS. The ISQ EC MS provides lower perchlorate detection limits in high-ionic-strength matrices than conductivity detection alone. Separation of perchlorate from the matrix ions combined with the use of a diverter valve has resulted in a method that minimizes interferences for environmental water samples. The recovery study demonstrated good method accuracy. The ionization interface of the ISQ EC MS instrumentation eliminates the need to add organic solvent to enhance ionization and thus detection.

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