

Determination of Perchlorate by U.S. EPA Method 332.0 Using an Updated IC-MS System

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ABSTRACT

Purpose: Our study evaluated the performance of a Thermo Scientific™ Dionex™ Integrion HPIC™ system coupled with a Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer to fulfill the requirements of EPA Method 332.0 for determination of perchlorate in environmental waters.

Methods: The method uses a Thermo Scientific™ Dionex™ IonPac™ AS20 column set, on a compact IC system (Dionex Integrion HPIC system) coupled with a recently introduced single quadrupole mass spectrometer (ISQ EC MS).

Results: The results showed this new IC-MS platform can successfully execute EPA Method 332 for the determination of perchlorate in drinking water. This study demonstrated great sensitivity, good precision and accuracy, and ruggedness. Method detection limit (MDL) values in deionized water are 20–60 ng/L, and MDLs in high-ionic-strength matrix are 30–60 ng/L.

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). Massachusetts and California have established standards for drinking water of 2 µg/L and 6 µg/L, respectively, according to EPA website (<https://www.epa.gov/dwstandardsregulations/perchlorate-drinking-water-frequent-questions#has-safe-level-determined>). Determination of perchlorate in environmental samples has also gained the attention of the International Standards Organization (ISO).

U.S. EPA Method 332.0 — Ion Chromatography with Suppressed Conductivity and Electrospray Ionization/Mass Spectrometry is one of the most sensitive and robust characterization methods available for perchlorate determinations. Mass spectrometry (MS) provides lower detection limits in high-ionic-strength matrices than conductivity detection alone. These low detection limits are achieved without sample preparation.

MATERIALS AND METHODS

System Configuration

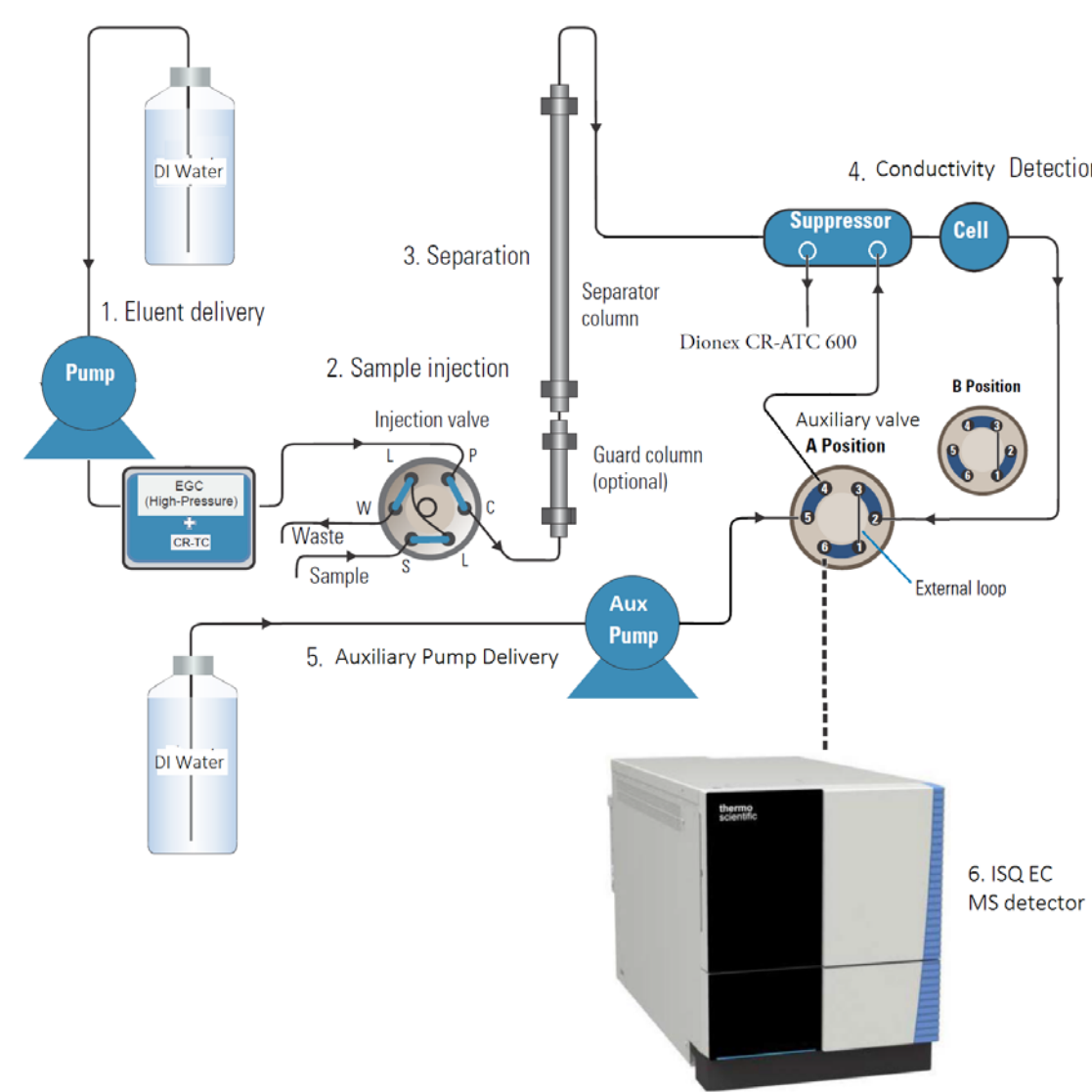


Figure 1. IC-MS Configuration with matrix diversion.

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.

In U.S. EPA Method 332, this valve may be placed between the exit of the column and the entrance of the suppressor, or alternatively, it may be placed between the conductivity detector and the MS. In the later configuration, a 50/50 water/acetonitrile mixture is mixed with the eluate before it enters the MS using a static mixing tee. Our study used the later configuration, but without the need for the acetonitrile (i.e. 100% DI water is sent to the MS when the flow from the cell is sent to the suppressor/regenerant channel). Ionization improvements to the electrospray source of the ISQ EC mass spectrometer eliminate the need for addition of organic solvents, and thus simplify operation.

Test Method

Conditions	
IC System:	Dionex Integrion HPIC system
MS Detector:	Thermo Scientific ISQ EC single quadrupole mass spectrometer
Columns:	Dionex IonPac AG20 Guard, 2 x 50 mm Dionex IonPac AS20 Analytical, 2 x 250 mm
Eluent Source:	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge with Thermo Scientific™ Dionex™ CR-ATC 600
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 Electrolytically Regenerated Suppressor (2 mm), AutoSuppression, 41 mA, external water mode via Thermo Scientific™ AXP™ Pump, external water flow rate (0.6 mL/min)
Background Conductance:	~ 0.3 µS
Run Time:	14 min
Mass Spectrometric Detection	
Ionization interface:	Electrospray ionization (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

Scan Name	Mass list (amu)	Dwell or Scan Times (sec)	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 107	107	1.2	0.3	Negative	0

Groups: Chrom. Filter Peak Width (sec): 25

Script for the matrix diversion method in the Thermo Scientific™ Chromeleon™ 7.2 Chromatography Data System (CDS) software

The ISQ EC MS method editor follows the same rules and logic as other IC modules and detectors. Once the MS instrument is properly connected and controlled by the Chromeleon CDS software, the user may create an instrument method. Due to the need for matrix diversion, we should manually insert commands to make a method that includes keeping the divert 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.

RESULTS

Separation

Figure 2 shows chromatograms of a 125 ng/L calibration standard with retention times for the ions monitored in this method (m/z 99, 101, and 107). Figure 3 shows chromatograms of a 1.0 µg/L perchlorate laboratory fortified synthetic sample matrix (LFSSM) solution containing 1000 mg/L of chloride, sulfate, and carbonate. Figure 3 also illustrates the effect of a high background at m/z 99 due to $H^3SO_4^-$.

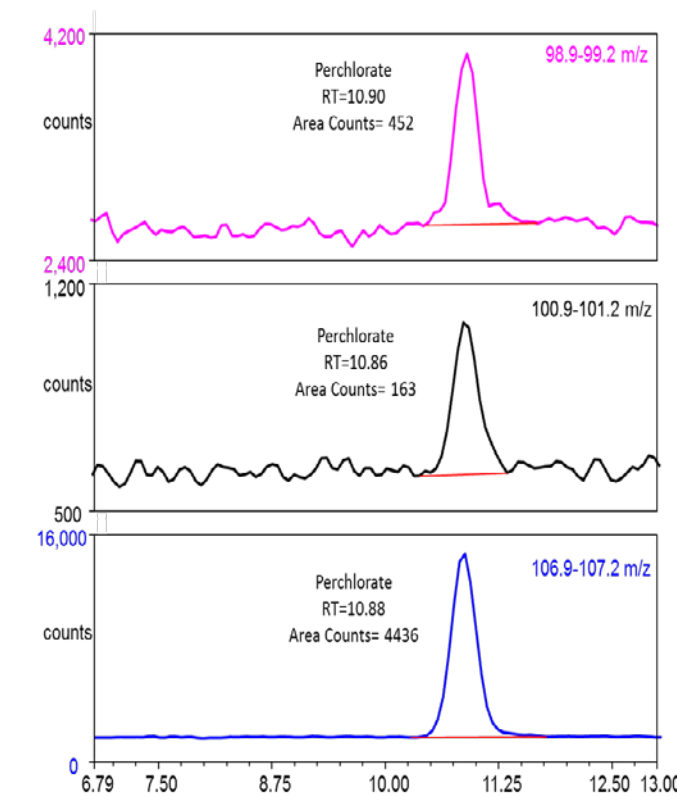


Figure 2. Mass chromatograms of a standard containing 125 ng/L perchlorate and 1.0 µg/L internal standard.

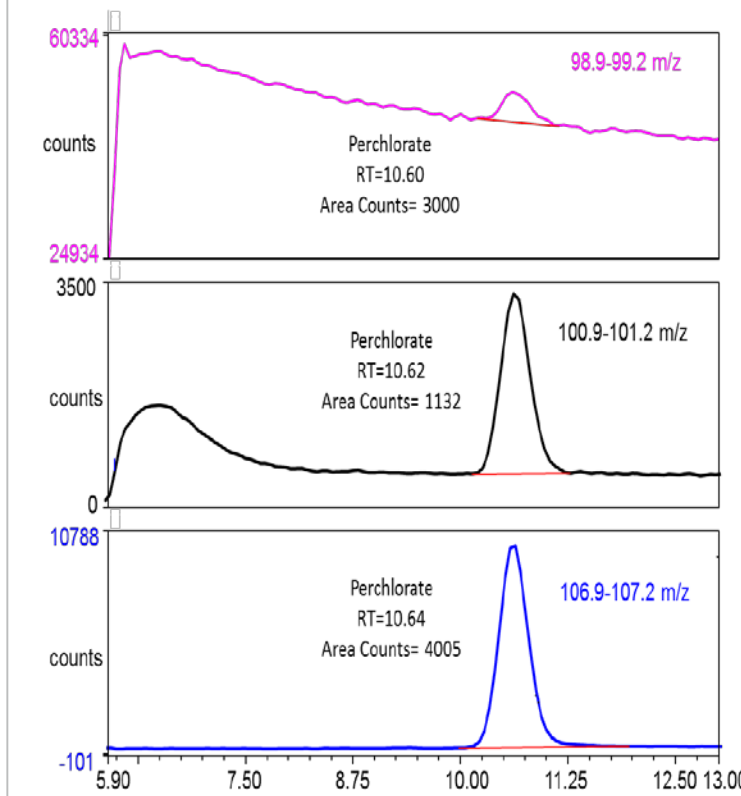


Figure 3. Mass chromatograms of an LFSSM containing 1.0 µg/L perchlorate and 1.0 µg/L internal standard.

Method Calibration and Limit of Detection

An ^{18}O -enriched perchlorate ($^{35}Cl^{18}O_4^-$) internal standard (m/z 107) is recommended to be used for quantitation to improve accuracy and ruggedness of the method in EPA Method 332. In our study, calibration curves with seven concentration levels ranging from 125 to 5000 ng/L were constructed for perchlorate in DI water and laboratory synthetic sample matrix (LSSM) using the internal standard method (Table 1).

Table 1. Method calibration and LOD for IC-MS of perchlorate.

	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	m/z 99	Internal standard	0.9994	20–60
	m/z 101	Internal standard	0.9997	30–60
Perchlorate in LSSM over the range of 400–5000 ng/L	m/z 99	Internal standard	0.9995	n.a.
Perchlorate in LSSM over the range of 125–5000 ng/L	m/z 101	Internal standard	0.9993	30–60

The calibration curves for perchlorate in the reagent water and high-ionic-strength matrix at 101 m/z over the range of 125–5000 ng/L using the internal standard method showed good linearity with the coefficients of determination being 0.9997 and 0.9993, respectively. The ISQ EC MS provides lower detection limits in high-ionic-strength matrices than conductivity detection alone. (See the details in AU72507)¹

Method Performance

Single laboratory precision in drinking waters, as measured by percent relative standard deviation (%RSD) of replicate analyses ($n=7$), was < 5% at concentrations > 150 ng/L perchlorate (Table 2). Accuracy, as measured by percent recoveries of fortified drinking water samples and external quality control samples, was 95.6–102% for concentrations > 150 ng/L perchlorate, and 111% for concentrations < 150 ng/L perchlorate (Table 3).

Table 2. Single laboratory precision in drinking waters.

Drinking water 1 (ng/L, n=7)	Mean (ng/L)	SD	RSD
635	622	20.3	3.26%
639			
651			
614			
609			
592			
615			
Drinking water 2 (ng/L, n=7)	Mean (ng/L)	SD	RSD
992	1007	36.9	3.66%
994			
1022			
1037			
976			
960			
1066			

Table 3. Single laboratory accuracy in drinking waters and external quality control samples.

Sample	Certified Concentration (ng/L)	Measured Concentration (ng/L)	Recovery (%)
Fortified Drinking Water 1	125	139	111
Fortified Drinking Water 2	1000	980	98.0
External Quality Control Sample 1	500	478	95.6
External Quality Control Sample 2	1000	1019	101.9

Single laboratory precision in fortified synthetic waters containing up to 1,000 mg/L of each of the common anions (LFSSM), as measured by %RSD of replicate analyses ($n=7$), was < 5% at concentrations > 150 ng/L perchlorate (Table 4). Accuracy, as measured by percent recovery of fortified synthetic high ionic waters containing up to 1,000 mg/L of each of the common anions (LFSSM), was 100–104% for concentrations > 150 ng/L perchlorate (Table 5).

Table 4. Single Laboratory Precision in LFSSM.

LFSSM (ng/L, n=7)	Mean (ng/L)	SD	RSD
1005	1035	24.4	2.36%
1046			
1013			
1056			
1072			
1035			
1019			

Table 5. Single Laboratory Accuracy in LFSSM.

Fortified LFSSM (ng/L)	Measured Concentration (ng/L)	Recovery (%)
200	200	100
400	400	100
800	814	102
1000	1035	104

Table 6 lists precision and recovery data for perchlorate in various drinking water and synthetic water samples at low and high fortification concentrations. Note: When it was unable to detect the m/z 99 ion in the LSSM fortified with 200 ng/L perchlorate due to the high-ionic-strength matrix, a remedial action was employed that consisted of using a Ba/Ag/H cartridge to reduce high background to a level that allows better integration of the perchlorate peak at m/z 99, and thus, better m/z 99/101 area ratios for confirmation (Figure 4).

Table 6. Precision and recovery data for perchlorate in various matrices ($n=7$).

Matrix	Background Conc. (ppt)	Fortification Conc. (ppt)	m/z 99/101 Area Ratio	Avg. Recovery (%)	RSD
Reagent Water	ND	50	3.54	87.5	19.6
		500	3.17	96.0	3.35
LSSM	ND	200	2.97 (after using Ba/Ag/H cartridge)	100	7.07
		1000	2.78	104	1.89
Tap water	ND	1000	2.85	101	3.66
Bottled water	270	200	2.96	100	3.24
		1000	3.07	98.8	2.47
Bottled water	<LCMRL	200	3.08	103	3.56
		1000	3.07	98.7	1.25

ND means "not detected"
LCMRL=125 ng/L

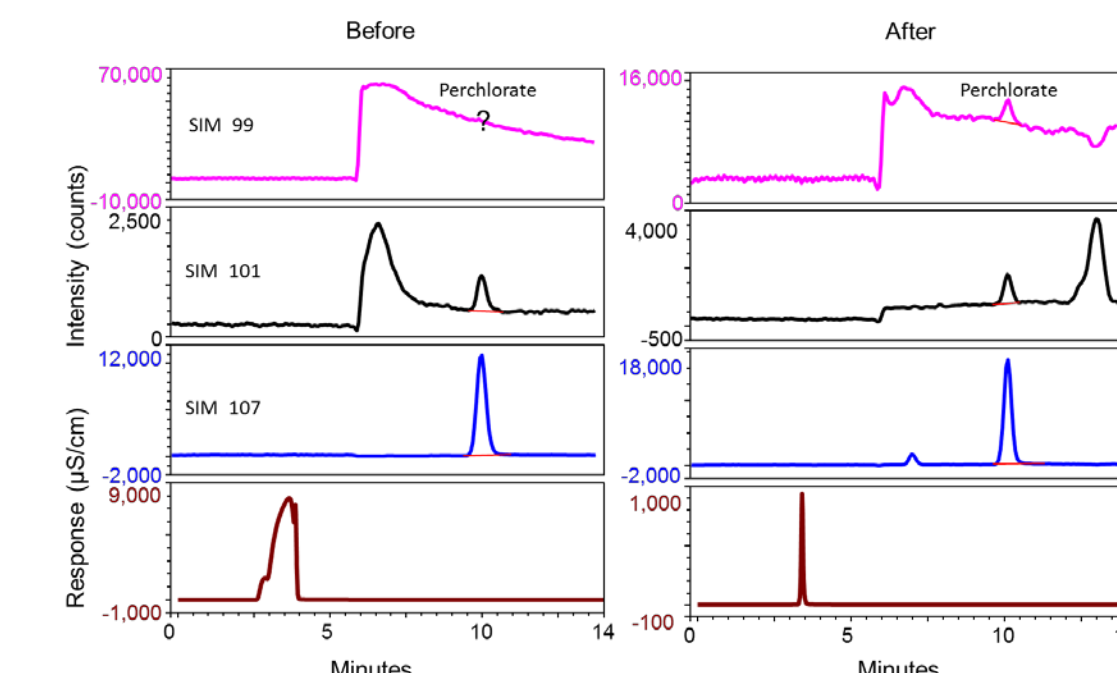


Figure 4. Conductivity and SIM chromatograms of 200 ng/L perchlorate in LSSM before and after using a Ba/Ag/H cartridge.

Note: See Thermo Scientific Application Update 72507¹ and Application Note 72587² for more details.

REFERENCES

- Thermo Scientific Application Update 72507: Determination of perchlorate in environmental waters using a compact ion chromatography system coupled with a single quadrupole mass spectrometer. Sunnyvale, CA. 2017.
- Thermo Scientific Application Note 72587: Determination of Perchlorate by U.S. EPA Method 332.0 Using a Compact Ion Chromatography System Coupled with Mass Spectrometry. Sunnyvale, CA. 2018.

TRADEMARKS/LICENSING

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