

Improved Determination of Trace Concentrations of Perchlorate in Environmental Waters Using EPA Method 314.1

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ABSTRACT

Perchlorate (ClO_4^-) is known to have serious health effects by interfering with the uptake of iodide by the thyroid gland. An increase in concerns over the perchlorate health effects at concentrations less than the current reporting limit of 4 ppb created the need for methods with lower detection limits. Currently, perchlorate is determined in drinking and ground waters using U.S. Environmental Protection Agency (EPA) Method 314.0, an ion chromatographic method with suppressed conductivity detection that provides a minimum reporting limit (MRL) of 4 ppb. However, perchlorate is often subject to interferences by matrix anions present at high concentrations that often preclude the determination of low-ppb perchlorate. In this paper, we demonstrate two methods, based on modifications to EPA Method 314.0, that significantly improve the determination of perchlorate in environmental waters. The linear range, limit of detection, and the recovery and precision of perchlorate spiked into drinking water and simulated water samples are reported.

EXPERIMENTAL

Ion Chromatography Conditions

Instrumentation: Thermo Scientific™ Dionex™ ICS-2500 Reagent-Free™ Ion Chromatography (RFIC™) System

Pump: GP50 Gradient Pump

Detector: ED50A Conductivity Detector

Chromatography

compartment: LC25 (set at 35 °C)

Eluent generator: EG50

Autosampler: AS50U

Table 1. Consumables

Consumables	Primary method	Confirmatory method
Columns	Thermo Scientific Dionex IonPac™ AG16, AS16, 2 mm	Dionex IonPac AG20, AS20, 2 mm
Eluent Generator Cartridge	Thermo Scientific Dionex IonPac Dionex EluGen™ EGC-NaOH	Dionex EluGen EGC-NaOH
Trap Column	Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column	Dionex CR-ATC Continuously Regenerated Anion Trap Column
Concentrator	Dionex IonPac Cryptand C1, 4 × 35 mm	Dionex IonPac Cryptand C1, 4 × 35 mm

PREPARATION OF STANDARDS AND SAMPLES

Perchlorate Standards

- The perchlorate stock standard was prepared according to EPA Method 314.1, Section 7.2.1.1. All calibration standards contained 100 mg/L each of chloride, sulfate, and bicarbonate to ensure that the IonPac Cryptand concentrator had sufficient capacity (from the presence of Na^+) to retain the target analyte.
- Laboratory Fortified Synthetic Sample Matrix (LFSSM) standards were prepared by adding 1000 mg/L each of chloride, sulfate, and bicarbonate (as the sodium salt) followed by the addition of 0.5 or 5 $\mu\text{g/L}$ perchlorate (Method 314.1, Section 7.5). This standard was used to monitor the integrity of the cryptand concentrator trapping efficiency throughout the analysis batch

Samples

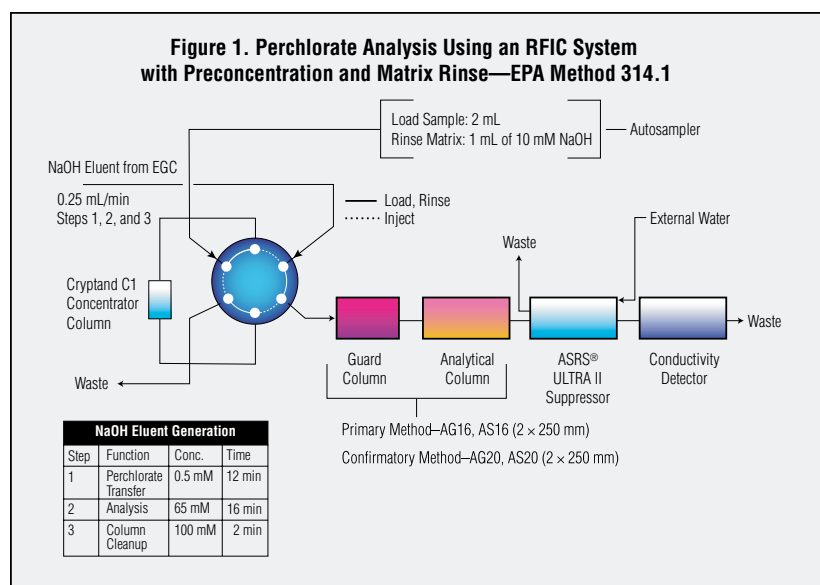
- Samples were collected according to the procedure in Section 8.1. Drinking water matrices were spiked with 0.5 or 5 $\mu\text{g/L}$ perchlorate followed by an additional 100 mg/L each of chloride, sulfate, and bicarbonate.

RESULTS AND DISCUSSION

Traditionally, laboratories that are required to analyze for perchlorate in environmental waters use the protocol described in EPA Method 314.0. This method reports a method detection limit (MDL) of 0.53 µg/L and an MRL of 4.0 µg/L perchlorate. Although modifications to Method 314.0 such as the use of a Reagent-Free IC combined with an improved suppressor, a Thermo Scientific Dionex ASRS ULTRA II, have significantly lowered the MDL for perchlorate; the determination of <4 µg/L perchlorate in high-ionic-strength matrices is still a challenging problem.

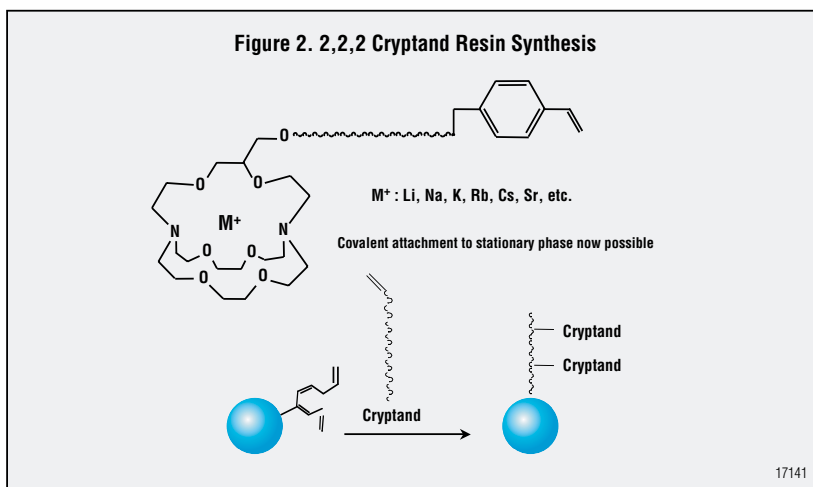
The U.S. EPA recently published Method 314.1 as an update to 314.0 to further reduce the MRL from 4.0 to 0.5 µg/L perchlorate. The method is based on the use of preconcentration/matrix diversion followed by separation using a 2 mm Dionex IonPac AS16 analytical column (primary method) or AS20 column (confirmatory method) and suppressed conductivity detection. This method significantly improves Method 314.0 by allowing the determination of perchlorate down to 0.5 µg/L in high-ionic-strength matrices, containing up to 1000 mg/L each of chloride, sulfate, and bicarbonate. Table 2 compares the analytical conditions required to perform EPA Methods 314.0 and 314.1. Figure 1 shows a schematic diagram of an RFIC system for U.S. EPA Method 314.1.

	EPA Method 314.0	EPA Method 314.1
Columns	Dionex IonPac AG16, AS16, 4 mm	Dionex IonPac AG16, AS16, 2 mm, (primary method) Dionex IonPac AG20, AS20, 2 mm, (confirmatory method)
Eluent	50 mM NaOH	0.5 mM NaOH 0–12 min, 65 mM 12.1–28 min, 100 mM 28.1–30 min
Temperature	30 C	35 C
Flow Rate	1.5 mL/min	0.25 mL/min
Sample Volume	1 mL	2 mL
Rinse Volume	—	1 mL (10 mM NaOH)
Concentrator	—	Dionex IonPac Cryptand C1, 4 × 35 mm
Detection	Suppressed conductivity, ASRS ULTRA II, 4 mm, auto-suppression, external water mode	Suppressed conductivity, ASRS ULTRA II, 2 mm, auto-suppression, external water mode



Cryptand Concentrator

In this work, a cryptand concentrator column was used to trap perchlorate in the standard or sample prior to eliminating the matrix ions with 10 mM NaOH. The cryptand concentrator is based on a cryptand stationary phase that is capable of complexing different metal ions. The capacity of the cryptand concentrator is directly proportional to the binding constant of the metal ion that occurs in the following order: $K^+ > Na^+ > Li^+$. Figure 2 shows the synthesis of a 2,2,2 cryptand monomer that is then covalently attached to a polymer based macroporous resin. Because Na^+ provides an intermediate capacity for the cryptand concentrator, a NaOH eluent was found to be ideal for this application, providing sufficient capacity and selectivity to retain perchlorate preferably over the matrix ions. Hence, removal of most interfering anions, such as chloride, sulfate, and bicarbonate, became possible with a low concentration base rinse.

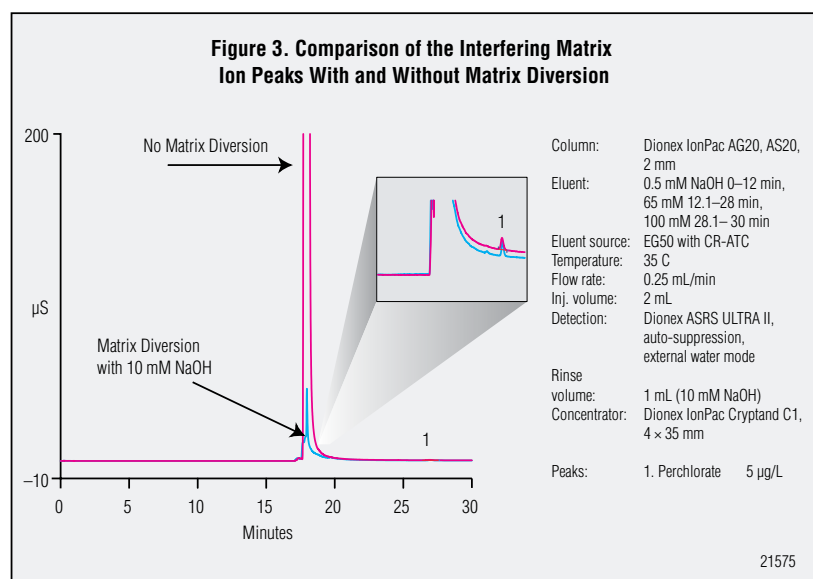


Matrix Diversion of Sample Anions

The elimination of most of the sample matrix anions is a critical step in determining sub- $\mu\text{g/L}$ perchlorate concentrations using EPA Method 314.1. The matrix ions are rinsed from the concentrator using 1 mL of 10 mM NaOH. The weak rinse solution allows the concentrator to retain the perchlorate while diverting the matrix ions to waste. Following the rinse procedure, the injection valve is switched in-line with the analytical column and the perchlorate is eluted from the concentrator column and refocused at the head of the guard column using a low concentration of an electrolytically generated NaOH eluent. Figure 3 demonstrates that $>90\%$ of the matrix ions are eliminated using this procedure.

In addition, this method uses the Dionex IonPac AS20 as a confirmation column that has a separation mechanism that is different from the AS16 column (primary column) to allow confirmation of the presence of perchlorate in the matrix.

The Dionex IonPac AS16 uses a low cross-linked vinyl aromatic quaternary monomer whereas the column chemistry of the AS20 is based on a cross-linked quaternary condensation polymer that is free of any pi electron containing substituents. Therefore, the retention of aromatic species with the Dionex IonPac AS20 column is reduced relative to the AS16. For example, *p*-chlorobenzenesulfonic acid is well resolved from perchlorate on the Dionex IonPac AS20 column, but co-elutes with perchlorate on the AS16 column.



LINEARITY AND METHOD DETECTION LIMITS

The system was calibrated by injecting a blank and six calibration standards to cover the perchlorate concentrations of interest. Although, the determination of the MDLs is not required by the method, according to Section 9.2.7, we determined the MDLs because this may be required by some regulatory bodies for compliance monitoring. The MDLs were determined by performing seven replicate injections of DI water containing 100 mg/L each of chloride, sulfate, and bicarbonate and fortified with 0.06 µg/L perchlorate. Table 3 summarizes the linearity, MDLs, and the retention time and peak area precisions for seven replicate injections of a perchlorate standard prepared at 0.5 µg/L.

Analyte ^a	Range (g/L)	Linearity ^b (r ²)	MDL ^c (g/L)	Standard Deviation of MDL (g/L)	Retention Time Precision (%RSD ^d)	Peak Area Precision (%RSD)
A) Perchlorate	0.3–10	0.9990	0.022	0.007	0.07	4.20
B) Perchlorate	0.3–10	0.9996	0.020	0.006	0.03	6.66

^aDesignations (A) and (B) refers to the primary method (AS16 column) and confirmatory method (AS20 column), respectively

^bQuadratic fit

^cMDL = $\alpha \sigma_{S,99}$ where $\alpha_{S,99} = 3.14$ for $n = 7$ using a concentration of 0.06 µg/L as the MDL standard

^dRSD = relative standard deviation, $n = 7$ for 0.5 µg/L perchlorate standard

ACCURACY AND PRECISION

All samples were analyzed in batches with each batch consisting of a laboratory synthetic sample matrix blank (LSSMB), a laboratory fortified synthetic sample matrix (LFSSM), lowlevel initial calibration check standard (ICCS), mid-level continuing calibration check standard (CCCS), and a high-level end calibration check standard (ECCS). The ICCS, CCCS, and ECCS contained 0.5, 5.0, and 10.0 µg/L perchlorate, respectively. All samples were spiked with 0.5 or 5.0 µg/L perchlorate. The first, second, and third sample batches included the LFSSM samples, Sunnyvale drinking water, and Cincinnati ground water, respectively.

Simulated Samples

– The LSSMB and LFSSM were prepared in 1000 mg/L each of chloride, sulfate, and bicarbonate and were filtered through a 0.20 µm filter.

Drinking Water Samples

– Sunnyvale, CA drinking water and Cincinnati, OH ground water samples were analyzed for perchlorate in this study. The Sunnyvale and Cincinnati water samples were filtered through a 0.20 µm filter.

Figure 4. Separation of 0.5 µg/L Perchlorate Standard Using the Confirmatory Method

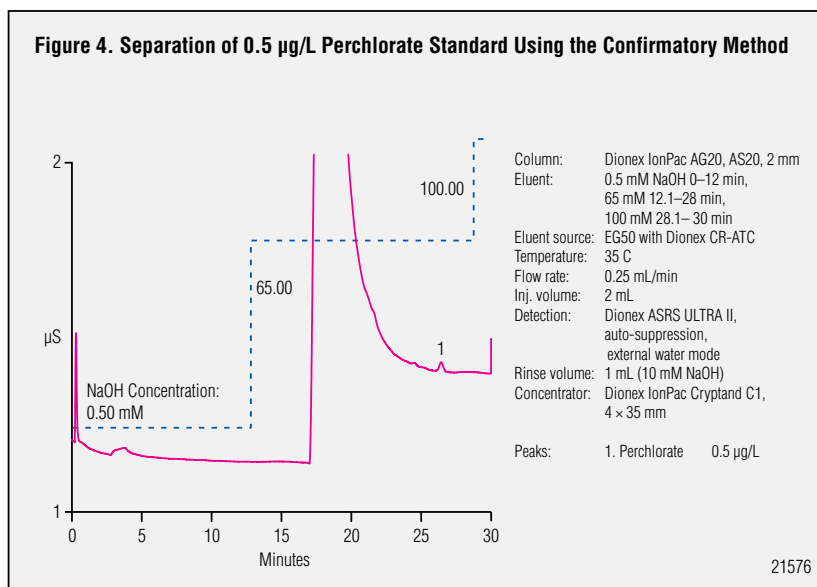


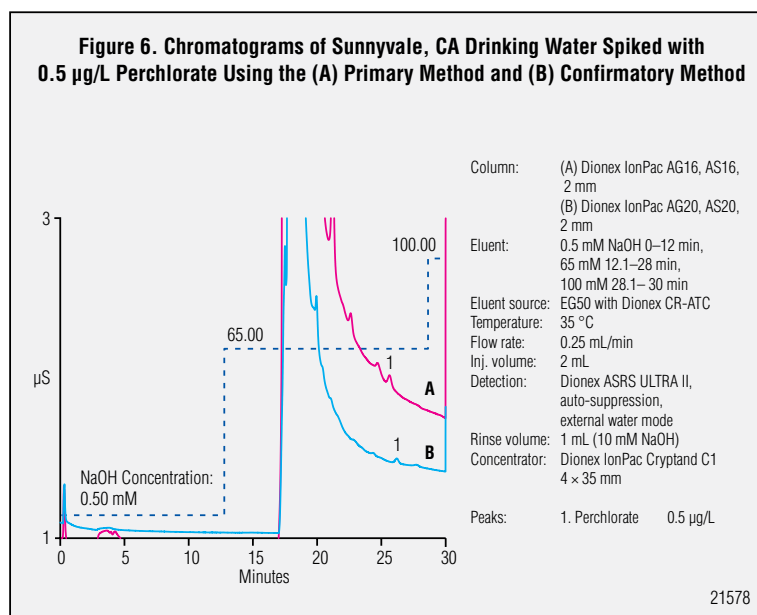
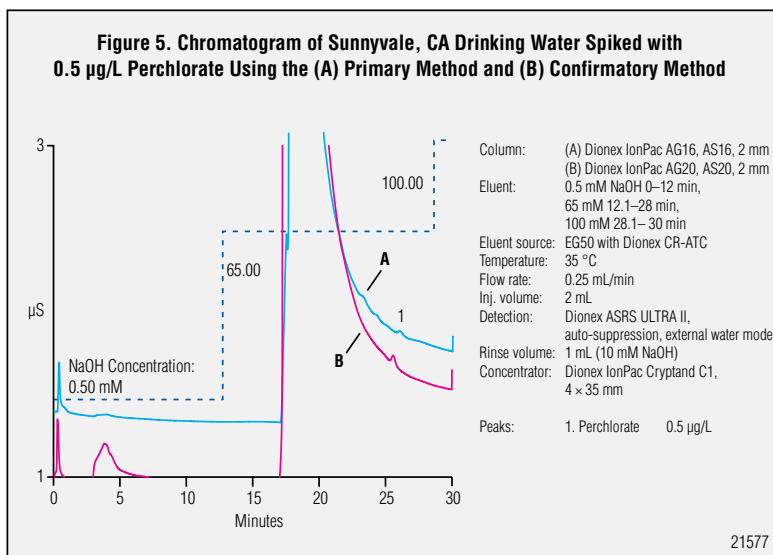
Table 4. Accuracy and Precision of Perchlorate Spiked in Simulated and Real Drinking Water Samples Using the Primary and Confirmatory Methods of U.S. EPA Method 314.1

Matrix	Spiked Perchlorate (µg/L)	# Replicates	Average Recovery (%)		Peak Area Precision (%RSD)	
			A ^a	B ^a	A	B
LFSSM	0.5	7	103	97.4	0.91	5.70
	5.0	7	103	86.3	0.56	1.34
Sunnyvale Drinking Water	0.5	7	117	108	5.60	2.80
	5.0	7	97.4	97.8	1.58	2.14
Cincinnati Drinking Water	0.5	7	93.6	96.2	5.90	11.2
	5.0	7	96.9	98.0	1.54	0.75

^aDesignations (A) and (B) refers to the primary method (AS16 column) and confirmatory method (AS20 column), respectively

CONCLUSION

- A preconcentration/matrix diversion method was validated using updated EPA Method 314.1 for trace concentrations of perchlorate by Reagent-Free ion chromatography.
- The use of the Dionex IonPac Cryptand concentrator column was found to be an effective procedure for quantitatively trapping perchlorate spiked in simulated and real drinking water samples in the presence of common matrix anions, such as chloride, sulfate, and bicarbonate.
- A method detection limit of 0.02 µg/L perchlorate and precision of <12% was determined using the primary and confirmatory methods of EPA Method 314.1.
- The average recoveries for 0.5 and 5.0 µg/L perchlorate fortified in the LFSSM (1000 mg/L each of chloride, sulfate, and bicarbonate) and in real drinking water samples were within 94–117% and 86–98%, respectively.
- A confirmatory column for perchlorate, the Dionex IonPac AS20, was found to produce similar results to the AS16 column, making it an ideal column for confirming the presence of perchlorate in environmental waters.



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