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An Improved Ion Chromatographic Method for the Determination of Trace Level Perchlorate in Drinking Water and Ground Water

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Introduction

Ammonium perchlorate is a key ingredient in solid rocket propellants; and perchlorate has recently been found in drinking water wells in regions of the U.S. where aerospace material, munitions and fireworks were developed, tested, or manufactured. To date, perchlorate has been found in ground and surface waters in states such as California, Nevada, Utah and West Virgina, however the total extent of the contamination problem in the U.S. is not known [1]. The locations where perchlorate concentrations in ground water are high can be predicted based on historic or current use of the surrounding land. When contamination occurs, it is widespread in a given area because of the high mobility of perchlorate [2].

Perchlorate poses a human health concern as it can interfere with the thyroid gland's ability to utilize iodine to produce thyroid hormones. Initial data from the U.S. EPA reported an exposure range of 4 - 18 µg/L (ppb) to provide adequate health protection [2]. Although perchlorate is not currently regulated under the Federal Safe Drinking Water Act, the California Department of Health Services (CDHS) has adopted an action level for perchlorate in drinking water of 18 µg/L [2]. The CDHS recommends that utilities remove drinking water sources from service that contain concentrations of perchlorate above the 18 µg/L action level.

The determination of perchlorate at trace levels is a difficult analytical task; and ion chromatography (IC) represents perhaps the only viable means for the quantification of such low concentrations of perchlorate. Large, polarizable anions, such as perchlorate, are strongly retained and often display poor peak shape on conventional anion exchange columns [3]. Consequently, the analysis of perchlorate is typically performed using an hydrophilic column (e.g. Dionex IonPac® AS5) with an organic modifier, such as methanol or p-cyanophenol, added to the mobile phase to minimize adsorption and improve peak shape [4].

This paper reports on a new method developed specifically for the determination of low level perchlorate in drinking water and ground waters using ion chromatography. This method uses a large loop injection with a Dionex IonPac AS 11 column, hydroxide eluent and suppressed conductivity detection to quantify perchlorate at levels as low as 2.5 µg/L in drinking water samples. The method is linear over the range of 2.5- 100 µg/L and quantitative recoveries were obtained for perchlorate in spiked tap water samples. Also, the applicability of a new polarizable anion analysis column, the IonPac AS 16, for the determination of low level perchlorate will be presented.

Experimental

Instrumentation and Conditions

A DX-500 ion chromatography (Dionex Corporation, Sunnyvale, CA) was used for this work. The system was configured with a GP40 Gradient Pump, CD20 Conductivity Detector, AS40 Automated Sampler and an LC20 Chromatography Enclosure with rear loading injection valve. Separations were carried using Dionex IonPac AS 11 and AS 16 (250 x 4.0 mm) analytical columns and IonPac AG11 and AG16 (50 x 4.0 mm) guard columns. Anions were detected by suppressed conductivity detection using an Anion Self-Regenerating Suppressor, ASRS®-ULTRA (4 mm) with AutoSuppression® at 300 mA in the external water mode.

Materials

All water used was deionized water, Type I reagent grade, 18 MΩ-cm resistance or better. Sodium hydroxide, 50% w/w aqueous solution was obtained from Fisher Scientific (Pittsburgh, PA). Sodium perchlorate, 99% ACS reagent grade was obtained from Aldrich (Milwaukee, WI). ACS reagent grade standards were used for the preparation of the standards for the interference and recovery studies, with the exception of humic acid and selenate standards, which were prepared from technical grade reagents.

Preparation of Solutions and Reagents

Perchlorate stock standard was prepared by dissolving 1.231 grams of sodium perchlorate in 1.000 L of deionized water to prepare a 1000 mg/L standard. This standard was stable for at least one month when stored at 4°C. Working standards were prepared daily by diluting the 1000 mg/L standard solution with deionized water as required. The 100 mM sodium hydroxide eluent for the AS 11 separation was prepared by weighing 992.0 g of deionized water into a 1.0 liter polypropylene eluent bottle. The water was then degased for five minutes, after which 8.000 g of 50% sodium hydroxide was carefully added directly to the eluent bottle. The solution was mixed and the bottle quickly transferred to the instrument and pressurized with helium (8 psi). Such precautions are necessary when preparing hydroxide eluents in order to avoid carbonate contamination.

Results and Discussions

In order to quantify perchlorate at low µg/L levels, it was essential to optimize chromatographic conditions in terms of retention time, peak shape and baseline noise. The IonPac AS 11 column is packed with highly cross-linked microporous resin coated with an aminated, hydrophilic latex layer. The use of this column with an eluent of 100 mM sodium hydroxide permits the elution of perchlorate in less than 10 minutes without the need for organic modifiers in the mobile phase, unlike the IonPac AS5 column used in the CDHS

method [4]. The perchlorate anion displays excellent peak shape and is well resolved from common inorganic anions, which essentially elute at the void volume under these conditions.

In order to minimize baseline noise, it was necessary to operate the ASRS at 300 mA in the external water mode. Also, a large loop injection (1000 µL) was used in order to achieve sub-ppb detection limits for perchlorate. Figure 1 shows a typical chromatogram of a 20 µg/L perchlorate standard obtained using the optimized conditions described above.

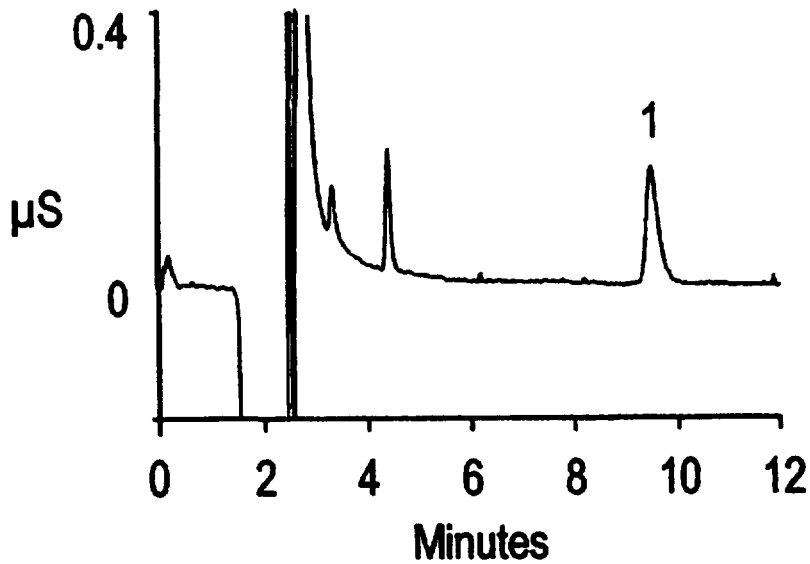

Figure 1. Perchlorate standard at 20 µg/L. Conditions: guard column, Dionex IonPac AG11; analytical column, Dionex IonPac AS 11; eluent, 100 mM sodium hydroxide; flow-rate, 1.0 mL/min; detection, suppressed conductivity; injection volume, 1000 pL; peak 1- perchlorate.

A linearity study was performed to ensure accurate quantification of perchlorate in the low µg/L range. A correlation coefficient of 0.9996 was obtained for a plot of peak area *versus* concentration, as shown in Figure 2, demonstrating that calibration is linear in the 2 - 100 µg/L range required for the quantification of perchlorate in drinking water and ground waters. The method detection limit (MDL) was determined using the procedure outlined in U.S. EPA Method 300.0 [5]. Seven replicates of a 2.5 µg/L perchlorate standard were injected and the MDL was calculated as follows:

$$MDL = (t) \times (S)$$

where, t = Students t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]; and S = standard deviation of the replicate analysis. The MDL for perchlorate was calculated to be 0.25 µg/L according to this

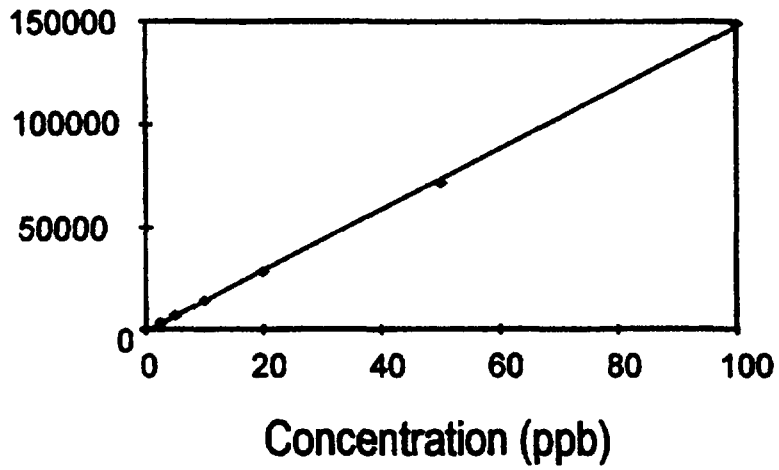

Figure 2. Perchlorate calibration curve. Conditions as for Figure 1.

procedure. The peak area precision was 2.4% RSD for the seven replicate injections with a retention time precision of 0.5% RSD for the same injections.

Despite the use of a large loop injection, no evidence of column overloading was observed when injecting samples. Figure 3 shows a chromatogram of Sunnyvale, CA, tap water spiked with 2.5 µg/L perchlorate.

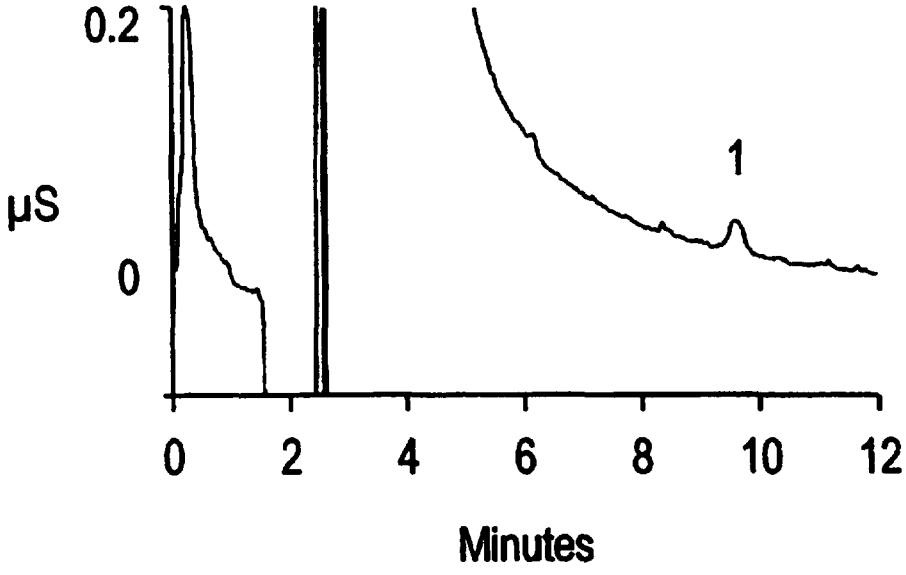

Figure 3. Sunnyvale, CA, tapwater spiked with 2.5 µg/L perchlorate. Conditions as for Figure 1; peak 1- perchlorate.

The method was tested for interferences by injecting 20 µg/L perchlorate in the presence of 100 µg/L solutions of the 22 anions shown below in Table I. This table shows that only cyanide, iodide, and thiocyanate display any significant retention under these elution conditions. Perchlorate is resolved by three minutes from the nearest eluting anion, thiocyanate, which would not be typically found at high levels in drinking or ground waters.

Table I. Comparison of the retention times of 22 common anions and perchlorate with the Dionex IonPac AS 11 column.

Anion	Anion Retention Time (minutes)	Perchlorate Retention Time (minutes)
Arsenate	<4	9.27
Arsenite	<4	9.27
Bromate	<4	9.2
Bromide	<4	9.22
Carbonate	<4	9.18
Chlorate	<4	9.13
Chloride	<4	9.12
Chromate	<4	9.08
Cyanide	4.38	9.08
Humic acid	<4	9.08
Iodate	<4	9.05
Iodide	4.38	9.07
Molybdate	<4	9.07
Nitrate	<4	9.07
Nitrite	<4	9.05
Phosphate	<4	9.07
Phthalate	<4	9.05
Selenate	<4	9.07
Sulfate	<4	9.07
Sulfite	<4	9.08
Thiocyanate	6.27	9.07
Thiosulfate	<4	9.05

The effect of mg/L levels of common anions on perchlorate recovery was investigated by injecting solutions of 20 µg/L perchlorate in the presence of 50, 200, 600 and 1000 ppm chloride, carbonate and sulfate, respectively. Quantitative recoveries were obtained for perchlorate in all cases, as shown in Table H, demonstrating that high mg/L levels of common anions have no significant effect on the recovery of low µg/L levels of perchlorate. Figure 4 shows chromatograms of 20 µg/L perchlorate in the presence of 50 - 1000 mg/L sulfate. No significant effect on the perchlorate peak shape is observed at high mg/L sulfate levels.

Table II. Effect of mg/L levels of common anions on perchlorate recovery with the Dionex IonPac AS 11 column.

Common Anion	Concentration (mg/L)	Perchlorate Recovery (%)
Carbonate	50	96.6
Carbonate	200	98.8
Carbonate	600	92.1
Carbonate	1000	94.2
Chloride	50	92.2
Chloride	200	99.2
Chloride	600	98.7
Chloride	1000	97.4
Sulfate	50	94.4
Sulfate	200	100.0
Sulfate	600	93.4
Sulfate	1000	97.4

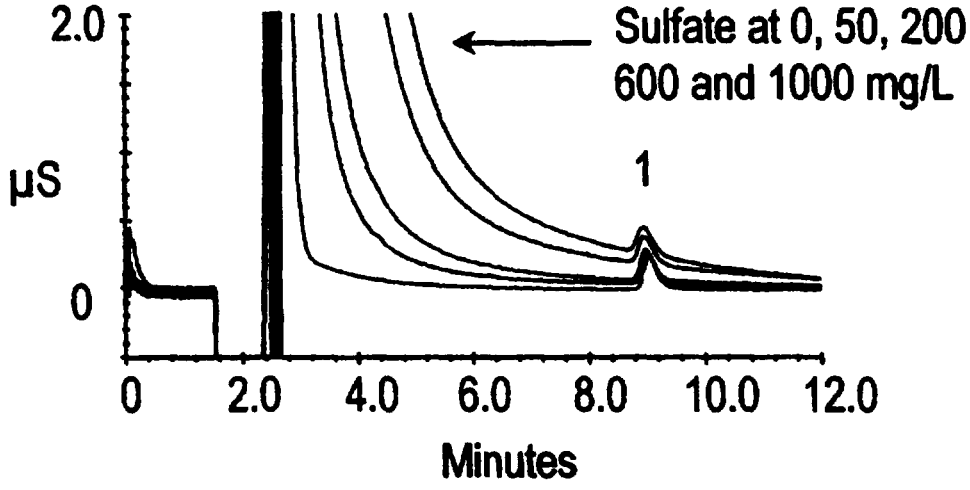

Figure 4. Effect of sulfate on perchlorate recovery. Conditions as for Figure 1; peak 1-perchlorate.

Dionex is currently developing a new column for the analysis of polarizable anions. The high capacity Ion Pac AS 16 column will allow the injection of even higher ionic strength samples and also provide improved peak efficiency compared to the AS 11 column. Figure 5 shows the application of the new AS 16 column for the analysis of low level perchlorate in a high ionic strength ground water sample.

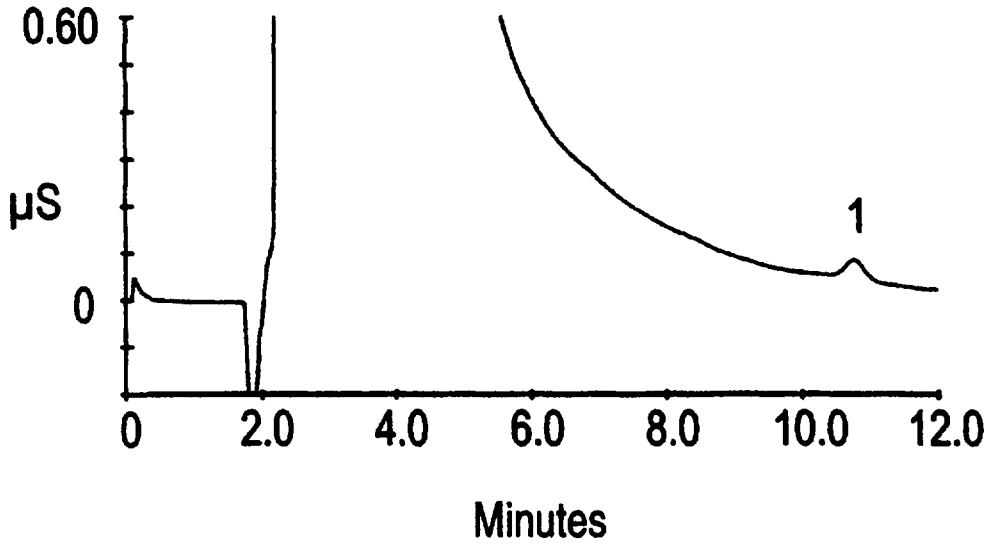

Figure 5. Perchlorate in high ionic strength ground water. Conditions: guard column, Dionex IonPac AG16; analytical column, Dionex IonPac AS 16; eluent, 50 mM sodium hydroxide; flow-rate, 1.5 mL/min; detection, suppressed conductivity; injection volume, 1000 µL; peak 1-perchlorate at 5 µg/L; sample matrix contains - chloride, 200 mg/L; nitrate, 50 mg/L, carbonate, 200 mg/L, and sulfate 1000 mg/L.

Conclusion

The use of ion chromatography with an IonPac AS 11 column, hydroxide eluent, a large loop injection and suppressed conductivity detection provides a simple, interference free method for the determination of perchlorate at low µg/L levels in drinking water and ground waters. The method is linear over the range of 2.5 - 100 µg/L perchlorate and quantitative recoveries were obtained for spiked tap water samples. The single operator MDL of 0.25 µg/L permits quantification of perchlorate below the levels which ensure adequate health protection (4 -18 µg/L), as recommended by the U.S. EPA.

References

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