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Journal of Chromatography A, 850 (1999) 131–135

JOURNAL OF
CHROMATOGRAPHY A

Determination of trace level perchlorate in drinking water and ground water by ion chromatography

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Abstract

Ammonium perchlorate, a key ingredient in solid rocket propellants, has recently been found in ground and surface waters in the USA in a number of states, including California, Nevada, Utah, and West Virginia. Perchlorate poses a health risk and preliminary data from the US Environmental Protection Agency reports that exposure to less than 4–18 $\mu\text{g}/\text{l}$ provides adequate human health protection. An ion chromatographic method was developed for the determination of low $\mu\text{g}/\text{l}$ levels of perchlorate in drinking and ground waters based on a Dionex IonPac AS11 column, a 100 mM hydroxide eluent, large loop (1000 μl) injection, and suppressed conductivity detection. The method is free of interferences from common anions, linear in the range of 2.5–100 $\mu\text{g}/\text{l}$, and quantitative recoveries were obtained for low $\mu\text{g}/\text{l}$ levels of perchlorate in spiked drinking and ground water samples. The method detection limit of 0.3 $\mu\text{g}/\text{l}$ permits quantification of perchlorate below the levels which ensure adequate health protection. A new polarizable anion analysis column, the IonPac AS16, and its potential applicability for this analysis is also discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Perchlorate; Inorganic anions

1. Introduction

Ammonium perchlorate, a key ingredient in solid rocket propellants, has recently been found in ground waters in regions of the USA where aerospace materials, munitions, and fireworks were developed, tested, or manufactured. To date, perchlorate has been found in ground and surface waters in California, Nevada, Utah, Texas, New York, Maryland, Arkansas, and West Virginia; although the total extent of the problem in the USA is not known [1,2]. The locations where perchlorate concentrations in ground water are high can be predicted based on historic or current use of the surrounding land. However, when contamination occurs, it is typically

widespread in a given area because of the high mobility of perchlorate [3].

The presence of perchlorate poses a considerable human health risk, even at trace levels, as it can interfere with the thyroid gland's ability to produce thyroid hormones. Preliminary data from the US Environmental Protection Agency (EPA) indicates that exposure to less than 4–18 $\mu\text{g}/\text{l}$ perchlorate provides adequate health protection [3]. The provisional reference dose (RfD) range of 4–18 $\mu\text{g}/\text{l}$ results from the use of different uncertainty factors applied to the same human data, although the EPA is currently gathering more toxicological data and intends to publish a definitive RfD for perchlorate in the near future [4].

Perchlorate contamination of public drinking water wells has recently become a serious problem in California. While perchlorate is listed on the EPA

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Contaminant Candidate List as a research priority, it is not currently regulated under the Federal Safe Drinking Water Act [5]. However, the California Department of Health Services (CDHS) has now adopted an action level for perchlorate in drinking water of 18 $\mu\text{g}/\text{l}$. The CDHS recommends that utilities remove drinking water sources that contain concentrations of perchlorate above the 18 $\mu\text{g}/\text{l}$ action level from service. To date, perchlorate has been detected in over 100 public drinking water wells in California, with more than 20 wells being closed due to contamination [3].

The determination of trace perchlorate is a difficult analytical task and ion chromatography (IC) is perhaps the only viable means for the quantification of such low levels of perchlorate. Large, polarizable anions, such as perchlorate, are strongly retained on conventional anion-exchange columns and often display poor peak shape [6]. Consequently, the analysis of perchlorate is typically performed using an hydrophilic column with an organic modifier, such as methanol or *p*-cyanophenol, added to the mobile phase to minimize adsorption and improve peak shape [7].

This article reports on a new method developed for the determination of trace level perchlorate in drinking water and ground waters using IC. This method uses a large loop injection with a Dionex IonPac AS11 column, hydroxide eluent, and suppressed conductivity detection to quantify perchlorate below 2.5 $\mu\text{g}/\text{l}$. The method detection limit (MDL), linear concentration range, and potential method interferences are discussed. Also, the applicability of a new polarizable anion analysis column, the IonPac AS16, for the determination of low level perchlorate is presented.

2. Experimental

2.1. Instrumentation

The ion chromatograph used for this work was a Dionex (Sunnyvale, CA, USA) DX-500 IC System consisting of a GP40 gradient pump, AS40 automated sampler, CD20 conductivity detector, and LC20 chromatography enclosure equipped with a with rear loading injection valve. Separations were

carried out using a Dionex IonPac AS11 (250 \times 4.0 mm) analytical column and an IonPac AG11 (50 \times 4.0 mm) guard column. The experimental conditions for the IC were as follows: sample loop, 1000 μl ; flow-rate, 1.0 ml/min; eluent, 100 mM NaOH. Anions were detected by suppressed conductivity detection; suppression was achieved using a Dionex ASRS-ULTRA, operated at 300 mA in the external water mode.

2.2. Reagents and procedures

All solutions were prepared from ACS reagent-grade chemicals (where possible) in 18 M Ω water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO, USA). Sodium hydroxide, 50% (w/w) aqueous solution, was obtained from Fisher (Pittsburgh, PA, USA). Sodium perchlorate standard, 99% ACS reagent-grade, was obtained from Aldrich (Milwaukee, WI, USA). ACS reagent-grade sodium salts, obtained from Fisher, Aldrich, Sigma (St. Louis, MO, USA), EM Science (Gibbstown, NJ, USA) and Fluka (Ronkonkoma, NY, USA), were used for the preparation of solutions for the interference study; with the exception of technical-grade humic acid from Aldrich and ACS reagent-grade potassium cyanide from Sigma.

The 100 mM sodium hydroxide eluent was prepared by weighing 992.0 g of deionized water into a 1.0 l polypropylene eluent bottle. The water was then degassed for 5 min, after which 8.00 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 p.s.i./0.055 MPa). Such precautions proved to be necessary when preparing the hydroxide eluents in order to avoid carbonate contamination [8].

3. Results and discussions

In order to quantify perchlorate at low $\mu\text{g}/\text{l}$ levels, it was necessary to optimize chromatographic conditions in terms of retention time, peak shape, and baseline noise. The IonPac AS11 column used for this work is packed with highly crosslinked microporous resin coated with an aminated, hydrophilic

latex layer. The use of this very hydrophilic column with an eluent of 100 mM sodium hydroxide permits the elution of the perchlorate ion within 10 min without the need for organic modifiers in the mobile phase [9]. Even a relatively hydrophilic column, such as the IonPac AS5, requires the addition of 2 mM *p*-cyanophenol to an eluent of 120 mM sodium hydroxide in order to achieve a similar retention time for perchlorate [7]. It was found that eliminating the use of organic modifiers when using the AS11 column resulted in lower background conductance after suppression and improved detection limits for this application. The perchlorate anion displays excellent peak shape on the AS11 column and is well resolved from common inorganic anions under these conditions.

In order to maximize sensitivity for this application, it was necessary to operate the ASRS at 300 mA in the external water mode. Also, a large loop injection (1000 μ l) was used to achieve sub- μ g/l detection limits for perchlorate. Fig. 1 shows a typical chromatogram of a 20 μ g/l perchlorate standard obtained with the optimized conditions described above. A linearity study was performed to ensure accurate quantification of perchlorate in the low μ g/l range. A correlation coefficient of 0.9996 was obtained for a plot of peak area versus concentration, demonstrating that calibration is linear in the 2.5–100 μ g/l range required for the determination of perchlorate in drinking water. The MDL was determined using the procedure outlined in EPA

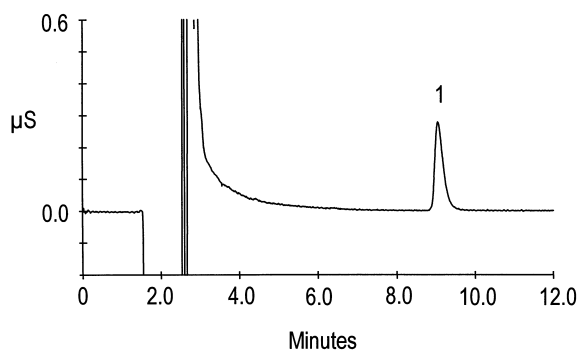


Fig. 1. Perchlorate standard at 20 μ g/l. Conditions: guard column, Dionex IonPac AG11; analytical column, Dionex IonPac AS11; eluent, 100 mM sodium hydroxide; flow-rate, 1.0 ml/min; detection, suppressed conductivity; injection volume, 1000 μ l; peak, 1=perchlorate (20 μ g/l).

Method 300.0 [10]. Seven replicates of a 2.5 μ g/l perchlorate standard were injected and the MDL was calculated as follows:

$$\text{MDL} = tS$$

where t =Student's 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 0.3 μ g/l according to this 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 drinking water samples. Fig. 2 shows a chromatogram of Sunnyvale (CA, USA) tap water spiked with 6.0 μ g/l perchlorate. The method was tested for interferences by injecting 100 μ g/l solutions of the 22 solutes listed in Table 1. These data show that only cyanide, iodide, and thiocyanate exhibited any significant retention under these elution conditions. Perchlorate is resolved by 3 min from the nearest eluting anion, thiocyanate, which would not be typically found at high levels in drinking waters.

Ground water samples may contain high concentrations of common anions, particularly chloride, carbonate, and sulfate. The effect of mg/l levels of these common anions on perchlorate recovery was investigated by injecting solutions of 20 μ g/l perchlorate in the presence of 50, 200, 600, and 1000

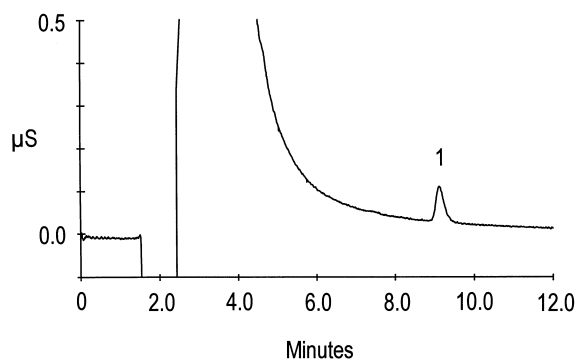


Fig. 2. Sunnyvale tap water spiked with 6.0 μ g/l perchlorate. Conditions: as for Fig. 1; peak, 1=perchlorate (5.9 μ g/l).

Table 1
Comparison of the retention times of 22 anions and perchlorate on the IonPac AS11 column

Anion	Anion retention time (min)	Perchlorate retention time (min)
Arsenate	<4	9.27
Arsenite	<4	9.27
Bromate	<4	9.20
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

Table 2
Effect of ppm levels of common anions on perchlorate recovery (20 $\mu\text{g}/\text{l}$) on the IonPac AS11 column

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

mg/l of chloride, carbonate, or sulfate. Fig. 3 shows an overlay of chromatograms of 20 $\mu\text{g}/\text{l}$ perchlorate in the presence of 50–1000 mg/l sulfate. Similar plots were obtained for perchlorate in the presence of 50–1000 mg/l chloride or carbonate. Quantitative recoveries were obtained for perchlorate in all cases, as shown in Table 2, demonstrating that high mg/l

levels of common anions do not significantly affect the recovery of perchlorate at low $\mu\text{g}/\text{l}$ levels.

Dionex is currently developing a new column for the simultaneous analysis of polarizable anions, such as iodide, thiosulfate, thiocyanate, and perchlorate. The IonPac AS16 is more hydrophilic than the AS11 column and has a higher capacity, 170 $\mu\text{equiv.}/\text{column}$ compared to 45 $\mu\text{equiv.}/\text{column}$ for the AS11 column. Hence, the AS16 column should allow the injection of even higher ionic strength samples and also provide improved peak efficiency compared to the AS11 column. Fig. 4 shows the application of the new AS16 column for the analysis of low level perchlorate in a high ionic strength ground water sample. A complete evaluation of the

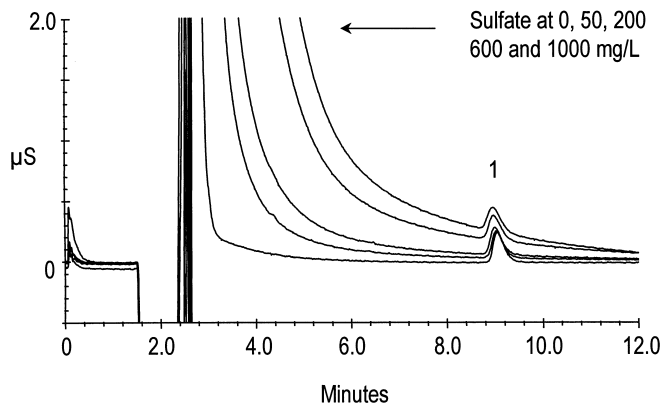


Fig. 3. Perchlorate (20 $\mu\text{g}/\text{l}$) in the presence of 0, 50, 200, 600 and 1000 mg/l of sulfate. Conditions: as for Fig. 1; peak, 1=perchlorate (20 $\mu\text{g}/\text{l}$).

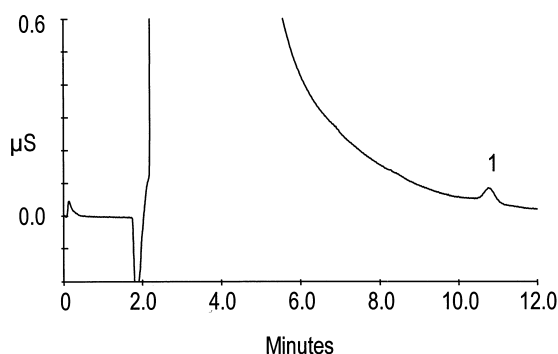


Fig. 4. Ground water spiked with 5 $\mu\text{g/l}$ perchlorate. Conditions: guard column, Dionex IonPac AG16; analytical column, Dionex IonPac AS16; eluent, 50 mM sodium hydroxide; flow-rate, 1.5 ml/min; detection, suppressed conductivity; injection volume, 1000 μl ; sample, synthetic ground water containing 200 mg/l chloride, 50 mg/l nitrate, 200 mg/l carbonate, 1000 mg/l sulfate; peak, 1 = perchlorate (5 $\mu\text{g/l}$).

use of the AS16 column for the analysis trace level perchlorate in a variety of sample matrices is currently underway, and the results will be the subject of a future publication.

4. Conclusions

The use of IC with an IonPac AS11 column, hydroxide eluent, large loop injection and suppressed conductivity detection provides a simple, interference-free method for determining perchlorate at low $\mu\text{g/l}$ levels in drinking and ground waters. The method is linear over the range of 2.5–100 $\mu\text{g/l}$ perchlorate and quantitative recoveries were obtained for low $\mu\text{g/l}$ levels of perchlorate in spiked drinking and ground water samples. The MDL of 0.3 $\mu\text{g/l}$

permits quantification of perchlorate below the levels that ensure adequate health protection, as recommended by the EPA.

Acknowledgements

The authors wish to thank N. Avdalovic, C.A. Pohl and C. Saini of Dionex for their assistance.

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