Anal. Chem. **2000,** *72,* 25−29

Determination of Perchlorate at Trace Levels in Drinking Water by Ion-Pair Extraction with Electrospray Ionization Mass Spectrometry

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Perchlorate has been added to the U.S. Environmental Protection Agency's Drinking Water Contaminant Candidate List (CCL). The present work describes the analysis of perchlorate in water by liquid−liquid extraction followed by flow injection electrospray mass spectrometry (ESI/MS). Cationic surfactants, mostly alkyltrimethylammonium salts, are used to ion-pair aqueous perchlorate, forming extractable ion pairs. The cationic surfactant associates with the perchlorate ion to form a complex detectable by ESI/MS. The selectivity of the extraction and the mass spectrometric detection increases confidence in the identification of perchlorate. The method detection limit for perchlorate based on $3.14\sigma_{n-1}$ of seven replicate injections was 100 ng L^{-1} (parts per trillion). Standard addition was used to quantitate perchlorate in a drinking water sample from a contaminated source, and the concentration determined agreed within experimental error with the concentration determined by ion chromatography.

Perchlorate is an environmental contaminant usually associated with the storage, manufacture, and testing of solid rocket motors which use ammonium perchlorate as an oxidizer.[1,2] One source of perchlorate contamination is the removal and recovery of propellant from solid rocket motors, which can result in wastewater that contains ammonium perchlorate. Another source of contamination is the frequent replacement of old stocks of ammonium perchlorate after its limited useful lifetime for rocket motor usage. Perchlorate infiltrates the watershed through a variety of mechanisms, such as leaching and groundwater recharge. This infiltration threatens the water supplies of several regions, such as the southwestern United States.[1,2] Potential health effects are associated with perchlorate, namely that perchlorate can interfere with the ability of the thyroid gland to produce thyroid hormones.[1,2] Therefore, perchlorate has been added to the U.S. Environmental Protection Agency's Candidate Contaminant List (CCL),[3,4] which is the list from which future regulated drinking water compounds will be selected. For a candidate to be selected for regulation, several requirements must be met. Namely, the contaminant must have sufficient data documenting adverse health effects, it must occur over a sufficiently wide area to qualify for federal interest, and there must be suitable methods to treat such contaminated water. To properly study treatment options, analytical techniques are needed to quantitate perchlorate in drinking water matrixes at suitable concentrations. It is meaningful in considering analytical techniques that the state of California has set a maximum drinking water action level at a concentration of 18 μg/L.[1,2]

Several methods exist for the analysis of perchlorate and have been reviewed elsewhere.[1,2] To summarize, gravimetry and titrimetry are applicable for determinations in the high mg/L range. Ion-selective electrodes function down to around 70 μg/L, which can be improved to 10 μg/L when combined with capillary electrophoresis, which separates interfering ions from perchlorate.[5] Addition of an ion-pairing agent to the aqueous perchlorate solution and extraction of the ion pair with an organic solvent have resulted in detection limits down to 3 μg/L. At this level, common ions such as nitrate can interfere with perchlorate determination.[6,7] Perchlorate is also determined through the use of ion chromatography (IC).[8] Limits of detection for IC with conductivity detection are ∼ 3−4 μg/L, and the analysis is often complicated by the presence of interfering species such as iodide. Due to chromatographic interference, the positive identification of perchlorate by retention time match in ion chromatography may not meet legal challenges.[1,2]

Another approach to perchlorate determination is through electrospray mass spectrometry, which provides additional confidence in the analysis through mass-based determination. Horlick[9] recently determined perchlorate with a reporting limit of 5 μg/L. Depending on the experimental conditions employed, the direct observation of perchlorate may be limited by the presence of

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10.1021/ac9909204 Not subject to U.S. Copyright. Publ. 2000 Am. Chem. Soc.

interfering species at the m/z of the most abundant ion, m/z 99, i.e., by hydrated bromide $Br(H_2O)^-$. The mass of perchlorate is also in the region of "chemical noise", the m/z range with abundant naturally occurring low-mass ions. Observation of interfering ions in electrospray mass spectrometry without recourse to chromatography or another on-line separation technique is common, and considerations for experimental protocol have been discussed in some detail.[10] Consequently, to increase the selectivity for perchlorate, we recently investigated the detection of perchlorate using selective associative complexes of perchlorate with organic bases and other substances.[11] By observation of a complex at a mass > 300 units higher than that of perchlorate, the classical chemical noise region was avoided. The complexation increased selectively, did not significantly decrease sensitivity (LOD ~ 10 $\mu g/L^{-1}$), and was relatively free of common spectroscopic interferences. The quantitation of species, via association of the ions in the electrospray process, has also been reported for other analytes such as Cr^{3+}, which has been electrosprayed as a negative chloro complex.[12] Horlick and co-workers refer to electrospray of the complex as the "intermediate" mode of observation.[13] Recently, in this laboratory, haloacetic acids were analyzed by electrospray mass spectrometry in a similar fashion.[14]

The use of a complexing agent for perchlorate increases selectivity[11] but does not necessarily improve sensitivity. One approach to increasing sensitivity for perchlorate determination is to add an ion-pairing agent to the aqueous solution and extract the ion pair with an organic solvent.[6,7] Conventionally, the ion pair is formed with a good chromophore, such as a dye, and the perchlorate may be determined spectrophotometrically.[6,7] It seemed reasonable to combine the enhanced selectivity of complexation in ESI/MS with the enhanced sensitivity of solvent extraction. In the present work, cationic surfactants (alkyltrimethylammonium salts) were investigated for their dual role in the formation of a solvent-extractable ion pair and an electrosprayable selective complex for mass spectrometric detection. Contaminated water from southern Nevada was analyzed by ion-pair extraction with ESI/MS detection, and the results compared favorably with those from ion chromatography.

EXPERIMENTAL SECTION

Reagents. Brilliant cresyl blue [81029-05-2 (CAS Registry number)], brilliant green [633-03-4], and crystal violet [548-62-9] were obtained from Spectrum (New Brunswick, NJ). Octyltrimethylammonium bromide (C8) [2083-68-3], decyltrimethylammonium bromide (C10) [2082-84-0], dodecyltrimethylammonium bromide (C12) [1119-94-4], tetradecyltrimethylammonium bromide (C14) [1119-97-7], and tributylheptylammonium bromide (THAB) [85169-31-9] were used as received from Fluka (Buchs, Switzerland). The organic solvents were obtained from Fisher (Fairlawn, NJ) and were of Optima or similar quality. Aqueous perchlorate fortifications were made with ammonium perchlorate [7790-98-9] (Aldrich, Milwaukee, WI). Dilutions were made with water deionized through reverse osmosis.

Table 1. Summary of Experimental Conditions

acquisition mode	negative ESI/MS
applied ESI spray potential (optimized)	4.0 kV
interface capillary temperature	200 °C
sheath gas pressure	70 psi (480 kPa)
injection mode/injection volume	flow injection/50.0 μL
carrier liquid	methanol/dichloromethane (70/30 v/v)
flow rate	0.3 mL/min
extractive ion-pairing agent (optimized)	decyltrimethylammonium bromide (C10)
concentration of ion-pairing agent in solution	1.0 mM
extraction solvent	dichloromethane
preconcentration factor	500/1
reconstitution solvent	methanol/dichloromethane (70/30 v/v)

Synthetic Tap Water. A soft synthetic tap water was prepared by adding appropriate ACS reagent grade salts to deionized water. The synthetic tap water, which represents an extreme tap water in terms of ionic strength, was prepared to contain the following anion concentrations: 5.6 mM (200 mg/L) chloride, 0.97 mM (60 mg/L) nitrate, 53 μM (1 mg/L) fluoride, 0.078 μM (10 μg/L) bromate, 0.12 μM (10 μg/L) chlorate, 0.10 mM (10 mg/L) sulfate, 0.16 mM (10 mg/L) carbonate, 63 μM (5 mg/L) bromide. These concentrations were selected to be greater than the average concentrations found in many source waters.[15] Sodium salts were used, except for bromide and bromate, which were prepared from potassium salts.

Apparatus. Injections were made with a Rheodyne (Rohnert Park, CA) model 7725 injector having a 200 μL loop. The pump for the carrier liquid was a Waters 600 (Waters, Milford, MA). The mass spectrometer was a Finnigan MAT TSQ-700 (Finnigan, San Jose, CA) equipped with a Finnigan electrospray interface. Mass spectra were acquired in the negative-ion mode by scanning Q3 over appropriate mass ranges. Other experimental parameters are listed in Table 1.

Procedure. A volume of 500 mL of the aqueous sample, cationic surfactant, and 100 mL of the extraction solvent were shaken together vigorously. A separatory funnel was used to collect the organic phase. The organic phase was then reduced through rotary evaporation to dryness at 60 °C (bath temperature). The residue was redissolved in 5−7 mL of dichloromethane, and the mixture was transferred to a disposable test tube and re-evaporated at 45−50 °C in a heater block. The localized residue was then reconstituted in 1.00 mL of the chosen solvent, and the solution was transferred to a 1.8 mL glass vial. Injections of 50 μL of this solution were then analyzed by flow injection (FI)−ESI/MS.

RESULTS AND DISCUSSION

1. Extraction Conditions. The extraction solvent for these experiments was dichloromethane. Methyl isobutyl ketone (MIBK), ethyl acetate, and *tert*-butyl methyl ether were also investigated.

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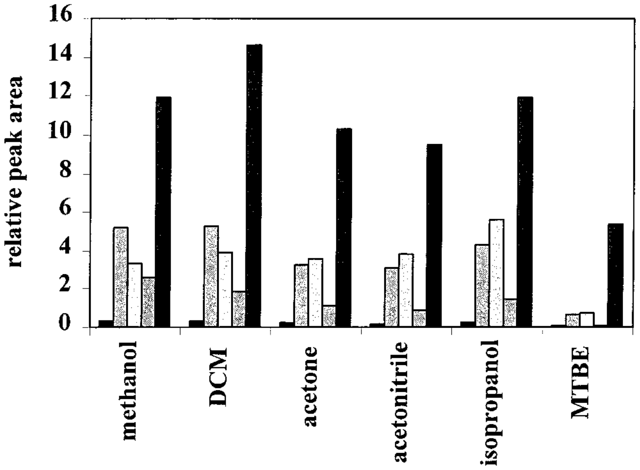

Figure 1. Effect of reconstitution solvent and cationic surfactant on relative perchlorate response. The bars for each solvent represent different cationic surfactants. From left right, the cationic surfactants are C8, C10, C12, C14, and THAB. DCM is dichloromethane, and MTBE is methyl *tert*-butyl ether.

Dichloromethane was chosen because it resisted emulsification in the presence of the surfactant. MIBK also resisted emulsification but was not easily rotary-evaporated due to its high boiling point. Because of its efficiency, a single dichloromethane extraction of the aqueous solution was made.

Brilliant cresyl blue[6] and brilliant green[7] dyes have been reported as ion-pairing agents for the extraction of perchlorate. These, along with crystal violet, were preliminarily investigated but were not used because of high levels of detectable impurities. Cationic surfactants (quaternary ammonium salts) were next considered because these are available in high purity. The cationic surfactants differed in their sensitivity and their selectivity for perchlorate. Among common anions in a synthetic tap water solution, only nitrate, bromide, and chloride were detected. These anions appear at masses different from that of perchlorate and do not present interference in perchlorate detection. The choice of the cationic surfactant represents a compromise between selectivity for perchlorate and sensitivity for the extraction. The selectivity for perchlorate was investigated using the synthetic tap water. Nitrate, bromide, and chloride were the dominant species for which surfactant complexes were detected. Of the surfactants, C10 appeared to have the highest selectivity for perchlorate compared to nitrate or chloride, judging from the ratios of the peak areas of the respective complexes relative to the perchlorate complex.

The analytical sensitivity for the perchlorate extraction was investigated for several surfactants. Figure 1 shows that C8 gives markedly less sensitivity, probably due to a decrease in extraction ability resulting from its shorter alkyl chains. Tributylheptylammonium bromide (THAB) produces a higher response than C10, C12, or C14, probably owing to more favorable extraction resulting from its longer alkyl chains but also perhaps because of its ability to associate with the anions during electrospray. However, THAB was observed to have an impurity which interfered with quantitation. Given the desirable ion-pairing abilities of C10, its high purity, and better sensitivity, C10 was chosen for future experiments. The concentration of surfactant was experimentally selected to provide a large excess of surfactant relative to perchlorate concentration. The amount of surfactant added to the aqueous solution resulted in a 1.0 mM surfactant concentration.

The reconstitution solvent is important for sensitivity. Figure 1 shows the peak areas resulting from the same perchlorate concentration reconstituted in several solvents. Although C10 was selected for future experiments, all five cationic surfactants were investigated; interestingly, every combination of surfactant and solvent behaved differently from the others. The solvent affects the electrospray properties via its dielectric strength, volatility, and viscosity.[16] Potentially, the dielectric strength of the solvent may also affect the association of the complex, but detailed analysis of these synergistic effects is beyond the scope of this paper.

In Figure 1, the response in methyl *tert*-butyl ether (MTBE) is lower due to limited surfactant solubility; a precipitate was observed. Both dichloromethane and methanol appear to have similar responses, but the flow injection peak shape for methanol is better than that for dichloromethane. In methanol, a slight precipitate was formed if the sample was placed in a cool room. A 30/70 (v/v) mixture of dichloromethane/methanol was chosen for better solubility properties and the ability to maintain flow injection peak shapes.

2. Flow Injection−Electrospray Ionization/Mass Spectrometry Analysis. Key parameters in the optimization of the FI-ESI/MS systems are the carrier liquid flow rate, the pressure of the sheath (nebulizing) gas, the interface capillary temperature, and the applied electrospray voltage. The carrier flow represents a compromise between signal intensity/stability and analysis time. The signal intensity/stability dropped off when the carrier flow increased above approximately 0.4 mL/min. A carrier flow rate of 0.3 mL/min was chosen to optimize the peak height and minimize peak width. This carrier flow rate is sufficiently low that it requires only the sheath gas, which was applied at 70 psi. The interface capillary temperature was investigated over the range 150−250 °C. The differences were small, and 200 °C was selected. The electrospray voltage was varied between 1 and 8 kV and underwent a shallow maximum at 4 kV. Removing the electrospray voltage resulted in an 80% reduction in signal. Table 1 is a summary of the experimental conditions.

Figure 2 is a mass spectrum of 100 μg/L perchlorate in distilled water using the extraction and analysis conditions determined above (Table 1). The peak assignments are shown for the various C10 complexes. Because C10 was used as the bromide salt, three complexes are detected: (1) the complex with C10 and two bromide ions, (2) the complex with C10 and bromide and perchlorate ions, and (3) the complex with C10 and two perchlorate ions. It is more reliable to quantitate using the bromide−perchlorate−C10 complex rather than the perchlorate−perchlorate−C10 complex. The bromide−perchlorate−C10 complex produces a larger signal, probably due to the larger amount of bromide present as result of the C10 surfactant solution being prepared from the bromide salt. The larger signal from the bromide−perchlorate−C10 complex may also reflect a greater tendency for this complex to form.

Figure 3 is the flow injection peak resulting from a 50 μL injection of an extract of 3 μg/L perchlorate in distilled water.

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[16] Niessen, W. M. A. *Liquid Chromatography-Mass Spectrometry;* Marcel Dekker: New York, 1999; passim.

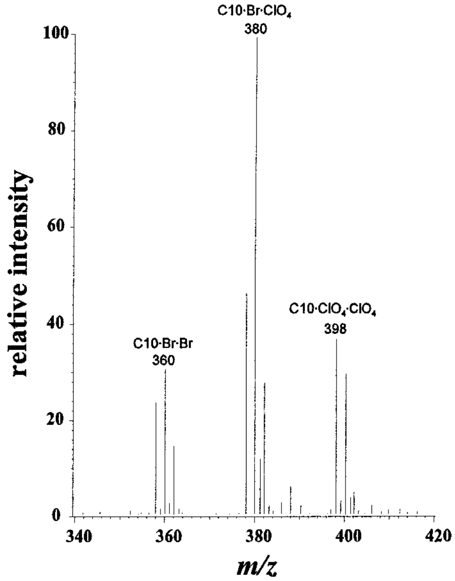

Figure 2. Mass spectrum of 100 μg/L perchlorate in a distilled water extract. The ions with which the decyltrimethylammonium (C10) cationic surfactant is complexed are indicated. The injection volume was 50 μL. The remainder of the m/z range contains noise.

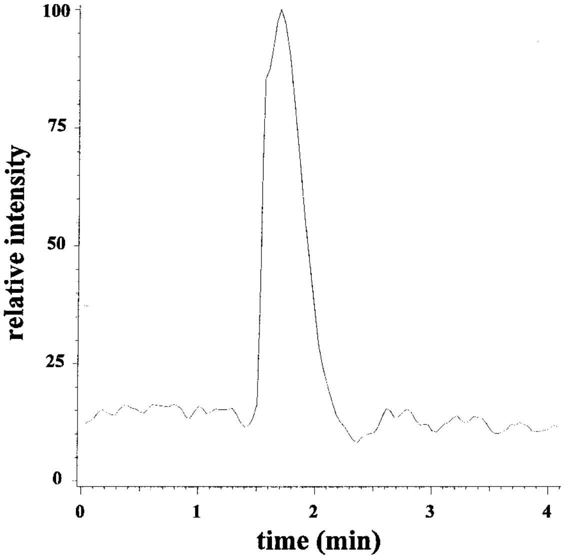

Figure 3. Flow injection peak resulting from a 50 μL injection of an extract of 3 μg/L perchlorate in distilled water. Selected-ion monitoring of mass 380 was used.

Selected ion monitoring of mass 380 was used. The baseline is observed to not be entirely flat; however, this does not present a quantitation problem using the instrument data analysis software.

3. Method Sensitivity and Detection Limit. The method detection limit (MDL),[17] as defined in the U.S. Federal Code of Regulations, is a measure of the precision of replicate injections of an analyte. The method detection limit for the FI-ESI/MS analysis of perchlorate using the optimized reaction conditions was calculated from $3.14\sigma_{n-1}$ of seven replicate injections of a low-level solution. For a 200 ng/L (200 part per trillion) solution, the MDL was calculated to be 100 ng/L. This MDL is probably a more conservative estimate of the detection limit than the $3\sigma_{n-1}$ of the noise, which is computed to be 4 ng/L. These detection limits are based on 500 mL of perchlorate-containing water being transferred through the extraction process into 1.00 mL of solvent.

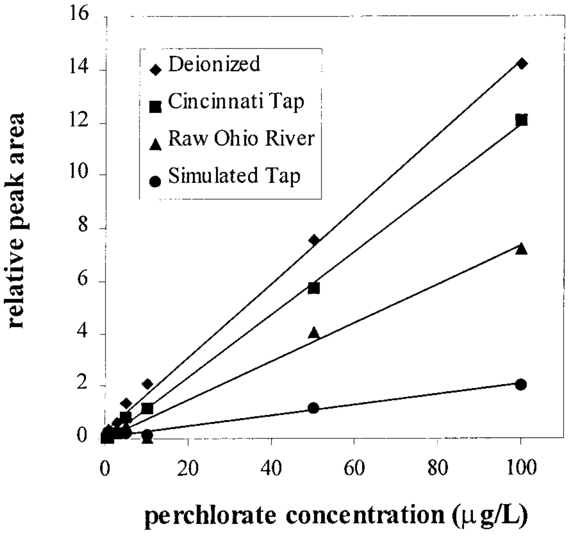

Figure 4. Peak areas (m/z 380) for fortified perchlorate concentrations for four source waters.

As demonstrated in Figure 1, the choice of another surfactant, such as a pure form of THAB, could improve the sensitivity of the analysis, since the most sensitive ion-pairing agent had to be rejected due to its impurity. However, since the chief anticipated purpose of the FI-ESI/MS determination is to be a technique complementary to ion chromatography to confirm the presence of perchlorate, the detection limit is sufficiently beneath the ion chromatography detection limit (3−4 μg/L) that concern over further decrease in the detection limit via better ion-pairing agents is not warranted at this point.

4. Perchlorate Determination in Different Water Matrixes. Figure 4 shows calibration plots for perchlorate in a variety of water matrixes: distilled water, Cincinnati (Ohio) tap water, Ohio River water filtered at 0.45 μm (cellulose acetate), and synthetic tap water. The correlation coefficients (R^2) for the waters were 0.998, 0.999, 0.997, and 0.992, respectively, indicating linearity for all waters to 100 μg/L. Concentrations above 100 μg/L were not systematically investigated because concentrations this high are well above both the detection limit and levels of interest (i.e., 18 μg/L in California). It is worthwhile to point out that linearity is observed even in the presence of much larger concentrations of competing anions (as in the case of the synthetic tap water), which tend to form mixed complexes,[11] similar to the bromide−perchlorate complex (Figure 2).

The slopes of the calibration plots for the water matrixes are different, but some comparative observations can be made. The Cincinnati tap water shows a larger slope than Ohio River water (the source water for Cincinnati tap water). Finishing drinking water alters the matrix; evidently matrix effects cause the slopes to be different. There are several possible explanations for these differences. The first, competition with nitrate, was investigated and ruled out by reducing the nitrate with zinc dust.[18] A second explanation for the matrix effects is that, during separation, a small amount of water is inadvertently transferred to the receiving vessel prior to solvent reduction. The resulting higher ionic content of the reconstituted extract may lead to suppression of the signal,

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(17) (a) 40CFR136.3. (b) Glaser, J. A.; Forest, D. L.; McKee, G. D.; Quave, S. A.; Budde, W. L. *Environ. Sci. Technol.* **1981**, *58*, 502−510.

which is often seen in the electrospray of solutions with many ionic species.[16] Thus, the synthetic tap water, with its high ionic content, would have a more suppressed signal. Careful use of the separatory funnel did not alleviate this problem. A third possible source of matrix effects is the species that are probably extracted, e.g., sulfate, but are not detected by ESI/MS. Although not a spectroscopic interference, their presence in the electrospray may chemically interfere with the association and/or electrospray of the perchlorate complex. Likewise, the presence of other detected species, namely the chloride complex and the bromide complex, may interfere with the association and/or electrospray of the perchlorate complex. Whatever the cause of the matrix effect, the slopes of the calibration plots (Figure 4) vary between waters, so accurate determination of perchlorate must be made through the use of standard additions. The high correlation coefficients of the calibration plots suggest that standard addition should result in accurate perchlorate determination.

For the plots in Figure 4, a blank was subtracted from the data. The background is probably due to the presence of natural organic matter (NOM) in the water. This material typically has a large m/z distribution range but is present in very small quantities and is not normally detected. Due to the large concentration factor (500-fold) in this experiment, the NOM is concentrated and results in a false positive of 0−2 μg/L depending on the water. Since the types and quantities of NOM vary with source water, it is necessary to determine the blank for each source water. This determination can be made on the basis of the following considerations: The cationic surfactant is essential for the extraction of perchlorate. Because the cationic surfactant (ion-pairing agent) is present below its critical micelle concentration,[19] it was assumed that the surfactant should not sufficiently affect the extraction of the natural organic matter. Experimentally, the background was determined to be the same with and without the surfactant. Therefore, when the extraction procedure is performed without the cationic surfactant, the blank value for the water is obtained (Figure 4).

To demonstrate the capabilities of ion-pair extraction with ESI/MS detection for determining perchlorate in contaminated water, drinking water was obtained from a source in southern Nevada. The perchlorate concentration in this drinking water was determined using ion chromatography at the water utility to be 8−9 μg/L. According to the procedure outlined above, the concentration of the perchlorate was determined to be 8.4 ± 0.2 μg/L ($n = 3$) by standard addition. The agreement between the two independent techniques increases confidence in the results, namely that the peak in the ion chromatograph is for perchlorate and not for an interfering species. The FI-ESI/MS determination, made at ∼40 times the detection limit, shows higher precision than the ion chromatography determination, made at 2−3 times the IC detection limit.

CONCLUSION

A sensitive technique for the analysis of perchlorate is demonstrated for measuring trace levels in a variety of water matrixes. The use of an ion-pairing agent for extraction reduces the spectroscopic interference for the nonchromatographically separated sample. The results for a drinking water sample obtained by FI-ESI/MS compare well to those obtained by another technique, ion chromatography with conductivity detection. The ion-pairing/extraction agent is selective for perchlorate among common ions. The method detection limit is among the lowest reported in the literature. Therefore, results from this technique could be compared with those from ion chromatography, as well as other emerging low-level techniques, for the purpose of increasing the confidence in the accuracy of the reported perchlorate concentration.

ACKNOWLEDGMENT

The authors thank microbiologist Peggy Roefer of the Southern Nevada Water Authority for supplying samples of raw and finished waters used in this work.

Received for review August 12, 1999. Accepted October 21, 1999.

AC9909204

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(18) For the reduction, 5 g of zinc dust and 100 μL of glacial acetic acid were added to 500 mL of the water sample. The sample was allowed to react 12−24 h, and the zinc dust was then filtered off at 0.45 μM (cellulose acetate). These quantities were optimized and mass spectrometrically observed to eliminate the nitrate signal. Acetic acid performed better than mineral acids at the same molarity.

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