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Talanta 52 (2000) 285–291

Talanta

www.elsevier.com/locate/talanta

Microscale extraction of perchlorate in drinking water with low level detection by electrospray-mass spectrometry

Matthew L. Magnuson *, Edward T. Urbansky, Catherine A. Kelty

US Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Treatment Technology Evaluation Branch, 26 W Martin Luther King Drive, Cincinnati, OH 45268 USA

Received 27 October 1999; accepted 14 February 2000

Abstract

Improper treatment and disposal of perchlorate can be an environmental hazard in regions where solid rocket motors are used, tested, or stored. The solubility and mobility of perchlorate lends itself to ground water contamination, and some of these sources are used for drinking water. Perchlorate in drinking water has been determined at sub-μg l^{-1} levels by extraction of the ion-pair formed between the perchlorate ion and a cationic surfactant with electrospray-mass spectrometry detection. Confidence in the selective quantification of the perchlorate ion is increased through both the use of the mass based detection as well as the selectivity of the ion pair. This study investigates several extraction solvents and experimental work-up procedures in order to achieve high sample throughput. The method detection limit for perchlorate based on $3.14\sigma_{n-1}$ of seven replicate injections was 300 ng l^{-1} (parts-per-trillion) for methylene chloride extraction and 270 ng l^{-1} for methyl isobutyl ketone extraction. Extraction with methylene chloride produces linear calibration curves, enabling standard addition to be used to quantify perchlorate in drinking water. Perchlorate determination of a contaminated water compared favorably with results determined by ion chromatography.

Keywords: Microscale extraction; Perchlorate; Drinking water; Low level detection; Electrospray-mass spectrometry

1. Introduction

Ammonium perchlorate is used in solid rocket motors, and their maintenance may result in perchlorate infiltrating watersheds by leaching and/or groundwater recharge. Perchlorate ingestion has potential health effects related to its ability to interfere with the proper functioning of the thyroid gland. Therefore, perchlorate has been added to the US Environmental Protection Agency's Drinking Water Contaminant Candidate List (CCL) [1], the list from which future regulated compounds will be selected. The CCL has identified treatment research as a research priority for perchlorate. Perchlorate is also subject to the Unregulated Contaminants Monitoring Regulation

* Corresponding author. Tel.: +1-513-5697321; fax: +1-513-5697658.

E-mail address: magnuson.matthew@epa.gov (M.L. Magnuson)

0039-9140/00/$ - see front matter
PII: S0039-9140(00)00342-8

(UCMR) [2]. In order to obtain reliable treatment data, it is necessary to accurately quantify perchlorate. The state of California (USA) has set a maximum drinking water action level at a concentration of 18 μg l^{-1} [3,4], which is a useful reference concentration in considering analytical techniques.

Several methods exist for the analysis of perchlorate and have been reviewed elsewhere [3,4]. Among techniques for low level determination (<20 μg l^{-1}), ion selective electrodes can achieve a detection limit of 10 μg l^{-1} but require combination with capillary electrophoresis to reduces interfering ions [5]. The extraction of an ion-pair between perchlorate and an organic dye [6,7], can achieve a 3 μg l^{-1} detection limit, but because the detection is spectrophotometric, co-extraction of interfering species such as nitrate may produce an interference. Ion chromatography [8] is popular for perchlorate determination, but interference can be caused by ions commonly found with perchlorate, such as iodide. Therefore, the identification of perchlorate solely on the basis of its retention time may not withstand legal challenges [3,4]. Mass based detection has recently been used to increase confidence in perchlorate identification. Horlick directly observed perchlorate with electrospray mass spectrometry (ESI-MS) with a report limit of 5 μg l^{-1} [9]. Lyophilization for sample concentration has been followed by direct detection by ESI-MS of perchlorate to achieve a 2 μg l^{-1} detection limit [10]. In this laboratory, we recently investigated electrospray mass spectrometry analysis to complement the ion chromatography analysis [11,12]. Detection limits of 100 ng l^{-1} were achieved through selective extraction of perchlorate from drinking water as an ion-pair with a cationic surfactant (quaternary ammonium salt) [12]. Selectivity for perchlorate in this analysis technique is enhanced in two ways. First, the extraction was selective for perchlorate–surfactant ion-pair. Second, the ion-paring agent also forms a selective surfactant–perchlorate complex in the ESI-MS analysis with a higher mass than perchlorate itself. This provides greater selectivity than observing the perchlorate mass directly. The perchlorate mass is in the 'chemical noise' region of the electrospray mass spectrum, which contains spectroscopic interferences from small mass ions in the sample as well as small mass ions formed by the electrospray process, i.e. hydrated bromide. The sample work-up procedure in the previous study [12] involved extraction with a large volume of organic solvent, removal of the solvent, and reconstitution in a different solvent. In our studies with larger numbers of samples, it was found to be advantageous to develop a different sample work-up in order to reduce analysis time and minimize the generation of excess organic solvents as hazardous waste. The results of the investigation into alternate sample work-up procedures are presented here. The resulting procedure was used to analyze perchlorate in several water matrices.

2. Experimental

2.1. Reagents

Decyl trimethyl ammonium bromide (C-10) [2082-84-0] was used as received from Fluka Chemical (Buchs, Switzerland) to make a 0.1 M stock solution. Methylene chloride (Optima®) was obtained from Fisher Scientific (Fairlawn, NJ), 1-butanol from EM Science (Gibbstown, NJ), and methyl isobutyl ketone was obtained from Spectrum Chemical (Gardena, CA). Perchlorate fortifications were made with ammonium perchlorate [7790-98-9] (Aldrich, Milwaukee, WI). Dilutions were made with water deionized through reverse osmosis.

2.2. Apparatus

Injections were made with a Rheodyne (Rohnert Park, CA) model 7725 injector with a 200 μl loop. The pump for the carrier liquid was a Waters 600 (Milford, MA). The mass spectrometer was a Finnigan MAT TSQ-700 (San Jose, CA) equipped with the standard 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.

2.3. Procedure

For comparing different extraction solvents, the following steps were preformed. Sufficient C-10 surfactant stock solution was added to make the aqueous solution 1.0 mM in surfactant. The C-10 is the ion-pairing agent, and this concentration was optimized previously [12]. For comparing solvents, the 96.0 ml of the water sample and 5.00 ml solvent were combined in a 100 ml, class A volumetric borosilicate flask. The flasks were stoppered, inverted, and vigorously shaken. The flasks were returned to upright and the phases were permitted to partly separate. This process was repeated four times to ensure >1 min of vigorous shaking, along with several minutes during which the phases were partly mixed. The combination of volumes forces the entire MIBK layer into the neck of the flask where it may easily be drawn off. For the MIBK, after the final shaking, a period of 10–30 min was allowed for adequate phase separation. The MIBK layer was drawn off with a Pasteur pipette and placed in a 1.8 ml screw cap glass vial with a PTFE-lined septum. For the methylene chloride, after the final shaking, solution was allowed to phase-separate (≈ 2 min) in a separatory funnel. The methylene chloride extracts were then placed in 1.8 ml screw cap glass vials with PTFE-lined septa.

The alternate procedure for the methylene chloride extraction was to place 38.0 ml of water sample, an appropriate amount of stock C-10 solution, 1.8 ml of methylene chloride in a 40 ml cylindrical glass screw cap vial with PTFE-lined septa. This is an approximately proportional reduction in the volumes discussed above, and fit conveniently in the vial. After shaking vigorously for 2 min, the phases were allowed to separate for 2 min. The vial could be tilted and sufficient methylene chloride could be drawn from the bottom edge of the vial with a Pasteur pipette. Because of the small amount of methylene chloride used, this extraction will be referred to below as the 'microextraction'.

Table 1
Summary of experimental conditions for 'microextraction' determination of perchlorate by electrospray ionization mass spectrometry

Acquisition mode	Negative ESI-MS on Q3
SIM scan window	0.5 amu
Scan time	0.5 s
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/flow rate	Methanol at 0.3 ml min^{-1}
Ion pairing agent	1.0 mM Decyltrimethylammonium bromide
Extraction solvent	Dichloromethane

3. Results and discussion

3.1. ESI-MS analysis

ESI-MS analysis using the flow injection mode produces signal intensity versus time plots, as shown in Fig. 1. Each peak in Fig. 1 represents a separate 50 μl injection of extracts of deionized water fortified with the perchlorate concentrations indicated. Elution of the peak begins a few seconds after injection, and the narrow peak width provides for rapid sample throughput. The intensity of the signal increases with increased perchlorate concentration. Selected monitoring of m/z 380 was used to prepare Fig. 1. This m/z is derived from an association complex between the surfactant, a perchlorate ion, and a bromide ion. The bromide is present in high concentration as the counter-ion for the surfactant. Detailed mass spectrometric analysis is presented elsewhere [12]. The shape of the flow injection peak is sufficient to allow quantification based on peak area. The injection to injection reproducibility of the measured peak area averaged 3% for the concentrations shown in Fig. 1. Optimized parameters for the mass spectrometric signal are shown in Table 1. The optimization of extraction is described below.

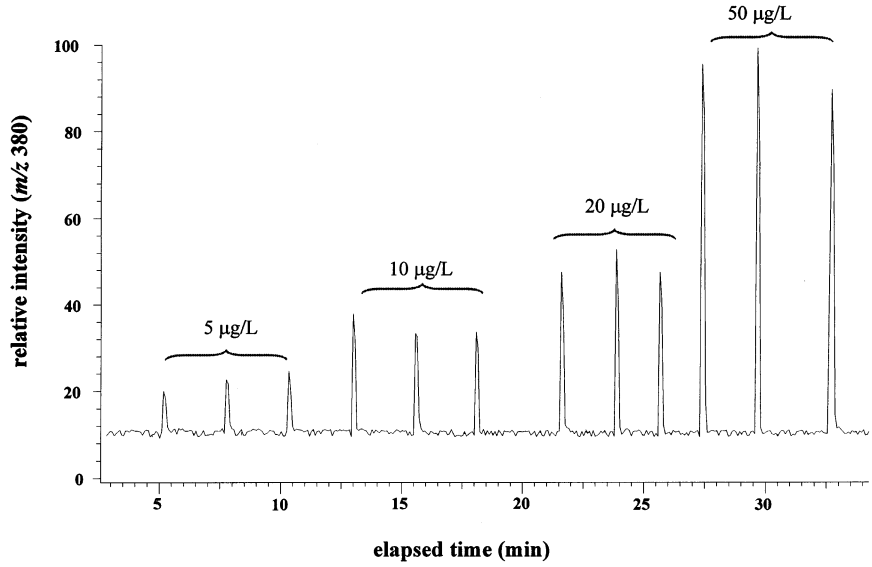

Fig. 1. Flow injection peaks for perchlorate extractions. Each peak represents a separate 50 µl injection of an extract of a perchlorate solution with the concentration shown. The injection-to-injection error in the measured peak area averages 3% for the four concentrations shown.

3.2. Choice of extraction solvents

Methylene chloride, 1-butanol, and methyl isobutyl ketone (MIBK) were investigated. Because the aqueous solution contains a surfactant, fairly stable emulsions are possible. Shaking methylene chloride or MIBK with the aqueous surfactant solution formed emulsions which were stable for less than a few minutes. 1-Butanol formed stable emulsions that did not breakdown in less than 12 h. 1-Butanol was not investigated further because of the much more rapid phase separation possible with methylene chloride or MIBK. Methylene chloride and MIBK were investigated in terms of analytical signal resulting from the extraction.

For the ESI/MS analysis, methylene chloride and MIBK behaved differently in several ways. Fig. 2 plots the relative peak area versus fortified perchlorate concentration. The response for extraction solvents differ by around a factor of 2. This response difference may be due to differences in the extraction efficiency of the solvent for the perchlorate–surfactant ion pair. Another cause of the response difference may be the electrospray process. Electrospray efficiency is related to a number of factors, such as solvent viscosity, surface tension, dielectric constant, and vapor pressure of the solvent [13]. These factors influence the ability of the perchlorate-surfactant complex to be formed and ionized in the electrospray interface and enter the mass spectrometer. These interactions are complex, fascinating, and beyond the scope of this paper.

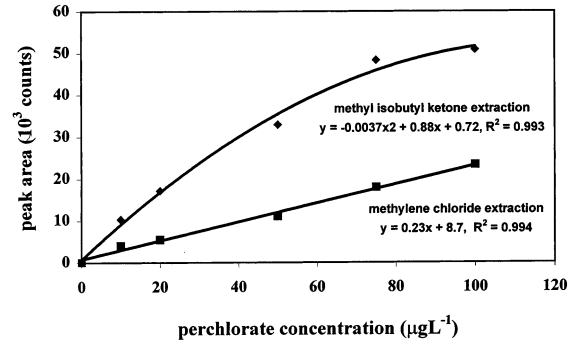

Fig. 2. Peak area versus perchlorate concentration for extraction with methyl isobutyl ketone and methylene chloride. Perchlorate solutions were prepared in deionized water. The solid lines represent the best fit to the equations shown.

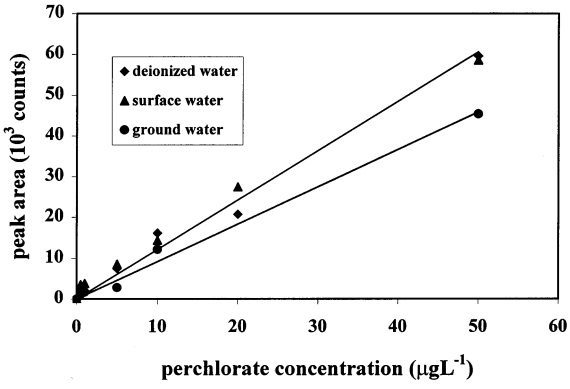

Fig. 3. Peak area versus fortified perchlorate concentration for three water matrices using the methylene chloride microextraction. The best fit linear lines are shown for distilled water and ground water. The best fit line for surface water is not shown since it falls almost on top of the distilled water line.

The other prominent feature of Fig. 2 is that the best fit of the data for the MIBK extraction is a second order polynomial ($R^2 = 0.993$). The linear fit of the same data results in $R^2 = 0.959$, indicating less correlation for the linear fit. By contrast, the best fit for the methylene chloride extraction is linear ($R^2 = 0.994$). The equations for the fit are shown on Fig. 2. The cause of the second order effects for MIBK is not entirely clear. The leveling out in the MIBK response suggests an extraction/solubility effect may be responsible, but it is possible that some electrospray-related phenomenon is partially responsible as well. At higher perchlorate concentrations, second order effects in the perchlorate analysis following the MIBK extraction may complicate data analysis. It is worth noting that the MIBK extraction appears to provide a fairly linear fit ($R^2 =$ 0.985) for points ≤ 20 μg l^{-1}.

Another difference between MIBK and methylene chloride as extraction solvents was in the choice of ions to monitor. In ESI/MS, perchlorate complexes appear at m/z 380 and 400 [12]. m/z 380 corresponds to the complex between the surfactant, a perchlorate, and a bromide, which is the counter-ion of the surfactant. m/z 400 corresponds to the complex with two perchlorates. The choice of ions for quantification was investigated for MIBK and methylene chloride. For MIBK, the correlation coefficients for the area versus concentration plots was higher when the sum of the areas of m/z 380 and 400 (Fig. 2) was used than when either mass was used separately. In general (experiments not shown), it was necessary to use the sum for quantification, i.e. it was not sufficient to use either mass by itself. For methylene chloride, a different case occurred. In other experiments, such as the ones reported below, it was sufficient to use m/z 380 by itself. For example, the correlation coefficient, 0.994, calculated for the sum of the peak areas (Fig. 2) did not differ much from the correlation coefficients for the plots in Fig. 3 (discussed later), which were all > 0.990.

3.3. Method detection limit

The method detection limit (MDL) [14], as defined in the US Federal Code of Regulations, is a measure of the precision of replicate injections of an analyte. The method detection limit for the ESI/MS analysis of perchlorate using the procedure above was calculated from $3.14\sigma_{n-1}$ of seven replicate injections of a low level solution. For a 1 μg l^{-1} solution, the MDL was calculated to be around 300 ng l^{-1} (300 part-per-trillion) for extraction with methylene chloride and around 270 ng l^{-1} for MIBK. These detection limits are based on 100 ml of perchlorate containing water being transferred through the extraction process into 5.00 ml of solvent. The MDLs are similar between the two solvents, possibly because as the concentration decreases, the peak areas from the two solvents become similar (Fig. 2).

In the large scale sample work-up [12], a volume of 500 ml, of water was extracted with 100 ml of methylene chloride and ultimately reconstituted in 1 ml of solvent. The MDL from this sequence was around 100 ng l^{-1}, which is only a factor of three less, even though the nominal extractive preconcentration factor was about 25 times less. This unexpected result allows for the use of the small volume extractions in the present study. The cause of this effect may be due to a change in the electrospray efficiency. As solutions become more ionic, the efficiency of the electrospray process typically drops. Thus, when the

preconcentration factor is very large, the ionic strength increases as the surfactant concentration increases. A smaller concentration factor may therefore increase the analytic signal via a higher electrospray efficiency, which partially makes up for the loss in analyte concentration due to a lower amount of analyte preconcentration in the extraction step. The MDL of the small volume extraction possibly may be lowered by careful study of the extraction ratio. However, at 300 ng l^{-1}, the MDL is sufficient to accomplish the goal of providing confirmation for ion chromatography, which has a detection limit of around 3 μg l^{-1} [8].

3.4. Standard addition analysis of drinking water

Based on the comparable MDLs of the MIBK and methylene chloride and the more simple data analysis resulting from the linearity of the response (Fig. 1), methylene chloride was used for further experiments. It was deemed inconvenient to use separatory funnels for the methylene chloride extraction. Therefore, 40 ml, glass vials with PTFE-lined septa were used as the 'microextraction' vessels, as described in the procedure section.

For the analysis of actual drinking water samples, it is necessary to subtract out the 'blank value' of the injection. For example, the blank value causes the intercepts in Fig. 2 to not have a value of zero, even for deionized water fortified with perchlorate. The value may result from a change in the noise of the instrument as the solvent changes from the flow injection carrier liquid, methanol, to the extraction solvent, methylene chloride or MIBK. The extraction solvent contains other substances extracted from the water matrix. These substances may vary from matrix to matrix and affect the electrospray process, so each matrix produces a different blank signal, typically < 2 μg l^{-1}, depending on the water matrix. Because the C-10 surfactant is necessary for the ion-pair extraction of perchlorate, when the extraction procedure is performed without the surfactant, the blank value for the water is obtained. For matrices not contaminated or fortified with perchlorate, the background was experimentally determined to be the same with and without the surfactant. Therefore, the blank value can be subtracted for quantification of perchlorate.

The 'microscale' extraction procedure with methylene chloride was applied to several drinking waters fortified with perchlorate. Calibration plots for these different water matrices are shown in Fig. 3. The correlation coefficient for the linear regression of these calibration curve were all greater than 0.990, indicating a high degree of linearity. The slopes for these calibration plots are somewhat different, especially for the ground water, which is expected to have a higher ionic content. It was shown previously that solutions with higher ionic content result in a suppressed signal [12]. Fig. 3 indicates that perchlorate can be determined in these water matrices by the use of standard additions.

In order to compare the perchlorate determined by this extraction procedure with another technique, water contaminated with perchlorate was obtained from a source in Nevada, USA. Using standard additions, this water was determined to contain 8.2 ± 0.2 μg l^{-1} ($n = 3$) perchlorate. The water utility determined the concentration to be 8–9 μg l^{-1} by ion chromatography. The same water was determined to contain 8.4 ± 0.2 μg l^{-1} ($n = 3$) perchlorate by the large volume extraction [12]. The ESI-MS determination of perchlorate is more precise due its lower detection limits (0.3 μg l^{-1}) than ion chromatography (≈ 3 μg l^{-1}). The concentration of perchlorate determined with this 'microextraction' is the same as the large volume extraction within experimental error, indicating the viability of the microextraction. The agreement between the ESI-MS results and the ion chromatography increases confidence that the peak quantified as perchlorate by ion chromatography is in fact perchlorate and not an interfering anion.

4. Conclusion

A microextraction of perchlorate has been developed which provides for the sample throughput needed for large scale studies of perchlorate in drinking water. The microextraction is performed

with methylene chloride, and methyl isobutyl ketone can be used for extraction, as well. The results compare well to ion chromatography, as well as a previously reported large scale extraction technique. The detection limit for the microextraction is greater than the large scale extraction, but the microextraction provides sufficient sensitivity to complement ion chromatography. In addition to increasing the efficiency of the analysis, the amount of hazardous waste is reduced 50-fold in the process.

5. Notice

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