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Challenges encountered in extending the sensitivity of US Environmental Protection Agency Method 314.0 for perchlorate in drinking water

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Abstract

Concerns about the potential adverse health effects of perchlorate at concentrations below the minimum reporting level (MRL) of US Environmental Protection Agency (EPA) Method 314.0 (generally recognized as 4.0 μg/l) have led to an interest in increasing the sensitivity of the method. This work describes the use of 2 mm columns with a large-loop direct injection method, a column concentration technique and this concentration technique with a background reduction step, to increase the sensitivity for the analysis of trace levels of perchlorate in high ionic strength matrices. The concentrator columns studied were the Dionex TAC LP-1 and a new Dionex high capacity Cryptand concentrator column. The use of a surrogate to monitor trapping efficiency for the concentration technique and the use of confirmational columns to minimize the potential for false positives are also discussed. The large-loop direct injection method and the column concentration methods provided acceptable data when the samples were pre-treated with solid phase pretreatment cartridges. The background reduction technique did not provide acceptable data with either of the concentrator columns evaluated.

Keywords: Water analysis; Perchlorate

1. Introduction

In 1997, perchlorate (ClO_4^-) concentrations up to 260 μg/l were found in the drinking water wells of some eastern Sacramento California Counties. Perchlorate can interfere with iodide uptake by the thyroid gland and consequently affect how the thyroid functions. This has the potential to cause effects that range from improper regulation of metabolism in adults to developmental and behavioral problems in infants and young children. Disruptions in thyroid hormone levels may also result in thyroid gland tumors [1]. Consequently, the California Department of Health Services (DHS) initiated sampling for perchlorate in hundreds of additional drinking water wells. Based on results from these and other sampling events, the California DHS established a drinking water action level for perchlorate at 18 μg/l [2]. In 2002, California DHS revised their drinking water action level for perchlorate to 4.0 μg/l [2].

Perchlorate was identified by the US Environmental Protection Agency (EPA) as a contaminant of potential concern in drinking water with its publication in the 1998 Contaminant Candidate List (CCL). The CCL program was developed by EPA as a means to determine which contaminants are priorities for future regulation in the most cost-effective way possible [3]. Following the CCL, the Unregulated Contaminant Monitoring Rule (UCMR) was proposed in 1999. It identified analytical methods and proposed a schedule for collecting data on 34 CCL contaminants for which additional data were needed [4]. In conjunction with this effort, EPA developed Method 314.0 to analyze trace levels of perchlorate in drinking water [5] based on work that had been done by the State of California and Dionex Corporation [6,7].

National monitoring for perchlorate under the UCMR began in January 2001 and will continue through December 2003. Initial data is indicating occurrence above 4.0 μg/l (the method minimum reporting level) in greater than 2% of the public water systems which have thus far reported. Final assessments of these results will take place after the end of the monitoring cycle [8].

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Interpretation of the health effects data for perchlorate has been a subject of active debate among stakeholders. This issue was recently referred to the National Academy of Sciences (NAS). The EPA's decision regarding potential regulation and establishing a drinking water maximum contamination level is pending the outcome of the NAS study and the completion of the UCMR survey. To support perchlorate monitoring at low levels, EPA is currently investigating three analytical approaches that could offer enhanced sensitivity and selectivity. These techniques include high performance-liquid chromatography/mass spectroscopy, ion chromatography/mass spectroscopy, and revising the current ion chromatography-based method.

This manuscript describes the work at EPA's Technical Support Center to increase the sensitivity for perchlorate using EPA Method 314.0 protocols with suppressed conductivity detection. Direct injection of a large volume (1.3 ml) of solid phase pretreatment (SPP) cartridge-treated samples onto 2 mm columns was investigated as one means of improving the sensitivity for perchlorate in high ionic strength matrices. A second procedure involved concentrating a large volume (5 ml) of a SPP cartridge-treated sample onto a concentrator column prior to injection onto the analytical columns. The use of a surrogate to monitor trapping efficiency was also evaluated. Addition of a background reduction step to the column concentration technique was evaluated to improve the sensitivity for the analysis of perchlorate in high ionic strength drinking water matrices and eliminate the need for SPP cartridge treatment. This procedure involved loading the sample, without SPP cartridge treatment, onto a concentrator column and then rinsing with a dilute eluent to remove the interfering anionic species, prior to injection onto the analytical columns. These investigations also used an autosampler to perform both the column concentration step and the background reduction step as well as to establish the capacity of the Cryptand trap column, and thereby eliminate the need for a step gradient with the Cryptand trap column.

Conductivity detection is a non-specific detection technique that can occasionally be subject to false positives; the potential for such with EPA Method 314.0 was addressed by including a number of quality control measures in the method. These investigations also included evaluation of a confirmational column to further reduce the potential for false positives for perchlorate using EPA Method 314.0.

2. Experimental

2.1. Reagents

The eluent, standards, surrogate and all dilutions were prepared using 18 MΩ water. Sodium hydroxide eluent was prepared with either NaOH pellets (Aldrich, catalog no. 30657-6, Milwaukee, WI, USA) or a 50% NaOH solution (Fisher Scientific, catalog no. SS254-500, Chicago, IL, USA). The eluent was membrane filtered (0.4 μm) and degassed with helium prior to use. Mellitic acid (Aldrich, catalog no. M270-5) was used to prepare the surrogate solution in reagent water (RW), which was fortified into all standards and samples prior to analysis. The high ionic strength water (HIW) was prepared from reagent water, which was fortified with 1000 mg/l of chloride as sodium chloride, carbonate as sodium carbonate and sulfate as sodium sulfate [5].

2.2. Standard and sample preparation

The calibration standards, continuing calibration check standards and spiking solutions were prepared using a 1000 mg/l perchlorate (ClO_4^-) standard stock solution prepared from sodium perchlorate (Sigma, catalog no. S1513, Milwaukee, WI, USA). Dionex autosampler vials were used to filter all standards and samples prior to analysis.

2.3. SPP cartridge procedure

The individual barium (Dionex OnGuard Ba, PN 057093), silver (Dionex OnGuard Ag, PN 057089) and hydrogen (Dionex OnGuard H, PN 057085) cartridges were conditioned with 100 ml of RW prior to use. The Millipore MillexGP 0.22 μm particulate filter (Millipore PN SLGP033RB) was rinsed with 50 ml of RW prior to use. The cartridges were stacked in the order barium, silver, particulate filter and hydrogen. All samples were placed in a disposable syringe and passed through the cartridges at a rate of 1 drop every 4 s [5]. The first 3 ml was discarded and the next 5 ml collected for analysis. Prior to injection, all HIW samples were purged with helium after the SPP cartridge treatment to remove carbon dioxide.

2.4. Instrumentation

A Dionex AS40 autosampler and a rear-loading Rheodyne load/inject valve with either a 1.3 ml sample loop or a concentrator column (50 mm × 4 mm TAC LP1 or 30 mm × 3 mm Cryptand) in the sample loop position, were connected to the Dionex DX500 microbore pump (GP40 and/or GP50), which delivered the eluent (0.40 ml/min) to either the Dionex 2 mm × 50 mm IonPac AG11HC guard and 250 mm × 2 mm IonPac AS16 or 30 mm × 3 mm Cryptand guard and 150 mm × 3 mm analytical columns for separation. Following electrolytic suppression of the eluent (ultra anion self-regenerating suppressor in the external water mode and/or in the recycle mode combined with the EG50 eluent generator), the suppressed eluent entered a Dionex CD20 conductivity detector. The effluent from the conductivity detector was directed to waste. A personal computer with Peak Net software (version 5.1 and/or 6.0) were utilized to control the instrument and to process data.

2.4.1. Large-loop direct injection conditions

The optimized conditions for the large-loop direct injection method used a 1.3 ml sample loop combined with the 2 mm AG11HC and AS16 columns at room temperature. The eluent was 75 mM NaOH at a flow rate of 0.4 ml/min.

2.4.2. Column concentration using a TAC LP1 with AG11HC and AS16 columns

The finalized conditions for the column concentration method used the AS40 autosampler to concentrate 5 ml of SPP cartridge-treated sample onto a 35 mm × 4 mm TAC LP1 column, with separation of the analytes on 2 mm AG11HC/AS16 columns with an 80 mM NaOH eluent. The trap, guard, analytical columns and suppressor were enclosed in the LC25/LC30 chromatography module and maintained at 35 °C.

2.4.3. Column concentration with background reduction using a TACLP1 with AG11HC and AS16 columns

These conditions used the AS40 autosampler to concentrate 5 ml of sample (without SPP cartridge treatment) and also used the AS40 autosampler to load the rinse solution to perform the background reduction step.

2.4.4. Column concentration using the Cryptand columns

The final conditions for the column-concentration method used the AS40 autosampler to concentrate 5 ml of sample onto a 3 mm Cryptand trap column, with separation of the analytes on a 3 mm Cryptand guard and analytical columns at 35 °C. A 35 mM NaOH eluent was used to set the capacity of the trap column, and a step gradient to 45 mM LiOH was used to elute the analytes. A return step to the NaOH eluent was used to re-establish the column capacity prior to injection of the next sample.

2.4.5. Column concentration with background reduction using the Cryptand columns

These conditions were identical to the column-concentration method above but also used the AS40 autosampler to load the rinse solution to perform the background reduction step.

3. Results and discussion

3.1. Refining cartridge cleanup techniques to prolong column life

High ionic strength drinking water matrices necessitated the use of the matrix conductivity threshold (MCT) protocols that were incorporated into EPA Method 314.0 [5]. All samples that exceed the MCT for a given laboratory require cartridge cleanup with SPP cartridges prior to analysis [5]. It is well established that use of the silver SPP cartridges to remove chloride has the potential to add silver ions to the solution [5,7]. Silver can have an extremely deleterious affect on the longevity of ion IC columns. Consequently, an additional SPP cartridge in the hydrogen form has been used in conjunction with the silver cartridge to remove soluble silver. Use of the hydrogen SPP cartridge has the added benefit of removing carbonate/bicarbonate as well (providing the treated solution is purged with helium prior to injection). In this work, an AG11HC, rather than an AG16, column was used in combination with AS16 column.

Table 1
ICAP-AES levels of silver in solution after SPP cartridge cleanup

Description	Silver (μg/l) ($n = 3$)
Cartridges with no particulate filter	14.0
Cartridges with 0.45 μm particulate filter after H^+ cartridge	33.1
Cartridges with 0.22 μm particulate filter after H^+ cartridge	12.1
Cartridges with 0.45 μm particulate filter between Ag^+ and H^+ cartridge	1.96[a]
Cartridges with 0.22 μm particulate filter between Ag^+ and H^+ cartridge	0.28

[a] $n = 2$.

A personal communication from Dionex, which was based upon one of their collaborators' work, suggested that colloidal silver, rather than soluble silver, was responsible for contaminating the columns. This work also suggested that use of a particulate filter, between the silver and hydrogen cartridge, would completely remove essentially all colloidal and soluble silver [7].

Additional work was conducted at our laboratory to confirm these findings. Standard inductively coupled plasma atomic emission spectrometry (ICAP-AES) protocols were utilized to determine the silver content of the solutions after treatment with the SPP cartridges and particulate filters. Two types of particulate filters were used, a 0.45 μm approximately 1.3 cm in diameter, and a 0.22 μm approximately 2.5 cm in diameter, either after the hydrogen (H^+) cartridge or between the silver (Ag^+) and H^+ cartridges. As indicated in Table 1, insertion of the 0.22 μm particulate filter between the individual Ag^+ and H^+ cartridges was successful in removing essentially all of the colloidal and soluble silver.

3.2. Large-loop direct injection with 2 mm columns

EPA Method 314.0 protocols incorporate 1.0 ml samples injected directly onto 4 mm columns using a 50 mM NaOH eluent with a flow rate of 1.5 ml/mm. It was hypothesized that an approximate four-fold increase in sensitivity could be obtained by direct injection of the same volume of sample onto 2 mm columns using an eluent flow rate of 0.4 ml/mm.

Seven replicates of a RW fortified with 1.0 μg/l ClO_4^- provided acceptable precision [<10% relative standard deviation (R.S.D.)] with the later approach. However, a large water dip was observed at approximately 2.5 min and the retention time (t_R) for ClO_4^- was lengthened to about 13 min when using the large-loop direct injection, compared to EPA Method 314.0 where ClO_4^- elutes near 10 min. This was

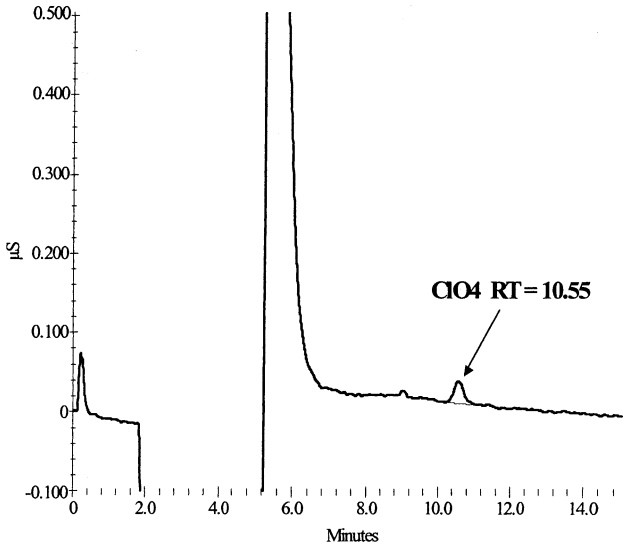

Fig. 1. Direct injection of SPP-treated RW 1.0 μg/l ClO_4^- on 2 mm AG11HC and AS16 columns (1.3 ml sample loop, 75 mM NaOH eluent at 0.4 ml/min.)

speculated to be due to dilution of the eluent by the large volume injection at the lower flow rate. The eluent strength was therefore increased to 75 mM to shorten the t_R for ClO_4^-. The size of the water dip was not significantly affected by the increase in eluent strength. A further increase in sensitivity was accomplished by increasing the sample loop to 1.3 ml. As shown in Fig. 1, acceptable chromatography and sensitivity were obtained for a 1.0 μg/l ClO_4^- RW standard with this modification. With this technique, all HIW samples require SPP cartridge cleanup to remove potential interfering matrix anions. Consequently, it was necessary to ensure that this sample pre-treatment did not affect the perchlorate quantitation. This was accomplished by preparing calibration standards in both RW and the simulated HIW matrix at 0.25, 0.50, 1.0, 2.0, 5.0, 10 and 20 μg/l. The RW calibration standards were analyzed directly, as well as after SPP cartridge treatment. The HIW calibration standards were analyzed after SPP cartridge treatment followed by sparging with helium prior to injection. The peak area data were similar for all three experiments indicating the sample pre-treatment did not substantially affect the quantitation of perchlorate.

The detection limits (DLs) for the large loop direct injection method were evaluated using EPA protocols [9] by analyzing eight replicates of a 0.50 μg/l ClO_4^- solution in both RW and the simulated HIW matrices over 3 days. The detection limits in the SPP-treated RW and HIW were 0.11 and 0.17 μg/l respectively. The reported detection limit for perchlorate in EPA Method 314.0 is 0.53 μg/l using a 4 mm column and a 1.0 ml injection volume. Acceptable precision was also obtained for SPP cartridge-treated replicate injections ($n = 8$) of both 0.50 and 1.0 μg/l concentrations of ClO_4^- in the RW (5.3 and 3.9% R.S.D.) and the HIW (7.8 and 6.0% R.S.D.) matrices.

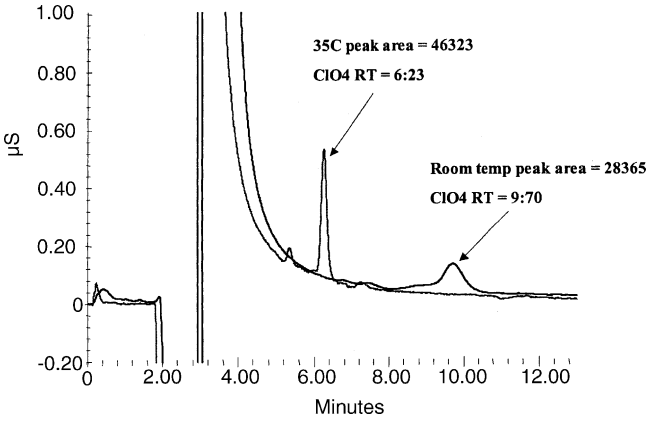

Fig. 2. Effect column of temperature on the chromatography using column concentration of 5 ml of 3.0 μg/l ClO_4^- in RW and 100 mM NaOH eluent.

3.3. Effect of temperature on the chromatography of perchlorate

Column concentration was also investigated for its potential to increase the sensitivity of EPA Method 314.0 using a TAC LP1 (4 mm) concentrator column in the sample loop position with the 2 mm AG11HC and AS16 columns. Since the Cryptand columns were to be investigated as confirmational columns and their performance is optimal at 35 °C, a LC25 and/or LC30 chromatography module (to control the temperature of the trap, guard and analytical columns and suppressor) was used to accurately control temperature. As shown in Fig. 2, the peak shape and peak area for ClO_4^- was dramatically improved when the temperature was increased from room temperature to 35 °C. As well, the retention time for ClO_4^- decreased from 9.7 to 6.1 min.

3.3.1. Surrogate evaluation for the column concentration method

When a column concentration technique is used to load a sample, some process to monitor the trapping efficiency and release of the analytes on and off of the trap column should be incorporated into the method to ensure acceptable quality control of the method. Tribromoacetic acid (TBA) and mellitic acid [benzenehexacarboxylic acid (MA)] were considered as potential surrogates for the trapping efficiency of ClO_4^-.

Ideally, the surrogate would behave very similar to and elute near ClO_4^-. While tribromoacetic acid elutes after perchlorate [10], it has been shown to be susceptible to both chemical and microbiological degradation [11–13] and was therefore not considered further.

Mellitic acid is a highly charged species and consequently its retention time can be easily adjusted to approximate that of ClO_4^-. As a result of MA's high charge, the eluent strength has a dramatic effect on the elution of MA while only a moderate effect on the elution of ClO_4^-. For example, the t_R for MA shifted from 11.8 to 4.1 min whereas the t_R for ClO_4^- moved from 7.2 to 6.2 min when the NaOH

Table 2
Precision for 1.0 μg/l ClO_4^- and 20 μg/l MA in RW, SPP cartridge-treated RW and SPP cartridge-treated HIW ($n = 4$)

Description	t_R (min)	ClO_4^- (area)	t_R (min)	MA (area)
RW average	6.93	14986	8.63	345411
R.S.D. (%)	0.34	2.15	0.29	1.62
SPP cartridge-treated RW average	6.95	11533	8.64	340272
R.S.D. (%)	0.42	6.04	0.33	2.01
SPP cartridge-treated HIW average	6.95	11021		
R.S.D. (%)	0.38	7.38		

eluent strength was increased from 75 to 100 mM. Studies with other potential surrogates are continuing.

3.3.2. Column concentration precision for ClO_4^- and MA in RW and HIW matrices

The ability to consistently trap and elute ClO_4^- using a TAC LP1 column was evaluated in RW and the HIW using conditions as outlined in Section 2.4.2. The precision obtained for fortified RW ($n = 8$) was acceptable both in terms of retention time reproducibility and trapped amount. The t_R and peak area precision for a 1.0 μg/l ClO_4^- solution were 1.38 and 8.22% R.S.D., respectively. The surrogate fortified at 40 μg/l MA, yielded R.S.D.s of 1.06 and 4.06%, respectively.

Once acceptable precision was achieved in RW, the precision was evaluated for ClO_4^- and MA in RW, SPP cartridge-treated RW, and SPP cartridge-treated HIW matrices. Perchlorate was again fortified at 1.0 μg/l and the MA concentration was reduced to 20 μg/l in order to have both peaks on scale. As shown in Table 2, acceptable precision ($n = 4$) for both t_R and peak areas was obtained in RW, and in the SPP cartridge-treated RW for ClO_4^- and MA. Acceptable precision was also obtained for ClO_4^- in the SPP cartridge-treated HIW matrix; however, the MA was not recovered in this matrix. Since the MA was fully recovered from fortified RW after SPP cartridge treatment, it was established that the HIW matrix anions interfered with the recovery of MA during SPP cartridge treatment. Consequently, MA cannot be added prior to SPP cartridge treatment but can still be added, prior to injection, to monitor the TAC LP1 trapping efficiency.

3.4. Column concentration with background reduction

While the column concentration method provided an acceptable technique for increasing the sensitivity for ClO_4^- in RW and HIW matrices, the required use of three SPP cartridges and a particulate filter for each sample dramatically increases the cost-per-analysis. Consequently, background reduction was investigated as a means of eliminating this added expense.

In these investigations, the AS40 was used to load the sample as well as to deliver the rinse solution to the TAC LP1 concentrator column as outlined in Section 2.4.3. A 5 ml aliquot of a 3.0 μg/l ClO_4^- solution in RW was first loaded onto the TAC LP1 column and the trap column was then rinsed with either 5 ml of RW or 1.0, 5.0, 10, 15 and 20 mM NaOH prior to switching the trap column in line with the guard and analytical columns. The peak areas for ClO_4^- progressively decreased from about 48,000 to 0 as the concentration of the NaOH rinse solution increased. Conversely, the retention time for ClO_4^- increased from 6.3 to 7.9 min as the concentration of the NaOH rinse solution increased. This was determined to be a consequence of loading and rinsing the trap column in one direction and eluting the analytes from the trap column in the opposite direction.

In the next series of experiments 5 ml of a 3.0 μg/l ClO_4^- solution containing 500 mg/l of either carbonate, chloride, or sulfate HIW matrices were evaluated. The peak shape for ClO_4^- was dramatically broadened and skewed by the background reduction step and the peak areas were significantly altered by the NaOH rinse solution in the carbonate, chloride and sulfate HIW matrices. The ClO_4^- retention times ranged from 5.93 to 6.90 min (5.4% R.S.D.) and peak areas ranged from 79,603 to 302,377 (56.2% R.S.D.). In contrast, MA was less affected by the NaOH rinse solution. The MA retention times ranged from 7.95 to 8.73 min (3.6% R.S.D.) and the peak areas ranged from 646,959 to 745,751 (4.3% R.S.D.).

3.5. Column concentration with Cryptand confirmational columns

The Dionex Cryptand columns utilize column capacity to accomplish separation of the target analytes. The capacity of the Cryptand column is altered by the eluent counter-ion. For example, sodium hydroxide establishes a higher capacity on the Cryptand column than does lithium hydroxide. As well, eluent concentration will have some effect on the capacity of the Cryptand column. Consequently, use of the Cryptand columns requires a step-gradient elution. A sodium hydroxide eluent is used to set the capacity of the columns and a switch to lithium hydroxide is used to lower the capacity of the columns and affect separation of the target analytes. A final switch back to sodium hydroxide is required to re-establish the capacity before injection of the next sample.

3.5.1. Column concentration with Cryptand trap, guard and analytical columns

The conditions as outlined in Section 2.4.4 were used to evaluate the column concentration technique using the Cryptand columns. As mentioned previously, with the column concentration/background reduction technique using the TAC LP1 trap column, an increase in t_R was observed when the sample was loaded and rinsed in one direction and eluted from the trap column in the opposite direction. As shown in Fig. 3, the same effect on t_R was not observed

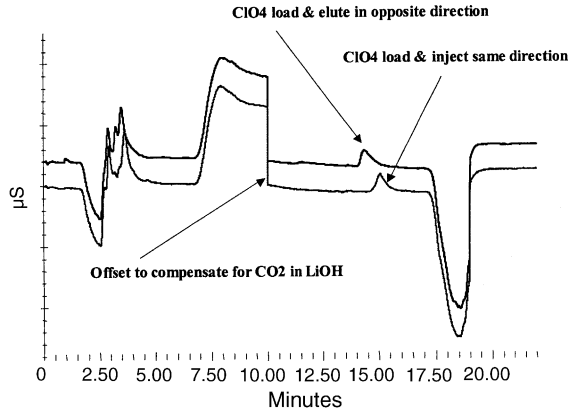

Fig. 3. Effect of loading and elution on the ClO_4^- (10 μg/l) peak shape and t_R using column concentration on Cryptand trap, guard and analytical columns. Chromatograms are "*y*"-axis offset 15% for clarity.

when loading and eluting a 10 μg/l solution of ClO_4^- in RW on the Cryptand trap column in the same or opposite directions. On the other hand, the peak shape for ClO_4^- in RW was improved (less tailing) when the sample was loaded and eluted in the same direction. The shift in baseline conductivity at about 7 min is a result of the presence of carbonate in the manually prepared LiOH eluent. An instrument offset at 10 min was incorporated to compensate for the baseline shift.

3.5.2. Cryptand trapping efficiency in the presence of sodium

It was suggested by Dionex that when using the Cryptand columns, the trapping efficiency and peak shape for perchlorate could be significantly improved by the addition of approximately 50 mg/l of Na^+ into the sample. Since our preliminary work with the Cryptand columns indicated that the peak shapes for MA and ClO_4^- were least affected by the presence of sulfate (compared to carbonate or chloride), it was decided to add 50 mg/l Na^+ in the form of sodium sulfate to all samples. As shown in Fig. 4, the peak shape for the ClO_4^- improved significantly and the peak area was doubled by the addition of 50 mg/l Na^+. The Cryptand columns require the presence of a small amount of Na^+ in the samples for optimal performance. Addition of Na^+ was made to the reagent water samples to improve performance for perchlorate. Although most drinking water matrices will contain sufficient Na^+ to ensure optimal performance, perchlorate standards prepared in reagent water will require the addition of Na^+.

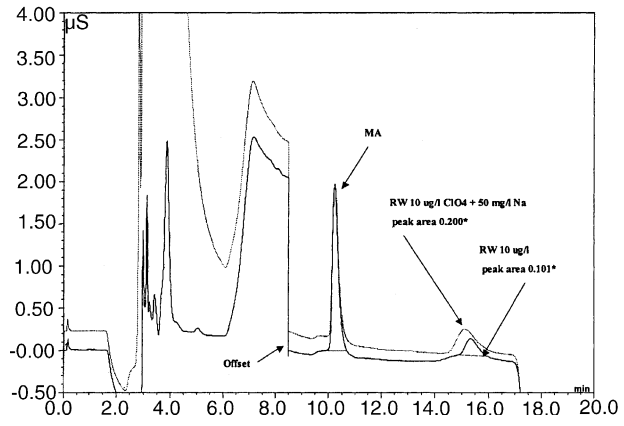

Fig. 4. Effect of 50 mg/l Na^+ on the ClO_4^- (10 μg/l) peak shape using column concentration on Cryptand trap, guard and analytical columns. Chromatograms are "*y*"-axis offset 15% for clarity.

3.6. Column concentration with background reduction using Cryptand confirmational columns

The column concentration method with the Cryptand confirmational columns (see Section 2.4.4) appeared to provide acceptable results for MA and ClO_4^- in RW matrices, with the addition of 50 mg/l Na^+. Consequently, column concentration with background reduction was investigated as a means of eliminating the interfering anions in the HIW matrices.

3.6.1. Cryptand column concentration with background reduction in RW matrices

The next step was to evaluate the effect on the peak shapes and areas for the MA and ClO_4^- peaks after concentrating samples on the Cryptand trap column and then rinsing with varying volumes of dilute hydroxide prior to injection of the sample (Section 2.4.5). A 5 ml portion of RW containing 10 μg/l of ClO_4^- in the presence of 50 mg/l of Na^+ was loaded onto the Cryptand trap column and washed with either 1, 2, 3, 4 or 5 ml of 10 mM NaOH. The control sample was not rinsed. As indicated in Fig. 5, the MA t_R and peak areas were not affected by the NaOH rinse solution. Although the peak shape and peak area for ClO_4^- were not dramatically affected, the ClO_4^- t_R shifted forward, from 15.1 to 14.1 min as the volume of NaOH rinse solution increased.

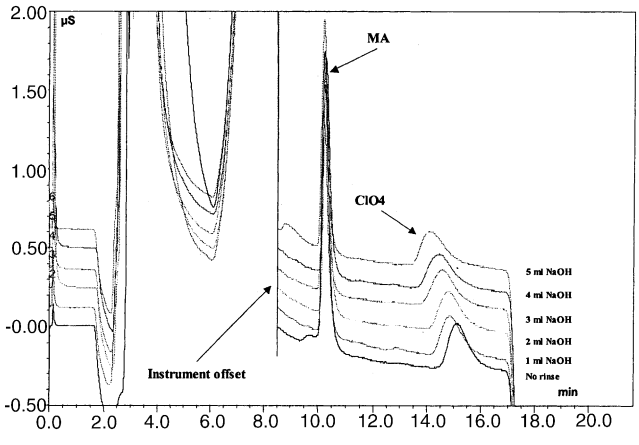

Fig. 5. Effect of NaOH rinse solution on MA and ClO_4^- (20 and 10 μg/l) in RW with 50 mg/l Na^+ on the peak shape and area using column concentration on Cryptand trap, guard and analytical columns. Chromatograms are "*y*"-axis offset 5% for clarity.

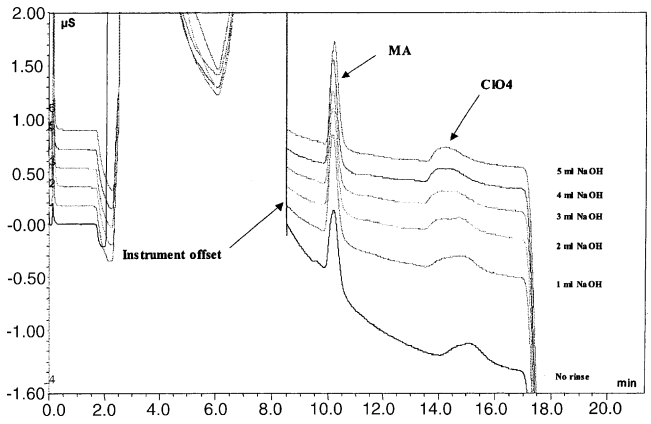

Fig. 6. Effect of NaOH rinse solution on MA and ClO_4^- (20 and 10 μg/l) in 375 mg/l HIW matrix on the peak shape and area using column concentration on Cryptand trap, guard and analytical columns. Chromatograms are "*y*"-axis offset 5% for clarity.

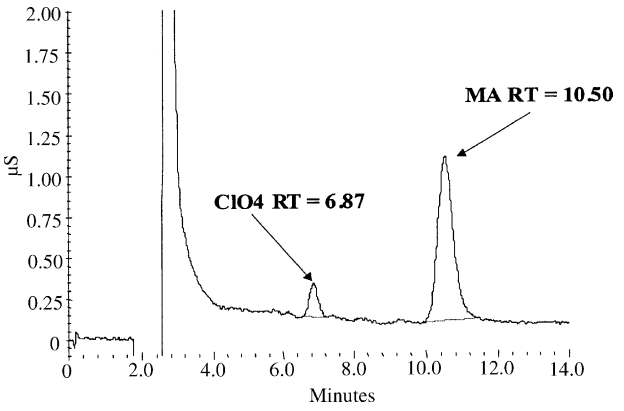

Fig. 7. Effect of eliminating the step gradient to LiOH on MA and ClO_4^- (20 and 10 μg/l) in a RW matrix on the peak shape and area using column concentration on Cryptand trap, and separation on an AG11HC guard and AS16 analytical column.

3.6.2. Cryptand column concentration/background reduction from HIW matrices

The experiments described above in Section 3.6.1 were repeated in a HIW matrix containing 10 μg/l of ClO_4^- and 375 mg/l of sodium chloride, carbonate and sulfate. As indicated in Fig. 6, the MA t_R was not significantly different than in the RW control. However, the peak area for MA was, on average, 31% lower in the HIW matrix. Although the peak shape for ClO_4^- was broadened and skewed, the peak area was not dramatically affected. Again, the ClO_4^- t_R shifted forward from 15.2 to 14.2 min, as the volume of NaOH rinse solution increased.

3.7. Use of the Cryptand concentrator column with AG11HC and AS16 columns

The step gradient to LiOH that is required with the Cryptand columns causes a shift in the baseline conductivity due to the presence of carbonate in the manually prepared LiOH eluent. Incorporation of an ATC column can help to decrease the baseline shift. However, the ATC column has a limited lifetime and requires frequent regeneration. In some instances, especially when monitoring trace levels of perchlorate in HIW matrices, an offset may still be required to monitor the small peaks produced by 0.5–1.0 μg/l ClO_4^-.

An effort to eliminate the need for the ATC column and the step gradient with the Cryptand concentrator column was investigated. The idea involved the use of the Cryptand trap column with the AG11HC and AS16 columns combined with isocratic elution of the analytes with 75 mM LiOH. The AS40 autosampler was used to load a 5 ml volume of 35 mM NaOH onto the Cryptand concentrator column to set the capacity of the Cryptand concentrator column prior to loading 5 ml of sample onto the Cryptand concentrator column (in the sample loop, load position). At injection, the concentrator column was switched in-line where the analytes were eluted from the Cryptand concentrator column onto the AG11HC/AS16 columns for separation using a single, 75 mM LiOH eluent. As shown in Fig. 7, both MA (20 μg/l) and ClO_4^- (3.0 μg/l) in a RW matrix were well separated and eluted from the columns in less than 14 min. Although there was no shift in baseline, the baseline appeared noisier with the LiOH eluent compared to a NaOH eluent.

4. Conclusions

Acceptable precision, detection limits and minimum reporting levels were obtained using the large-loop direct injection method for perchlorate in RW and HIW matrices that had been pretreated with SPP cartridges to remove the interfering anionic species prior to injection. However, the use of cartridge pre-treatment prior to injection increased the cost per analysis.

The column concentration method for perchlorate from RW samples was effective with both the TAC LP1 and Cryptand trap columns using the AS40 autosampler. High ionic strength matrices containing perchlorate, which had been pretreated with SPP cartridges prior to concentration on either the TAC LP1 or Cryptand trap columns, also provided acceptable data. The cost per analysis was also increased with this technique.

The AS40 autosampler can be used successfully to perform both the column concentration step as well as the background reduction step. However, the background reduction step did not perform successfully with either the TAC LP1 or Cryptand trap columns that were evaluated. The shifting retention times and changing peak shapes for perchlorate were unacceptable. Although the peak areas for perchlorate were relatively consistent, the perchlorate t_R and peak shape were dramatically affected by the concentration of the rinse solution, providing data, which was unacceptable.

The AS40 can also be used successfully to establish the capacity of the Cryptand trap column. Elution from the Cryptand trap column onto the AG11HC/AS16 columns with a single 75 mM LiOH eluent eliminates the need for

the step gradient that is normally required with the Cryptand columns.

The sensitivity of EPA Method 314.0 has the potential to be significantly increased using SPP cartridge treatment and either the large-loop direct injection or column concentration methods described above. However, work is continuing to develop an effective concentrator column for perchlorate to reduce the added cost of the SPP cartridges. Until a suitable trap or concentrator is developed, treatment with SPP cartridges will remain a viable approach for analyzing trace levels perchlorate in high ionic strength matrices using suppressed conductivity detection.

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