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Preconcentration/preelution ion chromatography for the determination of perchlorate in complex samples

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Abstract

The determination of perchlorate in complex matrices by ion chromatography (IC) with an online preconcentration and preelution technique is discussed. The method was applied to different sample types containing large concentrations of matrix anions that would otherwise interfere with analysis via conventional IC. The present approach was highly effective in removing most of the matrix anions and was thus resistant to the interferences commonly encountered in a high ionic strength background. Method performance was evaluated by analyzing for low-level perchlorate in synthetic high ionic strength solutions, tissue extracts, and hydroponic nitrate fertilizer samples. Not only is it easier to practice the present method compared to USEPA Method 314.0, but for most of these samples the present approach provided equal to or better recovery of perchlorate than Method 314.0. With a sample of specific conductance 12,650 μS cm^{-1}, for example, the present method provided a perchlorate recovery of 101% at the 25 μg L^{-1} level versus 89% by EPA Method 314.0. Method detection limits of perchlorate in hydroponic fertilizer samples with this method (130–190 μg kg^{-1}) are the lowest thus far reported.

Keywords: Ion chromatography; Non-water matrices; Perchlorate; Preconcentration; Hydroponic fertilizers

1. Introduction

The U.S. Environmental Protection Agency (EPA) has placed perchlorate on the drinking water contaminant candidate list [1]. At least 20 states in the U.S. have confirmed perchlorate releases. While perchlorate contamination in surface and groundwater is usually associated with the manufacture, storage, and testing of solid rocket motors, recent reports on the significant presence of perchlorate in groundwater in regions far from such known sources is enigmatic [2]. In addition to surface and groundwaters, perchlorate has been found in a variety of other matrices such as soil, vegetation, animal tissues, and milk [3–6]. Perchlorate has also been detected in fertilizers containing Chilean saltpeter [7] and in some cases in hydroponic fertilizers [8] with no link to Chilean saltpeter. Because of an increase in commercial hydroponic farming of fruits and vegetables, there is potential concern about the uptake of perchlorate from such fertilizers. In this journal, Collette et al. [9] recently reported that perchlorate was detected in three of seven hydroponic fertilizer samples.

Many methods, including UV–vis spectrophotometry [10–12], Fourier transform infrared spectrometry [13], Raman spectroscopy [8], ion-selective electrodes [14], capillary electrophoresis [15], mass spectrometry [16], etc. have all been described for the analysis of perchlorate. However, ion chromatography (IC) is the technique most widely used for the determination of perchlorate because of its sensitivity, ability to separate perchlorate from other ions, and its availability in many laboratories. Nevertheless, trace determination of almost any analyte by IC in the presence of high

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concentrations of other anions can be difficult. The case of perchlorate is a little more favorable than the typical ionic analyte because perchlorate is more strongly retained than most anions. Still, high salinity samples cause a high signal background from tailing peaks of the less retained ions and lead to poor analyte recovery [17]. In many cases, the matrix peak(s) will totally overlap the perchlorate response. In EPA Method 314.0, serial pretreatment by Ag^{+}-, Ba^{2+}-, and H^{+}-loaded cation exchangers are recommended for removal of chloride, sulfate, and carbonate [17]. This approach is at best partially effective in our experience and is not easily automated. Moreover, according to experimental results, this treatment is of little value with some biological tissue and fluid samples. For instance, egg [19] and milk [6] samples need to be processed for prior protein precipitation, ethanol is typically used as a non-ionic, removable agent for this purpose. However, after the pretreatment process and evaporation to remove ethanol, the extract still contains a small amount of residual ethanol that causes an elevated, slowly bleeding conductance background when that extract is directly injected into a conventional IC system. This leads to interference and quantitative inaccuracies in the determination of perchlorate. We present here a system that allows such an extract to be directly analyzed without problems.

Earlier, we developed an online preconcentration/preelution (PC/PE) approach for improved IC analysis of high conductivity and high background samples [18]. In this report, a more effective extension of this system is demonstrated for the determination of trace perchlorate in complex samples. A combination of two short preconcentration columns (PCs) replaces the sample injection loop. After sample preconcentration, these columns are preeluted with a dilute NaOH eluent before it is connected to the principal separation column. This permits the majority of the matrix ions to be eluted and removed before the perchlorate-containing preconcentrated and processed sample plug enters the principal separation system. Compared to the use of a single 35-mm column for preconcentration [18], the new system provides distinctly better performance with more complex matrix samples. We demonstrate the application of this approach for perchlorate analysis in high ionic strength samples and hydroponic fertilizers.

2. Methods

2.1. Reagents and standards

All solutions were prepared in 18.3 MΩ cm water (Milli-Q, Millipore) equipped with a 0.45 μm outlet filter. Sodium hydroxide, 50% (w/w) aqueous solution, sodium chloride, sodium sulfate, sodium carbonate, and potassium chloride were all analytical reagent grade (Fisher Scientific). A 100 mg L^{-1} sodium perchlorate standard (AccuStandard, Inc., New Haven, CT) was used as the stock perchlorate standard. Sodium hydroxide eluent (100 mM) was prepared by dissolving 5.2 mL (8.0 g) of 50% (w/w) NaOH in reagent water to a final volume of 1.0 L and used under a 5 psi helium blanket. Synthetic samples of known conductivity containing various common anions, perchlorate standard solutions, perchlorate-spiked samples, and conductivity calibration standards were prepared as prescribed in EPA Method 314.0 [17].

2.2. Instrumentation

Fig. 1 shows the system configuration. All chromatographic equipment was from Dionex. An IC25 chromatograph equipped with a LC25 chromatography oven (35 °C) and an AS40 automated sampler was used with a AG16 (4 mm × 50 mm) guard column and an AS16 (4 mm × 250 mm) analytical column. The flow rate of the eluent, 100 mM NaOH, was 1.0 mL min^{-1}. The wash solution (10 mM NaOH) was pumped at 0.80 mL min^{-1}. An ASRS-ULTRA suppressor was operated at 300 mA and used in the external water mode. The dashed enclosure in Fig. 1 is essentially the standard IC

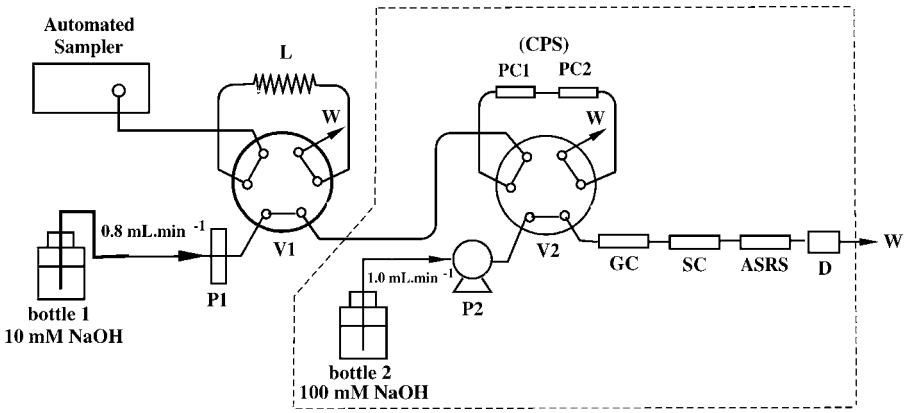

Fig. 1. Schematic diagram for present system. P1: peristaltic pump; L: sample loop; PC1 and PC2: preconcentration columns; GC: guard column; SC: separation column; ASRS: electrodialytic suppressor; D: conductivity detector; V1: low-pressure six-port valve; V2: six-port chromatographic injector; P2: chromatographic pump; W: waste.

configuration except for the sample loop being replaced by a preconcentration system composed of two preconcentration columns PC1 and PC2 (TAC-LP1, 4 mm × 35 mm). The other components of the PC/PE system outside the dashed enclosure were the same as those used previously [18]. The volume of loop (L) was 1.0 mL.

2.3. Operating conditions

Operating conditions (selectivity, sensitivity, wash volume, etc.) for the two-column system were optimised, as previously discussed [18]. With a 10 mM NaOH wash solution, ~1.8–6.0 mL can be used to effectively preelute the PC's without loss of perchlorate. The optimum value within this range is dependent on the specific sample type. For processed milk or biological tissue samples, the sample does not have particularly high conductivity but contains strongly retained ions other than perchlorate, leading to a high background. For these samples, we find a high wash volume (3.0–6.0 mL) is better. On the other hand, for fertilizer samples, which have a high conductivity background but not other ions that are as strongly retained as perchlorate, in general, a lower wash volume (1.8–2.0 mL) is better when the perchlorate concentration is low. When the perchlorate concentration is high, there is greater latitude in selecting the precise wash volume; greater wash volumes reduce the background further. For the present configuration, a minimum injection period (t_{inj}) of ~75 s is needed to fully transfer perchlorate to the separation system; this time increases at lower wash volumes and sample ionic strength. Perchlorate retention times for all sample analyses remained within the 5% window recommended by EPA Method 314.

2.4. Sample type and preparation

The tissue matrix was from an extract of a wood duck (*Aix sponsa*) egg prepared, extracted, and processed as described in [19]. Seven hydroponic nitrate fertilizer samples studied by Collette et al. [9] were kindly supplied by these researchers. These sample solutions were prepared by weighing 1.00 g of the fertilizer sample in a 100-mL volumetric flask and diluting to final volume with deionized, distilled water.

3. Results and discussion

3.1. Common anion standards with varying conductivities

A series of common anion solutions with different conductivities were prepared as described above with each solution containing 25 μg L^{-1} perchlorate and varying amounts of SO_4^{2-}, Cl^-, and CO_3^{2-}. The solutions were analyzed by (1) EPA Method 314.0 [17]; (2) single column preconcentration system [18] using 2.0-mL wash volume and 80 s injection duration; and (3) the two-column system with the same wash volume and injection duration as used in the single column configuration. The experimental results are shown in Table 1. When EPA Method 314.0 was used, perchlorate recovery markedly decreased at conductivities ≥10,850 μS cm^{-1}. These results clearly indicate the higher recoveries obtained by the present method over EPA Method 314.0 and the comparable if not higher recoveries than those obtained with the single preconcentration column system. The present method removed the background of the high salinity sample much more effectively and thus allowed better quantitation of the perchlorate peak (Fig. 2a).

Table 1
Recoveries of perchlorate in synthetic common anion matrix analyzed via the present method and EPA Method 314.0

Sample matrix conductance (μS cm^{-1})	Percentage recovery for EPA Method 314.0	Percentage recovery for single PC system	Percentage recovery for two PC system
<1	100	100	100
1767	99.4	98.8	98.3
3425	97.3	99.6	98.2
4850	96.5	99.0	97.7
8063	94.0	98.8	99.1
9451	93.7	99.7	97.1
10850	92.0	99.4	99.4
12650	88.9	96.4	101
14680	84.2	92.0	98.3

3.2. Bird egg extract

The bird egg extract was spiked with 10 μg L^{-1} perchlorate but no perchlorate was detectable by the EPA method and only a very high background was discernible (Fig. 2b). However, the present method provided a recovery of 99.3 ± 0.17% (n = 3), considered excellent for this highly complex sample. As can be seen from Fig. 2b, for common IC, the egg sample shows a high background, which interferes with the analytical results. The high background is caused by the sample matrix as well as residual ethanol used during sample processing. To fully remove the ethanol, time consuming repeated evaporation steps can be used but this cannot remove matrix interferences. In comparison, in the presently described system, the effect caused by both the ethanol and matrix can be effectively and conveniently reduced.

3.3. Hydroponic fertilizer samples

Seven hydroponic fertilizer samples were also analyzed by the present method. Triplicate analyses were conducted for each sample. To achieve qualified data in this experiment, some quality assurance (QA) samples, such as a quality control sample (QCS) and laboratory fortified sample matrix (LFM), were prepared according to the process described in EPA Method 314.0 [17]. The perchlorate concentration fortified in the QCS sample was 100 μg L^{-1}. The perchlorate concentration fortified in LFM for each fertilizer sample was

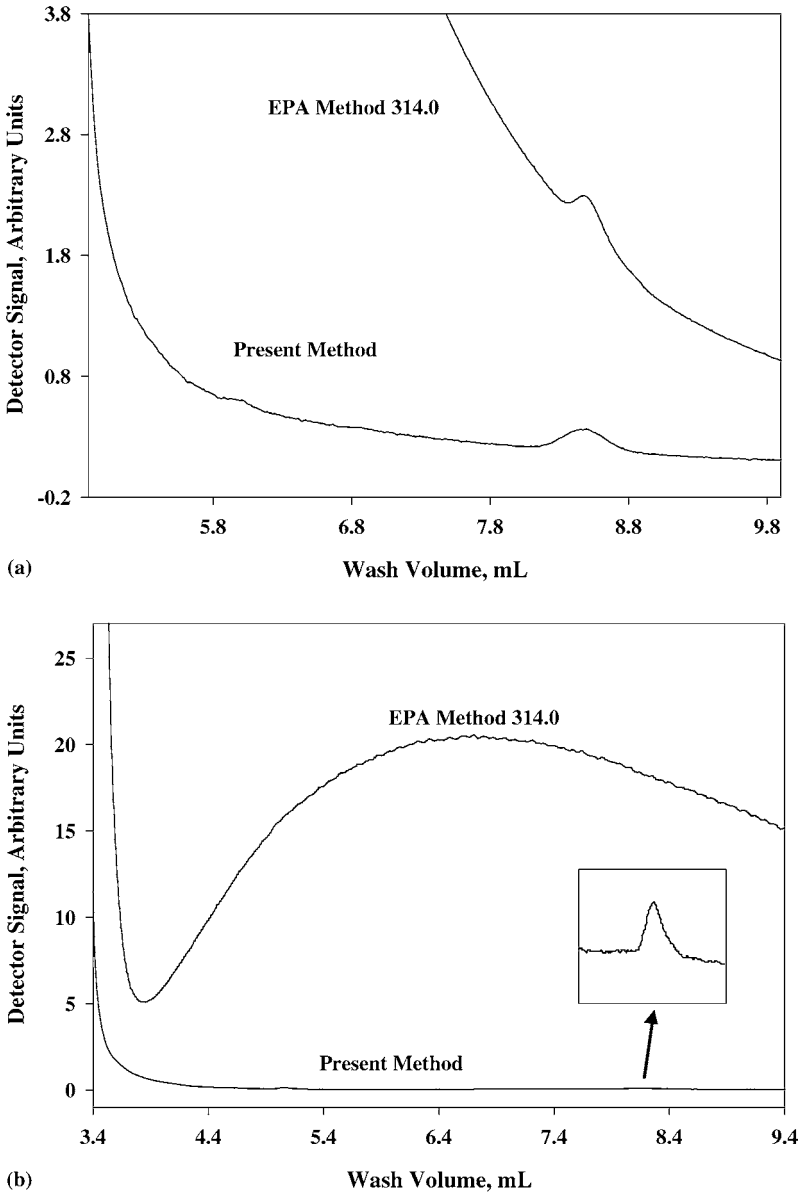

Fig. 2. Chromatographic comparisons between the present PC/PE Method and EPA Method 314.0 for perchlorate analysis in complex matrices. For the present method, 10 mM NaOH flowing at 0.80 mL min^{-1} was used for analysis with a wash volume of 2.0 mL for synthetic common anion samples, 3.2 mL for the bird egg extract, and with injection duration of 85 s. (a) Synthetic common anion sample fortified with 25 $\mu g\,L^{-1}$ perchlorate (G = 8074 $\mu S\,cm^{-1}$); (b) tissue sample fortified with 10 $\mu g\,L^{-1}$ perchlorate.

200 $\mu g\,L^{-1}$. The recovery of QCS was 97 ± 0.81%. The average recoveries for all LFMs were 95 ± 1.4%. The experimental data are reported in Table 2. The results are comparable to the data previously reported [9] but in general, there is less variability in the quantitation.

Hydroponic fertilizer samples #3, #5, and #6, which did not contain significant concentrations of perchlorate, were selected for recovery studies. Samples were diluted 100-fold and spiked with two levels of perchlorate. Recoveries were generally superior with the present method (Fig. 3 and Table 3) compared to the EPA Method for both high and low levels of perchlorate added. It is worth noting that while the recovery for the present system was 52.6 and 46.9%, respectively, for samples #3 and #6 spiked with 3.0 $\mu g\,L^{-1}$ perchlorate, this is due to the large amount of ionic equivalents injected. Either reducing the total injected volume or using greater sample dilution can overcome this problem. For samples diluted 250-fold and spiked with 2.5 $\mu g\,L^{-1}$ perchlorate, the respective recoveries increased to 90.5 ± 9.8% and 86.9 ± 6.4% (n = 3 for both).

Detection limits were determined with hydroponic fertilizer samples #3 (solid) and #6 (liquid) as matrix. Neither of these samples contained detectable perchlorate. Seven replicate samples were diluted 250-fold, spiked at 2.5 $\mu g\,kg^{-1}$, and analyzed. The MDL of the system was calculated according to EPA Method 314.0 to be 126 ± 40 and 191 ± 61

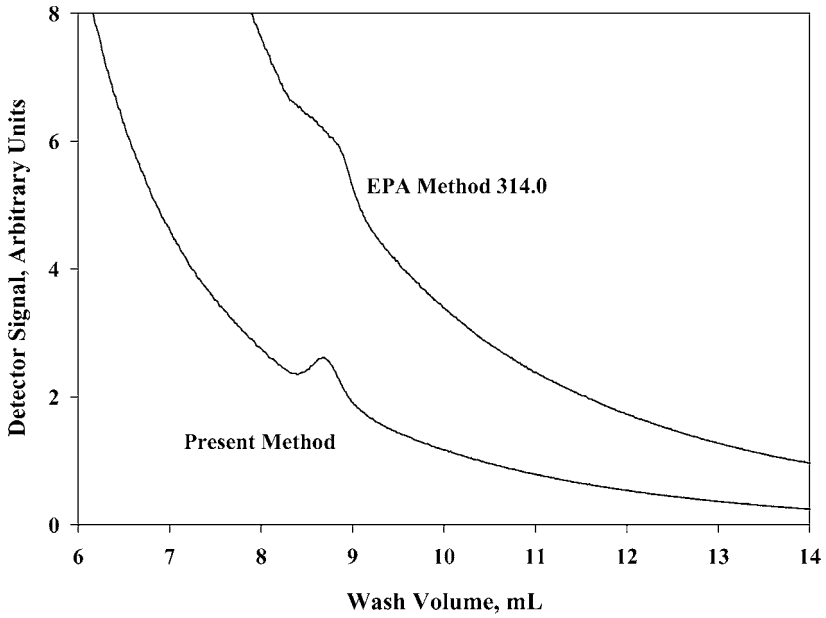

Fig. 3. Comparison of a hydroponic fertilizer (sample #6, 100 mg L^{-1} spiked with 100 μg L^{-1} perchlorate) analyzed by EPA Method 314.0 and the present method (2.0 mL 10 mM NaOH prewash, injection period = 85 s).

(μg kg^{-1}). In comparison, the best LOD among the methods in Table 2 as reported by Collette et al. [9] was 30 mg kg^{-1} (IC and cESI-MS). One obvious advantage of the present system is that good sensitivity can be achieved without the complex and time-consuming sample pretreatment necessary for the other methods. Even though Raman analysis does not often require extensive sample pretreatment, the method is not very sensitive with an LOD in fertilizers of 50 mg kg^{-1} [9].

The online preconcentration/preelution technique for perchlorate analysis reduces the matrix background efficiently for a variety of complex and high background samples and provides satisfactory recoveries.

Table 2
Perchlorate in hydroponic nitrate fertilizer samples analyzed by the present method compared to data from other methods [9]

Sample #	ClO_4^- concentration, mg kg^{-1} (mean ± S.D.)				
	Present method	Common IC[a]	cESI-MS[a]	ATR–FTIR[a]	Raman[a]
1	199 ± 3[b]	202 ± 2	230 ± 29	120 ± 40	92 ± 5
2	364 ± 2[b]	319 ± 16	483 ± 146	340 ± 30	352 ± 87
3	ND[c]	ND	ND	ND	ND
4	262 ± 7[b]	285 ± 9	323 ± 15	300 ± 100	268 ± 12
5	ND[c]	ND	ND	ND	ND
6	ND[c]	ND	ND	ND	ND
7	ND[c]	ND	ND	ND	ND

[a] Data from Collette et al. [9].
[b] Sample stock (10 g L^{-1}) diluted 5000-fold.
[c] Sample diluted 250-fold.

Table 3
Recovery of perchlorate in hydroponic fertilizer samples analyzed via the present method and EPA Method 314.0

Sample #	Spiked concentration (μg L^{-1})	Percentage recovery ± S.D.	
		EPA Method 314.0	Present method
3	100	82 ± 5	94 ± 1
5	100	80 ± 9	95 ± 0.75
6	100	101 ± 3	101 ± 1
3	3	0	52 ± 6
6	3	0	47 ± 12

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