

Determination of Perchlorate Levels in Food and Soil Samples Using Accelerated Solvent Extraction and Ion Chromatography

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Overview

Purpose: Demonstrate the use of accelerated solvent extraction and ion chromatography (IC) to determine perchlorate levels in complex matrices.

Methods: Samples contained within stainless steel extraction chambers were subjected to heat and pressure following addition of solvent. Extracted material was recovered, filtered, and then analyzed using IC.

Results: Accelerated solvent extraction yielded percent recovery for perchlorate of 89–119% with %RSD of 8.9–1.6. The method detection limit (MDL) and reliable quantitation limit (RQL) ranged from 0.72–2.0 and 2.0–8.0 µg/kg, respectively, depending on the matrix.

Introduction

Perchlorate (ClO_4^-) occurs naturally, but also as an environmental contaminant that has been found in drinking, ground, and surface waters in several U.S. states. Most of the contaminated sites have been traceable to sources near military installations or manufacturing sites where perchlorate salts are used to produce rocket propellant, munitions, or fireworks. The solubility, mobility, and persistence of perchlorate have resulted in the contamination of drinking water, soil, and vegetation.

Perchlorate has been shown to disrupt iodine uptake by the thyroid gland, inhibiting growth and development. For this reason, the U.S. Environmental Protection Agency (EPA) has defined perchlorate as a regulated contaminant for drinking water.¹ Plants grown with perchlorate-tainted water become contaminated with perchlorate.² Preparation of water samples for determination of perchlorate is generally not considered difficult. However, preparation of vegetation for analysis is much more challenging and tedious.

This poster describes the use of accelerated solvent extraction and IC for determination of perchlorate in soil, milk, and plant matrices.

A more precise and sensitive method for perchlorate determination using 2D-IC is outlined in Thermo Scientific Application Note 1024.³

Methods

Sample Preparation

Prior to extraction, 100 mL extraction cells were prepared from bottom to top as follows: two glass microfiber (GFB) filters, 3.0 g of Thermo Fisher™ Dionex™ OnGuard™ H (hydronium), a GFB filter, 6.0 g of Dionex OnGuard Ag (silver), a GFB filter, 3.0 g Dionex OnGuard Ba (barium), a GFB filter, 18 g basic alumina, a GFB filter, 1.8 g Dionex OnGuard RP (Poly-divinylbenzene), a GFB filter, and then the remainder of the cell was filled with Thermo Scientific Dionex ASE Prep DE (diatomaceous earth) plus sample. Representative samples (5 g) were placed into a mortar with 10 g of Dionex ASE Prep DE, ground with a pestle, and then added to the extraction cell. The mixture was then spiked with the appropriate amount of perchlorate standard. The cells were allowed to stand overnight at 4 °C. The final volume of each of the resulting extracts was adjusted to 100 mL. The 33 mL cells were prepared in the same manner with proportionally less of each resin.

Prior to analysis, each of the extracts was filtered using a 0.2 µm polyethersulfone syringe filter.

Accelerated Solvent Extraction Conditions

Instrument:	Thermo Scientific™ Dionex™ ASE™ 200 or 300 Accelerated Solvent Extractor system
Extraction Solvent:	18 MΩ-cm resistivity deionized water
Pressure:	1500 psi
Temperature:	80 °C
Equilibration Time:	5 min
Extraction Time:	5 min (static)
Solvent Flush:	30% (of cell volume)
Nitrogen Purge:	120 s (after extraction)
Extraction Cycles:	3
Cell Sizes:	33 mL and 100 mL

Chromatographic Conditions

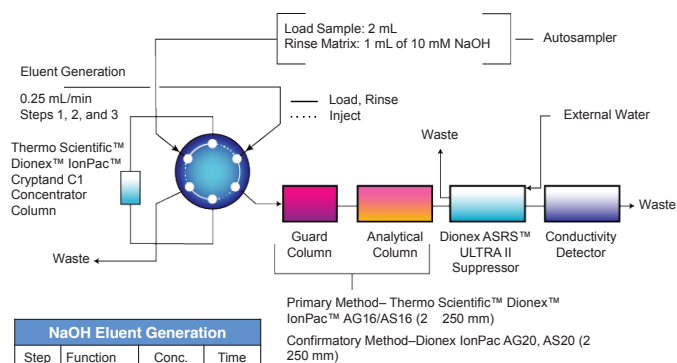
Instrument:	Thermo Scientific Dionex ICS-2500 IC System
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The chromatographic conditions used were as noted in figures 2–4. Figure 1 outlines the chromatographic system configuration. See Thermo Scientific Application Note 176 for more details.⁴

Data Analysis

Thermo Scientific™ Dionex™ Chromeleon™
Chromatography Data Systems software, version 6.6
(Service Pack 3)

FIGURE 1. Schematic of the system configuration for concentration and determination of perchlorate.



NaOH Eluent Generation			
Step	Function	Conc.	Time
1	Perchlorate Transfer	0.5 mM	12 min
2	Analysis	60 mM	16 min
3	Column Cleanup	100 mM	2 min

Results

Each sample matrix was extracted in replicates of five. The recovery data and reproducibility for each set of extractions are shown in Table 1.

TABLE 1. Recovery data for perchlorate in different matrices following accelerated solvent extraction and IC analysis.

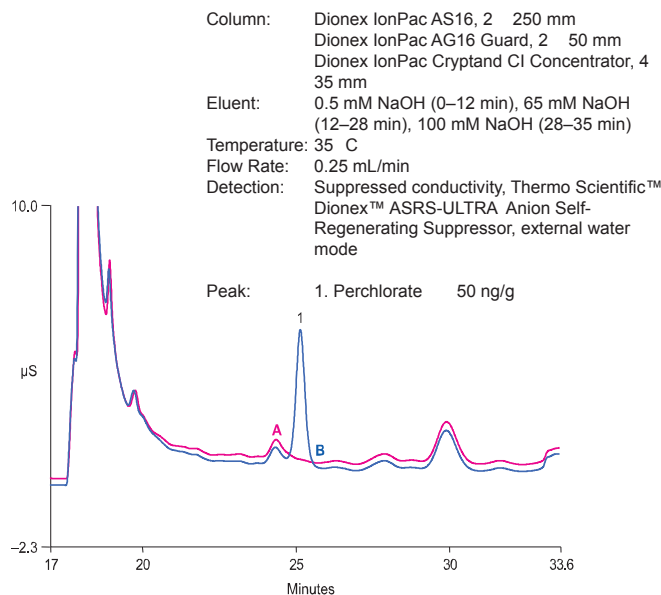
Matrix	Perchlorate (ppb)	% Recovery*	% RSD
Soil	50	106	7.89
Alfalfa	50	94.2	8.24
Corn	50	88.7	8.86
Milk	25	118.7	1.57

*Analysis was performed using EPA Method 314.1⁵ with a Dionex ICS-2500 IC system.

Perchlorate in Soil

Figure 2 compares chromatograms of a 3 g soil sample that had been spiked with 50 ppb (ng/g) perchlorate and extracted with water. Chromatogram A shows a blank soil extract, and chromatogram B shows a soil extract spiked with perchlorate. The perchlorate peak was well resolved with no observed sample-related interferences.

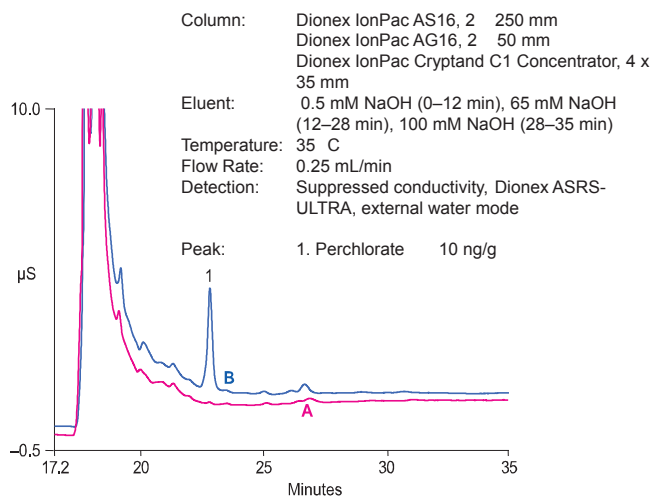
FIGURE 2. Chromatograms of (A) a soil “blank” obtained using accelerated solvent extraction, and (B) a 3 g soil sample spiked with perchlorate and extracted with water.



Perchlorate in Melon

Figure 3 shows the chromatogram resulting from an accelerated solvent extract of a 5 g melon sample spiked with 10 ppb (ng/g) perchlorate. The chromatogram of a “blank” melon extract is overlaid with the spiked sample to show that there are no extraneous peaks in the “blank” extract that interfere with the perchlorate peak.

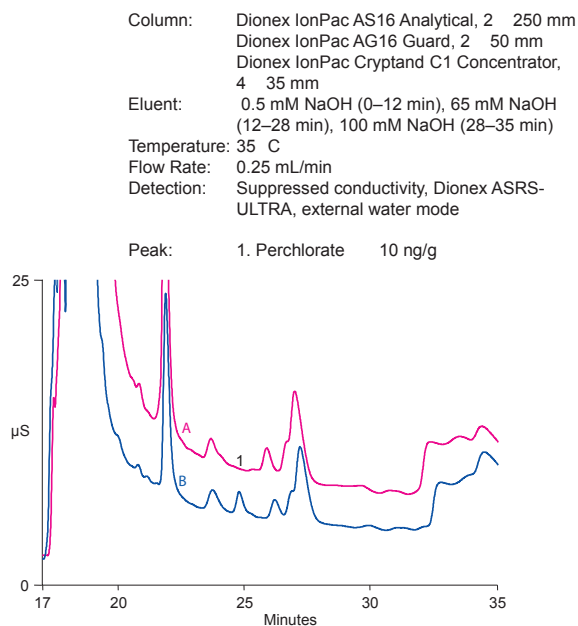
FIGURE 3. Chromatograms of (A) a melon “blank” obtained using accelerated solvent extraction, and (B) a 5 g melon sample spiked with perchlorate.



Perchlorate in Spinach

Figure 4 shows the chromatogram of a 5 g spinach sample spiked with 10 ppb (ng/g) perchlorate. The chromatogram of a spinach “blank” extract is again overlaid with the spiked sample to show that there are no interferences with the perchlorate peak.

FIGURE 4. Chromatograms of (A) a spinach “blank” obtained using accelerated solvent extraction, and (B) a 5 g spinach sample spiked with perchlorate.



Method Performance

The method performance was evaluated by calculating the method detection limit (MDL). This was done by multiplying the standard deviation of the seven replicates of the low-level samples by 3.143 (as per EPA guidelines). The reliable quantization limit (RQL) was calculated by multiplying the MDL by 4. See Table 2 for a summary.

TABLE 2. Summary of the method performance.

Matrix	Avg. Recovery (% , n = 21)	*MDL (µg/kg)	*RQL (µg/kg)
Melon	103.3	0.72	2.9
Corn	96.3	1.4	5.6
Spinach	101.6	2.0	8.0

*Analysis was performed using EPA Method 314.1⁵ with a Dionex ICS-2500 IC system.

Conclusion

The method described in this poster demonstrates:

- Use of accelerated solvent extraction as a labor, solvent, and time efficient way to perform extractions across a variety of matrices.
- Determination of perchlorate at ppb levels using IC.
- Detection and reliability limits that ranged from 0.72 to 8.0 µg/kg, depending on the matrix.

References

1. Technical Fact Sheet- Perchlorate. U.S. Environmental Protection Agency. **2012**. EPA Pub. No. EPA 505-F-11-003.
2. Perchlorate Accumulation in Forage and Edible Vegetation. W. A. Jackson, P. Joseph, P. Laxman, K. Tan, P. N. Smith, L. Yu, T. A. Anderson. *J. Agric. Food Chem.* **2005**, *53*, 369.
3. Improved Determination of Trace Perchlorate in Drinking Water Using 2D-IC. Thermo Fisher Scientific Application Note 1024. Document No. AN70213, Sunnyvale, CA, **2012**.
4. Determining Sub-ppb Perchlorate in Drinking Water Using Preconcentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection by U.S. EPA Method 314.1. Thermo Fisher Scientific Application Note 176. Document No. AN70398, Sunnyvale, CA, **2012**.
5. Method 314.1, U.S. Environmental Protection Agency, Cincinnati, OH, **2005**.

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