

Determination of Perchlorate in High Ionic Strength Fertilizer Extracts by Ion Chromatography

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Introduction

Perchlorate anion (ClO_4^-) is a water soluble, mobile, and persistent environmental contaminant most clearly linked with the disposal of ammonium perchlorate used in rocket propellants.¹ Perchlorate may cause hypothyroidism by interfering with the uptake of iodide (a similarly polarizable anion) needed by the thyroid to produce thyroid hormones. The prescribed method for determination of perchlorate in drinking and ground waters, as required in the assessment phase of the Unregulated Contaminant Monitoring Rule, is U.S. Environmental Protection Agency (EPA) Method 314.0.² Perchlorate determination in water at the low- $\mu\text{g/L}$ level is described in Dionex (now part of Thermo Scientific) Application Note 134.³

Beyond the need to monitor drinking and ground water for perchlorate, there is also interest in identifying other potential sources of perchlorate contamination of the environment. This will demand analysis of more complex matrices with higher ionic strength than drinking water. For example, Chilean caliche (sodium nitrate) may contain naturally occurring perchlorate. Products derived from Chilean caliche currently represent only about 0.14% of present U.S. fertilizer use, but were more widely used in the past. Among the materials surveyed for perchlorate in recent reports were fertilizers and fertilizer feed stocks. One survey confirmed the occurrence of perchlorate in Chilean caliche, but did not identify perchlorate in any of the other materials tested.⁴

This application note provides a procedure for preparing aqueous leachates of fertilizers, inorganic salts, and other materials. The perchlorate anion in these extracts or similar high ionic strength matrices can be determined in 15 min by using a Thermo Scientific™ Dionex™ IonPac™ AS16 column, EG40-generated hydroxide eluent, a 500- μL injection, and suppressed conductivity detection.

The Dionex IonPac AS16 column is a high capacity, hydroxide-selective anion exchange column with ultra low hydrophobicity designed for the isocratic separation of polarizable anions including perchlorate, iodide, thiocyanate, and thiosulfate. The Dionex IonPac AS16 column's capacity of approximately 170 $\mu\text{eq/column}$ allows large loop injections without column overloading. The higher capacity extends the method's linear range and improves its performance for trace-level determinations of perchlorate in high ionic strength matrices.

Equipment

- Thermo Scientific™ Dionex™ DX-600 Chromatography System:
 - GP50 Gradient Pump with Vacuum Degas Option
 - EG40 Eluent Generator Module
 - Thermo Scientific™ Dionex™ EluGen™ Hydroxide Cartridge (EGC-KOH) (P/N 053921)
 - ED50 Conductivity Detector with DS3
 - SRS Gas-Assisted Regeneration Kit (P/N 56886)
 - AS50 Automated Sampler with Thermal Compartment
 - 1.0 mL sample syringe for AS50 (P/N 55066)
 - Thermo Scientific™ Dionex™ PeakNet™ 6 Chromatography Workstation
- Syringe filters (Gelman IC Acrodisc, 0.2 μm , PN 4483)
- Orbital shaker (LAB-LINE 3520)
- Centrifuge (Beckman GS-6R)

Conditions	
Columns:	Dionex IonPac AS16 Analytical, 4 × 250 mm (P/N 55376) Dionex IonPac AG16 Guard, 4 mm, 4 × 50 mm (P/N 55377)
Eluent:	65 mM potassium hydroxide (KOH)
Eluent Source:	EG40
Flow Rate:	1.2 mL/min
Temperature:	30 °C
Injection:	500 µL partial loop w/10 µL cut volume from a 1000-µL sample loop
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA, 4 mm, gas-assisted external water mode, current setting – 300 mA DS3 Cell (P/N 044130), 35 °C, 1.7% /°C
Background:	1–3 µS
Noise:	5–10 nS peak-to-peak
Backpressure:	Adjust to ~2500 psi
Run Time:	15 min

Reagents and Standards

Ammonium perchlorate (NH₄ClO₄), A.C.S. grade

Preparation of Solutions and Standards

Reagent Water

Type I Reagent Grade distilled or deionized water with a specific resistance of 17.8 MΩ-cm or greater, filtered through a 0.2-µm filter immediately before use.

Eluent Solution

Generate the 65 mM KOH eluent on-line by pumping reagent water through the EG40. Dionex PeakNet software tracks the amount of KOH used and calculates the remaining lifetime of the EGC-KOH cartridge.

Alternatively, prepare 65 mM NaOH by pipetting 5.2 g of 50% (w/w) aqueous NaOH from the middle portion of the reagent bottle into a 1.00-L volumetric flask containing about 500 mL of degassed reagent water. Do not shake the 50% (w/w) NaOH bottle or pipette from the top of the solution where sodium carbonate may have formed. Dispense the aliquot of NaOH below the surface of the water to avoid the introduction of carbon dioxide from the air into the eluent. Bring to volume with degassed reagent water. Mix and degas by sparging with helium or sonicating under vacuum for 10 min. Atmospheric carbon dioxide readily dissolves in dilute basic solutions, forming carbonate. Carbonate contamination of eluents can affect the retention times of the analytes, resulting in performance that may not be equivalent to that achieved with the EG40 eluent generator. Store the eluent in plastic labware. Maintain an inert helium atmosphere of 3–5 psi in the eluent reservoir to minimize carbonate contamination.

Stock Standard Solutions

Prepare a 1000 mg/L stock standard solution of perchlorate anion by dissolving 0.1181 g of ammonium perchlorate in reagent water and diluting to 100 mL. Store in glass, high density polyethylene or polypropylene bottles at 4 °C. This stock standard is stable for at least one month.

Working Standard Solutions

Prepare working standards at lower concentrations by diluting appropriate volumes of the 1000 mg/L stock standard with reagent water. Prepare working standards daily if they contain less than 100 mg/L of perchlorate.

Sample Preparation

Dilute liquid samples as necessary and filter through a 0.2-µm IC syringe filter. Use a hydrophilic polypropylene or polyethersulfone filter; do not use polyvinylidene fluoride (PVDF). Discard the first 300 µL of filtrate and filter the remainder directly into a clean plastic autosampler vial. Qualify filters by analyzing a reagent water blank and a 10-µg/L perchlorate standard that has been passed through the filter. The blank should be free of peaks within the retention time window of perchlorate, and the recovery of the 10-µg/L standard should fall between 80% and 120%.

Use standard sampling practices to obtain a representative sample of the matrix to be analyzed, for example, a fertilizer or soil sample.⁵ Extract perchlorate anion from solid samples by combining 4.00 g solid with 40.0 mL reagent water in a 100-mL glass, high-density polyethylene or polypropylene bottle. Place the capped bottle on an orbital shaker and vigorously mix at 250 rpm for 8–15 h. Allow suspended material to settle, then decant into a 50-mL polypropylene centrifuge tube and centrifuge the supernatant at 6000 rpm for 10 min or until clear. Filter supernatant through a 0.2-µm IC syringe filter as above and inject.

In this study, high chloride samples (for example, KCl) were analyzed after simply diluting and filtering the extract. Alternatively, reduce the concentration of chloride by treating the sample with the Thermo Scientific™ Dionex™ OnGuard™ Ag cartridge (PN 39637) or the Dionex OnGuard II Ag 1 cc (PN 057089) followed by an OnGuard H cartridge (PN 39596) or OnGuard II H 1 cc (PN 057085). Prepare the Dionex OnGuard cartridges by passing 10 mL of reagent water through the cartridge at 2 mL/min. After preparing the cartridge, pass 5 mL of the undiluted sample through the cartridge. Discard the first 3 mL and collect the remainder for dilution or direct injection. (For details, consult Dionex (now part of Thermo Scientific) Application Note 134 and the Dionex OnGuard cartridge manual, Document No. 032943, or the Installation Instructions and Troubleshooting Guide for the OnGuard II Cartridges, Document No. 031688.)

System Preparation and Setup

Prepare the Dionex ASRS ULTRA for use by hydrating the eluent chamber. Use a disposable plastic syringe to slowly push approximately 3 mL of 200 mN H₂SO₄ through the ELUENT OUT port and 5 mL of 200 mN H₂SO₄ through the REGEN IN port. Allow the suppressor to sit for approximately 20 min to fully hydrate the suppressor screens and membranes. Install the Dionex ASRS ULTRA for use in the gas-assisted external water mode by following the Installation and Troubleshooting Instructions for the Dionex ASRS ULTRA, Document No. 31367, and the Dionex ASRS ULTRA Gas-Assisted Regeneration Kit, Document No. 31665. Adjust the head pressure on the external water reservoir to deliver a flow rate of 5–10 mL/min (~ 10–15 psi). Use a current of 300 mA.

Install the EG40 and configure it with the Dionex PeakNet Chromatography Data System. Make sure the high pressure degas tubing assembly (Degas Assembly, P/N AAA-053721) is installed to remove the electrolysis gas from the freshly generated eluent. Condition the Dionex EluGen KOH cartridge as directed in the EG40 Eluent Generator manual by running a gradient from 1 to 60 mN KOH in 20 min, then 60 mN for 40 min at 1 mL/min. (For instructions on EG40 installation and use, see the Operator's Manual for the EG40 Eluent Generator System, Document No. 031373).

Install a 4 mm × 50 mm Dionex IonPac AG16 and a 4 mm × 250 mm IonPac AS16 column. Make sure the system pressure displayed by the pump is at least 2000 psi when 65 mM KOH is delivered at 1.2 mL/min, so that the Degas Assembly can effectively remove hydrolysis gas from the eluent. If necessary, install backpressure coils supplied with the EG40 ship kit to bring the system pressure to between 2000 and 2800 psi. Because the system pressure can rise over time, trim the backpressure coil as necessary to maintain system pressure under 3000 psi. Do not exceed 3000 psi or the Degas Assembly tubing may rupture.

The storage solution that the Dionex IonPac AS16 column is shipped with is 35 mM NaOH. Equilibrate the column with 65 mM KOH eluent for 60 min; then analyze a system blank of reagent water. An equilibrated system has a background signal of less than 3 μS and peak-to-peak noise of less than 10 nS. There should be no peaks eluting within the retention time window of the perchlorate anion.

This application uses a partial-loop injection with a 1000-μL sample loop for a 500-μL injection. If injecting a different volume in the partial-loop injection mode, use a sample loop that is at least 2X the volume to be injected. Refer to the AutoSelect AS50 Autosampler Operator's Manual (Document No. 31169) for a complete discussion of the different injection modes.

Install a 1 mL sample syringe and set the syringe speed to 4 or 5 to make faster large-loop injections. Enter the correct sample loop size and sample syringe volume in the AS50 Plumbing Configuration screen. Inject a 100-μg/L standard. The column is equilibrated when two consecutive injections of the standard produce the same retention time for perchlorate. Confirm that the resulting chromatogram resembles the chromatogram of the 100 μg/L standard shown in Figure 1.

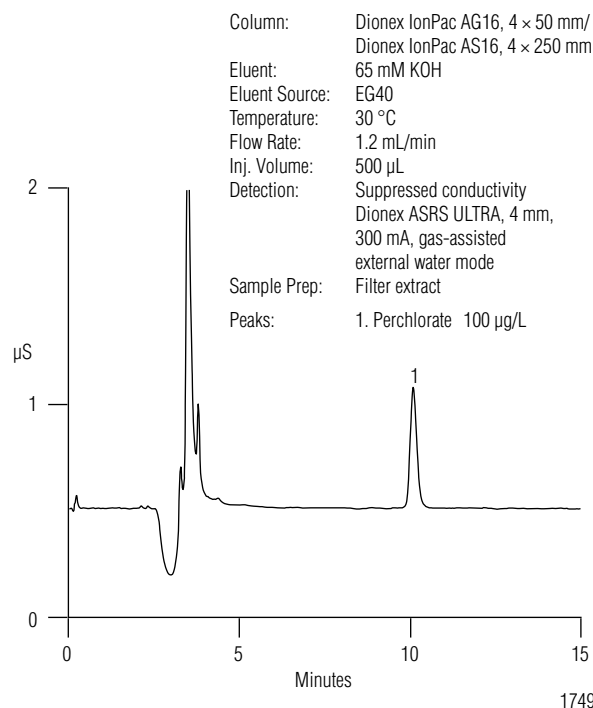


Figure 1. Perchlorate standard at 100 μg/L.

Results and Discussion

Figure 2 summarizes the calibration data for perchlorate anion obtained by using the partial-loop injection mode with a 10- μ L cut volume to make duplicate 500- μ L injections of calibration standards at 3, 5, 10, 15, 20, 30, 50, 100, 125, 150, 175, and 200 μ g/L. The calibration curve is linear over two orders of magnitude because of the high capacity of the Dionex IonPac AS16 column and the good peak shape for the perchlorate anion.

The method detection limit (MDL) is a measure of the precision of replicate injections of a low-level solution and is defined as the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.⁶ The MDL for perchlorate was determined by making seven injections of reagent water fortified with perchlorate at a concentration of 3 μ g/L (five times the estimated instrument detection limit). Using the concentration values calculated from the calibration curve, the MDL is calculated as:

$$\begin{aligned} \text{MDL} &= (t) \times (S) \\ &= (3.14) \times (0.136) \\ &= 0.43 \mu\text{g/L} \end{aligned}$$

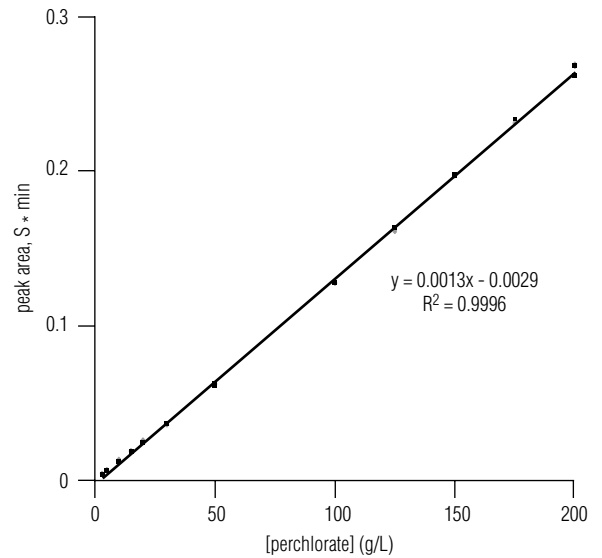
where, t = Student's t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom [$t = 3.14$ for seven replicates].

S = the standard deviation of the replicate analyses.

The MDL of 0.43 μ g/L obtained by this method, which uses a 500- μ L sample injection and an anion self-regenerating suppressor in gas-assisted external water mode with suppressed conductivity detection, is similar to the MDL reported in U.S. EPA Method 314.0, which uses a 1000- μ L sample injection and an anion self-regenerating suppressor in external water mode. The gas-assisted recycle mode consumes less water than does the external water mode, which may benefit some labs.

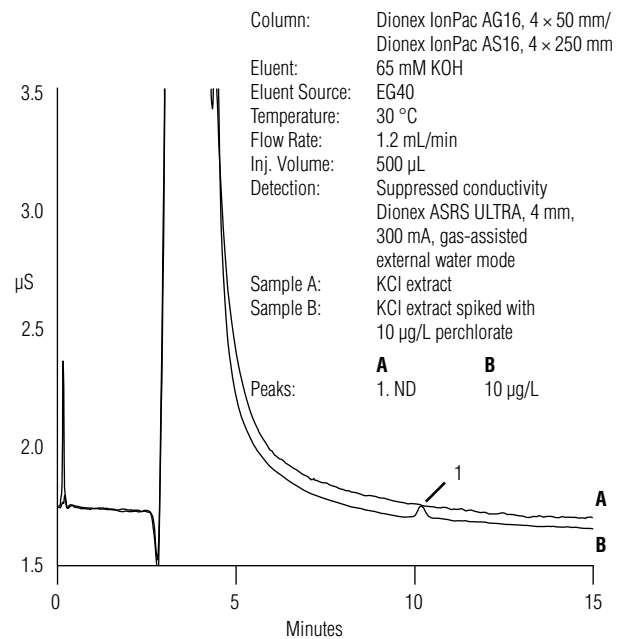
The performance of this method was evaluated by analyzing fortified samples to confirm retention time and assess recovery. First, the level of perchlorate was determined in various fertilizer extracts that were diluted 10-fold, filtered, and analyzed.

Samples with no detectable perchlorate peak were fortified with 10 μ g/L perchlorate and reanalyzed. If the perchlorate spike was not quantitatively recovered (80–120%), the sample was diluted 100-fold, fortified with 10 μ g/L perchlorate and reanalyzed. This was repeated at increasing dilutions until the perchlorate spike could be quantitatively recovered. The final dilution factor was multiplied by the MDL to calculate the reported detection limit for each sample. Figure 3 shows the chromatogram (A) of a 10-fold dilution of a KCl fertilizer extract with no detectable perchlorate compared with (B) the same sample spiked with 10 μ g/L of perchlorate. The calculated recovery of the perchlorate spike in this case is 100%.



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Figure 2. Calibration curve for perchlorate. See text for details.



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Figure 3. Recovery of a 10 μ g/L spike from a perchlorate-free KCl extract.

Samples observed to have a detectable peak within the perchlorate retention time window were diluted to bring the peak area within the linear range of the calibration curve. The diluted sample was fortified with perchlorate at a level 50–100% of the observed level and reanalyzed. Only if the spiked sample showed a single perchlorate peak with quantitative recovery of the spike was the sample reported as containing perchlorate.

Table 1 summarizes the spike recovery of perchlorate from various extracts analyzed as part of a recent U.S. EPA survey of fertilizers and related materials for perchlorate.⁴ Generally, the higher the ionic strength of the original extract, the greater the dilution required to achieve acceptable spike recovery. The highest ionic strength samples, salts such as KCl or NaNO₃, could be successfully analyzed with a 100- or 1000-fold dilution. (A 100-fold dilution of a KCL sample prepared according to this method has a Cl⁻ concentration of about 500 mg/L). After an appropriate dilution, this method provides acceptable recovery (that is 80–120%) of the perchlorate anion from each of these matrices.

Figure 4 shows the chromatogram (A) of a 2000-fold diluted extract of Chilean sodium nitrate fertilizer (Chile saltpeter)⁴ containing perchlorate compared with (B) the same sample spiked with 100 µg/L perchlorate. The identity of the perchlorate peak is confirmed and the spike recovery is 106%.

Column: Dionex IonPac AG16, 4 × 50 mm/
Dionex IonPac AS16, 4 × 250 mm
Eluent: 65 mM KOH
Eluent Source: EG40
Temperature: 30 °C
Flow Rate: 1.2 mL/min
Inj. Volume: 500 µL
Detection: Suppressed conductivity, Dionex ASRS ULTRA, 4 mm, 300 mA, gas-assisted external water mode
Sample Prep: Filter extract
Sample A: Extract of Chilean nitrate fertilizer, diluted 2000x
Sample B: Extract of Chilean nitrate fertilizer, diluted 2000x and spiked with 100 µg/L perchlorate

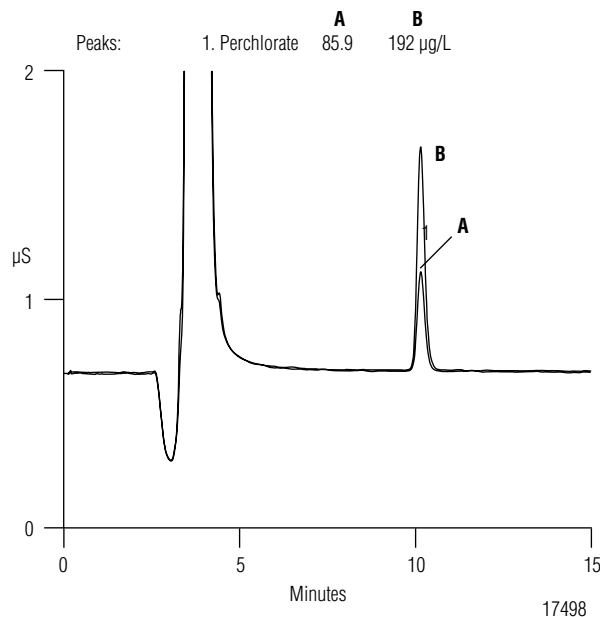


Figure 4. Recovery of a 100 µg/L spike from a perchlorate-containing Chilean nitrate fertilizer extract.

Table 1. Spike recovery of perchlorate.

Item ^a	Materials surveyed for perchlorate ^b (NPK ratio)	Dilution ^c	[ClO ₄ ⁻] found, µg/g	[ClO ₄ ⁻] added, µg/L	Spike Recovery
4	Potassium chloride	100	ND	10	103%
7	Potassium magnesium sulfate	100	ND	10	96%
9	Osmocote (18-6-12)	100	ND	10	98%
10	Lawn fertilizer (36-6-6)	100	ND	10	96%
16	Ammonium sulfate	100	ND	10	106%
23	Ammonium dihydrogen phosphate	100	ND	10	106%
29	Urea	100	ND	10	110%
33d	Potassium sodium nitrate	5000	3850	100	101%
34d	Ammonium nitrate	100	ND	10	102%
35	Potassium nitrate	2000	2240	100	106%
36	Sodium nitrate	2000	1920	100	103%
38	Granular triplesuperphosphate (GTSP)	1000	ND	10	98%
41	Limestone	100	ND	10	99%
47	Ammonium monohydrogen phosphate	100	ND	10	100%
49	Potassium chloride + 6.8 mg/g ClO ₄ ⁻	10000	6140	50	95%
50	Soluble plant food + 6.2 mg/g ClO ₄ ⁻	10000	5430	40	99%
51	GTSP + 2.7 mg/g ClO ₄ ⁻	10000	2300	20	105%
52	Urea + 1.8 mg/g ClO ₄ ⁻	10000	1810	20	102%
55	Chilean sodium nitrate (Chile saltpeter)	2000	1700	100	102%

^a Item numbers are consistent with Table 2.1 in Reference [4]; see [4] for definitions and sources.

^b See text for sample preparation and analysis details.

^c Refers to the final dilution of the original sample for liquids, or of the extract for solids.

^d Perchlorate was added to the final dilution to augment the native perchlorate concentration by this amount.

Interferences

Dionex (now part of Thermo Scientific) Application Note 134 lists 22 potentially interfering anions that are eluted well before perchlorate by using a 65 mM KOH eluent. Once again, with the 65 mM KOH eluent used in this study, most of the potential interferences, including chloride, nitrate, sulfate, and phosphate elute earlier and do not interfere with the determination of perchlorate.

The potential for interference from some additional polyvalent analytes that might be found in phosphate-containing fertilizers was also investigated. KOH concentrations ranging from 35–65 mM were used to elute dipolyphosphate ($P_2O_7^{4-}$, also called pyrophosphate), tripolyphosphate ($P_3O_{10}^{5-}$), and perchlorate anion. Depending on the eluent composition, column temperature, and sample matrix, either pyrophosphate or tripolyphosphate can coelute with perchlorate.

The results are plotted in Figure 5 as the logarithm of the retention time versus the logarithm of the eluent concentration. As the concentration of KOH increases, the retention time of the polyvalent phosphates decreases faster than that of monovalent perchlorate. Theory predicts that for a hydroxide eluent, the slope of the line for each anion should be equal to the charge on that anion.⁷ Figure 5 shows that perchlorate and pyrophosphate coelute at around 35 mM KOH (1.54 on the log scale), while perchlorate and tripolyphosphate coelute at around 45 mM KOH (1.65 on the log scale). At 65 mM KOH, pyrophosphate and tripolyphosphate should not interfere with the determination of perchlorate. However, because other unidentified polyvalent analytes could behave similarly, we recommend reanalyzing any sample that shows a peak within the retention time window of perchlorate, after fortifying it with perchlorate at a level 50–100% of that seen in the sample. The calculated recovery of the added perchlorate should be between 80% and 120%. There should be no indication of a peak coeluting with perchlorate in the chromatogram of the fortified sample. If necessary, reanalyze the spiked sample at 70 mM KOH. It is unlikely that an interfering anion will coelute with perchlorate at both 65 mM KOH and 70 mM KOH.

Precautions

Peak area precision and accuracy depend on autosampler performance. Replace the water in the flush reservoir daily with freshly filtered and degassed water. Inspect the AS50 Autosampler daily for bubbles in the sample syringe or its tubing. Purge to remove any bubbles by following the instructions in the AS50 manual.

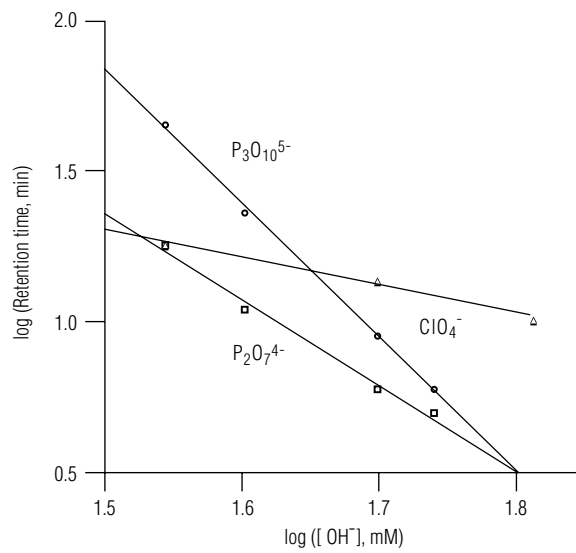


Figure 5. Effect of eluent concentration on retention of perchlorate and potential interfering anions.

Strongly retained compounds from injected samples can accumulate on the column and degrade its performance. Signs of a fouled column include loss of capacity, loss of resolution, shortened retention times, higher noise and background, spurious peaks, and peak tailing. The Dionex IonPac AS16 column can be flushed with up to 100% acetonitrile to help remove contaminants from the column. (For more information on column troubleshooting and cleanup, see the Installation Instructions and Troubleshooting Guide for the Dionex IonPac AS16 Analytical Column, Document No. 031475).

Some fertilizer extracts contain soluble aluminosilicates (clays) or potassium magnesium sulfate (langbeinite) that will plug the column and increase the backpressure despite careful centrifugation and filtering. Use a guard column to protect the analytical column; change the guard column if such a sample causes a sudden increase in total backpressure to greater than 3000 psi.

Summary

This application note describes an EG40-based IC system for the determination of perchlorate in high-ionic strength matrices such as fertilizer extracts. It provides guidelines for system setup and sample preparation. Expected operating conditions for well-performing systems are given as an aid to troubleshooting. The system uses a Dionex IonPac AS16 analytical column, 65 mM KOH eluent electrolytically generated by the EG40, and suppressed conductivity detection.

References

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3. Application Note 134, "Determination of Low Concentrations of Perchlorate in Drinking and Ground Waters Using Ion Chromatography", Dionex Corporation (now part of Thermo Scientific), Sunnyvale, CA.
4. "Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-)", U.S. Environmental Protection Agency Report EPA/600/R-01/049, Cincinnati, Ohio, May 2001.
5. American Society for Testing and Materials (ASTM), 1999, "Standard Practice for Sampling Industrial Chemicals", West Conshohocken, PA, Methods D5679-95A and E300-92.
6. "The Determination of Inorganic Anions in Water by Ion Chromatography", U.S. Environmental Protection Agency Method 300.0, Cincinnati, Ohio, 1993."
7. Madden, J. E., Avdalovic, N., Jackson, P.E. and Haddad, P.R., *J. Chromatogr. A.* 837 (1999) 65.

Suppliers

- VWR Scientific Products, 3745 Bayshore Blvd., Brisbane, CA 94005, USA, 1-800-932-5000. www.vwrsp.com
- www.pall.com/gelman
- Sigma Chemical Co., P.O. Box 14508, St. Louis, MO 63178 USA, 1-800-325-3010, www.aldrich.sial.com
- LAB-LINE, Melrose Park, IL
- Beckman Coulter, Inc., P.O. Box 3100, Fullerton, CA 92834-3100 USA, 800-233-4685 www.beckman.com
- Alpha Aesar, 30 Bond Street, Ward Hill, MA 01835-8099 USA, 1-800-343-0660. www.alfa.com

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