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Field Screening Method for Perchlorate in Water and Soil

Philip G. Thorne

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ABSTRACT

Low concentrations (µg/L) of the perchlorate anion, ClO_4^-, have been measured in drinking water supplies in many states throughout the United States. Federal and state regulatory agencies are concerned about the possible adverse effects of perchlorate contamination, as the anion is known to target the human thyroid gland and its metabolic-hormone-producing function. The provisional action level for drinking water established by the EPA and adopted by several states is 18 µg/L (18 ppb) perchlorate; however, other states have set levels as low as 1–4 µg/L. The major sources of perchlorate contamination in surface and ground waters are propellant manufacturers, military installations, defense contractors, and agriculture. A reliable and inexpensive colorimetric method for perchlorate in water and soil extracts has been developed and tested with surface water, well water, bioreactor effluent, and soil extracts. The detection limit for water is 1 µg/L and 0.3 µg/g for spiked soils. A 0.5-L sample of water or a 1-mL sample of aqueous soil extract is passed through a solid-phase extraction cartridge that has been conditioned with a perchlorate-specific ion-pair reagent. Perchlorate, as well as small quantities of chlorate and major ions, is retained. A rinse step removes the interferences and the perchlorate is eluted into an ion-pairing dye in a 13- × 100-mm test tube. A 1-mL aliquot of xylene is added, the tube is shaken, and the dye-pair extracts into the xylene that separates into a layer lying in the light path of a standard portable spectrophotometer. Results from nearly 100 well water and bioreactor samples show excellent agreement with EPA Method 314 over the range of 1–225 µg/L (slope = 1.11, $R^2 = 0.913$). Some false positives were encountered in some wells. A cleanup method was developed that can eliminate false positives due to humic substances. The colorimetric method is being adapted to an automated on-line monitor.

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PREFACE

This report was prepared by Philip G. Thorne, Senior Scientist, Applied Research Associates, Inc., South Royalton, Vermont.

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The Commander of the Engineer Research and Development Center is Colonel James R. Rowan, EN. The Director is Dr. James R. Houston.

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PHILIP G. THORNE

1 INTRODUCTION

Background

The perchlorate anion (ClO_4^-) was first discovered in 1997 in western U.S. (California, Nevada, and Utah) ground and surface waters; attendant with the discovery has been increasing interest in the health effects resulting from chronic exposure to low parts per billion (µg/L) levels. With authority under the Safe Drinking Water Act (SDWA), in March 1998, the U.S. Environmental Protection Agency's Office of Water formally added perchlorate to the drinking water contaminant candidate list (CCL) (Urbansky 1998, Urbansky and Schock 1999). A National Primary Drinking Water Regulation (NPDWR) has not yet been promulgated for perchlorate, but monitoring will continue under the Unregulated Contaminants Monitoring Rule (UCMR).

An NPDWR is promulgated for contaminants that may have an adverse effect on public health, are known to exist or are likely to exist in public water systems, and for which there is an opportunity for health risk reduction. Prior to the issuance of a perchlorate NPDWR, the USEPA is required to prepare a health-risk-reduction-versus-cost analysis for alternative maximum contaminant levels (MCLs). Ultimately, an MCL will be established where the health benefits justify the costs of compliance with the regulation. Currently, the agency is far from this goal. Toxicological studies are incomplete and a safe, but non-zero, concentration that ensures no adverse human health effects remains unknown.

Considerable controversy over the methodological details of existing toxicological and epidemiological studies (Greer et al. 2002, Chang et al. 2003, Kelsh et al. 2003, Strawson et al. 2004) have resulted in the National Academy of Sciences being tasked with reviewing all studies and making its own recommendations. Research continues toward establishing an oral Reference Dose

(RfD) and corresponding "no observable adverse effects level" (NOAEL). The RfD is the exposure level considered to be without significant risk to humans, including sensitive or vulnerable subgroups (e.g., fetuses exposed via placental transport and neonates drinking perchlorate-contaminated breast milk), when the contaminant is ingested daily over protracted periods.

The latest statement from the EPA (Farland and Jarabek 2003) reiterates its opinion that 1 µg/L is the appropriate MCL; however, California recently set the Action Level at 6 µg/L (CADHS 2004) and Massachusetts at 1 µg/L (MADEP 2004). Detection of a contaminant at greater than the Action Level triggers an advisory from the state that consumers not drink the water and that municipal water suppliers withdraw suspect wells from public use.

Perchlorate Uses and Environmental Occurrence

Perchlorate is an environmental contaminant that seldom occurs naturally except in evaporite deposits in extremely arid regions (Orris et al. 2003). Recent analyses of Chile saltpeter (sodium nitrate) by USEPA and the Department of Energy have found concentrations of approximately 1 g ClO_4^-/kg $NaNO_3$ (Urbansky and Schock 1999). Chile saltpeter is used as a fertilizer, particularly favored by tobacco farmers, resulting in accumulation of perchlorate in tobacco products (Ellington et al. 2001). Commercial quantities of sodium perchlorate are usually prepared by electrolysis of aqueous solutions of sodium chloride, in which the chloride ion is successively oxidized through hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-), and finally to perchlorate (ClO_4^-).

Large commercial quantities of ammonium perchlorate are used in 1.3-inch-diameter solid rocket motors and to a limited extent in pyrotechnic and explosive compositions. Potassium perchlorate is used extensively in pyrotechnic compositions and in black-powder-substitute gun propellants. It is used in some spotting charges that enable range control personnel to assess the accuracy of inert (non-explosive) rounds. Perchlorate salts are also used in nuclear reactors, electronic tubes, as additives in lubricating oils, in tanning and finishing of leather, as mordents for dyed fabrics, in electroplating and electropolishing, aluminum refining, rubber manufacture, and in the production of paints and enamels.

Commercial production of chlorate used for herbicides and bleaching agents is by the incomplete electrolysis of sodium chloride. Analysis of laboratory-grade chlorate found nearly % levels of perchlorate (Burns et al. 1989). It is reasonable to assume that industrial-grade chlorate may contain several % of perchlorate as a result of slight variations in process conditions.

In years past, railroads used sodium chlorate as an ingredient in herbicides to suppress the growth of foliage along rail corridors. Where rainfall is low or intermittent, soils around railbeds may still be contaminated with perchlorate. Another uninvestigated source of perchlorate contamination around railways is from spillage of chlorate salts used for bleaching at paper mills.

Quantitative Analytical Chemistry

EPA Method 314 can be improved by utilizing the latest ion chromatography (IC) systems that include an eluent generator, refined suppressor, low noise conductivity detector, temperature-controlled column oven, and either on-line or off-line sample preparation cartridges ion (Susarla et al. 1999, Urbansky et al. 2000, Ellington et al. 2001, De and Urbansky 2002, Liter 2003). Detection limits are now routinely reported at 0.2 µg/L. Regardless, this method produces only a non-specific response (conductivity) at a retention time that is compared to a perchlorate standard. There is no guarantee that an ionic interference that elutes in a peak at that given time is perchlorate.

Several alternative detection schemes have appeared in the literature (with their detection limits): capillary electrophoresis (5–10 µg/L) (Avdalovic et al. 1993, Nann and Pretsch 1994, Susarla et al. 1999, Ellington et al. 2001), ion selective electrode (3 µg/L) (Nann and Pretsch 1994), ion-pair extraction (IPE) coupled with electrospray ionization/mass spectrometry (ESI-MS) (0.1 µg/L) (Urbansky et al. 1999, Magnuson et al. 2000), and ion chromatography/tandem mass spectrometry (LC-MS/MS) (0.02 µg/L) (Flaherty et al. 2002, Winkler et al. 2004). Development work is continuing on a second column confirmation that uses a novel cryptand support (Liter 2003, Woodruff 2003). In this project, a flow injection colorimetric analysis (36 µg/L) (Burns et al. 1989) was modified to increase sensitivity and provide an analytical screening method that could be performed rapidly on site with limited equipment. This new method will, in turn, be adapted to a sequential injection process monitor in a future project.

2 METHOD DEVELOPMENT

Method developments began by looking for substitutes for the reagents used in the Burns et al. 1989 report. The method was based on the liquid/liquid partition behavior of Brilliant Green (BG) dye, a hydrophilic cation and the BG/perchlorate ion-pair that is un-ionized and hydrophobic. Briefly, the starting method used a flow injection apparatus to mix Brilliant Green, dissolved in absolute ethanol, with an aqueous buffer carrier to ion-pair with perchlorate in a water sample injected into the carrier mixture. Benzene was added and the two phases passed into a mixing coil. The mixture was then passed into a dual-chamber separator where the benzene diffused through a hydrophobic membrane separating the chambers. The benzene that contained BG/perchlorate ion-pairs was drawn into a spectrophotometer and absorbance at 640 nm recorded.

In our method, xylene (available locally at hardware stores as "Xylol") was used in place of the known carcinogen benzene as the receiving liquid for the hydrophobic BG/perchlorate ion-pair. Acetone (also hardware-store grade) was used to replace the absolute ethanol as the solvent for the BG dye. Because the original flow injection method required the chemical destruction of chlorate ions and had a detection limit (36 µg/L) far above the expected perchlorate drinking water limits (1 µg/L), a separation/pre-concentration step was also developed.

Separation/Pre-concentration

Separation/pre-concentration was accomplished by the careful selection of a solid-phase extraction (SPE) cartridge conditioned with a perchlorate-selective ion-pairing reagent and by manipulation of elution conditions. Ion-pair/SPE is used routinely in medical research (Carson and Heller 1998, Jorgensen 1998) but has rarely been applied to environmental samples (Wolf et al. 2000, Alonso and Barcelo 2002). SPE cartridges are small plastic syringe barrels packed with 50-µm beads of chromatographic material.

Initially, two candidate cartridges were investigated: C-18 (Supelco, 3 mL) and SDVB (styrene-divinylbenzene-WATERS Sep-PakRDX, 6 mL). Research into the selectivity and efficiency of perchlorate ion-pair reagents by the USEPA (Magnuson et al. 2000) suggested several quaternary ammonium salts as candidates. Three reagents were investigated in the current project: tetrabutylammonium hydroxide (TBAH), tetraheptylammonium bromide (THAB), and decyltrimethylammonium bromide (DTAB). Ion-pair chromatography on a C-18 column with TBAH/aqueous ACN eluent system with suppressed conductivity detection was used to monitor the retention, rinsing, and elution behaviors of

chloride, nitrite, nitrate, sulfate, phosphate, carbonate, chlorate, and perchlorate. DTAB was superior to TBAH and THAB for both retention capacity for perchlorate and selectivity over common ions found in groundwater.

The C-18 SPE did not retain much of the ion-pair reagent, thus it did not extract much of the perchlorate. The SDVB cartridge retained all DTAB and extracted all chlorate and perchlorate from 3 mL of sample while not retaining nitrate or other common ions. When 20 mL of sample was applied to a cartridge, some chlorate and perchlorate was not retained. When the concentration of ion-pair reagent was increased from 10 mM to 50 mM, all of the chlorate and perchlorate in 20 mL was retained. Differential elution of the chlorate and perchlorate was investigated by using increasing percent concentrations of methanol dissolved in deionized water. As predicted by ion-pair chromatographic behavior, chlorate was eluted from the SPE cartridge before perchlorate. Partial separation of the pair was accomplished using 30% methanol; however, there was significant perchlorate lost to the initial chlorate extract and residual chlorate remained in the secondary perchlorate extract.

Substituting the eluent used for the chromatographic method (80% 2 mM aqueous tetrabutyammonium hydroxide ([TBAH]/20% acetonitrile) allowed complete separation of the chlorate/perchlorate pair and 100% recovery of perchlorate. A 20-mL sample containing 25 mg/L of chlorate and 50 mg/L of perchlorate was passed through an SPE preconditioned with 500 µL of 50 mM DTAB. All of the chlorate and some of the DTAB plus 10% of the perchlorate were recovered by extracting the SPE with 12 mL of TBAH/acetonitrile. The remaining 90% of the perchlorate was recovered with no interfering compounds using 2 mL of methanol, resulting in a tenfold concentration. A second 2-mL extract of methanol was blank, indicating that the SPE was ready to be reconditioned and reused for subsequent extractions.

In one attempt to achieve a concentration factor of over a hundredfold, an extraction was performed on 250 mL of sample. No chlorate or perchlorate was recovered in the fractions. This is explained by the relationship between the amount of ion-pair applied and the retention of ions from increasing amounts of sample. As shown above, more DTAB had to be applied to the SPE when the sample volume was increased from 3 to 20 mL. This is because the ion-pair is itself only retained by the SPE material—it is not bound to the substrate. Apparently, when the sample volume was increased to 250 mL, the ion-pair (with all of the “paired” chlorate and perchlorate) was washed from the SPE.

A new brand of SDVB-SPE introduced in 2001 (Phenomenex STRATA, 3 mL) had significantly better retention characteristics. Although the amount of STRATA SPE bed-support is half that of the WATERS Sep-PakRDX, it retained

all the conditioning ion-pair. One-L samples could be extracted with no breakthrough of perchlorate. Because the bed-volume was less, the volumes of conditioning, rinsing, and eluting solutions could be further reduced and optimized: 1 mL of 25 mM DTAB was used to condition each SPE; 500 mL of water sample was extracted; 5 mL of 2.5 mM DTAB in 15% v/v acetone/water was used to remove any retained chlorate ions; 1 mL of acetone was used to elute all of the retained perchlorate.

Colorimetric Reagent and Liquid/Liquid Extraction

The next phase of modifying the Burns et al. 1989 method was to determine the optimal conditions for the BG and liquid/liquid extraction step. The field method differed from the original method because the perchlorate was in an acetone extract containing some DTAB rather than in a simple water sample.

Originally, the method called for pH control using a buffer system, although pH had little effect in the range 2.6–7.3. In our system, pH less than 3.5 resulted in very rapid fading of the BG in the xylene layer. Furthermore, even very low concentrations of buffer salts caused the xylene layer to be slightly turbid and therefore unreadable by the spectrophotometer. This may not have been a problem with the original method that performed the liquid/liquid extraction across a Teflon membrane. Buffering the BG was found to be unnecessary and was eliminated. Effort was directed at optimizing the quantity of BG added to the acetone extract and to address problems with BG stability that were noted in the original paper. The more BG added, the more BG-perchlorate ion-pair is transferred to the organic layer. The trade-off was between sensitivity and some transfer of hydrophobic BG dimer into the xylene, resulting in a non-zero blank. A BG solution containing 150 mg/L BG was found to be a reasonable compromise; however, stability of this solution was a problem. Fresh BG had to be made each day or the background would increase. Furthermore, the 1500-mg/L stock that was originally made in water was also unstable over a few weeks. Stock solution made up in 95% acetone/5% water was stable for several months. Rather than dilute stock BG each day, 100 µL of 1500-mg/L stock could be added to test tubes in advance of the analysis. Racks of tubes could be prepared, dried, and stored in the dark for several months. BG was reconstituted by adding 1 mL of water immediately prior to extracting the SPE into each tube.

The problem with slight turbidity in the xylene layer could not always be completely eliminated. Some acetone and DTAB dissolved in the xylene. The 1 mL of xylene added separated in about 10 minutes but resulted in a floating layer that was about 1.3 mL. Two drops of acetone added to the completely separated top layer cleared up the turbidity. Occasionally, small patches of aqueous/acetone

BG from the bottom layer adhered to the sides of the test tube in the xylene zone and produced a very high absorbance if they were in the spectrophotometer beam. In this case, the reading was obviously wrong and the tube had to be rotated until the aqueous BG was out of the beam. This problem is related to the condition of the DTAB.

Quaternary ammonium compounds are degraded by oxygen when in dilute solutions. Therefore, the stock solution of 250 mM DTAB, which was stable for one month, was diluted daily to 25 mM in water. The 2.5 mM DTAB/15% acetone rinse was also made fresh daily. Upon receipt, solid DTAB was transferred from its nitrogen-filled shipping container to a 20-mL syringe so that all air could be expelled after weighing out each batch of stock. This syringe was wrapped in Parafilm-M and stored in the dark. Batches of SPEs can be conditioned with acetone, rinsed with water, pre-loaded with DTAB, and kept in resealable bags for one week. This is a convenient way to eliminate a few steps in the field. If the DTAB degrades, the absorbance of the blank control will rise significantly above the normal 0.10 ABS units—an absorbance that appears colorless at 640 nm where the eye is not particularly sensitive.

Water Method

A standard curve and linear range were determined using 500-mL samples of spiked well water (Fig. 1). A method detection limit (MDL = standard deviation of the mean × 2.7) determined by analyzing eight replicates containing 1.0-µg/L perchlorate was 0.3 µg/L. Eight common ions were also tested with the final method. Nitrite, nitrate, sulfate, chloride, phosphate, and carbonate produced no detectable color when 500 mL of 10-mg/L solutions were tested. A solution of 10- mg/L chlorate produced a positive color response equivalent to 5 µg/L perchlorate.

Although the calculated MDL is 0.3 µg/L, this value is not a realistic detection limit for the test. A higher level of certainty is achieved when the difference between a sample containing 1 µg/L and a blank sample is apparent to the “naked eye.” Daily calibrations should always include a blank and 1-µg/L standard. The blank value should be less than 0.200 ABS units. Higher values indicate that the DTAB is degraded and should be replaced with fresh stock.

The second calibration point can be adjusted to accommodate expected values. If higher perchlorate concentrations are found or anticipated, extracting less volume of sample can extend the linear range. In this case a blank and two-point standard curve should be acquired with the same sample volume, since the amount of DTAB that is removed during the sample extraction is proportional to sample volume and has some effect on the absorbance of the blank and standards.

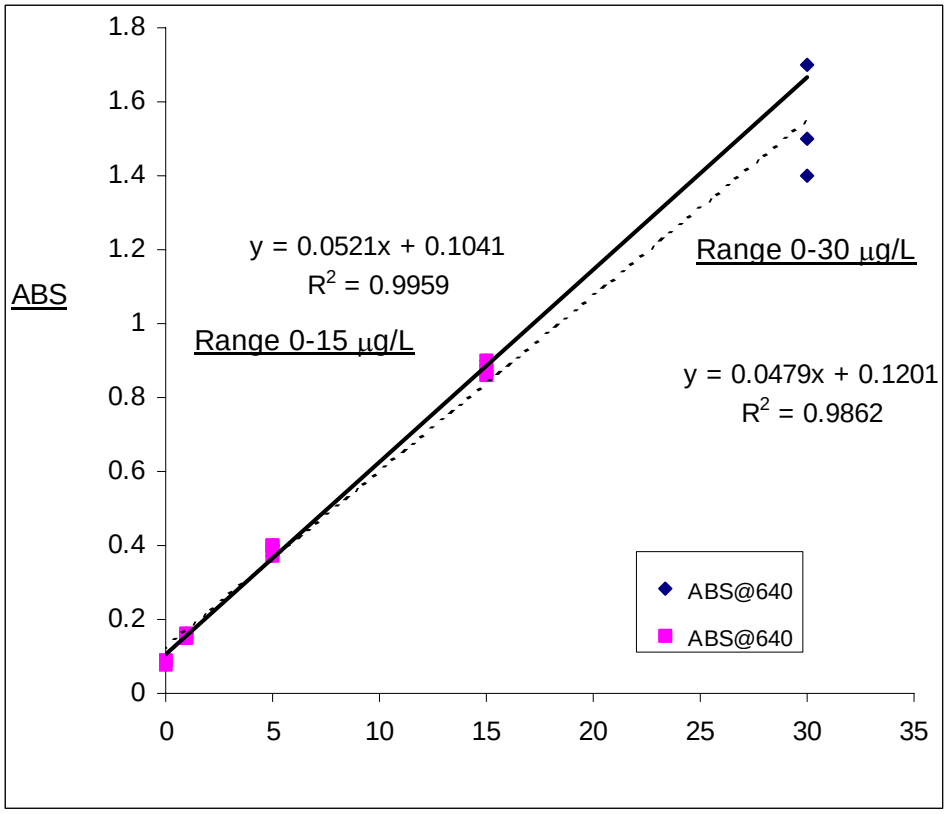


Figure 1. Linear range of colorimetric water method.

Soil Method

Work on a soil method was restricted to spike/recovery studies because no source of authentic perchlorate-contaminated soils was available. A 50-mL aliquot of perchlorate-spiked water was added to 50 g of soil and stirred until the soil was completely suspended. This suspension was allowed to dry over several days, and then 50 mL of deionized water was added to produce a simulated aqueous extract. The suspension was allowed to settle until a layer of relatively clear extract formed at the top of the extraction vessel.

The initial studies indicated quickly that plant material from the surface or the root zone caused major interference with the method. Either the green chlorophyll was extracted into the xylene layer, causing a false positive, or the recovery of spiked perchlorate was extremely low—presumably the result of naturally occurring ion-pairing compounds in the biologically active root zone. When soil from beneath the root zone was spiked, recoveries were complete;

however, the quantity of extract had to be kept quite low to eliminate positive interferences from matrix components and plugging of the SPE due to fines. Although 10-mL samples could be filtered using several 0.45-µm syringe filters to remove the fines, the soluble interferences were not eliminated.

Furthermore, a minimum of 50 mL of sample must be passed through the SPE to remove some of the DTAB that is loaded in excess and causes a high "blank." A 1-mL sample was withdrawn and diluted to 50 mL with deionized water prior to extraction in the SPE cartridge. A standard curve and linear range were determined (Fig. 2). An MDL was determined using seven replicate samples spiked at 1.0 mg/kg. The MDL was calculated as 0.4 mg/kg, which was also a realistic (visual) limit of detection. For some soils, it may be possible to add more sample volume to the 50 mL of diluted extract.

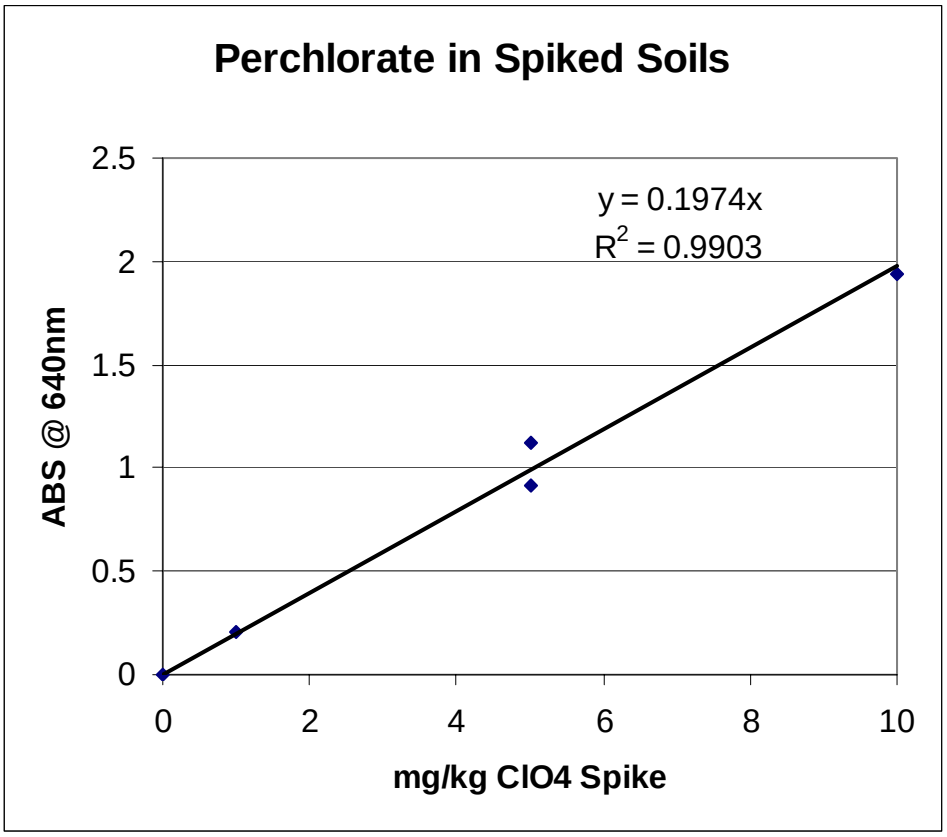


Figure 2. Linear range of colorimetric soil method.

Surface Water

Surface water samples must be pre-filtered through 0.45-µm filters to remove diatoms and bacteria. If residual color from dissolved substances remains, alternative cleanup steps may be required.

Interferences: Biological Polymers and Machine Oils

If the pre-concentration extract contained any colored biological materials, such as chlorophyll from surface water samples or from plant material in surface soils, some was invariably transferred into the xylene layer, producing either a false positive or some increased absorbance added to the BG-perchlorate complex. Some organic interference had no color but produced poor spike-recoveries. These compounds were probably acting as ion-pairs that were stronger than the DTAB loaded onto the SPE.

Two cleanup methods were found to be effective. Passing a water sample through an SPE containing neutral Alumina (Supelco Alumina-N, 6 mL) upstream of the DTAB-loaded SDVB-SPE removed most interfering substances from bituminous activated carbon and bioreactor effluents. In either case the false positive was only 1–3 µg/L. The Alumina-N cleanup reduced the result to less than 1 µg/L. The Alumina-N tubes should NOT be activated as recommended by the manufacturer (by rinsing with acetone followed by water) since this caused perchlorate in spiked samples to be retained. These tubes must be used without conditioning.

When samples contained brown humic materials, some color would pass through the Alumina-N and cause a false positive. The brown color could be destroyed by adding acid (20 µL 1.0 M acetic acid) and 50 mg Zn powder to the acetone extract, allowing enough time for the color to disappear (5–15 minutes) and then passing it through a 13-mm syringe filter into the 1-mL BG solution. Neither cleanup method removed interferences caused by chlorophyll. Filtration of surface water samples to remove algae and diatoms and removal of all green plant material from surface soil is the only option for such samples.

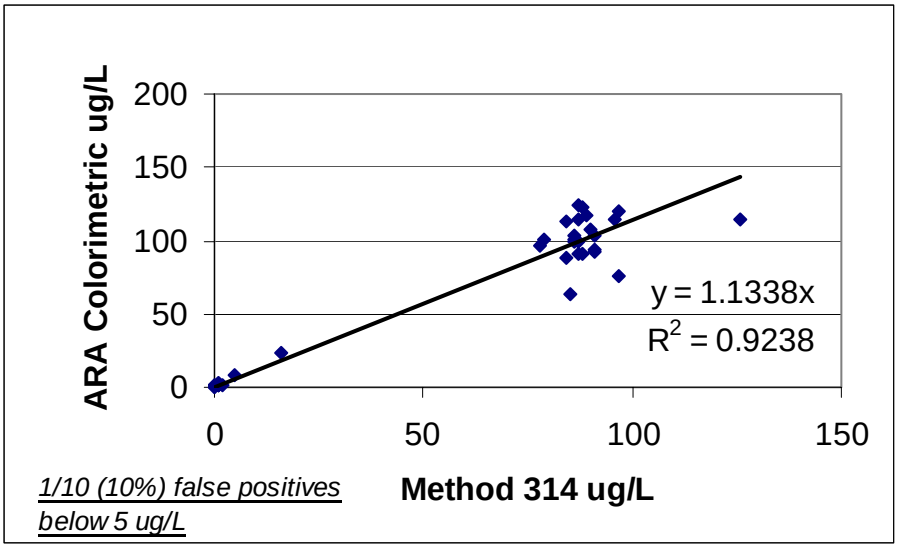
It will be critical to perform careful spike experiments for each new sample matrix. If interferences cause either false positives or poor recoveries, then both of these cleanup steps may be tried. It is still possible, as in the case for drilling-fluid-contaminated well-water samples, that no cleanup steps will solve the problem. In this case the method may be usable at a higher detection limit or with less confidence, i.e., as a high level yes/no screen rather than as a semi-quantitative assay at drinking water level.

3 RESULTS AND CONCLUSIONS

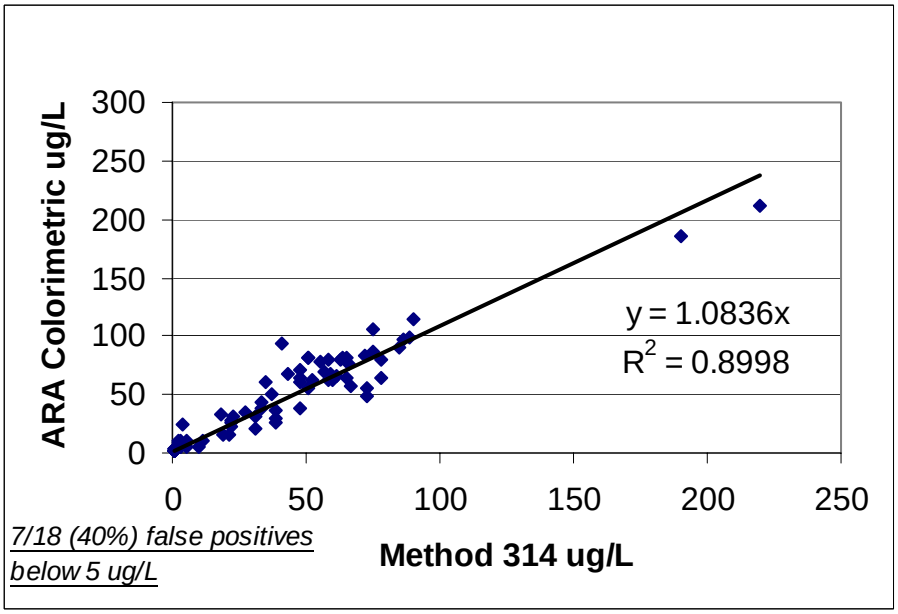
Well-water samples from a perchlorate-contaminated aquifer were tested using the field method and the results compared to EPA Method 314 analyses performed at a commercial laboratory. The wells had been installed in aquifers that contained either more than 100 µg/L or less than 5 µg/L perchlorate. Some samples were available from municipal wells that had less than 1 µg/L perchlorate. Water from the highly contaminated aquifer was used to test various bioreactors that were under investigation for remedial actions.

Results were very encouraging (Fig. 3). The slight positive bias (slope 1.11) was consistent so that this in itself is not important. The more significant problem is with accurate quantification near the detection level of 1 µg/L. Here the positive bias is more problematic (Fig. 4). False positives at this level were encountered at 10% for well water and 40% for bioreactor effluent. The Alumina-N cleanup was helpful in reducing “perchlorate” values determined by the field method for one of the bioreactors.

The linear range of the test was extended up to 225 µg/L by extracting variable quantities of sample depending on the expected values, i.e., 50 mL for samples above 200 µg/L, 100 mL for samples around 100 µg/L, and 500 mL for the wells from the municipal supplies and low-level aquifer and bioreactor effluents. If this method is used to extend the linear range, the standards and samples must be the same volume, since more or less DTAB is removed during the extraction.

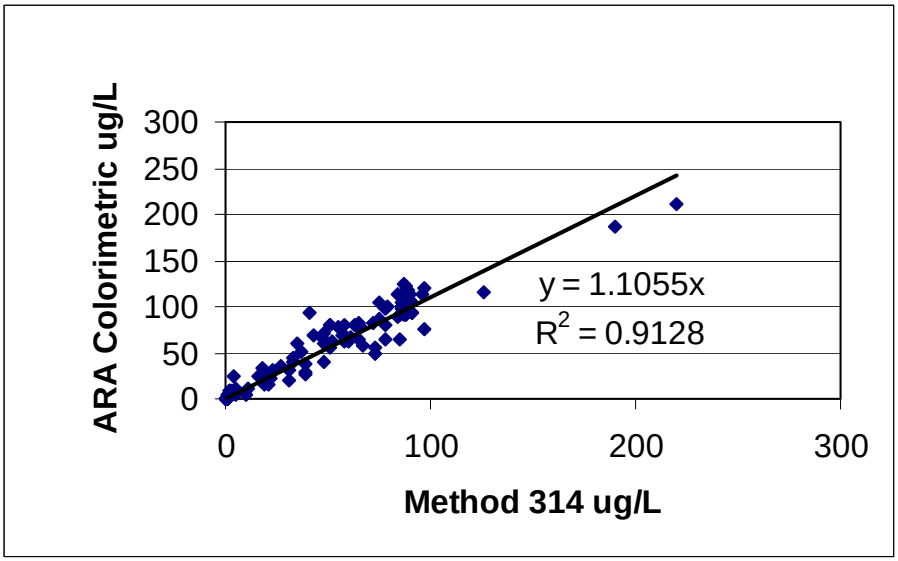


a. Method 314 vs. ARA for well water.



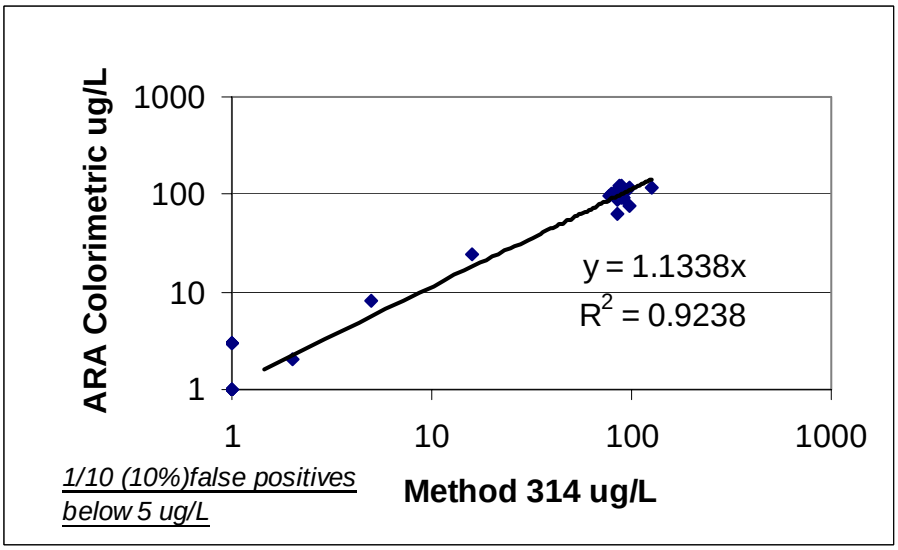
b. Method 314 vs. ARA for bioreactor effluent.

Figure 3. Performance of colorimetric water method compared to Method 314 ion chromatography.



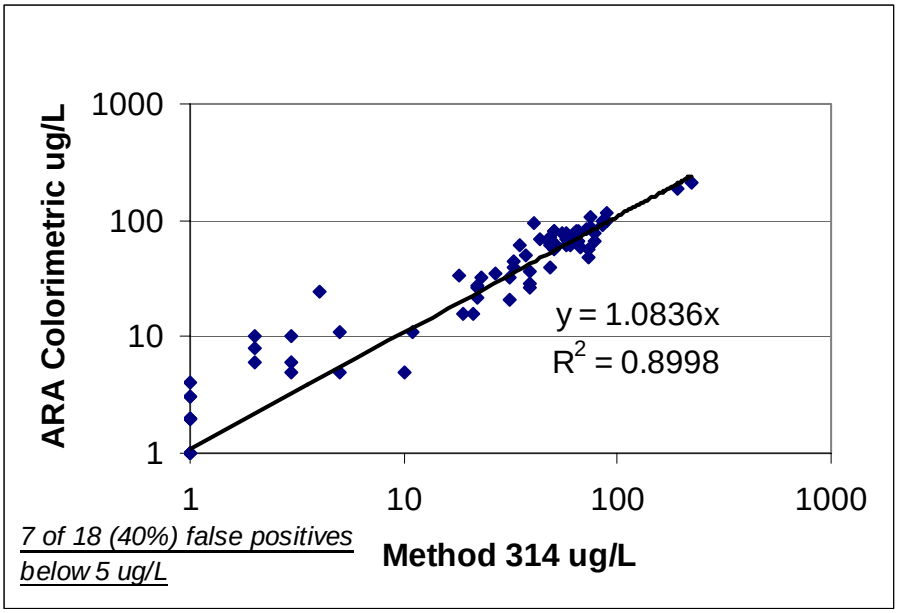
c. Method 314 vs. ARA for well water and bioreactor effluent.

Figure 3 (cont'd).

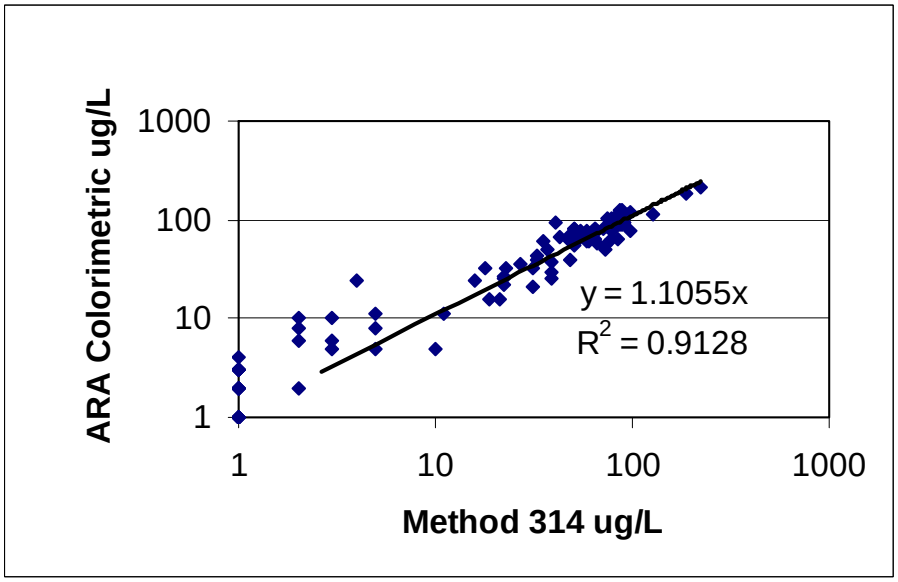


a. Method 314 vs. ARA for well water.

Figure 4. Performance of colorimetric viewed as log relationship to emphasize low-level positive bias.



b. Method 314 vs. ARA for bioreactor effluent.



c. Method 314 vs. ARA for well water and bioreactor effluent.

Figure 4 (cont'd). Performance of colorimetric viewed as log relationship to emphasize low-level positive bias.

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APPENDIX A. WATER METHOD

1.0 SCOPE AND APPLICATION

This method is suitable for the field-screening determination of perchlorate ions in well water or bioreactor effluent, using a battery-operated spectrophotometer.

2.0 SUMMARY OF METHOD

A 50- to 500-mL water sample is passed through a styrene divinylbenzene solid-phase extraction (SPE) tube that has been conditioned with an ion-pairing reagent. Perchlorate ions are retained on the resin. Ionic interferences are removed by washing the resin with an aqueous solution containing acetone and dilute ion-pair reagent. Perchlorate ions are eluted from the resin by washing with 1 mL of acetone into a test tube containing an ion-pairing dye. If matrix-spike samples indicate poor recovery or the extract is colored, cleanup procedures are attempted as described in detail below. A 1-mL aliquot of deionized water is added to the acetone dye solution. The tube is swirled to mix, then a 1-mL aliquot of xylene is added and the tube capped and shaken vigorously. Wait 15 minutes for the xylene to separate from the aqueous acetone. Place tube in a spectrophotometer and read the absorbance at 640 nm of the perchlorate-dye ion-pair. The absorbance is converted to µg perchlorate/L water based on the response from calibration standards.

3.0 REAGENTS

Potassium perchlorate
MW: 138.6
CAS# 7778-74-7

Decyltrimethylammonium bromide
MW: 280.29
CAS#2082-84-0

Brilliant Green
MW: 482.65
CAS#633-03-4

Acetone
MW: 58.08
CAS#67-64-1

Xylene
MW: 106.17
CAS#1330-20-7

Acetic Acid
MW: 60.05
CAS#64-19-7

Zinc powder (< 10 µm)
MW: 65.37
CAS#7440-66-6

4.0 INTERFERENCES

Highly colored biological materials may cause major interference with the method. Humic or fulvic acids and chlorophyll are extracted into the xylene layer, causing a false positive. The recovery of spiked perchlorate may be extremely low if naturally occurring ion-pairing compounds are present. Two procedures listed below may be used to reduce or eliminate these interferences.

5.0 SAFETY

The normal safety precautions associated with the use of flammable organic solvents, strong acids and bases, and potentially toxic chemicals should be employed.

6.0 EQUIPMENT AND SUPPLIES

Instrumentation

Field-portable, battery-operated spectrophotometer (Hach DR2000 or equivalent) that can accommodate a 100-mm × 13-mm test tube.

Analytical balance for preparation of standards.

Labware and equipment

Adjustable pipette: 10–1000 µL.

Glass syringe: 100 µL.

10-, 50-, and 500-mL graduated cylinders.

Syringe filter units, 0.5 mm, hydrophilic.

Disposable culture tubes with caps, 100 mm × 13 mm.

Disposable plastic syringes: 60 mL, 10 mL, 1 mL.

22-mL glass vials with Teflon-lined caps.

Phenomenex STRATA-SB, solid-phase extraction (SPE) tubes, 1 mL.

Supelclean Alumina-N SPE tube, 6 mL.

500-mL squirt bottles (two).

Timer or wristwatch to measure liquid/liquid separation time.

7.0 REAGENTS AND STANDARDS

Potassium perchlorate.

Acetone, commercial grade.

Xylenes (xylol), commercial grade.

Decyltrimethylammonium bromide (DMAB). Solid DMAB should be transferred from the inert-gas-packed shipping bottle to a plastic syringe for storage. Expel all air and wrap in ParaFilm to prevent oxidation. Store in the dark.

Stock solution: 250 mM in deionized water.

Daily working solution: 25 mM in deionized water.

Rinse solution: 2.5 mM in 15% acetone/deionized water.

Water, deionized.

Brilliant Green dye.

Stock solution: 1500 ug/ mL in 90% acetone/deionized water.

Pre-dying of Test Tubes: Add 100 µL stock to each test tube. Dry overnight in the dark, cap, and store in the dark.

1 M acetic acid.

Zinc powder: 100 µm.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

This method may be used on water from fully developed wells and on bio-reactor effluents. It cannot be used on surface waters if chlorophyll-containing organisms are present.

9.0 QUALITY CONTROL

9.1 GENERAL

The accuracy and precision of this method are subject to the common errors associated with poor-quality measurements of weights and volumes.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

An initial calibration curve for the method should be performed as directed in CALIBRATION AND STANDARDIZATION. The calibration curve should be linear, with a zero intercept and a range of approximately 0.0–30 µg/L for a 500-mL sample. **The linear range of this method may be extended to 300**

µg/L by extracting a 50-mL sample. The volumes of calibration solutions extracted must be equal to the intended sample volumes.

9.3 ASSESSING PERFORMANCE

A method detection limit (MDL) analysis should be performed. A 4000-mL sample of deionized water is spiked with 40 µL of the 100-mg/L working standard to produce a perchlorate concentration of 1 µg/L. Seven 500-mL samples are processed according to the method. The concentration of perchlorate in the samples is determined using the initial calibration curve. The standard deviation (SD) of the seven determinations is calculated. The MDL = 3.14 × SD and should be about 0.3 µg/L. The recovery of the spiked perchlorate should be between 95 and 105%.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

Blank and spiked water samples should be analyzed for each site as directed in CALIBRATION AND STANDARDIZATION. The background-corrected absorbance of a 15-µg/L spike should be above 95% of the 15-µg/L calibration solutions processed according to the directions for the daily calibration of response factor. The blank water sample should produce an absorbance less than 0.2 units at 640 nm.

10.0 CALIBRATION AND STANDARDIZATION

10.1 PREPARATION OF STANDARDS

About 0.2 g of solid potassium perchlorate is dried to constant weight in a vacuum desiccator in the dark; 0.139 g is weighed out to the nearest 0.1 mg, transferred to a 100-mL volumetric flask, and dissolved in deionized water. The concentration of perchlorate in this stock is 1000 mg/L. A working standard is made by diluting 10 mL of the stock with deionized water to 100 mL in a volumetric flask. The concentration of the working standard is 100 mg/L. Calibration solutions are prepared by diluting the working standard with deionized water as described in Table A1. An adjustable pipette is used. A 500-mL graduated cylinder is used to measure the dilution water.

10.2 INITIAL CALIBRATION

A 50- to 500-mL aliquot of each aqueous calibration solution is processed according to the PROCEDURE. Absorbance readings of Solutions A–D should range from 0.2 to about 2.0 absorbance units. The slope of the relationship between concentration of perchlorate and background-corrected absorbance should be linear, with a zero intercept.

10.3 DAILY CALIBRATION

A 50- to 500-mL aliquot of Calibration Solution C (15 µg/L) is processed according to the method. The daily response factor is calculated:

daily response factor = (15 µg/L)/(Absorbance @ 640 nm).

10.4 DAILY BLANK AND MATRIX SPIKES

A blank is produced by processing a 50- to 500-mL aliquot of deionized water. For each new site, a water sample is spiked at a concentration of 15 µg/L and performing the method.

11.0 PROCEDURE

1. Condition SDB-L SPE with 3 mL acetone (fill SPE tube from acetone squirt bottle, then push through slowly with empty 20-mL syringe), then 20 mL DI, then 20 mL air, quickly, to remove DI.

2. Add 1 mL 25 mM DMAB, push through cartridge using empty syringe.

3. Extract 50- to 500-mL water sample using 60-mL syringe with repeated fillings. Push through so that sample exits SPE as very rapid drops rather than as a stream (500-mL can be extracted in about 15 minutes). Finish by pushing 20 mL air through SPE.

4. Rinse SPE with 5 mL of 2.5 mM DMAB in acetone/water.

5. Expel rinse with 20 mL air.

6. Add 1 mL acetone to SPE tube and force through slowly into pre-dyed culture tube.

7. Add 1 mL DI to acetone extract and dye, swirl to mix. Cap immediately.

8. Rinse SPE with 3- × 3-mL acetone rinses. Cartridges may be reused until visibly dirty or plugged.

9. Add 1 mL xylene, start timer, cap tube, and shake vigorously for 30 seconds.

10. Wait until timer is at one minute to start second tube, etc. (During initial training the interval can be extended to two minutes between samples.)

11. At 10 minutes, gently tap and swirl tube to dislodge bubbles or foam. If spectrophotometer is to be used for quantification, add two drops acetone to xylene layer. Swirl gently to mix acetone and remove colloidal “haze.”

12. At 15 minutes, compare Sample to Control and Action Level or place tube in spectrophotometer and measure at 640 nm. Take several measurements,

rotating the tube slightly each time. Use the lowest value, because slight deposits of dyed foam/scum often spot the sides of the tube up into the xylene layer.

13. At 16 minutes, measure second tube, etc.

Two cleanup methods should be attempted if needed:

a. If the acetone extract is colored, repeat the extraction but elute the acetone into an undyed culture tube. Add 20 µL 1 M acetic acid and 50 mg zinc powder. Shake and allow 5–15 minutes for destruction of color. This process does not destroy chlorophyll. Filter through a 0.45-µm syringe into a new dyed culture tube and proceed from Step 7.

b. If extract is not colored but recovery is lower than expected, repeat the extraction by passing the sample through an SPE-Alumina-N followed by the ion-pair conditioned SDB-L.

12. DATA ANALYSIS AND CALCULATIONS

The absorbance data are converted to perchlorate concentration in the sample by the following formula:

µg/L perchlorate = daily response factor (µg/L–ABS unit) X ABS (Sample-Blank).

This is based on a 50- to 500-mL sample compared to a similar-sized calibration solution.

13. METHOD PERFORMANCE

The method has been applied only to a series of authentic and spiked water samples and bioreactor effluents. The results were compared to laboratory analyses using EPA Method 314 (Fig. 3).

14. POLLUTION PREVENTION

All containers of organic solvents and extraction solutions should be kept capped to prevent evaporation. A large tray should be used under the work area to contain any spilled solvents.

15. WASTE MANAGEMENT

All solid waste contaminated with solvents, acid, base, dye, and extracted chemicals should be disposed of according to Federal, state, and local regulations. This includes extraction bottles and soils, filters, syringes, disposable pipettes, SPE tubes, and eluent tubes. All waste organic solvents from the extraction procedures and rinses should be disposed of according to Federal, state and local regulations.

16. REFERENCE

Burns, D.T., N. Chimpalee, and M. Harriott (1989) Flow-injection extraction-spectrophotometric determination of perchlorate with Brilliant Green. *Analytica Chimica Acta*, **217**: 177–181.

17. TABLE

Table A1. Preparation of calibration solutions from 100-mg/L working standard, diluted to 500 mL with deionized water.*

		µL 100 mg/mL
A	Blank	0
B	1 µg/L	5
C	15 µg/L	75
D	30 µg/L	750

* Dilute 1 mL of each to 50 mL with deionized water and analyze by water method.

APPENDIX B. SOIL METHOD

1.0 SCOPE AND APPLICATION

This method is suitable for the field screening determination of perchlorate ions in field-moist or dried soil, using a battery-operated spectrophotometer.

2.0 SUMMARY OF METHOD

A 50-g sample of soil is placed in a bottle and extracted by adding 50 mL of deionized water and shaking for three minutes. A 1-mL aliquot is filtered into a graduated cylinder and diluted to 50 mL with deionized water. The diluted extract is then passed through a styrene divinylbenzene solid-phase extraction (SPE) tube that has been conditioned with an ion-pairing reagent. Perchlorate ions are retained on the resin. Ionic interferences are removed by washing the resin with an aqueous solution containing acetone and dilute ion-pair reagent. Perchlorate ions are eluted from the resin by washing with 1 mL of acetone into a test tube containing an ion-pairing dye. If matrix-spike samples indicate poor recovery or the extract is colored, cleanup procedures are attempted as described in detail below. A 1-mL aliquot of deionized water is added to the acetone dye solution. The tube is swirled to mix, then a 1-mL aliquot of xylene is added and the tube capped and shaken vigorously. Wait 15 minutes for the xylene to separate from the aqueous acetone. Place tube in a spectrophotometer and read the absorbance at 640 nm of the perchlorate-dye ion-pair. The absorbance is converted to mg perchlorate/g soil based on the response from calibration standards.

3.0 REAGENTS

Potassium perchlorate
MW: 138.6
CAS# 7778-74-7

Decyltrimethylammonium bromide
MW: 280.29
CAS#2082-84-0

Brilliant Green
MW: 482.65
CAS#633-03-4

Acetone
MW: 58.08
CAS#67-64-1

Xylene
MW: 106.17
CAS#1330-20-7

Acetic Acid
MW: 60.05
CAS#64-19-7

Zinc powder (<10 µm)
MW: 65.37
CAS#7440-66-6

4.0 INTERFERENCES

Biological materials from the soil surface or the root zone may cause major interference with the method. Humic and fulvic acids and chlorophyll are extracted into the xylene layer causing false positive. The recovery of spiked perchlorate may be extremely low if naturally occurring ion-pairing compounds in the biologically active root zone are extracted. Two procedures listed below may be used to reduce or eliminate these interferences.

5.0 SAFETY

The normal safety precautions associated with the use of flammable organic solvents, strong acids and bases, and potentially toxic chemicals should be employed.

6.0 EQUIPMENT AND SUPPLIES

Instrumentation

Field-portable, battery-operated spectrophotometer (Hach DR2000 or equivalent) that can accommodate a 100-mm × 13-mm test tube.

Mechanical or battery-operated balance to measure soils.

Analytical balance for preparation of standards.

Labware and equipment

8-oz. paper or plastic cups.

Disposable wooden spatulas.

Adjustable pipette: 10–1000 µL.

Glass syringe: 100 µL.

50-mL graduated cylinder.

10-mL graduated cylinders.

Syringe filter units, 0.5 mm, hydrophilic.

Disposable culture tubes with caps, 100 mm × 13 mm.

Disposable plastic syringes: 60 mL, 10 mL, 1 mL.

22-mL glass vials with Teflon-lined caps.

Phenomenex STRATA-SDB-L, solid-phase extraction (SPE) tubes, 200 mg/3 mL.

Supelclean Alumina-N SPE tube, 500 mg/6 mL.

500-mL squirt bottles (two).

Timer or wristwatch to measure liquid/liquid separation time.

7.0 REAGENTS AND STANDARDS

Potassium perchlorate.

Acetone, commercial grade.

Xylene (xylol), commercial grade.

Decyltrimethylammonium bromide (DMAB). Solid DMAB should be transferred from the inert-gas-packed shipping bottle to a plastic syringe for storage. Expel all air and wrap in ParaFilm to prevent oxidation. Store in the dark.

Stock solution: 250 mM in deionized water.

Daily working solution: 25 mM in deionized water.

Rinse solution: 2.5 mM in 15% acetone/deionized water.

Water, deionized.

Brilliant Green dye.

Stock solution: 1500 ug/ mL in 90% acetone/deionized water.

Pre-dying of test tubes: Add 100 µL stock to each test tube. Dry overnight in the dark, cap, and store in the dark.

1 M acetic acid.

Zinc powder: 100 µm.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

This method may be used with field-moist or dried soil samples. A soil sample is mixed as thoroughly as possible and a 50-g sample added to an 8-oz. paper or plastic cup. Fifty mL of deionized water is added and mixed with the sample using a disposable wooden spatula.

9.0 QUALITY CONTROL

9.1 GENERAL

The accuracy and precision of this method are subject to the common errors associated with poor-quality measurements of weights and volumes.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

An initial calibration curve for the method should be performed as directed in CALIBRATION AND STANDARDIZATION. The calibration curve should be linear, with a zero intercept and a range of approximately 0.0–10 mg/g.

9.3 ASSESSING PERFORMANCE

A method detection limit (MDL) analysis should be performed. A 500-g sample of blank soil is spiked with 500 mL of the 1 µg/mL working standard to produce a perchlorate concentration of 1 mg/g. The soil is homogenized as completely as possible. Seven 50-g subsamples are processed according to the method. The concentration of perchlorate in the subsamples is determined using the initial calibration curve. The standard deviation (SD) of the seven determinations is calculated. The MDL = 3.14 × SD and should be about 0.4 mg/g. The recovery of the spiked perchlorate should be between 75 and 125%.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

Blank and spiked soil samples should be analyzed for each new soil as directed in CALIBRATION AND STANDARDIZATION. The background-corrected absorbance of a 5-mg/g soil spike should be above 75% of the 5-µg/g calibration solutions processed according to the directions for the daily calibration of response factor. The blank soil should produce an absorbance less than 0.2 units at 640 nm.

10.0 CALIBRATION AND STANDARDIZATION

10.1 PREPARATION OF STANDARDS

About 0.2 g of solid potassium perchlorate is dried to constant weight in a vacuum desiccator in the dark; 0.139 g is weighed out to the nearest 0.1 mg, transferred to a 100-mL volumetric flask, and dissolved in deionized water. The concentration of perchlorate in this stock is 1000 µg/mL. A working standard is made by diluting 10 mL of the stock with deionized water to 100 mL in a volumetric flask. The concentration of the working standard is 100 µg/mL. Calibration solutions are prepared by diluting the working standard with deionized water as described in Table B1. An adjustable pipette is used. A 100-mL graduated cylinder is used to measure the dilution water.

10.2 INITIAL CALIBRATION

A 1-mL aliquot of each aqueous calibration solution is processed according to the PROCEDURE starting at Step 4. Absorbance readings of Solutions A–D should range from 0.2 to about 2.0 absorbance units. The slope of the relationship between concentration of perchlorate and background-corrected absorbance should be linear, with a zero intercept.

10.3 DAILY CALIBRATION

A 1-mL aliquot of Calibration Solution C (5 mg/mL, equivalent to 5 mg/g in soil) is diluted to 50 mL with deionized water and processed according to the method. The daily response factor is calculated:

daily response factor = (5 mg/g)/(Absorbance @ 640 nm).

10.4 DAILY BLANK AND MATRIX SPIKES

A blank is produced by processing a 50-mL aliquot of deionized water. For each new soil type or new site, a soil is spiked at a concentration of 5 mg/g by adding 50 mL of the 5-µg/mL working standard to 50 g of blank soil and performing the method.

11.0 PROCEDURE

1. Collect a 50-g sample from below the root zone. Exclude all chlorophyll-containing material.

2. Place sample in plastic bottle with 50 mL deionized water and shake for three minutes. Allow suspension to settle.

3. Withdraw 5 mL of supernatant and force a few mL through a 0.45-µm filter into an undyed culture tube.

4. Dilute 1 mL of extract to 50 mL with deionized water and analyze as above for water.

5. Two cleanup methods should be attempted if needed:

a. If the acetone extract is colored, repeat the extraction but elute the acetone into an undyed culture tube. Add 20 µL 1 M acetic acid and 50 mg zinc powder. Shake and allow 5–15 minutes for destruction of color. Chlorophyll is not destroyed by this process. Filter through a 0.45-µm syringe into a new dyed culture tube and proceed as for a water sample.

b. If extract is not colored but recovery is lower than expected, repeat the extraction by diluting 1 mL of filtered sample to 50 mL with deionized water and passing it through a SPE-Alumina-N followed by the ion-pair conditioned SDB-L.

12. DATA ANALYSIS AND CALCULATIONS

The absorbance data are converted to perchlorate concentration in the sample by the following formula:

µg/g perchlorate = daily response factor (µg/g–ABS unit) X ABS (Sample-Blank).

Based on a 50-g wet-weight subsample extracted using 50 mL of deionized water.

13. METHOD PERFORMANCE

The method has been applied only to a series of spiked soil samples.

14. POLLUTION PREVENTION

All containers of organic solvents and extraction solutions should be kept capped to prevent evaporation. A large tray should be used under the work area to contain any spilled solvents.

15. WASTE MANAGEMENT

All solid waste contaminated with solvents, acid, base, dye, and extracted chemicals should be disposed of according to Federal, state, and local regulations. This includes extraction bottles and soils, filters, syringes, disposable pipettes, SPE tubes, and eluent tubes. All waste organic solvents from the extraction procedures and rinses should be disposed of according to Federal, state and local regulations.

16. REFERENCE

Burns, D.T., N. Chimpalee, and M. Harriott (1989) Flow-injection extraction-spectrophotometric determination of perchlorate with Brilliant Green. *Analytica Chimica Acta*, **217**: 177–181.

17. TABLE

Table B1. Preparation of calibration solutions from 100-µg/mL working standard to simulate extracts of 50-g soil subsamples with 50 mL of deionized water.*

		mL 100 µg/mL	mL Deionized water
A	Blank	0.00	10.0
B	1 µg/g	0.100	9.90
C	5 µg/g	0.500	9.50
D	10 µg/g	1.00	9.00

* Dilute 1 mL of each to 50 mL with deionized water and analyze by water method.

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14. ABSTRACT

Low concentrations (µg/L) of the perchlorate anion, ClO_4^-, have been measured in drinking water supplies in many states throughout the United States. Federal and state regulatory agencies are concerned about the possible adverse effects of perchlorate contamination, as the anion is known to target the human thyroid gland and its metabolic-hormone-producing function. The provisional action level for drinking water established by the EPA and adopted by several states is 18 µg/L (18 ppb) perchlorate; however, other states have set levels as low as 1–4 µg/L. The major sources of perchlorate contamination in surface and ground waters are propellant manufacturers, military installations, defense contractors, and agriculture. A reliable and inexpensive colorimetric method for perchlorate in water and soil extracts has been developed and tested with surface water, well water, bioreactor effluent, and soil extracts. The detection limit for water is 1 µg/L and 0.3 µg/g for spiked soils. A 0.5-L sample of water or a 1-mL sample of aqueous soil extract is passed through a solid-phase extraction cartridge that has been conditioned with a perchlorate-specific ion-pair reagent. Perchlorate, as well as small quantities of chlorate and major ions, is retained. A rinse step removes the interferences and the perchlorate is eluted into an ion-pairing dye in a 13- × 100-mm test tube. A 1-mL aliquot of xylene is added, the tube is shaken, and the dye-pair extracts into the xylene that separates into a layer lying in the light path of a standard portable spectrophotometer. Results from nearly 100 well water and bioreactor samples show excellent agreement with EPA Method 314 over the range of 1–225 µg/L (slope = 1.11, $R^2 = 0.913$). Some false positives were encountered in some wells. A cleanup method was developed that can eliminate false positives due to humic substances. The colorimetric method is being adapted to an automated on-line monitor.

15. SUBJECT TERMS

Colorimetric Field screening Perchlorate

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