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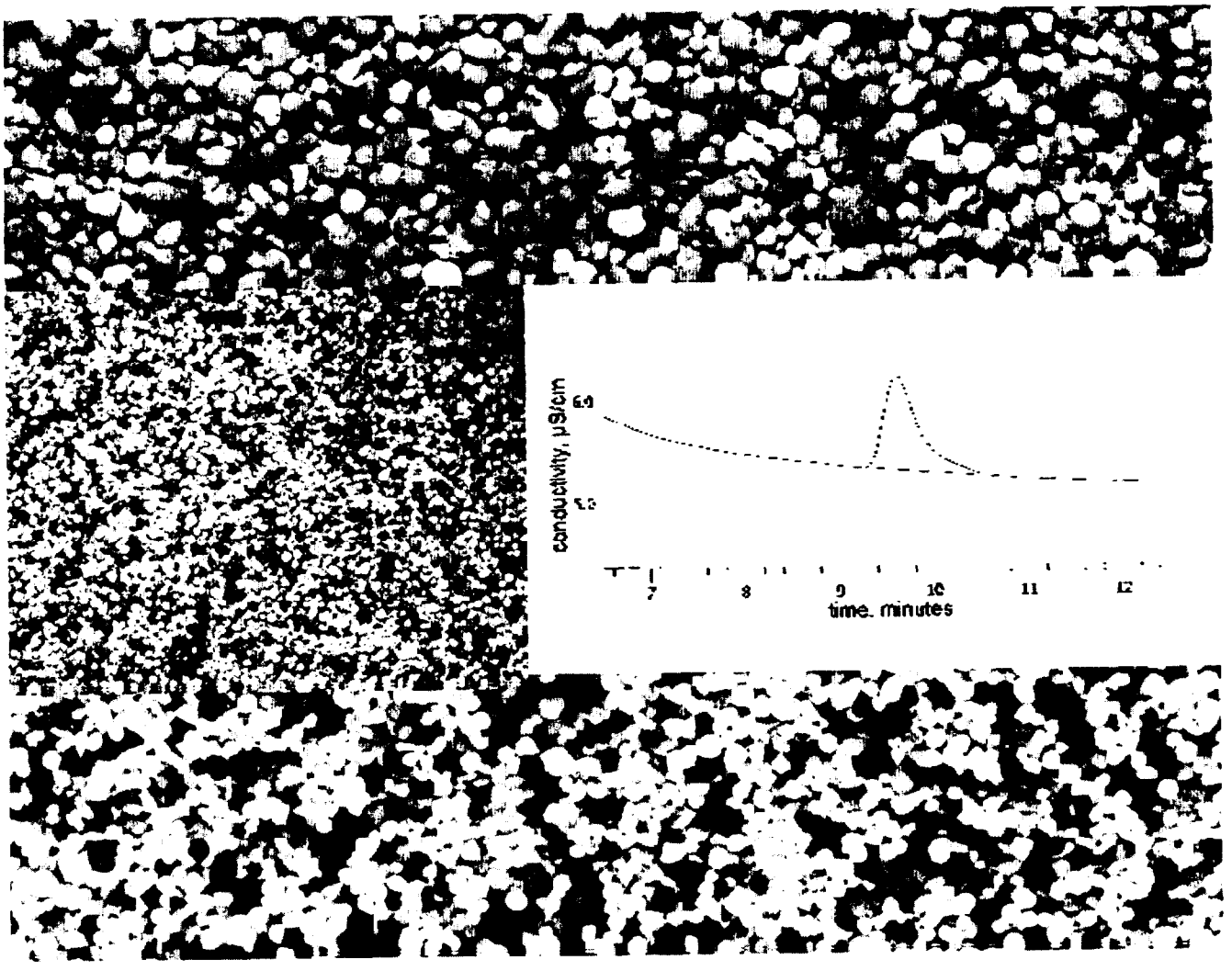
Ion Chromatographic Determination of Perchlorate

Analysis of Fertilizers and Related Materials



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Ion ChromatographicDetermination of Perchlorate

Analysis of Fertilizers and Related Materials

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Notice

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Foreword

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The National Risk Management Research Laboratory is the agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

A solid fertilizer sample is dissolved or leached to solubilize the perchlorate as the aqueous anion. If needed, the liquid is filtered or centrifuged. The resulting solution is subjected to ion chromatography using an adaptation of EPA Method 314.0. Preliminary screening is required to ensure the sample is amenable to ion chromatography and within the calibration range. Quality control and reporting requirements have been modified for the fertilizer matrices. Equipment and detailed procedures must be documented as part of the supporting information.

Contents

Notice iii

Foreword iv

Abstract v

Contents vi

List of tables vii

Sections

1 Sample procurement and reduction 1

2 Leaching or dissolution of solid materials 2

3 Instrument calibration and liquid sample analysis 3

4 Instrumental analysis of solutions 4

5 Data analysis 9

6 Quality control requirements 16

Appendices

1 Suggested approaches for determining whether insoluble components retain perchlorate or otherwise inhibit its detection 17

2 Recommended calibration standards for alternate size sample loops 24

List of tables

1 Recommended volumes of stock standard and post-dilution concentrations of calibration standards for 500-µL and 1.0-mL sample loops 4

2 Values of Student's *t* used to compute the 90% confidence interval 13

A2-1 Recommended volumes of stock standard and post-dilution concentrations of calibration standards for 10-µL and 100-µL sample loops 24

1. Sample procurement and reduction

1. Using a clean Missouri D tube sampler, obtain approximately 500–1000 g of the material to be tested by repeated insertions into the pile(s). Ideally, raw materials (i.e., specific chemical compounds) rather than multiple-component formulations are sampled. This affords two advantages. First, it minimizes matrix effects by keeping the number of matrix constituents as small as possible. Second, it ensures the highest possible analyte concentrations since there is a presumption that most components are essentially perchlorate-free. Accordingly, multiple-component formulations dilute the analyte.

2. Transfer the Missouri D tube contents to a new polyethylene bag (e.g., Ziploc or OneZip) and seal the bag. This represents a *bulk sample*. Ensure the chain of custody for all samples by appropriate measures. It is assumed that each laboratory has established its own guidelines for the number of bulk samples needed to represent a given mass (e.g., tonnage) or volume (e.g., cubic yardage) of material, consistent with industrial or regulatory practices and data use objectives. Record relevant sample information, e.g., location, date, time, manufacturer, lot number, product name, grade/guaranteed analysis.

3. In the laboratory, riffle the sample at least three times, re-combining all of the riffled portions after each round of riffling. Do this in a fume hood so that dust is carried out of the laboratory. This mixes the bulk sample thoroughly. Through 2–3 (or so) additional rounds of riffling, divide the sample repeatedly (e.g., 1000 g → 500 g → 250 g → 125 g), riffling each subsample until about 125–150 g of material is obtained.

The following steps do not apply to pure nitrate salts! However, they do apply to multiple component formulations (e.g., soluble plant foods) that contain nitrate salts as ingredients.

4. Transfer about 125–150 g of material to a blender, grinder, or mill equipped with stainless steel blades. Make sure the container is well-sealed to minimize loss of sample as fine dust. In our experience, kitchen blenders and coffee grinders give good results, with the blender being superior to the coffee grinder. Ball mills do not give good results; these materials tend to cake to the wall of the container when a ball mill is used (regardless of choice of grinding media). Operate the blender or grinder for at least 2 minutes to reduce the material to a fine powder. A glass blender jar allows visual inspection of particle size. As in step 3, use a fume hood so that dust is carried out of the laboratory.

5. Allow sufficient time for the dust to settle in the grinder or blender jar (about 2–5 minutes). Use a metal spatula to scrape the contents from the wall of the container, and operate the grinder or blender for another 30–90 seconds to re-mix the sample. After the dust has settled, carefully transfer the pulverized sample to a new screw-cap polypropylene or high density polyethylene bottle free of plasticizers (e.g., Nalgene). This is the *laboratory sample*.

6. Label the bottle and store the ground sample at ambient temperature.

2. Leaching or dissolution of solid materials

1. (a) *This step does **not** apply to materials identified as nitrate salts; see (b).* Prepare at least two individual portions of a ground sample as follows. Tare a polypropylene or high density polyethylene screw-cap bottle (or tube). Place **4.00 ± 0.01 g** of the pulverized solid material directly into the tared container. Now add **40.0 ± 0.5 mL** of deionized water into the bottle and cap tightly. In order to get the right ratio, you must use 40.0 mL of water. Do **not** put the fertilizer into a 40.0-mL volumetric flask and simply fill to the mark. That would be wrong! When done correctly, this procedure yields an *initial* fertilizer mass-to-leachate/solution (water) volume ratio of C° = (4.00 g) ÷ (40.0 mL) = 0.100 ± 0.003 g solid (mL liquid)$^{-1}$. It is incorrect to call this ratio a concentration because some of the materials are insoluble. It is essential that the measured physical quantities be kept to this level of exactness to minimize propagation of error. Although it is true that dissolving a salt in liquid water brings about a change in volume for the resulting solution, studies of the partial molar volumes of strong electrolytes suggest that this change should be ≤ 0.6% relative to the initial volume of water under our conditions. For convenience, we will refer to the fertilizer mass-to-leachate/solution (water) volume ratio as the *f/w ratio* (fertilizer to water).

   (b) **NITRATE SALTS ONLY!** Combine 100 ± 0.4 g of the solid sample with 1.00 ± 0.005 L of deionized water. *For safety reasons, **DO NOT GRIND THE SAMPLE!*** Stir magnetically or shake vigorously until the soluble material dissolves (usually 10–15 min). When all of the soluble material dissolves, a small amount of insoluble material (floating froth or sediment) may remain behind. Remove and discard this insoluble material. Froth may be removed by suction, and sediment should be allowed to settle out. Collect and save the solution phase.

2. *This step does **not** apply to materials identified as nitrate salts.* Place the capped bottle into a mechanical shaker and vigorously mix the contents of the bottle as follows. Shaking should be vigorous enough to keep the particulates suspended in the liquid phase. End-over-end (rotating/revolving), oscillating, wrist-action, or back-and-forth (reciprocating) shakers may be used. As a general rule, orbital, rocking, and some rotary shakers are inadequate to suspend the solid phase in the liquid phase.

   For completely soluble plant foods or fertilizers (e.g., potassium chloride, urea), shake for 20 minutes. For any sample that contains one or more insoluble components, including any fillers or coatings, shake for 8–15 hours.

3. If the liquid portion is sufficiently particulate-free to permit it to be injected in the ion chromatograph, no further treatment is needed. On the other hand, if suspended matter is visible, decant the liquid portion into a disposable polypropylene centrifuge tube and centrifuge until visually clear (usually 15–60 minutes).

4. Alternately (or additionally), filter through hydrophilic polypropylene or hydrophilic polyethersulfone filters. Do not use any membrane that has not been tested to ensure perchlorate is not lost to the filter. Acceptable performance of the membrane filter must be demonstrated using at least 2 DI water blanks and recovery of duplicate 10 ng mL^{-1} standards (prepared in DI water).

3. Instrument calibration and liquid sample analysis

1. **Stock standard**. Make a stock standard containing 1.000 mg ClO_4^- mL^{-1} = 1.000 g ClO_4^- L^{-1} by dissolving ACS reagent grade ammonium perchlorate, NH_4ClO_4 [7790-98-9], as follows. Weigh out 1.181 ± 0.004 g NH_4ClO_4 into a tared vessel. Alternately, ACS reagent grade anhydrous sodium perchlorate, $NaClO_4$ [7601-89-0], may be substituted for ammonium perchlorate. Weigh out 1.231 ± 0.004 g $NaClO_4$ into a tared vessel. Hydrous/hydrated forms must not be used. Using other grades or salts is prohibited. Quantitatively transfer the material to a 1.000-L volumetric flask. Add sufficient deionized water to dissolve the solid. Dilute to volume and stir magnetically until completely mixed. Retain this solution in high density polyethylene or polypropylene bottles at ambient temperature. Other than risks from evaporation or contamination, this solution is essentially good indefinitely if kept sterile. Under typical laboratory circumstances, it should last 30-60 days without difficulty; it should be made fresh at least every 60 days.

2. **Working standards**. Make a 100-µg mL^{-1} working standard by pipetting 10.00 mL of the stock standard into a 100-mL volumetric flask and diluting to volume. Make a successive working standard at 10.00 µg mL^{-1} using a second volumetric dilution. Always pipet a 10.00-mL portion of a standard and dilute to volume in a 100-mL volumetric flask. Use Class A volumetric glassware for this section.

3. **Calibration standards for ion chromatography**. Dilute the following volumes (Table 1) of the 10.00-µg mL^{-1} working standard in 100-mL volumetric flasks to obtain the following calibration standards. Use of a calibrated automatic pipettor is permitted in this step (e.g., Eppendorf, Oxford, Pipetman). Prepare duplicate standards at each concentration.

   Analyze the 3.00 ng mL^{-1} standard 8 times (8 injections) to obtain replicate measurements of peak area for the IC MDL determination. Subject each remaining standard to duplicate or triplicate analyses (injections) on the ion chromatograph to obtain at least two satisfactory peak areas. *All calibration solutions must be run at least in duplicate. Triplicate is encouraged, and additional replicates are at the discretion of the analyst.*

Table 1. Recommended volumes of stock standard and post-dilution concentrations of calibration standards for 500-µL and 1.0-mL sample loops. (1) Note alternative approaches to standards g, h, and i. (2) Standards a_1, a_2, and a_3 are used for the optional lower limit of detection calculation. (3) If a smaller sample loop is used (e.g., 100 µL or 200 µL), then the concentrations should be raised to account for the difference in the amount of analyte injected. See also Appendix 2.

volume of **10.0-µg mL^{-1}** working standard		concentration after dilution to 100 mL	volume of **100-µg mL^{-1}** working standard		concentration after dilution to 100 mL
a_0	none (blank)	0.00 ng mL^{-1}	g	100 µL	100 ng mL^{-1}
a_1	5.0 µL	0.50 ng mL^{-1}	h	200 µL	200 ng mL^{-1}
a_2	10.0 µL	1.00 ng mL^{-1}	i	500 µL	500 ng mL^{-1}
a_3	20.0 µL	2.00 ng mL^{-1}	j	1.00 mL	1.00 µg mL^{-1}
b	30.0 µL	3.00 ng mL^{-1}	k	2.00 mL	2.00 µg mL^{-1}
c	50.0 µL	5.00 ng mL^{-1}	l	5.00 mL	5.00 µg mL^{-1}
d	100 µL	10.0 ng mL^{-1}	m	10.0 mL	10.0 µg mL^{-1}
e	200 µL	20.0 ng mL^{-1}			
f	500 µL	50.0 ng mL^{-1}			
g	1000 µL	100 ng mL^{-1}			
h	2000 µL	200 ng mL^{-1}			
i	5000 µL	500 ng mL^{-1}			

4. Instrumental analysis of solutions

1. **Instrumentation.** The ion chromatograph and guard/separation columns must be demonstrated to provide a discrete retention time for perchlorate relative to other common anions. This has already been done for the Dionex IonPac AG11/AS11 and IonPac AG16/AS16 columns using Dionex DX300 and DX500 chromatographs. The AG16/AS16 column combination outperforms the AG11/AS11 combination. Recommended eluent is 0.10 M NaOH(aq). Recommended flow rate is 1.0 mL min^{-1}. Detection is by suppressed conductivity, with a suppressor current of 300 mA. Laboratories must demonstrate acceptable resolution and retention behavior for any other columns or instruments and must provide supporting documentation.

   Sample loops of 100 µL, 200 µL, 500 µL, or 1000 µL may be used to determine perchlorate concentration in routine samples. The initial choice of sample loop is up to the analyst. However, once that choice is made, it must be used throughout. **The same size of sample loop must be used for all standards, samples, and fortified samples.**

   About the choice of sample loop size. The choice of sample loop is not a simple matter for fertilizer matrices and can have profound effects on the quality of the results, especially sensitivity, particularly near the lower limit of detection. Primarily, there are two competing factors: (1) the need to maximize sensitivity by loading as much analyte as possible (i.e., injecting the largest possible volume of solution) onto the column, and (2) the need to minimize diffusion and undesirable mass-transport phenomena by diluting the eluent anion (hydroxide) as little as possible. Because of the

properties of fertilizer components, but especially their high concentrations relative to that of the analyte, the guidelines that apply to analyses of drinking water samples (which are considerably lower in ionic strength and dissolved matter) are inapplicable here. There are few simple rules or general guidelines that may be set down. Rather, the analyst must understand the potential chemical interactions and the principles of ion chromatography. The analyst is therefore alerted to the following considerations.

As a general guide, it is preferable to inject 100 μL of a 1.0% w/w leachate rather than 1000 μL of a 0.10% leachate. With leachates of insoluble compounds (e.g., clays or ferric oxides) or solutions of nonionic compounds (e.g., urea), the primary effect is the dilution of the eluent, 0.10 M NaOH(aq). Because of the sizes and shapes of the columns and the tubing, the flow is not very turbulent, and the mixing is therefore poor. This leads to regions of varying hydroxide concentrations in the column as well as requires a longer time for the hydroxide concentration to return to its pre-injection value, resulting in poorer separation, more diffusion, longer retention time, and peak broadening. In light of the column's diameter and loading capacity, it is important to consider the fact that large injections result in ions having to migrate farther into the stationary phase to reach an available binding site. However, at the same time, the eluent is flowing, which can sweep the analyte anions along before they have a chance to equilibrate with the quaternary ammonium sites on the column. Such undesirable mass transport produces a broader peak and can make some low analyte concentrations unrecoverable. The dilemma results from trying to use a large enough injection volume to load the column with as much analyte as possible while simultaneously trying to avoid undesirable mass transport. In other words, spreading of the peak negates the benefit of the additional loading. There is no easy resolution to this dilemma, and some experimentation (trial and error) may be warranted to achieve optimal recovery, given practical limitations (e.g., time or sample load). In select cases, it may even be acceptable to use a 10-μL or 20-μL sample loop, but this size of loop should not be used routinely. Of course, any change in sample loop requires obtaining a suitable calibration graph with each size of loop.

Best results are generally obtained using the smallest possible sample loop and the highest possible *f/w* ratio. In the case of urea or urea-containing products, there is an additional problem. While not normally significant for IC analyses, it must be kept in mind that urea undergoes hydrolysis to ammonium carbamate and ammonium carbonate when dissolved in water. Consequently, the ionic strength of a urea solution changes with time until equilibrium is reached. Best results are obtained by analyzing urea solutions as soon as possible after dissolution.

In the case of some soluble materials [e.g., KCl, $(NH_4)_2SO_4$, $NaNO_3$], the large injection of ions not only overloads the column, but also competes with the hydroxide and the perchlorate for the cationic sites on the column. Although these ions are essentially unretained when present at low concentrations, the sheer magnitude of their concentration is responsible for a huge tailing peak that can overlap with the perchlorate peak. Noise in the signal generally raises the lower limit of detection when the perchlorate peak falls on this tail. Best results are generally obtained using the smallest possible sample loop and the highest possible *f/w* ratio; however, even this guideline has limits because a solution with an ionic strength exceeding 0.10 M will suffer from Schlieren-type mixing problems when it meets the eluent.

In the case of phosphate fertilizers, the dihydrogen phosphate and monohydrogen phosphate ions must be neutralized to tribasic phosphate after injection onto the column. In addition to the dilution

effect, this causes a drop in pH and release of heat. By consuming hydroxide, the neutralization causes an additional delay in the hydroxide concentration returning to its pre-injection value.

2. **Preliminary screening**. Before a solution is injected in duplicate, the analyst should verify that the concentration is in fact within the calibration range. Experience suggests that the upper limit for perchlorate concentration in a solution prepared using 0.1 g of solid per mL falls below 200 $\mu g\ mL^{-1}$ (ppm). In order to reach the instrument calibration range specified in this procedure, a 1/1000 v/v dilution would be required. Such dilutions should be made in serial steps of pipetting 10.00-mL aliquots into 100-mL volumetric flasks using Class A glassware. For example, a solution that contains 150 $\mu g\ mL^{-1}$ would require three consecutive 10-mL to 100-mL (10% v/v) dilutions.

   Preliminary screening requires a single injection to verify (1) the location of the peak (retention time) and (2) the approximate range of concentration. Note that a solution containing 200 $\mu g\ mL^{-1}$ is 20× the upper limit of calibration. Because adsorbing so much perchlorate to the column can take a long time to remove, it is advisable to run a 1/1000 (0.1% v/v) dilution first. If no peak is visible, and the baseline rapidly recovers after the injection, the 1% dilution, 10% dilution, or the original solution may be run at the discretion of the analyst. The choices of what solutions to run and what order are matters for the analyst and will not be rigorously dictated in this procedure. It is a matter of balancing the risk of fouling the column (probably only temporarily) with the time required for the total number of screening injections.

   While not a requirement, it is useful to run a fortified sample (with ~10–100 ng mL^{-1} spike) immediately after the screening injection to make sure that the perchlorate retention time is correct and that a peak is visible. Complicated matrices with large amounts of dissolved material can influence retention time, peak shape, and general performance. The exact nature of the effect is dependent on the ionic strength, ionic medium, hydrophilicity/phobicity, and concentration of the matrix constituents. We accept that most analysts have developed strategies for dealing with complicated matrices, and we will not impose our own preferences on anyone else. Nonetheless, it is the responsibility of the analyst to ensure that the final tested solution contains a perchlorate concentration within the calibration range set by Table 1. Dilution should not put the concentration below either the LLOD or the MDL (vide infra).

3. **Test solution analysis**. Once a dilution factor has been settled upon for the leachate or solution derived from a particular solid sample based on the preliminary screening, this solution shall be injected in duplicate. Test solutions that show a perchlorate peak shall be injected in triplicate or more. Test solutions that show no observable perchlorate peak shall be injected in duplicate or more.

4. **Fortified samples and recovery**. Fortified (spiked) samples must be subjected to IC analysis. First, they verify that retention time has not shifted, or—if it has—they allow that shift to be determined. Second, they ensure that recovery is satisfactory within a particular matrix, in other words, that the peak area for a given analyte concentration remains constant. Once a final dilution is settled on for a particular sample, an aliquot of that diluted solution must be fortified with perchlorate concentration spikes equal to 20% and 50% of the concentration found in the sample.

   In this method, the term ***p%-spike*** ($10 \le p < 100$) shall denote a fortification (addition of analyte) that raises the analyte concentration to $(1 + p/100)c_0$, where c_0 is the measured analyte concentration

in the original (unspiked) test solution. For instance, if the perchlorate concentration in a solution is determined to be 1.0 μg mL^{-1}, a *20%-spike* requires that the concentration increase 0.20 μg mL^{-1} to a total (i.e., original + spike) concentration of 1.2 μg mL^{-1}. Likewise, a *50%-spike* would require that the total perchlorate concentration (i.e., after spiking) be raised to 1.5 μg mL^{-1}.

Similarly, the term ***m*-spike** (m, a concentration) shall denote a fortification (addition of analyte) that raises the analyte concentration to ($c_0 + m$), where c_0 is the concentration in the original (unspiked) test solution. For example, a 5.0-ng mL^{-1} spike raises the concentration of a 10 ng mL^{-1} solution to 15 ng mL^{-1}.

The volume of the spiking solution must be kept negligible compared to the volume of tested solution to which it is added so that the original solution is not measurably diluted. Therefore, the volume of spiking solution must not contribute more than 1.9% to the volume of the solution. If a 5.0 mL aliquot of test solution is to be spiked, the volume of spiking solution must not exceed 0.095 mL (95 μL) and is best kept to 50–60 μL. Note that a standard Dionex autosampler vial has a capacity of 5.5 mL of solution and is conveniently filled with 5.0 mL of solution using a dispensing pipettor.

Satisfactory recovery of a 20%-spike suggests that that measured concentration is significantly above the lower limit of detection and that the matrix does not proportionately attenuate the signal or increase the noise to the extent that the error is increased. All fortified solutions shall be run in duplicate or triplicate and the results averaged.

It is important to note that this method assumes that perchlorate is present in the form of a simple salt that completely dissolves and completely dissociates under the conditions used to leach or to dissolve the sample. It must be clearly understood that this method cannot be used to determine the concentration of perchlorate in insoluble substances capable of retaining it from (or incapable of releasing it to) the aqueous phase during leaching.

In the case of potassium fertilizers, there can be a risk of precipitating potassium perchlorate. This is especially true when the fertilizer is entirely soluble, especially KCl (0-0-62), because the K^+ molarity is the largest for that compound. When an aliquot of a concentrated analyte solution is used to spike a 10% w/w solution of KCl, precipitation may be observed. Although the $KClO_4$ will usually dissolve upon mixing, it is imperative that the analyst ensure the solubility product has not been exceeded.

Example. Suppose a liquid solution made at 0.100 g solid mL^{-1} is found to contain 50 ng ClO_4^- mL^{-1} by IC. The 20%-spike requires an increase in concentration, $\Delta[ClO_4^-]$, of +10 ng ClO_4^- mL^{-1}, so that the total (after spiking) concentration is 60 ng ClO_4^- mL^{-1}. If a 5.0-mL aliquot of test solution is placed in the vial, the 20%-spike requires the addition of 50 ng of perchlorate. So that the total volume remains approximately constant, the volume of spiking solution is constrained to 50 μL. This requires a spiking solution with a concentration of 1.0 ng μL^{-1} = 1.0 μg mL^{-1} (= 50 ng ÷ 50 μL).

The 50%-spike requires $\Delta[ClO_4^-]$ = +25 ng mL^{-1}, so that the total (after spiking) concentration is 85 ng ClO_4^- mL^{-1}. This corresponds to an addition of 125 ng of perchlorate in a 5.0-mL volume. Again, the volume of spiking solution is constrained to 50 μL. However, now the spiking solution must have a concentration of 2.5 ng μL^{-1} = 2.5 μg mL^{-1} (= 125 ng ÷ 50 μL).

Perchlorate-free solutions. If the liquid is found to contain no perchlorate (no distinguishable peak) at the right retention time, a spike of 10.0 ng mL^{-1} shall be used. This requires pipetting 55 μL of a 1000 ng mL^{-1} stock solution into the filled autosampler vial. If the analyst prefers not to fortify directly into the autosampler vials, it would also be acceptable to use 20.0 mL of the liquid sample and

pipet in 200 μL of the 1000 ng mL^{-1} standard. To be acceptable, recovery of spikes must be in the range of 80–120%, i.e., 8.0–12 ng mL^{-1}.

If the 10.0-ng mL^{-1} fortification cannot be recovered satisfactorily, the analyst shall dilute the test solution 1/10, 1/100, 1/1000, etc., using serial 10.00 mL to 100.0 mL volumetric dilutions. Each of the dilutions shall be spiked at 10.0 ng mL^{-1}. The process shall continue until a concentration is identified for which the recovery is acceptable. That concentration shall be called $c/10$, and the concentration of the previous solution from whence it was made shall be called c. The solution of concentration c shall be diluted to give solutions with concentrations of $0.90c$, $0.80c$, $0.70c$, ..., $0.20c$, and each of these fortified at 10.0 ng mL^{-1} and injected. The process shall continue until the highest leachate concentration is identified for which the recovery is acceptable. If none shall have satisfactory recovery, the previously successful solution shall be used, i.e., the one with concentration equal to $c/10$. The final concentration settled upon for fortification shall be used to compute the *assured reporting level* (vide infra).

Recovery. Recovery must be calculated for fortified samples. The first step is to choose a value for the spike. Suppose a solution tests positive for perchlorate at 117 ng mL^{-1}. We choose 20 and 60 ng mL^{-1} as the fortifications. For the larger spike: (60 ng mL^{-1})(5.5 mL) = 330 ng needed. We have a 10.0-ppm standard (10 μg mL^{-1} = 10 ng μL^{-1}). Thus, the volume required is (330 ng) ÷ (10 ng μL^{-1}) = 33 μL. However, this is too small to accurately measure.

Consequently, we dilute the 10.0-ppm standard in half to produce a 5.00-ppm standard. Now we require 66.0 μL (this is 1.2% of 5.5 mL, so the volume is not a problem). An autosampler vial is filled (5.5 mL) with the test solution, and a 66.0-μL aliquot of 5.00-ppm standard is pipetted into the vial. The vial is capped partly and mixed, then the cap is fully depressed. The final concentration of the perchlorate in the solution is computed as follows.

$$[ClO_4^-]_T = \frac{[ClO_4^-]_{test} \times V_{test} + [ClO_4^-]_{spike} \times V_{spike}}{V_{test} + V_{spike}} \tag{1}$$

$$[ClO_4^-]_T = \frac{(117 \text{ ng mL}^{-1})(5500\ \mu\text{L}) + (5000 \text{ ng mL}^{-1})(66\ \mu\text{L})}{5500\ \mu\text{L} + 66\ \mu\text{L}} \tag{2}$$

$$[ClO_4^-]_T = 175 \text{ ng mL}^{-1} \tag{3}$$

Running this fortified solution on the ion chromatograph, we obtain values of 176 and 182 ng mL^{-1}. These average to 179 ng mL^{-1} for the perchlorate concentration. Duplicate injections should be made and the results averaged.

$$\text{Recovery} = (179 \text{ ng mL}^{-1})/(175 \text{ ng mL}^{-1}) \times 100\% = 102\% \tag{4}$$

This is within the acceptable range of recovery. If an acceptable recovery cannot be obtained for a particular sample even after $1/10^4$ dilution, the laboratory must report that the sample is refractory to ion chromatographic analysis. To date, we have found no material that meets this criterion. If the recovery is reproducible, but not accurate, an attempt should be made to determine if the matrix brings about the nonlinearity and whether the behavior can be estimated by running additional spiked samples. If a sample is reported as refractory to analysis, an explanation of what steps were taken and how this conclusion was drawn must be written on the reporting form. Supporting data should be attached to the reporting form, including chromatograms, calculations, and other information necessary to justify the assertion that the sample is not amenable to the method.

5. **Continuing check: recovery of standards.** Once a calibration curve has been generated, standards prepared at 10, 50, and 150 ng mL^{-1} must be reanalyzed (for a 500-μL or 1000-μL loop). A recovery of 90–110% of the concentration must be obtained. Otherwise, additional standards at intermediate concentrations must be used in the construction of the calibration curve.

   As a continuing check on the calibration of the instrument, a 50 ng mL^{-1} standard must be run and fall between 45 and 55 ng mL^{-1} at the beginning and end of each sequence of injections and after every 10th-15th injection.

5. Data analysis and results reporting

1. **Calibration.** Plot integrated peak area against concentration. Plot all values, not averages. Compute the least squares slope, *y*-intercept, their standard errors, and the regression coefficient. Use an unweighted least squares fit to the data. Use all data for the plot, not averages (using averages skews the statistical calculation of the standard errors for the least squares parameters). To be satisfactory, the standard error in the slope must be <10% of the value of the slope and the *y*-intercept must be statistically indistinct from zero, i.e., less than its standard error in magnitude. Examine the plot to verify that there are no significant deviations from linearity in any region or discordant data that should be rejected.

   It is recommended that at least two calibration curves be constructed for various ranges of concentration so long as each curve is constructed from at least six duplicate ordered pairs (concentration, peak area), the data span the domain fully (no extrapolation), and no single concentration value is separated from another by more than 30% of the domain. This approach can give improved accuracy and precision, especially when analyzing samples that contain only a 5.0-ng mL^{-1} spike. Otherwise, the unweighted least squares regression biases the slope and *y*-intercept in favor of the higher concentration standards. The following are recommended domain intervals, but other splits are also valid: [0, 200 ng mL^{-1}], [0.50 μg mL^{-1}, 10.0 μg mL^{-1}]; samples falling in the interval (200 ng mL^{-1}, 500 ng mL^{-1}) may be diluted to bring them into the lower calibration interval.

2. **Signal-to-noise.** The signal-to-noise ratio should be at least 3. The signal-to-noise ratio may be calculated by integrating a nearby section of the baseline equal in time to the elution time period of the perchlorate peak. For example, if the perchlorate peak begins to elute at 8.40 min and finishes eluting at 8.60 min, the elution time period is 0.20 min. Therefore, a 0.20-min section of the nearby baseline should be integrated to estimate the noise. Generally, *S/N* will be greater than 3; this can usually be

checked by simple inspection. However, near the lower limit of detection, this must be verified using the procedure described.

3. **Detection limits.** The lower limit of detection should be below 3 ng mL^{-1}. Keep a calibration plot with your results. Note that this detection limit is based on a 1000-µL sample loop. The detection limit will vary with choice of loop size.

(a) Definitions

A_{av} = average of the eight peak area values for the 3.00 ng mL^{-1} sample

A_i = the integrated peak area associated with the *i*th injection

σ_{n-1} = sample standard deviation (estimated standard deviation) for *peak areas*

$$\sigma_{n-1} = \sum_{i=1}^{i=8} [(A_{av} - A_i)^2/7]^{1/2} \tag{5}$$

(b) Lower limit of detection (LLOD) in deionized water (optional)

For the 1000-µL loop, estimate the lower limit of detection (a concentration) from the calibration curve, using 5 or more replicate injections each of a_0 (blank), a_1 (0.5 ng mL^{-1}), a_2 (1.0 ng mL^{-1}), a_3 (2.0 ng mL^{-1}), b (3.0 ng mL^{-1}), and c (5.0 ng mL^{-1}). At the analyst's discretion, additional intermediate concentrations (e.g., 0.2, 0.7 ng mL^{-1}) may be used. Perform a least squares linear regression using only these points, and interpolate the LLOD from the data as follows, so long as $S/N \geq 3$, where the signal is the integrated peak area for the perchlorate peak at a specific concentration, and the noise is estimated by integrating an equivalent section of the baseline. First, calculate the sample standard deviation of the area at each concentration:

$$s = \sum_{i=1}^{i=n} [(\bar{A} - A_i)^2/(n-1)]^{1/2} \tag{6}$$

where n is the number of replicates at a specific concentration, A_i is the peak area for the individual *i*th injection, and $\bar{A}$ is the arithmetic mean of all n replicates at a specific concentration. Next, calculate the estimated standard deviation of the mean, which reflects the uncertainty in the arithmetic mean of the area for a specific concentration value.

$$s_m = s/n^{1/2} \tag{7}$$

For each concentration, plot the arithmetic mean peak area and vertical error bars based on the estimated standard deviation of the mean: $\bar{A} \pm 3s_m$. If desired, the propagated error in the concentration may be used to plot horizontal error bars as well. Draw a smooth curve through the upper limit established by the vertical error bars. Locate the point(s) where the vertical distance between the error-limit curve and the least squares line reaches its maximum. The largest value of the abscissa where an error maximum occurs represents the lower limit of detection. In the case of constant relative error (which is usually accepted to be a best case scenario), the LLOD is accepted

as being represented by the concentration of the lowest standard tested, but actually lies somewhere between that value and zero.

(c) Method detection limit (MDL) in deionized water

Compute the method detection limit in deionized water at the 99% confidence level for 7 degrees of freedom (8 replicates) using Student's t. In this case, $t_{0.01,7} = 2.998$.

$$\mathrm{MDL} = t_{0.01,7} \times \sigma_{n-1} \times [\mathrm{ClO_4^-}]/A_{\mathrm{av}} \tag{8}$$

$$\mathrm{MDL} = (2.998)(\sigma_{n-1})[3.00\ \mathrm{ng\ mL^{-1}}]/(A_{\mathrm{av}}) \tag{9}$$

(d) Assured reporting level (ARL) for the solid sample

The *assured reporting level* substitutes for a method detection limit for the solid. The important distinction between the ARL and the MDL is that it is possible to obtain an ARL even when the solid MDL is unknown. Furthermore, the ARL makes assumptions that simplify the experimental procedure, but put limits on our knowledge about the behavior of the analyte in a specific matrix. The solid MDL attempts to answer the question: "What is *the smallest concentration* of perchlorate we can detect and know it is really there?" On the other hand, the ARL answers a less rigorous question: "What is *a concentration* of perchlorate we can likely measure in this matrix?" In some cases, the ARL is approximately equal to the solid MDL and can be used as an estimate of it. However, if a measured value is far from the MDL, it is sufficient to know an ARL and not necessary to know the MDL. Some examples will clarify the matter. A *preliminary assured reporting level* (pARL) is found based on the recovery of a 20%-spike. In the case of a perchlorate-free sample, the pARL is equal to the ARL. The pARL is given by

$$\mathrm{pARL} = [\mathrm{ClO_4^-}]_{\mathrm{spike}} \div C^{\bullet} \div \Pi_{\mathrm{all}\ i}\, D_i \tag{10}$$

where $[\mathrm{ClO_4^-}]_{\mathrm{spike}}$ is the concentration increase due to the spike (e.g., 10 .0 ng mL), $C^{\bullet}$ is the *f/w* mass:volume ratio, and $\Pi_{\mathrm{all}\ i}\, D_i$ is the product of all dilution factors to give the overall dilution from each D_i, an individual dilution step (e.g., 1/10, 1/100).

Example 1. Suppose that a 10% w/w solution of urea is diluted 1/10 and that solution shows no distinguishable peak when injected using a 1000-μL loop. However, when fortified at 10.0 ng mL^{-1}, the recovered analyte concentration is 7.0 ng mL^{-1} in the 1/10 dilution, falling below the 80% cut-off, but a 1/100 dilution (c/10) shows acceptable recovery. Subsequently, the 1/10 solution (c) is diluted 90%, 80%, 70% v/v etc., each is spiked at 10.0 ng mL^{-1}, and injected. In the 70% v/v dilution (0.70c), the recovered concentration is 10.0 ng mL^{-1}. Without knowing *exactly* what dilution would have been necessary to get adequate recovery of a 10.0-ng mL^{-1} fortification, we simply make use of the information available. We know for sure that a 10.0 ng mL^{-1} fortification was adequately recovered under these conditions. Thus, we calculate the ARL = (10.0 ng mL^{-1}) × (40 mL/4.0 g) × (10/1) × (1/0.7) = 1430 ng g^{-1}. In this case, the ARL is an estimate of the detection limit for this particular matrix, and there is confidence that this urea sample contains less perchlorate than 1430 ng g^{-1}. If there are constraints on resources (especially time), this process may be truncated or fewer dilutions may be done, but the analyst must use a test solution for which recovery is satisfactory. It

must be realized that the more the process is shortened, the higher the ARL is, and the greater the potential for a false negative value is, especially for low analyte concentrations.

Example 2. Suppose that a 10% w/w solution of sodium nitrate is diluted 1/100 and the resulting solution has a perchlorate peak consistent with a concentration of 1.0 $\mu g\ mL^{-1}$. Fortifications of 200 and 500 ng mL^{-1} are satisfactorily recovered. Therefore, a *preliminary assured reporting level* (pARL) is determined as follows: (200 ng mL^{-1}) × (40 mL/4.0 g) × (100 mL/1 mL) = 200,000 ng g^{-1} = 200 $\mu g\ g^{-1}$. The concentration of perchlorate in the solid material is determined as follows: (1.0 $\mu g\ mL^{-1}$) × (40 mL/4.0 g) × (100 mL/1 mL) = 1000 $\mu g\ g^{-1}$ = 1.00 mg g^{-1}. Even without explicit knowledge of the lower limit of detection, there is reasonable confidence that a solid material containing perchlorate at a concentration equal to the pARL could in fact be measured. It should be noted, nonetheless, that this assertion is predicated on the presumption that the matrix does not induce a threshold response in the detector, below which, the analyte is utterly unobservable as opposed to merely being attenuated. Furthermore, it requires that *S/N* be sufficiently well-known and large. While not equivalent to a detection limit, the pARL is not an unreasonable approximation of the impact of the matrix upon the signal. We must rely upon the pARL because (1) the matrix cannot be duplicated so as to prepare a calibration curve in the matrix, and (2) the analyte cannot be removed from the sample to evaluate the true detection limit.

If the fortification at 20% of the measured concentration (20%-spike) cannot be successfully recovered, the solution may be spiked at up to 50% of the measured concentration. The highest fortification that may be used to calculate a pARL is 50% of the measured concentration. If a 50%-spike cannot be satisfactorily recovered, a dilution procedure similar to that specified in Example 1 shall be used to determine the pARL.

Subsequently, the concentrations found by triplicate (or n replicate) injections of the original (unspiked) test solution shall be used to estimate the 90% confidence interval. The 90% confidence interval shall be used as a check on the pARL determined from the recovery of the 20%-spike. The estimated standard deviation (s, as in equation 6) and the estimated standard deviation of the mean (s_m, as in equation 7) shall be calculated, but using concentrations, *not* peak areas. The 90% confidence interval represents an error in the measured concentration is given by

$$\Delta_{90\%} = t_{0.1,\nu} \cdot s_m \tag{11}$$

where ν is the number of degrees of freedom, $\nu = n - 1$ for n replicate measurements, and $t_{0.1,\nu}$ is the 90% confidence value of Student's t at ν, found from Table 2. Computationally similar to the MDL, $\Delta_{90\%}$ can be used to approximate the detection limit. Contrast the pARL [found from the (preferably 20%) spike] with $\Delta_{90\%}$, and report the larger of the two values as the ARL.

Table 2. Values of Student's t used to compute the 90% confidence interval

$t_{0.1,\nu}$	1.886	1.638	1.533	1.476	1.440	1.415	1.397	1.383	1.372	1.356	1.341	1.325	1.316
ν deg. of freedom	2	3	4	5	6	7	8	9	10	12	15	20	25
n replicates	3	4	5	6	7	8	9	10	11	13	16	21	26

4. Reporting results

1. Laboratories must report the unweighted least squares slope(s), y-intercept(s), their standard errors, and the regression coefficient(s) for their calibration curve(s). Print-outs of calibration plots must be retained and cataloged so as to be readily associated with the results of actual analyses for which they were used.

2. Laboratories must provide a sample chromatogram of 3.00 ng mL^{-1} calibration standards for inspection, report the calculated MDL, and report *S/N* values for the 3.00 ng mL^{-1} calibration standards. As long as $S/N > 3$, it is acceptable to report "$S/N > 3$."

3. For liquid aqueous samples, the analytical results (i.e., perchlorate concentrations) are to be reported in units of **(ng ClO_4^-) (mL soln)$^{-1}$**. In the case of solutions that contain more than 1000 ng mL^{-1}, laboratories may express aqueous concentrations in µg mL^{-1} at their discretion.

4. For solid samples that are dissolved or subjected to leaching at the testing laboratory, the analytical results (i.e., perchlorate concentrations) are to be reported on a <u>mass of perchlorate</u>-to-<u>mass of fertilizer</u> basis. All perchlorate concentrations in solid samples and assured reporting levels (ARLs) shall be expressed in units of **(µg ClO_4^-) (g solid)$^{-1}$**. Note that reporting is for the perchlorate anion and not a perchlorate compound.

$$1 \text{ mg } ClO_4^- \text{ (g solid)}^{-1} = 10^3 \text{ µg } ClO_4^- \text{ (g solid)}^{-1} = 10^6 \text{ ng } ClO_4^- \text{ (g solid)}^{-1} \quad (12)$$

5. For analytical results below the LLOD, MDL, or ARL, any positive result (i.e., integrable peak area distinct from the baseline noise) must be reported. A numerical value shall be reported for the concentration in the aqueous solution with the notation that the value is below the LLOD, MDL, ARL, etc. The solid sample shall then be described using the phrase "POSSIBLY DETECTED, NOT QUANTITATED." The ARL must be specified for the solid. If, however, the fortification indicates that the perceived peak is inconsistent with the retention time for perchlorate, the analyst shall rely on his/her best judgment to decide whether the concentration should in fact be listed as "UNDETECTABLE."

   If no peak is distinct from the baseline noise (as should be the case when no perchlorate is present), this null result for the aqueous solution and the solid shall be reported as "UNDETECTABLE." The ARL must be specified for the solid. If the ARL is less than 500 ng g^{-1} for a sample, and no perchlorate peak is distinguishable from the baseline noise in chromatograms from injections of duplicate solutions, then that material may reasonably be viewed as perchlorate-free.

5. Sample calculations

1. From IC, a solution prepared from a solid fertilizer was found to contain 22 ng mL^{-1} = **(22 ng ClO_4^-) (mL soln)$^{-1}$**.

$$W = [ClO_4^-]_{IC} \div C^{\bullet} \quad (13)$$

$$W = \frac{22.0 \text{ ng } ClO_4^-}{1.00 \text{ mL liquid}} \times \frac{40.0 \text{ mL liquid}}{4.00 \text{ g fertilizer}} = \frac{220 \text{ ng } ClO_4^-}{\text{g fertilizer}} \quad (14)$$

analyte concn obtained by IC	mass:vol (*f/w*) combining ratio 4 g per 40 mL (reciprocal, i.e., *w/f*)	mass:mass perchlorate concn

where W is the perchlorate:fertilizer mass:mass ratio.

2. From the IC screening run, a leachate prepared from a fertilizer was found to contain approximately 800 ng mL^{-1} = **(800 ng ClO_4^-) (mL soln)$^{-1}$**.

   This was outside the calibration range; therefore, a 10% v/v dilution was made by pipetting 10.00 mL into a 100-mL volumetric flask and diluting to volume. (This is alternately referred to as a 1 + 9 volume dilution or as 1/10 v/v dilution.)

   The 10% v/v dilution was run again and found to contain 77.2 ng mL^{-1}.

$$W = [ClO_4^-]_{IC} \div C^{\bullet} \div D \quad (15)$$

$$W = \frac{77.2 \text{ ng } ClO_4^-}{1.00 \text{ mL liquid}} \times \frac{40.0 \text{ mL liquid}}{4.00 \text{ g fertilizer}} \times \frac{10}{1} = \frac{7720 \text{ ng } ClO_4^-}{\text{g fertilizer}} \quad (16)$$

analyte concn obtained by IC	mass:vol (*f/w*) ratio (reciprocal, *w/f*)	dilution factor (reciprocal)	mass:mass perchlorate concn

where D is the dilution factor (1/10 in this case). A unit conversion is required:

$$W = \frac{7720 \text{ ng } ClO_4^-}{\text{g fertilizer}} \times \frac{1 \ \mu g}{10^3 \text{ ng}} = \frac{7.72 \ \mu g \ ClO_4^-}{\text{g fertilizer}} \quad (17)$$

3. For all tested fertilizers, the final reported result will be the average concentration obtained from multiple injections of duplicate solutions. For example, duplicate liquid solutions, L1 and L2, are prepared for solid sample XYZ. The following perchlorate concentrations are obtained by IC analysis.

   L1: 16.5, 16.6, 16.7 ng mL^{-1}; average of 3 injections: 16.6 ng mL^{-1}
   L2: 16.8, 16.9, 17.0 ng mL^{-1}; average of 3 injections: 16.9 ng mL^{-1}

Average = 16.75 ng mL^{-1}; report 16.8 ng mL^{-1}.
Convert back to solid basis for XYZ: 168 ng g^{-1}.

Round down even numbers followed by 5: 16.85 → 16.8
Round up odd numbers followed by 5: 16.55 → 16.6
Maintain 3 significant figures on final answers, even if only 2 significant figures are appropriate.

4. An ***assured reporting level*** must be given for quantitation of perchlorate in *each* solid sample. The term *ARL* will refer only to solids (vide supra). Any dilution factors must be taken into account. If no dilutions are done, the best case scenario results:

$$\text{ARL} = \underbrace{\frac{5.00\ \text{ng}\ ClO_4^-}{1.00\ \text{mL liquid}}}_{\text{fortification}} \times \underbrace{\frac{40.00\ \text{mL liquid}}{4.00\ \text{g fertilizer}}}_{\text{mass:vol } (f/w) \text{ ratio (reciprocal, } w/f)} = \underbrace{\frac{50.0\ \text{ng}\ ClO_4^-}{\text{g fertilizer}}}_{\text{mass:mass ARL}} \qquad (18)$$

If the leachate/solution prepared from this sample would have been diluted 10% v/v prior to analysis, the solid ARL would necessarily be 10 times the original value, i.e., 500 ng perchlorate per gram of solid (500 ng g^{-1} = 0.500 μg g^{-1}). Any undiluted leachate/solution would have the same solid ARL unless baseline noise precludes integrating the peak of the spike. For this reason, baseline noise (i.e., *S/N*) must be evaluated for each IC run, and appropriate dilutions made.

6. Quality control requirements

Each laboratory must do the following:

1. Establish an MDL ≤ 3 ng mL^{-1} in deionized water (if using a 1000-μL loop) and provide supporting information.

2. Using the standards specified in Table 1, obtain smooth six-point calibration line(s) for concentration range(s) in deionized water and report least squares equation(s) for the line(s) with all $R^2 > 0.99$, standard errors in slope < 10% of its value, and *y*-intercepts statistically indistinct from zero. A nonlinear fit may be used if it can be justified empirically, but should be avoided as much as possible. Estimates of error in the fitting parameters must be made for regions of data fit to a particular function.

3. Recover 90–110% of standards prepared at 10, 50, and 150 ng mL^{-1} in deionized water using the calibration curve prepared in (2). Each day, recover 90–110% of a 50 ng mL^{-1} standard (i.e., 45-55 ng mL^{-1}) as part of a continuing check.

4. Recover 80–120% (i.e., 8.0-12 ng mL^{-1}) of a 10.0-ng mL^{-1} perchlorate spike in solutions classified as UNDETECTABLE.

5. Determine an ARL for each solid sample using (1) the 10.0-ng mL^{-1} spike in samples classified as UNDETECTABLE, or (2) the larger of the recovered concentration of a fortification at 20% of the measured concentration in samples found to contain perchlorate and the 90% confidence interval. If the 20%-spike is not satisfactorily recovered, a higher spike may be used instead. However, no spike used to compute a pARL or ARL may exceed 50% of the measured concentration. The pARL must be compared with the best case solid MDL and the 90% confidence interval found from triplicate injections of the unspiked solution before an ARL is specified and the concentration is reported as falling below some value.

6. Retain all data and results, including supporting information. This includes sufficient information that another practitioner might be able to repeat calculations and computations in case an error is discovered.

7. Prepare a brief narrative that includes information about the following: instrumentation and columns, filtration/centrifugation details, mechanical shaking, means of detection, and other details that would be needed to exactly reproduce the laboratory's procedure.

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Appendix 1

Suggested approaches for determining whether insoluble components retain perchlorate or otherwise inhibit its detection

Previously, it was stated that this method assumes that perchlorate is present in the form of a simple salt that completely dissolves and completely dissociates under the conditions used to leach or dissolve the sample. This may not always be a valid assumption. For example, when tetrabutylammonium perchlorate is used to fortify any matrix, recovery is always unsatisfactory (low or zero), regardless of the matrix. Not only is tetrabutylammonium perchlorate sparingly soluble in water, but the ion pairs are apparently extremely favorable relative to aquation of the individual ions. Consequently, there is little association of the perchlorate ion with the stationary phase and reduced response at the conductivity detector. Accordingly, the presence of hydrophobic cations (e.g., large quaternary ammonium ions) in the matrix may lead to false negative values. On the other hand, $N(CH_3)_4ClO_4$ and $N(CH_2CH_3)_4ClO_4$ do not exhibit this behavior.

The fortification procedure used in this method is not intended to demonstrate that perchlorate is unretained by insoluble components. Rather, it is intended to show that the soluble components of the matrix do not adversely affect the analysis. In order to demonstrate that an insoluble component does not retain perchlorate, it would be necessary to spike a perchlorate salt into either (1) the solid before leaching, or (2) the leachate while still in contact with the insoluble solid phase. This is not a straightforward matter because the exact identity and location of perchlorate in contaminated materials remain mysteries. Moreover, it is impossible to know whether the partitioning equilibrium has been reached during the leaching time if spiking is done by adding a soluble salt at the start of the leaching step.

Because all of the insoluble components are finely pulverized prior to leaching, it is not unreasonable to assume that the perchlorate-bearing components become exposed during the grinding process and therefore become available to be dissolved so long as they are soluble. Past experience with contaminated materials supports this assertion. Consequently, the exact means of fortifying the sample may be unimportant for those components that were in fact responsible for previously observed contamination. Nevertheless, it must be clearly understood that this method is incapable of measuring the concentration of perchlorate in insoluble substances capable of retaining it from—or incapable of releasing it to—the aqueous phase during leaching.

Specifically, clays, soils, and some minerals can present special problems in terms of their ability to retain perchlorate due to their ion-exchange and/or molecular sieve characteristics. While these substances are not necessarily used as fertilizers, we emphasize that this method is not necessarily applicable to their analysis. With some materials, ions may be adsorbed to charged surfaces (e.g., goethite), but with others, ions may become trapped within cages at the molecular level (e.g., zeolites). Soils rich in organic matter may also exhibit ion-exchange properties. These materials require careful tests to determine analyte recovery using fortified samples. Sometimes, other ions may be used to displace adsorbed species by treating the sample with dilute mineral acids (e.g., H_3PO_4, H_2SO_4, HNO_3) or their sodium salts. Any such treatment requires balancing the effects of the lowered pH and higher ionic strength against the need to release trapped analyte. Such treatments are not recommended here. As written, this method does not address analyzing substances that absorb or adsorb perchlorate. That notwithstanding, this appendix offers suggested approaches for evaluating the impacts of insoluble components. At various times, these have been employed by the authors.

1. *Spiking a soluble salt into the leachate solution.* An aliquot of a concentrated solution of $NaClO_4$ or NH_4ClO_4 is spiked into the leachate solution prior to the 8-15 hour shaking period. It is probably best to spike several leachates at different concentrations so as to determine if any loss is relative (e.g., always 30% low) or absolute (e.g., always 50 ppb low). An advantage is that this is one of the easiest and most straightforward approaches experimentally. A disadvantage is that partitioning of the perchlorate between the phases (if it occurs) may not have sufficient time to reach equilibrium. In other words, the penetration and adsorption may be too slow to be observable.

2. *Spiking a methanolic solution of a soluble perchlorate salt into the dry solid and allowing the methanol to evaporate.* Sodium, ammonium, and tetramethylammonium perchlorate are sufficiently soluble in methanol to allow them to be used as spiking solutions. An advantage to this approach is that the analyte may be delivered deeper into the particles. A disadvantage is that the perchlorate is only delivered to those particles in contact with the methanolic solution. Moreover, if the solution strikes the container wall, it is possible for none of the analyte to be delivered to the matrix.

3. *Suspending the sample in methanol, delivering an aliquot of methanolic perchlorate solution to the sample, and evaporating off the methanol.* The sample is supsended in a sufficient volume of methanol to cover it, and a methanolic solution of a soluble perchlorate salt is delivered. Using rotary evaporation under vacuum, the methanol is removed. Advantages to this approach are that the analyte may be delivered deeper into the particles, is more homogeneously distributed, and water is not introduced. Disadvantages are that it may be difficult to fully remove methanol residues and that the methanol may affect the surface properties of some materials.

4. *Spiking the solid sample with an aqueous solution of a soluble perchlorate salt and allowing the water to evaporate.* As with the methanolic solutions, this can be done by pipetting a small portion of concentrated perchlorate solution onto the solid or by first suspending the solid in the water. An advantage of adding and evaporating a large amount of water is that plenty of time is available for partitioning of the perchlorate between the phases. Disadvantages are that the soluble materials are no longer available for adsorption and distribution of the perchlorate salt, possibly reducing recovery. In addition, the differing solubilities and concentrations of the primary soluble ingredients will lead to heterogeneity as these compounds re-precipitate distinctively during evaporation of the water. Some components may be changed by hydration or hydrolysis.

5. *Spiking a solid perchlorate salt directly into the solid sample.* A major disadvantage to this approach is its implementation. In actual practice, it is not possible to weigh out and disperse 1 mg of potassium perchlorate into 100 g of potassium chloride. Instead, 1 g of potassium perchlorate should be blended into 99 g of potassium chloride. Next, 1 g of the 1% w/w $KClO_4$/KCl mixture is blended into 99 g of fresh KCl. Finally, 10 g of the 0.1% w/w $KClO_4$/KCl mixture is blended into 90 g of fresh KCl. Serial grindings in a kitchen blender with masses under 150 g tend to yield satisfactorily uniform mixtures. Additional disadvantages stem from the hygroscopic (or even deliquescent nature) of some materials, which result in caking and clumping, especially to the blender jar wall and blades. The principal advantage is that no solvents are introduced into the material, and the fortified sample may be retained essentially indefinitely. If this approach is used, it is most reasonable to match the choice

of cation in the perchlorate salt with the primary cation in the matrix, for example, sodium perchlorate in sodium nitrate, ammonium perchlorate in ammonium nitrate, potassium perchlorate in potassium chloride.

If concern over uniformity of distribution outweighs concern over accuracy, transition metal salts (e.g., nickelous perchlorate, cupric perchlorate, or cobaltous perchlorate) may be used instead of sodium or ammonium perchlorate. The distribution of the metal cation (as determined by atomic absorption spectrometry or another suitable technique) provides a check on the distribution of the perchlorate. ***Warning! Danger!*** **Transition metal perchlorates are available commecially only as hydrated forms due to the explosive nature of anhydrous transition metal perchlorate salts. Anyone unfamiliar with these properties should use the more innocuous sodium salt instead. Caution must be exercised even when the hydrated transition metal perchlorates are used because contact with hygroscopic compounds may result in partial or complete loss of hydrated water molecules from the perchlorate salt, thereby producing an unstable species.**

Whatever approach is used, there will always be some limitations on its applicability and utility. The analyst should be prepared to defend any tests for sorption in terms of both the objectives for analyzing a particular matrix and the likelihood of specific mechanisms that might interfere with the leaching procedure. Useful discussions of sorption phenomena can be found in Donald L. Sparks' *Environmental Soil Chemistry*, Academic Press, 1995, ISBN 0-12-656445-0, and Garrison Sposito's *The Chemistry of Soils*, Oxford University Press, 1989, ISBN 0-19-504615-3.

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Appendix 2

Recommended calibration standards for alternate size sample loops

Table A2-1. Recommended volumes of stock standard and post-dilution concentrations of calibration standards for 10-µL and 100-µL sample loops. For 20-µL or 200-µL sample loops, the respective working standard volumes used for 10-µL or 100-µL loops should be multiplied by 0.50 (divided by 2) since twice as much analyte is loaded during injection via the larger loop size.

loop	10 µL		100 µL	
use for first (low concentration) calibration curve (routine analyses):				
	volume of **100-µg mL^{-1}** working standard	concentration after dilution to 100 mL	volume of **10.0-µg mL^{-1}** working standard	concentration after dilution to 100 mL
a_0	none (blank)	0.00 ng mL^{-1}	none (blank)	0.00 ng mL^{-1}
b	30 µL	30.00 ng mL^{-1}	30 µL	3.0 ng mL^{-1}
c	50 µL	50.00 ng mL^{-1}	50 µL	5.0 ng mL^{-1}
d	100 µL	100.0 ng mL^{-1}	100 µL	10.0 ng mL^{-1}
e	200 µL	200.0 ng mL^{-1}	200 µL	20.0 ng mL^{-1}
f	500 µL	500.0 ng mL^{-1}	500 µL	50.0 ng mL^{-1}
g	1000 µL	1000 ng mL^{-1}	1000 µL	100 ng mL^{-1}
h	2000 µL	2000 ng mL^{-1}	2000 µL	200 ng mL^{-1}
use for second (high concentration) calibration curve (for materials that contain high concentrations of perchlorate, i.e., > 200 µg g^{-1}:				
	volume of **1000-µg mL^{-1}** working standard	concentration after dilution to 100 mL	volume of **100-µg mL^{-1}** working standard	concentration after dilution to 100 mL
i	0.500 mL	5.00 µg mL^{-1}	0.500 mL	0.500 µg mL^{-1}
j	1.00 mL	10.0 µg mL^{-1}	1.00 mL	1.00 µg mL^{-1}
k	2.00 mL	20.0 µg mL^{-1}	2.00 mL	2.00 µg mL^{-1}
l	5.00 mL	50.0 µg mL^{-1}	5.00 mL	5.00 µg mL^{-1}
m	10.00 mL	100 µg mL^{-1}	10.00 mL	10.0 µg mL^{-1}

□ □ □ □