METHOD 6860

PERCHLORATE IN WATER, SOILS AND SOLID WASTES USING ION CHROMATOGRAPHY/ELECTROSPRAY IONIZATION/MASS SPECTROMETRY (IC/ESI/MS OR IC/ESI/MS/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method uses ion chromatography (IC) coupled with electrospray ionization (ESI) mass spectrometry (MS) or tandem mass spectrometry (MS/MS) for the determination of perchlorate in surface water, groundwater, salt water and soil (See Refs. 1-3). The following analyte has been determined by this method:

Analyte	CAS No.[a]
ClO_4^-	14797-73-0

[a]Chemical Abstract Service Registry Number

1.2 This method has not been fully validated for complex matrices, such as wastewater treatment sludges, using the recommended extraction procedure. Additional studies are necessary to confirm whether alternate extraction approaches are able to provide more efficient perchlorate recoveries.

1.3 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3600 and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and properly trained in the use of IC/MS or IC/MS/MS instrumentation and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Perchlorate is separated, detected and quantified using one of three instrument system options as described in Secs. 2.1.1-2.1.3.

2.1.1 IC/MS – An appropriate volume of sample or sample extract is introduced into an IC/MS instrument. Perchlorate (ClO_4^-) is separated by IC from the sample matrix. The IC effluent is ionized in the electrospray source and transferred to the mass spectrometer where the perchlorate is detected and quantified using mass-to-charge (*m/z*) ratios 99 (ClO_4^-), 101 ($^{37}ClO_4^-$) and 107 ($Cl^{18}O_4^-$). Quantitation is performed using *m/z* 99 and internal standard calibration. Isotopically-labeled perchlorate ($Cl^{18}O_4^-$), serves as an internal recovery and calibration standard (IRCS) to correct for perchlorate loss from the sample preparation procedure as well as during IC/MS analysis. The 99/101 isotopic ratio reflects the isotopic ratio of naturally occurring $^{35}Cl/^{37}Cl$ and is used for additional confirmation of perchlorate identification.

2.1.2 IC/MS/MS – Following IC separation and ionization, the perchlorate is isolated in the first mass spectrometer and transferred to a collision cell for fragmentation. The resulting fragments 83 (ClO_3^-), 85 ($^{37}ClO_3^-$) and 89 ($Cl^{18}O_3^-$) are introduced into the second mass spectrometer where they are detected and quantified.

2.1.3 IC/MS with fragmentation – This analysis option is similar to Sec. 2.1.1, except that the separated perchlorate is partially fragmented and detected by MS using *m/z* ratios 83 (ClO_3^-), 85 ($^{37}ClO_3^-$) and 89 ($Cl^{18}O_3^-$).

2.2 Matrix diversion may be used to direct early-eluting, matrix components to waste prior to the introduction of perchlorate into the mass spectrometer in order to minimize the accumulation of salt deposits in the electrospray source and mass spectrometer (Sec. 6.10.1.2).

2.3 A conductivity suppressor (Sec. 6.10.1.4) may be used to replace cations, such as potassium ion, with hydronium ion in the post-column eluent stream in order to minimize salt accumulation in the electrospray source and mass spectrometer. A conductivity detector (Sec. 6.10.1.5) may also be used in order to monitor the conductivity of the eluent stream entering the mass spectrometer.

2.4 Just prior to introduction into the mass spectrometer, the addition of solvent may be necessary to ensure adequate sample ionization in the electrospray source (Sec. 6.10.1.6)

2.5 Solids are first extracted prior to analysis using reagent water (Sec. 11.2). The filtered extracts are then analyzed by IC/MS or IC/MS/MS as described in Sec. 11.3.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware.

4.2 All reagent solutions and samples (including QC samples) should be filtered through a 0.45-µm nominal pore size or smaller (e.g., 0.2-µm) membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Filters specifically designed for IC or HPLC applications should be used.

4.3 Hydrogen sulfate ion ($H^{34}SO_4^-$), *m/z* 99, formed from a minor sulfur isotope, is commonly present in samples. $H^{34}SO_4^-$ elutes before perchlorate but at high concentrations can tail into the retention time of the perchlorate peak and elevate its baseline at *m/z* 99. Quantitation of perchlorate based on *m/z* 83, 85 and 89 avoids this potential interference from $H^{34}SO_4^-$.

4.4. Retention time shifts may occur as competing anions in the sample take up active sites on the stationary phase. In such samples, perchlorate will elute earlier than in the calibration standards. The $Cl^{18}O_4^-$ peak from the IRCS will also shift, and therefore is used to confirm the identification of the native perchlorate peak.

4.5 Potential problems may arise when analyzing samples containing high levels of total dissolved solids (TDS) (i.e. salts of chloride, sulfate, carbonate/bicarbonate, etc.). Ionization suppression can occur when high levels of dissolved salts are introduced into the mass spectrometer, resulting in a reduction in the perchlorate analyte peak. The degree of ionization suppression will depend on the type and concentration of interfering ions present, and whether or not they overlap with perchlorate when eluted. The $Cl^{18}O_4^-$ peak from the IRCS will similarly be affected and the internal standard calibration will correct for this effect. However, significant ionization suppression can result in failure to meet the ± 50% IRCS response verification acceptance criterion (Sec. 9.9). Additionally, ionization suppression can result in the complete loss of the analyte signal, particularly when the perchlorate levels of the sample are at or near the lower limit of quantitation (LLOQ) (Sec. 9.10). Sample dilution, the use of a smaller injection volume or sample cleanup can be used to help minimize this effect.

4.5.1 A conductivity limit study (Sec. 9.4.1) may be performed in order to determine the approximate level of TDS that can be tolerated by a particular IC/MS system before deleterious effects to chromatographic performance and quantification occur.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Protective clothing should be worn when working with corrosive or potentially corrosive materials or samples.

5.4 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation.

5.5 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Volumetric flasks, 100-mL and other sizes as needed.

6.2 Automatic precision pipetters and disposable tips – 10-10,000 µL capacity.

6.3 Disposable autosampler vials.

6.4 Disposable plastic centrifuge tubes – 15- and 50-mL.

6.5 Disposable plastic micro-beakers.

6.6 Sample bottles – polyethylene or glass of sufficient volume to allow replicate analyses.

6.7 Disposable 0.45-µm or 0.2-µm surfactant-free, PTFE-membrane syringe filters.

6.8 Plastic 5-mL luer-lock syringes or equivalent.

6.9 C_{18} (2000 mg) chromatography columns or equivalent for extract solution cleanup.

6.10 Ion chromatograph/mass spectrometer – An analytical system combining an ion chromatograph for separation of the sample components, electrospray ionization source and mass spectrometer for fragmentation and detection of sample components. Single stage MS or

MS/MS instruments may be used, but either MS/MS or MS with fragmentation is preferred due to superior selectivity. The respective instrument components are provided below. An example of an IC/MS setup is provided in Figure 1. Example IC/MS and IC/MS/MS conditions are provided in Tables 1-3.

6.10.1 Ion chromatograph – The instrument should contain a programmable solvent delivery system and all necessary accessories including injection loop, analytical columns, chromatography pump, purging gases, etc. A conductivity suppressor is used to remove mobile phase ions before introduction into the mass spectrometer.

6.10.1.1 Analytical column – Any anion exchange column capable of providing adequate separation of perchlorate from common anions such as sulfate, carbonate and chloride may be used. Several different analytical column/mobile phase conditions have been evaluated and found to be suitable for use in perchlorate quantitation. Examples of suitable columns and corresponding mobile phases are presented below.

Column	Suitable Corresponding Mobile Phase
Dionex IonPac® AS20 column, 2.0 mm x 50 mm	45 mM KOH
Dionex IonPac® AG16 column, 2.0 mm x 50 mm	2.5 mM NH_4OH
Dionex IonPac® AS16 column, 2.0 mm x 250 mm	35, 45 or 55 mM KOH
Metrohm Metrosep ASUPP5-150 column, 4.6 x 100 mm	12.8 mM Na_2CO_3, 4 mM $NaHCO_3$, 8.6 mM CH_3CN

NOTE: **These analytical columns and mobile phases are NOT listed in order of preference.**

NOTE: The AS20 column and 45mM KOH mobile phase and the AS16 column and 55 mM KOH mobile phase combinations were evaluated and found to provide acceptable results using an IC/MS system, with conductivity suppression and early matrix diversion, in which acetonitrile, 90% and 50% concentration, respectively, was added post-column to aid in matrix ionization. The AG16 column and 2.5 mM NH_4OH mobile phase combination was evaluated and found to provide acceptable performance using an IC/MS/MS system, without conductivity suppression, matrix diversion or post-column solvent addition. The AS16 column and 35 mM KOH mobile phase combination was evaluated and found to provide acceptable performance using an IC/MS/MS system, with conductivity suppression and early matrix diversion, in which 0.01 M $NaCH_3CO_2$ was added post-column to aid in matrix ionization. The AS16 column and 45 mM KOH mobile phase combination was evaluated and found to provide acceptable results using an IC/MS/MS system, with conductivity

suppression and early matrix diversion, in which 90% acetonitrile was added post-column to aid in matrix ionization. The Metrohm column and corresponding mobile phase combination was evaluated and found to provide acceptable results using an IC/MS system with fragmentation and conductivity suppression.

NOTE: Other chromatographic conditions may be used, provided that the data quality meets the project-specific goals.

6.10.1.2 Matrix diversion valve – A Rheodyne® or equivalent 6-port valve may be used if necessary to divert pre-eluting common anions to waste, prior to the elution of perchlorate from the analytical column. The use of matrix diversion will help to reduce buildup of salt deposits in the electrospray source and mass spectrometer.

6.10.1.3 Guard column – An optional low-capacity anion exchange chromatography column may be used before the analytical column to remove sample impurities and prevent them from passing onto the analytical column. The column is typically packed with the same material as the analytical column.

6.10.1.4 Conductivity suppressor – An electrolytic suppressor operated with an external source of reagent water. The conductivity suppressor removes potassium ions from the eluent stream prior to entry into the MS. A chemical conductivity suppressor is acceptable, although sulfuric acid should not be used as the chemical regenerant due to mass spectrometric interferences caused by HSO_4^- at *m/z* 99. Examples of conductivity suppressors include the Dionex Anion Self Regenerating Suppressor ASRS® ULTRA II, Metrohm Advanced IC Liquid Handling Suppressor Unit or equivalent.

6.10.1.5 Conductivity detector – A flow-through detector with an internal volume that does not introduce analyte band broadening. Though not necessary, the conductivity detector is useful in measuring the output and effectiveness of the conductivity suppressor. Examples of conductivity detectors include the Dionex CD25A Conductivity Detector, Metrohm Advanced IC Detector or equivalent.

6.10.1.6 Auxiliary pump – A single-piston isocratic pump used for introducing organic additives into the eluent stream just prior to introduction into the mass spectrometer for improved electrospray efficiency. An example of such a pump is the Dionex AXP-MS or equivalent.

6.10.1.7 Static mixing tee – A mixing tee used for the introduction of organic additives from the auxiliary pump into the eluent stream. An example is the Upchurch Scientific Micro Static Mixing Tee or equivalent.

6.10.1.8 Chromatography oven – An optional temperature-controlled chromatography oven is recommended for maintaining the temperature of the IC components and reducing analytical variability. The chromatography oven houses the 6-port injection valve, guard and analytical columns, conductivity suppressor and detector and maintains the temperature at 30 °C. Examples include the Dionex LC30 Chromatography Oven, Metrohm Advanced IC Separation Center or equivalent.

6.10.2 Electrospray ionization (ESI) source – The ESI source generates gas phase ions of perchlorate from the liquid phase. An example of an ESI setup is provided in Table 1.

6.10.3 Mass spectrometer – A single quadrupole mass spectrometer (MS), triple quadrupole mass spectrometer (MS/MS) or other mass analyzer. Refer to the manufacturer's instructions for instrument tuning, conditions and verification. Tuning parameters are available from the instrument manufacturer, along with mass tuning solutions and instructions on how to optimize the mass spectrometer. See Tables 1-3 for examples of IC/MS and IC/MS/MS instrument parameters and settings.

6.11 Data system capable of performing analyte signal acquisition, peak integration, instrument calibration and analyte quantification.

6.12 Analytical balance capable of ± 0.0001 g accuracy.

6.13 Sonicator

6.14 Vortexer

6.15 Centrifuge – Adequate for clarifying soil extracts prior to filtration.

6.16 Conductivity meter capable of measuring specific conductance over a range of 1-10,000 µS/cm.

6.17 Conductivity cell appropriate for performing measurements over the range of 1-10,000 µS/cm.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade or HPLC-grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water - All references to water in the method refer to organic-free reagent water unless otherwise specified. Refer to Chapter One for a definition of organic-free reagent water.

7.3 Acetonitrile, CH_3CN, HPLC-Grade

7.4 Ammonium hydroxide, NH_4OH, HPLC-grade

7.5 Potassium hydroxide, KOH

7.6 Ammonium acetate, $CH_3CO_2NH_4$

7.7 Sodium carbonate, Na_2CO_3.

7.8 Sodium bicarbonate, $NaHCO_3$.

7.9 100 mM NH_4OH – Prepare by diluting 6.8 mL of concentrated NH_4OH to 1 L using reagent water.

7.10 2.5 mM NH_4OH mobile phase – Prepare by diluting 25 mL of 100 mM NH_4OH to 1 L using reagent water.

7.11 35 mM KOH mobile phase – Prepare by dissolving 1.964 g KOH in approximately 700 mL reagent water. Dilute to a final volume of 1 L using reagent water.

7.12 45 mM KOH mobile phase – Prepare by dissolving 2.525 g KOH in approximately 700 mL reagent water. Dilute to a final volume of 1 L using reagent water.

7.13 55 mM KOH mobile phase – Prepare by dissolving 3.086 g KOH in approximately 700 mL reagent water. Dilute to a final volume of 1 L using reagent water.

7.14 12.8 mM Na_2CO_3, 4 mM $NaHCO_3$, 8.6 M CH_3CN mobile phase – Prepare by dissolving 1.357 g Na_2CO_3 and 0.336 g $NaHCO_3$ in 550 mL reagent water. Add 450 mL CH_3CN and mix well.

7.15 90% CH_3CN post-column eluent additive – Prepare by combining 900 mL CH_3CN with 100 mL reagent water. This solution may be used to improve electrospray efficiency.

7.16 50% CH_3CN post-column eluent additive – Prepare by combining 500 mL CH_3CN with 500 mL reagent water. This solution may be used to improve electrospray efficiency.

7.17 0.01 M $CH_3CO_2NH_4$ post-column eluent additive – Prepare by dissolving 0.771 g $CH_3CO_2NH_4$ in approximately 700 mL reagent water. Dilute to a final volume of 1 L using reagent water. This solution may be used to improve electrospray efficiency.

7.18 Sodium chloride, NaCl.

7.19 Sodium sulfate, Na_2SO_4.

7.20 Sodium perchlorate, anhydrous, $NaClO_4$,

7.21 Sodium perchlorate[$^{18}O_4$], anhydrous, $NaCl^{18}O_4$,≥ 90% enrichment, Isotec Inc. or equivalent.

7.22 Stock standard solution (1000 mg/L ClO_4^-) – This solution can be purchased commercially as a certified standard or prepared from the sodium salt as described below (Sec. 7.22.1). Stock standards may be stored at room temperature for a period of up to 12 months. Expiration dates should be clearly specified on the label.

7.22.1 Dissolve 0.123 g of anhydrous sodium perchlorate in reagent water and dilute to 100 mL in a volumetric flask.

7.23 Intermediate standard solution (10 mg/L ClO_4^-) – Dilute 1000 µL of stock standard solution (Sec. 7.22) to 100 mL with reagent water. Intermediate standards may be stored at room temperature for a period of up to 12 months. Expiration dates should be clearly specified on the label.

7.24 Calibration standards – Prepare by using various dilutions of the intermediate standard solution (Sec. 7.23). Spike each calibration each standard using the exact same volume of IRCS spiking solution (Sec. 7.26), such that the final IRCS concentration is exactly the same (i.e., approximately 5.0 µg/L $Cl^{18}O_4^-$) for each calibration standard. A minimum of six calibration standards is recommended as well as a blank standard. A sufficient number of standards should be analyzed to allow an accurate calibration curve to be established. Recommended standard concentrations for establishing a calibration curve are: 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 µg/L ClO_4^-. This range may be extended provided that the linear response can be adequately verified through satisfaction of all calibration criteria and quality control requirements. The low standard must be equivalent to or below the lowest result to be reported. All reported results must be within the calibration range.

7.25 IRCS stock solution (approximately 10.0 mg/L $Cl^{18}O_4^-$) – Dissolve 1.21 mg of ($^{18}O_4$)sodium perchlorate in reagent water and dilute to 100 mL in a volumetric flask. Stock standards may be stored at room temperature for a period of up to 12 months. Expiration dates should be clearly specified on the label.

7.26 IRCS spiking solution (approximately 1000 µg/L $Cl^{18}O^{4-}$) – Dilute 1.0 mL of the IRCS stock solution (Sec. 7.25) to 10 mL with reagent water. Store at ≤ 6 °C when not in use. The solution is also available commercially.

NOTE: Each standard and sample is spiked with 50 µL of IRCS spiking solution per 10 mL of sample or standard to obtain a final IRCS concentration of approximately 5 µg/L $Cl^{18}O_4^-$. An alternate IRCS spiking solution volume or final IRCS concentration may be used, provided that it falls within the same concentration range as the external calibration curve. **The volume of the IRCS spiking solution added to the sample or sample extracts should be such that minimal dilution of the extract occurs.** Refer to Method 8000 for further internal standard calibration procedures.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect water samples in clean, 125-mL polyethylene bottles.

8.2 Whenever possible, water samples should be sterilely filtered in the field at the time of collection using 0.2-µm PTFE membrane filtration in order to remove potentially perchlorate-degrading microbes.

8.3 For solids, collect samples in 4-oz amber glass bottles.

8.4 Extract solids within 28 days of sample acquisition.

8.5 Analyze water samples and extracts of solid samples within 28 days of collection or preparation, respectively.

8.6 Store all samples and extracts with headspace to reduce potential anaerobic biodegradation.

NOTE: Care should be taken to avoid temperature extremes during shipment and storage.

8.7 Also, see the introductory material to Chapter Three, "Inorganic Analytes".

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on QA and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal QA program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000 or 3600.

9.3 Quality control procedures necessary to evaluate the IC/MS system operation are found in Method 8000 and include calibration verification and chromatographic analysis of samples.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish an initial demonstration of proficiency.

9.4.1 For laboratories that analyze samples containing high levels of TDS (i.e., > 1000 mg/L), a conductivity limit study may be performed for each individual IC/MS system in order to determine the approximate sample matrix conductivity that may be tolerated before the loss of column capacity brings about a significant reduction in analyte signal. The specific conductivity of each aqueous sample or extract may be measured and recorded and compared to the conductivity limit (CL) in order to determine the approximate amount of sample dilution that may be necessary to produce acceptable perchlorate recovery.

9.4.1.1 Using the sodium salts of chloride, sulfate and carbonate, prepare a 250-mL dissolved salt solution (DSS) fortified with 0.5 µg/L perchlorate and containing 500 mg/L each of the anions chloride, sulfate and carbonate (i.e. 0.206 g NaCl, 0.277 g Na_2SO_4, 0.221 g Na_2CO_3, respectively, in 250 mL reagent water).

9.4.1.2 Measure the specific conductivity of this solution. It should be approximately 10,000 µS/cm.

9.4.1.3 Prepare a sample of the fortified DSS for analysis as described in Sec. 11.1. Analyze the prepared sample as described in Sec. 11.3. The perchlorate recovery should be within 80-120% of the theoretical value and the IRCS recovery within ± 50% of that of the ICV or CCV (Sec. 9.9). If the recovery meets these criteria, then perchlorate may be accurately

analyzed in samples having a conductivity of approximately 10,000 µS/cm. Thus the CL, the highest matrix conductivity level from which perchlorate can be effectively recovered, is approximately 10,000 µS/cm. Some IC/MS systems may be capable of accurately analyzing perchlorate in matrices having conductivities as high as 20,000 µS/cm. If acceptable perchlorate and IRCS recoveries can be obtained in a 10,000 µS/cm DSS, then a higher conductivity DSS may be prepared in order to find the true CL of the analytical system.

9.4.1.4 If the perchlorate and IRCS recoveries do not meet the acceptance criteria, then decrease the anion concentrations in the DSS, while maintaining the perchlorate level at 0.5 µg/L. Measure the specific conductivity and perchlorate concentration of this new solution. If the perchlorate and IRCS recoveries meet the acceptance criteria, then the measured conductivity of this solution is the conductivity limit. If not, continue to incrementally decrease the anion concentrations until the perchlorate and IRCS recoveries meet the acceptance criteria in order to establish the CL for the IC/MS system.

9.5 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed at or in close proximity to the expected retention time of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis.

9.6 Initial calibration verification (ICV) – Immediately after the calibration standards have been analyzed, the accuracy of the calibration must be verified by the analysis of an ICV standard. The ICV is prepared at a concentration level within the calibration range of the method and using a second source standard (prepared using standards different from the calibration standards) spiked into reagent water. The control limit for the ICV is ±15% of the true value. When the ICV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.7 Continuing calibration verification (CCV) – Once the calibration curve has been established, the continuing accuracy must be verified by analysis of a CCV prior to conducting any field sample analysis, after every tenth field sample, and at the end of the analysis sequence. The CCV is prepared from the intermediate standard solution (Sec. 7.23) at a concentration level within the calibration range of the method. CCV concentrations alternating between the low- and mid-range calibration standard concentrations are recommended. The control limit for the low-range CCV is ± 50% and for the mid-range CCV is ± 15% of the true value. When the CCV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified. Samples that are not bracketed by acceptable CCV runs must be reanalyzed.

9.8 Sample quality control for preparation and analysis.

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of IRCS to each field sample and QC sample. Any method blanks, matrix spike samples, and replicate samples must be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch.

9.8.1 A method blank (MB) is prepared from reagent water and treated exactly as a field sample, including exposure to all glassware, equipment, solvents, filtration, and reagents that are used with field samples. Analysis of a MB is used to assess contamination from the laboratory environment, equipment, and/or reagents. A perchlorate concentration in the MB exceeding the lower limit of quantitation (LLOQ) (Sec. 9.10) indicates that contamination is present. The source of the contamination should be determined and corrected prior to performing any sample analysis. Any sample included in an analysis batch that has an unacceptable MB should be reanalyzed in a subsequent batch after the contamination problem is resolved.

9.8.2 At least one matrix spike (MS) sample should be analyzed within each analysis batch for determining method bias and/or sample matrix effects.

9.8.2.1 The MS %R is calculated as follows:

$$\%R = \frac{(MSSR - SR)}{SA} \times 100$$

Where:
MSSR = MS sample result
SR = Sample result
SA = Spike added

When the sample concentration is less than the LLOQ, use SR = 0 for purposes of calculating %R.

9.8.2.2 The method control limits for %R are 80-120% for water matrices and 70-130% for solid matrices. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the MS %R criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem. If %R is outside the control limits and all other QC data is within limits, a matrix effect is suspected. The associated data should be flagged according to project specifications or noted in the comments section of the report.

9.8.3 A duplicate or matrix spike duplicate (MSD) should be analyzed within every analytical batch in order to establish the precision of the method.

9.8.3.1 Calculate the relative percent difference (RPD) between the sample and duplicate result as follows.

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where:

RPD	=	Relative percent difference
S	=	Sample or MS sample result
D	=	Duplicate or MSD result

9.8.3.2 The method control limit for RPD is 15% for all sample concentrations that are near or above the mid-range of the calibration curve. The method control limit for RPD is 50% for sample concentrations that are near the low-range of the calibration curve. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the duplicate RPD criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem.

9.8.4 An LCS is prepared as described in Chapter One and treated exactly as a field sample, including exposure to all glassware, equipment, solvents, filtration, and reagents that are used with field samples. Data produced are used to assess efficiency of the instrument performance and preparation procedures. The %R of the LCS should be within 80–120%. Alternate limits, may be used for specific projects. If the LCS %R is outside the specified control limits, corrective action should be undertaken to resolve the problem and the preparation batch in question should be re-prepared and reanalyzed.

NOTE: A high TDS QC standard may also be analyzed to further demonstrate sufficient analyte separation and lack of excessive ionization suppression. The standard should be prepared at the mid-range concentration level and contain each of the anions, chloride, carbonate and sulfate, at an equivalent concentration level, such that the final specific conducitivity of the solution is approximately equivalent to the samples being analyzed. The %R of the high TDS QC standard should be within 80–120%.

9.9 IRCS response verification – The IRCS area counts for each sample and QC standard must be monitored throughout the analysis and compared with the average of the IRCS area counts of the calibration standards, if the calibration is performed on the same day as the analysis, or otherwise, using either the ICV or the first CCV of the analytical batch, whichever is appropriate, if using a calibration curve established during a previous analytical run. If the IRCS area counts exceed ± 50% that of the ICV or CCV, a second sample aliquot should be analyzed. If the IRCS area count of second sample aliquot still exceeds the criterion, then check the area count of the most recent CCV. If the criterion is met in the most recent CCV and not the sample, then the sample result should be considered to be suspect. The associated data should be flagged according to project specifications or noted in the comments section of the report. If the IRCS area count criterion is not met in either the sample or the most recent CCV, then corrective action, such as instrument maintenance, should be undertaken to resolve the problem and the entire preparation batch in question should be re-prepared and reanalyzed.

9.10 The laboratory should establish the LLOQ as the lowest point of quantitation or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project-specific requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LLOQ recovery must be within 50% of the true value to verify the data reporting limit. The low-range CCV standard (Sec. 9.7) may also serve as the LLOQ verification for confirming method sensitivity.

9.11 It is recommended that the laboratory adopt additional QA practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

10.1 ESI/MS system – Refer to the manufacturer's instructions for instrument tuning and conditions.

10.2 IC/MS system

10.2.1 Prepare the calibration standards as outlined in Sec. 7.24.

10.2.2 Inject an equivalent volume of each calibration standard into the IC. Use an injection volume that is optimal for the specific column and instrument system. An injection volume of 100 µL is recommended.

10.2.3 Establish the initial calibration curve by plotting the area ratio response for each standard against the concentration using the internal standard calibration method. For a first-order linear regression calibration model (i.e., $y = ax + b$ function), the acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher. If a second-order or third-order, polynomial linear regression model is used (i.e., $y = ax^2 + bx + c$ or $y = ax^3 + bx^2 + cx + d$), the weighted coefficient of determination (COD) should be 0.995 or higher. Refer to Method 8000 for guidance on internal standard calibration.

10.2.4 Verify the accuracy of the initial calibration curve as described in Sec. 9.6 before proceeding to analyze samples.

NOTE: A retention time window study is not necessary when using internal standard calibration (See Method 8000 for further details). However, it is always a good practice and can be a useful diagnostic tool to monitor analyte and IRCS retention times and peak area counts in all samples and QC standards, including blanks, to effectively observe drifting method performance, poor injection execution, unintended changes in eluent strength or flow rates, column overloading, and high ionic matrix effects or fouling, so as to anticipate the need for system inspection and/or maintenance.

11.0 PROCEDURE

11.1 Water sample preparation

11.1.1 Dispense 10.0 mL of sample or standard into a 15-mL disposable centrifuge tube.

11.1.2 Add 50 µL of IRCS spiking solution (Sec. 7.26) to the sample tube, cap and shake until mixed well.

NOTE: The final concentration of IRCS in the sample extract must be exactly the same as that in the calibration standards (Sec. 7.24). Proportionally smaller volumes of sample and IRCS may be used to reduce laboratory waste or when limited sample volume is supplied to the laboratory.

11.1.3 Filter the sample solution using a plastic syringe fitted with an 0.45-µm or 0.2-µm PTFE membrane filter. Dispense the sample into an autosampler vial for analysis.

NOTE: Filtration may be omitted for calibration standards and for samples that have been previously filtered in the field (Sec. 8.2).

NOTE: If a CL has been determined (Sec. 9.4.1), a separate aliquot of sample may be used to determine its matrix conductivity for comparison against the CL in order to determine the need for sample dilution prior to analysis.

11.1.4 Proceed to Sec. 11.3.

11.2 Solid sample preparation

11.2.1 Weigh 1 g of solid sample, recording the weight to 0.01 g. Transfer the sample to a 15-mL centrifuge tube.

11.2.2 Add a sufficient quantity of reagent water to the 15-mL centrifuge tube containing the sample to bring the total volume to 10 mL.

11.2.3 Add 50 µL of IRCS spiking solution (Sec. 7.26) to the sample tube.

NOTE: The final concentration of IRCS in the sample must be exactly the same as that in the calibration standards (Sec. 7.24).

11.2.4 Vortex the mixture, followed by sonication for a minimum of 10 minutes, followed by additional vortexing.

11.2.5 Centrifuge the sample for 5 min, if necessary, to separate the solids from the extract solution. Use centrifuge settings that provide a visibly adequate separation and yield a clear extract solution.

11.2.6 Filter the supernatant extract solution using a plastic syringe fitted with an 0.45-µm or 0.2-µm PTFE membrane filter. Dispense the extract sample into an autosampler vial for analysis.

11.2.7 If large quantities of organic contaminants are not believed to be present in the solid sample extract (i.e., supernatant extract is relatively clear and not highly colored), proceed to Sec. 11.3. If necessary, however, a cleanup step using a C_{18} column may be performed to remove organic contaminants from the supernatant extract solution. The C_{18} column cleanup step is described in Secs. 11.2.7.1-11.2.7.5. However, other cleanup cartridges or procedures may be used as long as the data quality meets the project-specific goals. Alternate cleanup columns and media include the Supelclean™ ENVI Carb-II column from Supelco or graphitized carbon by United Chemical Technologies, Inc. Follow the manufacturer's instructions for use.

11.2.7.1 Activate the C_{18} cartridge column (Sec. 6.9) by pushing approximately 5 mL of methanol through the column, followed by 5 mL of reagent water. A flow rate of approximately 0.5 mL/min is recommended. Care should be taken not to let the column become dry.

11.2.7.2 Using gentle pressure, push approximately 6 mL of the supernatant extract solution through the activated column.

11.2.7.3 Discard the first 2 mL of eluted sample extract.

NOTE: The initially eluted sample extract is discarded because it is diluted by the solution remaining in the column following the activation process.

11.2.7.4 Collect the remaining eluted sample extract (approximately 4 mL) in a clean container.

NOTE: Quantitative recovery of the eluted extract sample is not necessary because there is no dilution or concentration of the sample.

11.2.7.5 Filter the eluted extract using a plastic syringe fitted with a 0.45-µm or 0.2-µm PTFE membrane filter. Dispense the extract sample into an autosampler vial for analysis.

NOTE: If a CL has been determined (Sec. 9.4.1), a separate aliquot of sample may be used to measure its matrix conductivity for comparison against the CL in order to determine the need for sample dilution or cleanup prior to analysis. A proportionally larger volume extract solution may need to be prepared in order to provide enough sample quantity for such a conductivity measurement.

NOTE: Evaluation studies have demonstrated that the use of alternate extraction methods may achieve improved perchlorate recoveries in matrices such as wastewater treatment sludges (See Sec. 13.2). Based on knowledge of the matrix of interest, the method user may consider an alternate extraction procedure to the primary method (Sec. 11.2) for extracting perchlorate from solids. The method user should ensure that the data quality obtained using any alternate extraction procedure meets the project-specific goals.

11.2.7.6 Proceed to Sec. 11.3.

11.3 Water and extract sample analysis

11.3.1 Set up the IC/MS instrumentation. Examples of suitable settings for IC and MS instruments are provided in Tables 1-3.

11.3.2 With mobile phase running through the system, establish a stable baseline. This should take approximately 15-30 min.

11.3.3 Establish a valid initial calibration as outlined in Sec. 10.2. Examples of chromatograms are provided in Figures 2 and 3.

11.3.4 Inject a suitable volume of sample into the IC instrument. Use an injection volume that is optimal for the specific analytical column and instrument system. An injection volume of 100 µL is recommended. The volume of sample injected must be consistent with that used for calibration (Sec. 10.2.2). Record the resulting perchlorate peak size at *m/z* 99 (or 83), 101 (or 85) and 107 (or 89) in area units as well as the peak retention times.

11.3.5 If the peak area response exceeds the calibration range of the system, dilute the sample and reanalyze.

11.3.6 If the IRCS peak area response exceeds the ± 50% criterion, reanalyze a fresh aliquot of the sample (See Sec. 9.9).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify and confirm the presence of perchlorate in all analytical and QC sample chromatograms:

12.1.1 Compare the retention times of the ClO_4^- *m/z* 99 peak (or ClO_3^- *m/z* 83 peak) and the IRCS $Cl^{18}O_4^-$ *m/z* 107 peak (or $Cl^{18}O_3^-$ *m/z* 89 peak). The retention times should not vary by more than 0.2 min.

12.1.2 Evaluate the relative abundances of the ClO_4^- *m/z* 99 (or ClO_3^- *m/z* 83) and $^{37}ClO_4^-$ *m/z* 101 (or $^{37}ClO_3^-$ *m/z* 85) ions in the chromatogram. To confirm the presence of perchlorate, the 99/101 (or 83/85) peak area count ratio should be within ± 30% of the average peak area count ratio of the mid-range calibration standard, if the calibration is performed on the same day as the analysis, or otherwise, using the average peak area count ratios of all of the CCV runs of the analytical batch, whichever is appropriate.

NOTE: All samples and QC standards should meet the ± 30% 83/85 (or 99/101) peak area counts ratio criterion, including those that are at or near the LLOQ. The failure of any low-range concentration samples or QC standards to meet this criterion is an indication that the method is not sensitive enough to measure accurately at the established LLOQ. In such cases, method sensitivity studies should be undertaken to establish a higher, more representative LLOQ.

12.2 Calculate the perchlorate concentration for each sample and QC standard using the internal standard calculation described in Method 8000. Use ClO_4^- *m/z* 99 (or ClO_3^- *m/z* 83) and $Cl^{18}O_4^-$ *m/z* 107 (or $Cl^{18}O_3^-$ *m/z* 89) from the IRCS for quantitation. Report the concentration of each of the sample matrices as follows:

12.2.1 Water samples

Final result (µg/L ClO_4^-) = (C)(D)

Where:
C = Concentration from calibration curve (µg/L ClO_4^-)
D = Dilution factor (if needed)

12.2.2 Solid samples

$$\text{Final result } (\mu g/g\ ClO_4^-) = \frac{(C)(V)(D)}{M}$$

Where:
C = Concentration in extract from calibration curve (µg/L ClO_4^-)
V = Final volume of sample extraction solution (L)
D = Dilution factor (if needed)
M = Mass of initial sample extracted (g)

13.0 METHOD PERFORMANCE

Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.1 The instrumentation and chromatographic options described in this method have been evaluated in a round robin study for a variety of environmental matrices. The results of the interlaboratory validation testing are summarized in Table 4. These data are provided for guidance purposes only.

13.2 Comparative results obtained for soils and wastewater treatment sludges using the primary extraction method (Sec. 11.2) versus alternate extraction methods are presented in Table 5. Nearly equivalent results were obtained for soils using the various extraction techniques. However, the results varied significantly when using different extraction techniques for the analysis of wastewater treatment sludges (See Table 5). These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Science Applications International Corporation, “Interlaboratory Study Plan for Validation of Method 6850,” Submitted to the U.S. Environmental Protection Agency, May 24, 2005.

2. EPA Office of Solid Waste, "Methods 6850 and 6860 Validation Study: Phase I Initial Demonstration of Proficiency Validation Study Results," January 23, 2007.

3. EPA Office of Solid Waste, "EPA/OSW Methods 6850 and 6860 Validation Study: Phase II Validation Study Results," January 23, 2007.

4. Krynitsky, A. J., Niemann, R. A., Nortrup, D. A., "Determination of Perchlorate Anion in Foods by Ion Chromatography–Tandem Mass Spectrometry," Anal. Chem., 2004, 76, 5518-5522.

5. EPA Office of Solid Waste, "Single-laboratory Comparative Perchlorate Analysis Testing Results Using Alternate Extraction Methods," January 23, 2007.

6. Mathew, J., Yang, S., Gandhi, J., "Perchlorate Study," U.S. EPA 16th Annual Quality Assurance Conference, Dallas, TX, October, 2006.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method. A flow diagram of the procedure follows the tables and figures.

TABLE 1

EXAMPLE INSTRUMENT SETTINGS FOR IC/MS[a]

IC Parameters and Settings	
Injection Volume	100 µL
Columns:	IonPac® AG20 guard column IonPac® AS20 separator column
Eluent:	45 mM KOH • Isocratic • 0.3 mL/min
IC Oven Temperature:	30 °C
Conductivity Suppressor:	ASRS MS, 2 mm • External water mode, 15 psi • 50 mA
Matrix Diversion Time:	2-9 min
Auxiliary Pump:	90% CH_3CN • 0.2 mL/min
Mass Spectrometer Parameters and Settings	
ESI Polarity:	Negative
Cone Voltage:	70 V
ESI Probe Voltage:	-3 kV
ESI Probe Temperature:	400 °C
SIM Channels:	99, 101 and 107 *m/z*
SIM Span:	0.3 amu
Dwell Time:	0.3 sec for each channel
Nitrogen Pressure:	70 psi

[a]Based on a Dionex Corp. ICS 2500 Ion Chromatography System and MSQ™ Plus Mass Spectrometric Detector

TABLE 2

EXAMPLE INSTRUMENT SETTINGS FOR IC/MS/MS[a]

IC Parameters and Settings	
Injection Volume:	250 µL
Columns:	IonPac® AG16 guard column IonPac® AS16 separator column
Eluent:	35 mM KOH • Isocratic • 0.3 mL/min
IC Oven Temperature:	30 °C
Conductivity Suppressor:	ASRS MS, 2 mm • External water mode, 15 psi • 50 mA
Auxiliary Pump:	0.01 M $CH_3CO_2NH_4$ • 0.1 mL/min
Mass Spectrometer Parameters and Settings	
ESI Polarity:	Negative
Capillary Current:	0.5 kV
Multiplier Voltage:	650 V
Desolvation Temperature:	500 °C
Source Temperature:	120 °C
Desolvation Gas Flow:	500 L/hr
Cone Gas Flow:	50 L/hr

[a]Based on a Dionex Corp. DX-600 Ion Chromatography System and Waters Micromass Quattro Ultima Mass Spectrometric Detector

TABLE 3

EXAMPLE INSTRUMENT SETTINGS FOR IC/MS WITH FRAGMENTATION[a]

IC Parameters and Settings	
Injection Volume:	100 µL
Columns:	Metrosep RP guard column Metrosep ASUPP5-150 separator column
Column Temperature:	35 °C
Eluent:	12.8 mM Na_2CO_3, 4 mM $NaHCO_3$, 8.6 mM CH_3CN • Isocratic • 0.7 mL/min
Conductivity Suppressor:	Metrohm 833 Suppressor Module • 100 mM HNO_3 • 0.5 mL/min • Reagent water rinse
Mass Spectrometer Parameters and Settings	
Scan Mode:	Single Ion Monitoring
ESI Polarity:	Negative
Tune File:	"Autotune" – Electrospray Negative Mode
Fragmentor Voltage:	• 100 V • 210 V for in-source fragmentation
Desolvation Temperature:	350 °C
Desolvation Gas:	• N_2 • 10 L/min
Source Temperature:	100 °C
Resolution:	0.1 amu
Capillary Voltage:	-1500 V

[a]Based on a Metrohm Advanced IC System and Agilent 1100SL Mass Spectrometric Detector

TABLE 4

RESULTS OF INTERLABORATORY TESTING FOR PERCHLORATE BY IC/MS AND IC/MS/MS[a]

	Phase I: Initial Demonstration of Proficiency		Phase II: Real-world Matrices					
Matrix	**Reagent Water**		**Salt Water**		**Soil**			
ID	**1**	**2**	**1**	**2**	**1**	**2**	**3**	**QC Standard[b]**
Selected Matrix Characterization Data								
Conductivity[c]	< 1 µS/cm	< 1 µS/cm	44,600 µS/cm	44,600 µS/cm	243 µS/cm	243 µS/cm	3200 µS/cm	[d]
Aluminum	---	---	[d]	[d]	3700 mg/kg	3700 mg/kg	3700 mg/kg	[d]
Calcium	---	---	299 g/L	299 g/L	8900 mg/kg	8900 mg/kg	8900 mg/kg	[d]
Iron	---	---	[d]	[d]	3120 mg/kg	3120 mg/kg	3120 mg/kg	[d]
Magnesium	---	---	1050 g/L	1050 g/L	288 mg/kg	288 mg/kg	288 mg/kg	[d]
Potassium	---	---	332 g/L	332 g/L	138 mg/kg	138 mg/kg	138 mg/kg	[d]
Sodium	< 5 µg/L	< 5 µg/L	9910 g/L	9910 g/L	[e]	[e]	[e]	[d]
TOC	< 50 µg/L	< 50 µg/L	[d]	[d]	670 mg/kg	670 mg/kg	670 mg/kg	[d]
Round Robin Testing Results								
Number of Laboratories	7	7	7	7	8	7	8	7
Perchlorate True Value	1.75 µg/L	47.0 µg/L	1.70 µg/L	8.30 µg/L	16.0 µg/kg	150 µg/kg	63.0 µg/kg	564 µg/kg
Relative Bias	-7.56%	-5.56%	-1.15%	-2.76%	-14.4%	-9.38%	-7.59%	-14.1%
Repeatability[f] (RSD)	4.47%	2.70%	7.22%	5.11%	8.59%	3.76%	3.61%	8.53%
Reproducibility[g] (RSD)	9.52%	6.57%	14.8%	9.59%	11.5%	6.84%	11.0%	10.7%

[a]Samples were prepared and analyzed using the conditions described in the test method.
[b]Soil and Hazardous Waste QC Standard, Wibby™ Environmental, Inc., Golden, Colorado.
[c]For solids, the conductivity values were based on a 1 g/10 mL extraction solution.
[d]Not determined
[e]Not detected
[f]Intralaboratory precision
[g]Interlaboratory precision

Data taken from References 1-3. These data are provided for guidance purposes only.

TABLE 5

COMPARATIVE PERCHLORATE TESTING RESULTS USING DIFFERENT EXTRACTION TECHNIQUES®[a-f]

Matrix ID	Soil 1[f]				Soil 2[f]				Soil 3[f]				Soil QC Standard[g,h]			
Comparative Testing Results																
Extraction Solvent	RW	ASE®	50% CH_3CN	M-P	RW	ASE®	50% CH_3CN	M-P	RW	ASE®	50% CH_3CN	M-P	RW	ASE®	50% CH_3CN	M-P
Measured Perchlorate Concentration (mg/kg)	12.5	13.7	14.8	14	130	136	147	130	56.4	57.3	55.7	62	445	491	[j]	[j]
Repeatability (RSD) (%)	10.0	23.7	[i]	[i]	3.05	2.02	[i]	[i]	4.87	3.14	[i]	[i]	6.52	14.0	[j]	[j]

Matrix ID	Sludge 1				Sludge 2				Sludge 3			
Selected Matrix Characterization Data												
Conductivity[k]	5100 µS/cm				5100 µS/cm				26000 µS/cm			
Aluminum	3220 mg/kg				3220 mg/kg				3220 mg/kg			
Calcium	42.4 g/kg				42.4 g/kg				42.4 g/kg			
Iron	17.3 g/kg				17.3 g/kg				17.3 g/kg			
Magnesium	6390 mg/kg				6390 mg/kg				6390 mg/kg			
Potassium	3100 mg/kg				3100 mg/kg				3100 mg/kg			
Sodium	4820 mg/kg				4820 mg/kg				4820 mg/kg			
TOC	4880 mg/kg				4880 mg/kg				4880 mg/kg			
Comparative Testing Results												
Extraction Solvent	RW	ASE®	50% CH_3CN	M-P	RW	ASE®	50% CH_3CN	M-P	RW	ASE®	50% CH_3CN	M-P
Measured Perchlorate Concentration (mg/kg)	2.73	13.9	54.3	25	4.99	13.9	123	130	38.2	46.5	119	120
Repeatability (RSD) (%)	3.38	20.6	[i]	[i]	4.79	7.46	[i]	[i]	5.92	8.26	[i]	[i]

TABLE 5 CONTINUED

[a]Reagent water (RW) extracts were prepared using the conditions described in the test method.
[b]ASE® extracts were prepared as described in Figure 4.
[c]RW soil extracts and ASE® soil and sludge extracts were analyzed by IC/MS with conductivity suppression using a Dionex IonPac® AG20/AS20 column with 45 mM KOH mobile phase and early matrix diversion, in which 90% acetonitrile was added post-column.
[d]Acetonitrile extracts were prepared similarly to the RW extracts, except using 50% (v/v) CH_3CN solution. See Reference 4 for more information.
[e]Metrohm-Peak (MP) extracts were prepared as described in Table 6.
[f]RW sludge extracts and all 50% CH_3CN and M-P extracts were analyzed by IC/MS/MS with conductivity suppression using a Dionex IonPac® AS16 column with 35 mM KOH mobile phase and early matrix diversion, in which 0.01 M $NaCH_3CO_2$ was added post-column.
[g]See Table 4 for soil matrix true values and characterization data.
[h]Soil and Hazardous Waste QC Standard, Wibby™ Environmental, Inc., Golden, Colorado.
[i]Result based on a single analysis.
[j]Not analyzed.
[k]Based on a 1 g/10 mL extraction solution
[l]Analysis results could not be effectively computed due to the poor chromatographic quality resulting from interferences in the sample extract matrix.

Data taken from Reference 5. These data are provided for guidance purposes only.

TABLE 6

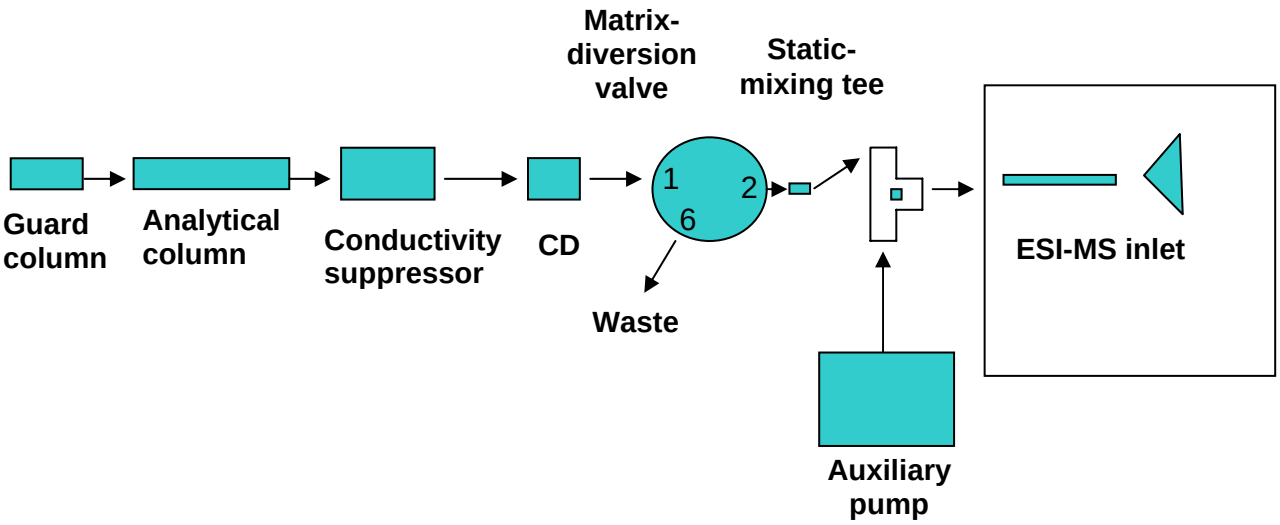
METROHM-PEAK ACID-BASED EXTRACTION AND CLEANUP PROCEDURE FOR THE ANALYSIS OF SOLID MATRICES

Step 1:	Prepare the extraction solution with a final concentration of 15 mM HCl and 5 mM HNO_3.
Step 2:	Add internal standard to a 15 mL centrifuge tube. To that same tube add 1 g of soil or sludge (having recorded the exact weight used to within 0.01 g) and 10 mL of the extraction solution from Step 1.
Step 3:	Vortex, sonicate and centrifuge the sample mixture, as described in this test method.
Step 4:	Filter the supernatant extract solution as described in the test method.
Step 5:	Prepare a 500 mg x 6 mL Supelclean ENVI-Carb SPE cleanup cartridge (PN# 57094) by passing 0.5 mL of fresh extraction solution from Step 1 through it. Discard the effluent from the cartridge.
Step 6:	Process the filtered supernatant extract solution from Step 4 through the prepared cleanup cartridge from Step 5.
Step 7:	Analyze the processed, filtered supernatant from Step 6 for perchlorate by IC/MS.

Procedure obtained from Reference 6.

FIGURE 1

EXAMPLE IC/MS INSTRUMENTATION SET-UP



(**CD** = Conductivity detector)

Figure obtained from R. Slingsby; (408) 481-4542; Rosanne.Slingsby@dionex.com

FIGURE 2

EXAMPLE REAGENT WATER SAMPLE CHROMATOGRAM CONTAINING 0.01 µg/L PERCHLORATE AND OBTAINED USING A DIONEX IONPAC® AS16 COLUMN AND IC/MS/MS ANALYSIS

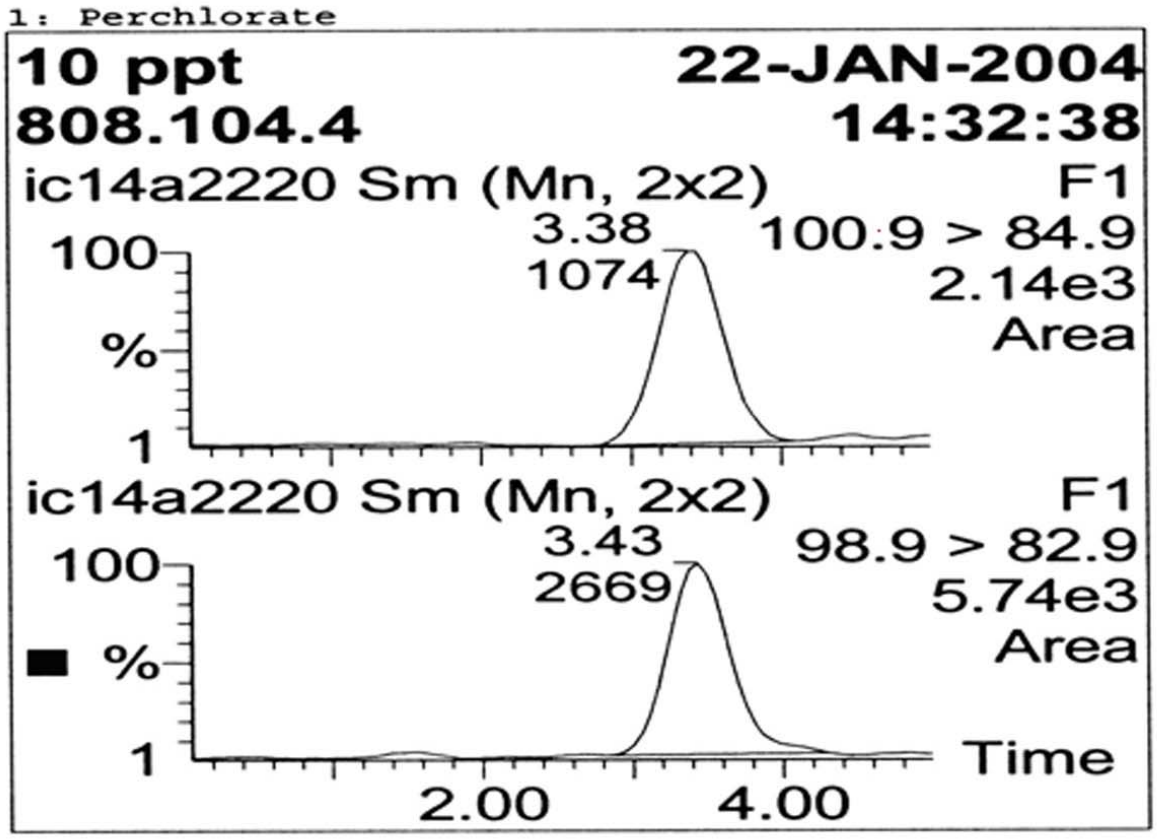


Figure obtained from R. Burrows; (303) 736-0100; rburrows@stl-inc.com

FIGURE 3

EXAMPLE SOIL EXTRACT CHROMATOGRAM OBTAINED USING A
METROSEP ASUPP5-150 COLUMN AND IC/MS ANALYSIS WITH FRAGMENTATION

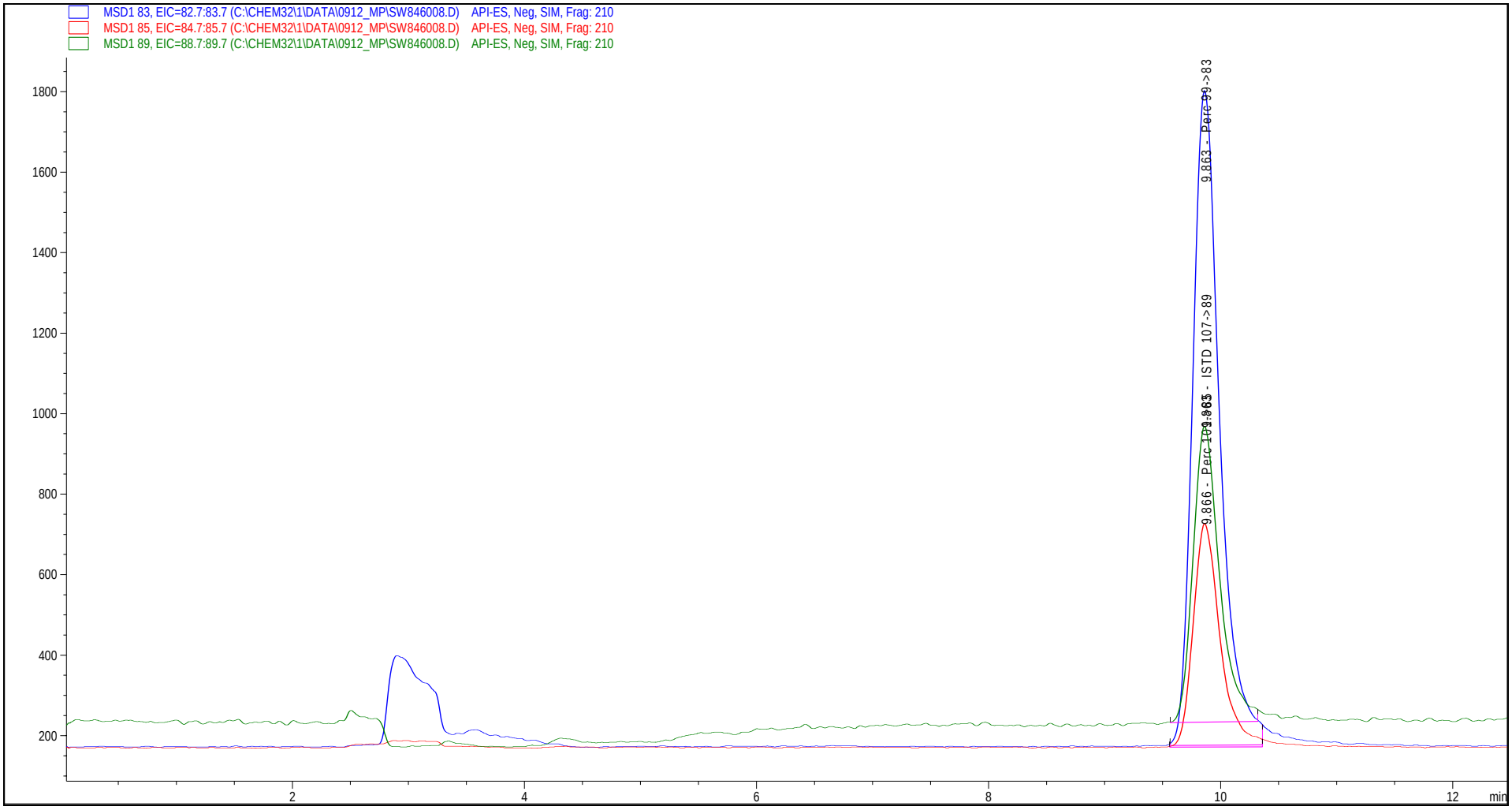


Figure obtained from J. Gandhi; (281) 484-5000; jay@mp-ic.com and J. Mathew; (281) 983-2132; mathew.johnson@usepa.gov

FIGURE 4

IN-LINE ASE® SAMPLE PREPARATION METHOD FOR THE DETERMINATION OF PERCHLORATE IN SELECTED SOILS AND WASTEWATER TREATMENT SLUDGES

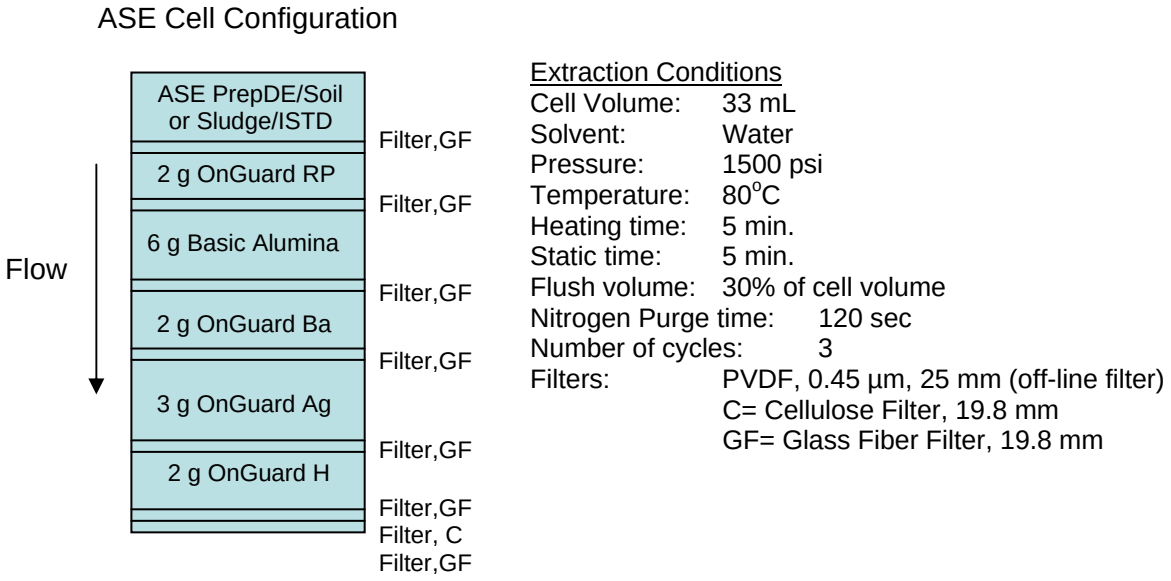
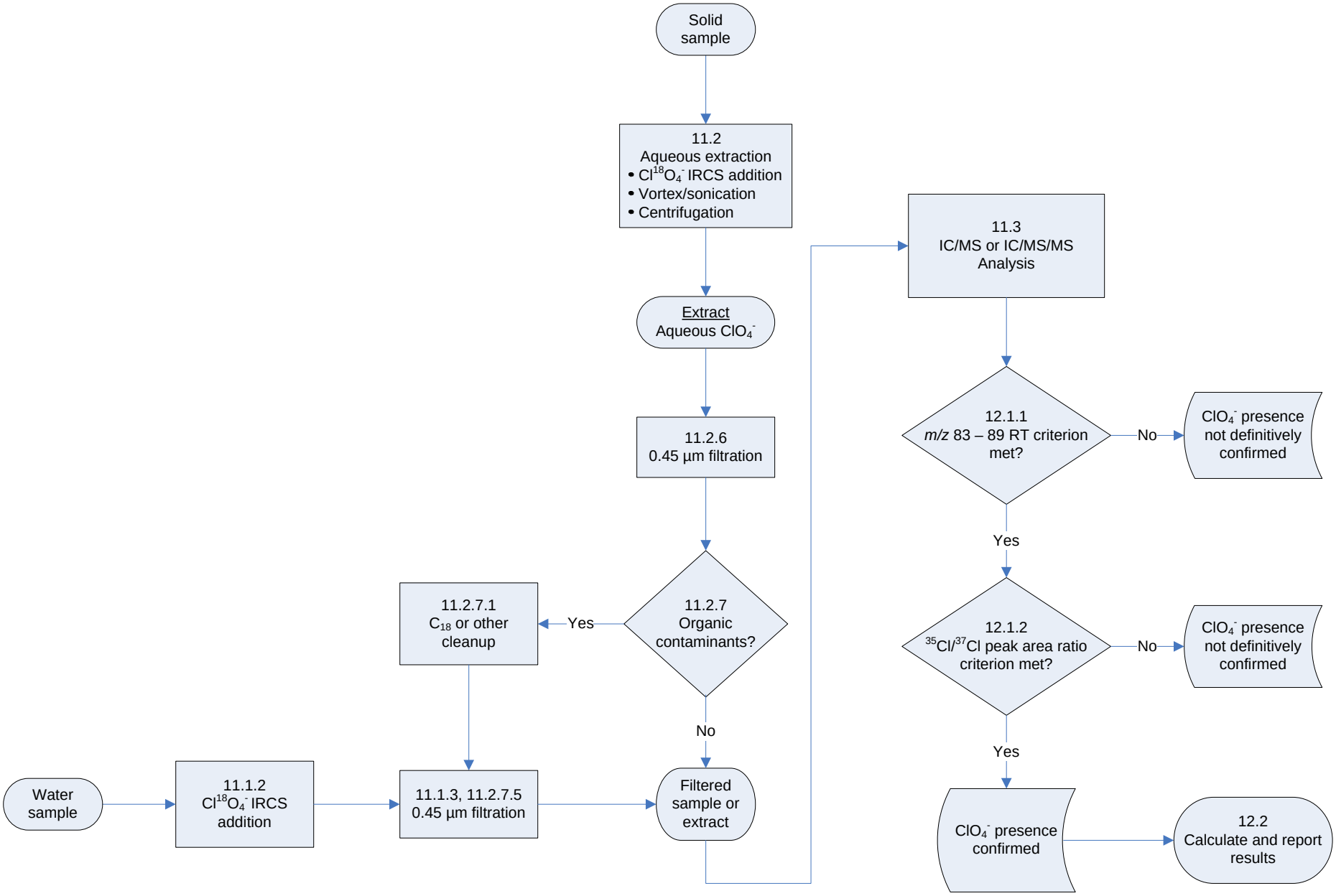


Figure obtained from R. Slingsby; (408) 481-4542; Rosanne.Slingsby@dionex.com


Solid sample
11.2 Aqueous extraction
• $Cl^{18}O_4^-$ IRCS addition
• Vortex/sonication
• Centrifugation
Extract Aqueous ClO_4^-
11.2.6 0.45 µm filtration
11.2.7 Organic contaminants?
Yes
11.2.7.1 C_{18} or other cleanup
No
Water sample
11.1.2 $Cl^{18}O_4^-$ IRCS addition
11.1.3, 11.2.7.5 0.45 µm filtration
Filtered sample or extract
11.3 IC/MS or IC/MS/MS Analysis
12.1.1 *m/z* 83 – 89 RT criterion met?
No
ClO_4^- presence not definitively confirmed
Yes
12.1.2 $^{35}Cl/^{37}Cl$ peak area ratio criterion met?
No
ClO_4^- presence not definitively confirmed
Yes
ClO_4^- presence confirmed
12.2 Calculate and report results