

METHOD 6850

PERCHLORATE IN WATER, SOILS AND SOLID WASTES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION /MASS SPECTROMETRY (HPLC/ESI/MS OR HPLC/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 high performance liquid chromatography (HPLC) coupled with electrospray ionization (ESI) mass spectrometry (MS) or tandem mass spectrometry (MS/MS) for the determination of perchlorate in surface water, groundwater, wastewater, salt water and soil (See Refs. 1-4). The following analyte has been determined by this method:

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

^aChemical 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 3500, 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 HPLC/MS or HPLC/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 HPLC/MS with fragmentation – An appropriate volume of sample or sample extract is introduced into a HPLC/MS instrument. Perchlorate (ClO_4^-) is separated by HPLC from the sample matrix, ionized via negative electrospray ionization, partially fragmented and detected by MS using mass-to-charge (m/z) ratios 83 (ClO_3^-), 85 ($^{37}\text{ClO}_3^-$) and 89 ($\text{Cl}^{18}\text{O}_3^-$). Quantitation is performed using m/z 83 and internal standard calibration. Isotopically-labeled perchlorate ($\text{Cl}^{18}\text{O}_4^-$), serves as an internal recovery and calibration standard (IRCS) to correct for perchlorate loss from the sample preparation as well as in the HPLC/MS. The 83/85 isotopic ratio reflects the isotopic ratio of naturally occurring $^{35}\text{Cl}/^{37}\text{Cl}$ and is used for additional confirmation of perchlorate identification.

2.1.2 HPLC/MS/MS – Following HPLC 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 ($^{37}\text{ClO}_3^-$) and 89 ($\text{Cl}^{18}\text{O}_3^-$) are introduced into the second mass spectrometer where they are detected and quantified.

2.1.3 HPLC/MS without fragmentation – This alternate analysis option is similar to Sec. 2.1.1, except that the separated perchlorate is detected and quantified without fragmentation. The m/z ratios used for analysis in this case are 99 (ClO_4^-), 101 ($^{37}\text{ClO}_4^-$) and 107 ($\text{Cl}^{18}\text{O}_4^-$). HPLC/MS without fragmentation was not evaluated for performance. However, this alternate option may be used, provided that it generates data of acceptable quality, such that the data meet the quality assurance (QA) and quality control (QC) criteria established in this test method or otherwise meet project-specific goals.

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

2.3 Matrix diversion may be used prior to perchlorate introduction to minimize the accumulation of salt deposits in the electrospray source and mass spectrometer (Sec. 6.10.1.2).

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 Chapter Three for general guidance on the cleaning of glassware.

4.2 All reagent solutions and samples (including QC samples) should be filtered through 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 ($\text{H}^{34}\text{SO}_4^-$), m/z 99, formed from a minor sulfur isotope, is commonly present in samples. $\text{H}^{34}\text{SO}_4^-$ 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 $\text{H}^{34}\text{SO}_4^-$.

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 $\text{Cl}^{18}\text{O}_4^-$ 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 $\text{Cl}^{18}\text{O}_4^-$ 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 $\pm 50\%$ 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 HPLC/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 pipettors and disposable tips – 10-10,000 μ L 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- μ m or 0.2- μ m, surfactant-free, PTFE-membrane syringe filters.
- 6.8 Plastic 5-mL luer-lock syringes or equivalent.
- 6.9 C₁₈ (2000 mg) chromatography columns or equivalent for extract solution cleanup.
- 6.10 High performance liquid chromatograph/mass spectrometer – An analytical system combining a high performance liquid chromatograph for separation of the sample components, electrospray ionization source and mass spectrometer for fragmentation and detection of sample components. A single state MS instrument with fragmentation or an MS/MS instrument is preferred due to superior selectivity. An example of such a system is the Agilent 1100 LC/MSD or equivalent. The respective instrument components are provided below.

6.10.1 High performance liquid chromatograph – The instrument should contain a programmable solvent delivery system and all necessary accessories including injection loop, analytical columns, column heater, chromatography pump, in-line degasser, etc. If a solvent gradient is used to obtain separation, then a binary solvent delivery system is necessary. The chromatographic system must be capable of interfacing with a mass spectrometer.

6.10.1.1. Analytical column – Any column capable of providing adequate separation of perchlorate from the sample matrix 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
K' (Prime) Technologies, Inc. Reversed-phase, HPLC column, 4 x 250 mm, PN KP-RPPX250	9.6 M CH ₃ CN, 0.035 mM CH ₃ CO ₂ H
Waters IC-Pak™ Anion HR column, 4.6 x 75 mm	100 mM CH ₃ CO ₂ NH ₄ , 9.6 M CH ₃ CN or 25 mM NH ₄ HCO ₃ , 9.6 M CH ₃ CN, pH 10
Dionex IonPac® AG16 column, 2.0 x 50 mm	0.2 mM CH ₃ CO ₂ NH ₄ , 2 mM NH ₄ OH
Dionex IonPac® AS16 column, 2.0 x 250 mm	65 mM KOH, 9.88 M CH ₃ OH
Dionex IonPac® AS21 column, 2.0 x 250 mm	231 mM CH ₃ NH ₂ (See note below regarding the use of Vespel®-blend rotor seals)
Metrohm LCMS column-1, 4 x 150 mm	15 mM NH ₄ CO ₂ H, 7.5 mM (NH ₄) ₂ CO ₃ , 13.4 M CH ₃ CN, pH 9.6

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

NOTE: The K'(Prime) Technologies and Metrohm columns and corresponding mobile phases were evaluated and found to provide acceptable performance using an HPLC/MS system with fragmentation. All other columns and mobile phases were evaluated and found to provide acceptable performance using an HPLC/MS/MS system.

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

NOTE: The standard rotor seal in most HPLC systems is made from a Vespel® blend, which will dissolve when operating at pH > 10. If using high-pH buffers, such as 200 mM methylamine (pH 12), all Vespel® rotor seals that could come in contact with the mobile phase should be replaced with a PEEK-blend rotor seal. This would include the rotor seals in both the HPLC and matrix diversion valve (Sec. 6.10.1.2).

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.

6.10.2 Electrospray ionization (ESI) source – The ESI source generates gas phase ions of perchlorate from the liquid phase. An example of an ESI setup for HPLC/MS analysis with fragmentation 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 1-2 for examples of HPLC/MS with fragmentation and HPLC/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 $\mu\text{S}/\text{cm}$.

6.17 Conductivity cell appropriate for performing measurements over the range of 1-10,000 $\mu\text{S}/\text{cm}$.

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, CH₃CN, HPLC-Grade.

7.4 Acetic acid, glacial, CH₃COOH.

7.5 Ammonium acetate, CH₃CO₂NH₄.

7.6 Ammonium bicarbonate, NH₄HCO₃.

7.7 Ammonium hydroxide, NH₄OH, HPLC-Grade.

7.8 Methanol, CH₃OH.

7.9 Methylamine, CH₃NH₂, 40% w/w.

7.10 Ammonium formate, NH₄CO₂H.

7.11 Ammonium carbonate, (NH₄)₂CO₃.

7.12 100 mM CH₃CO₂NH₄ – Prepare by dissolving 0.77 g CH₃CO₂NH₄ in 500 mL reagent water. Dilute to a final volume of 1 L using reagent water.

7.13 100 mM NH₄OH – Prepare by diluting 6.8 mL of concentrated NH₄OH to 1 L using reagent water.

7.14 9.6 M CH₃CN, 0.035 mM CH₃CO₂H mobile phase – Prepare by combining 500 mL CH₃CN, 500 mL reagent water and 1-2 mL acetic acid.

7.15 100 mM CH₃CO₂NH₄, 9.6 M CH₃CN mobile phase – Prepare by dissolving 7.71 g CH₃CO₂NH₄ in 500 mL reagent water. Add 500 mL CH₃CN and mix thoroughly. Filter the final solution through a 0.20 μm membrane filter.

7.16 25 mM NH₄HCO₃, 9.6 M CH₃CN, pH 10 mobile phase – Prepare by dissolving 1.98 g NH₄HCO₃ in 450 mL reagent water. Add 500 mL CH₃CN and mix thoroughly. Adjust pH to 10 using NH₄OH. Bring final volume to 1 L using reagent water.

7.17 8 mM CH₃CO₂NH₄, 4.94 mM CH₃OH mobile phase – Prepare by dissolving 0.617 g CH₃CO₂NH₄ in 500 mL reagent water. Add 200 mL CH₃OH and bring the final volume to 1 L using reagent water.

7.18 0.2 mM CH₃CO₂NH₄, 2 mM NH₄OH mobile phase – Prepare by combining 20 mL 100 mM NH₄OH (Sec. 7.13) and 2.0 mL 100 mM CH₃CO₂NH₄ (Sec. 7.12). Dilute the solution to 1 L using reagent water. Prepare fresh daily.

7.19 65 mM KOH, 7.4 M CH₃OH mobile phase – Prepare by dissolving 3.65 g KOH in 500 mL reagent water. Add 300 mL CH₃OH and dilute to a final volume of 1 L with reagent water.

7.20 231 mM CH₃NH₂ mobile phase – Prepare by diluting 20 mL of 40% w/w CH₃NH₂ (Sec. 7.9) to 1 L using reagent water.

7.21 15 mM $\text{NH}_4\text{CO}_2\text{H}$, 7.5 mM $(\text{NH}_4)_2\text{CO}_3$, 13.4 M CH_3CN , pH 9.6 mobile phase – Prepare by dissolving 0.946 g $\text{NH}_4\text{CO}_2\text{H}$ and 0.721 g $(\text{NH}_4)_2\text{CO}_3$ in 250 mL reagent water. Add 700 mL CH_3CN and mix well. Adjust pH to 9.6 using NH_4OH . Bring final volume to 1 L using reagent water. An HPLC instrument equipped with an in-line degasser is necessary when using this mobile phase to prevent bubble formation. Otherwise, the solution may be degassed off-line prior to use.

7.22 Sodium chloride, NaCl .

7.23 Sodium sulfate, Na_2SO_4 .

7.24 Sodium carbonate, Na_2CO_3 .

7.25 Sodium perchlorate, anhydrous, NaClO_4 .

7.26 Sodium perchlorate [$^{18}\text{O}_4$], anhydrous, $\text{NaCl}^{18}\text{O}_4$, $\geq 90\%$ enrichment, Isotec Inc. or equivalent.

7.27 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. 7.27.1). 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.

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

7.28 Intermediate standard solution (10 mg/L ClO_4^-) – Dilute 1000 μL of stock standard solution (Sec. 7.27) 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.

7.29 Calibration standards – Prepare by using various dilutions of the intermediate standard solution (Sec. 7.28). Spike each calibration standard using the exact same volume of IRCS spiking solution (Sec. 7.31), such that the final IRCS concentration is exactly the same (i.e., approximately 5.0 $\mu\text{g/L}$ $\text{Cl}^{18}\text{O}_4^-$) 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 in order 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 $\mu\text{g/L}$ 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.

7.30 IRCS stock solution (approximately 10.0 mg/L $\text{Cl}^{18}\text{O}_4^-$) – Dissolve 1.21 mg of ($^{18}\text{O}_4$)sodium perchlorate in reagent water and dilute to 100 mL in a volumetric flask or purchase commercially. 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.

7.31 IRCS spiking solution (approximately 1000 $\mu\text{g/L}$ $\text{Cl}^{18}\text{O}_4^-$) – Dilute 1.0 mL of the IRCS stock solution (Sec. 7.30) to 10 mL with reagent water. Store at $\leq 6^\circ\text{C}$ 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 Cl¹⁸O₄. 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 clean, 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. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the HPLC/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 the 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 HPLC/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 Na₂SO₄, 0.221 g Na₂CO₃, 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 HPLC/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 HPLC/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 $\pm 15\%$ 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. 7.28) 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 $\pm 50\%$ and for the mid-range CCV is $\pm 15\%$ 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 an 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 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 percent recovery (%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 conductivity 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 $\pm 50\%$ 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 HPLC/MS system

10.2.1 Prepare the calibration standards as outlined in Sec. 7.29.

10.2.2 Inject an equivalent volume of each calibration standard into the HPLC. Use an injection volume that is optimal for the specific column and instrument system. An injection volume of 5-50 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. 7.31) to the sample tube, cap and shake until mixed well.

NOTE: The final concentration of IRCS in the sample must be exactly the same as that in the calibration standards (Sec. 7.29). 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 a 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. 7.31) 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. 7.29).

11.2.4 Vortex the mixture, followed by sonication for a minimum of 10 min, 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 a 0.45-µm or 0.2-µm PTFE membrane filter. Dispense the filtrate 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 C₁₈ column may be performed to remove organic contaminants from the supernatant extract solution. The C₁₈ 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 C₁₈ 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 filtrate 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 an alternate extraction method 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 HPLC/MS instrumentation. Examples of instrument settings for an HPLC/MS with fragmentation and HPLC/MS/MS system are provided in Tables 1-2.

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. Example chromatograms are provided in Figures 1-3.

11.3.4 Inject a suitable volume of sample into the HPLC instrument. Use an injection volume that is optimal for the specific analytical column and instrument system. An injection volume of 5-50 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 83, 85 and 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 a fresh aliquot of the sample and reanalyze.

11.3.6 If the IRCS peak area response exceeds the $\pm 50\%$ 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_3^- m/z 83 peak and the IRCS $\text{Cl}^{18}\text{O}_3^-$ 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_3^- m/z 83 and $^{37}\text{ClO}_3^-$ m/z 85 ions in the chromatogram. To confirm the presence of perchlorate, the 83/85 peak area counts ratio should be within $\pm 30\%$ 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 $\pm 30\%$ 83/85 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_3^- m/z 83 and $\text{Cl}^{18}\text{O}_3^-$ m/z 89 from the IRCS for quantitation. Report the concentration of each of the sample matrices as follows:

12.2.1 Water samples

$$\text{Final result } (\mu\text{g/L ClO}_4^-) = (C)(D)$$

Where:

C = Concentration from calibration curve ($\mu\text{g/L ClO}_4^-$)

D = Dilution factor (if needed)

12.2.2 Solid samples

$$\text{Final result } (\mu\text{g/g ClO}_4^-) = \frac{(C)(V)(D)}{M}$$

Where:

C = Concentration in extract from calibration curve ($\mu\text{g/L ClO}_4^-$)

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 3. 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) and an alternate extraction method are presented in Table 4. Nearly equivalent results were obtained for soils using either of the two extraction techniques. However, the results varied significantly when using different extraction techniques for the analysis of wastewater treatment sludges (See Table 4). 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. Di Rienzo, R. P., Lin, K., McKay, T. T., Wade, R. W., "Analysis of Perchlorate in Difficult Matrices by LC/MS," Fed. Fac. Environ. J., 2004, 15, (4), 27-42.
2. Science Applications International Corporation, "Interlaboratory Study Plan for Validation of Method 6850," Submitted to U.S. Environmental Protection Agency, May 24, 2005
3. EPA Office of Solid Waste, "Methods 6850 and 6860 Validation Study: Phase I Initial Demonstration of Proficiency Validation Study Results," January 23, 2007.
4. EPA Office of Solid Waste, "EPA/OSW Methods 6850 and 6860 Validation Study: Phase II Validation Study Results," January 23, 2007.
5. 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.
6. EPA Office of Solid Waste, "Single-laboratory Comparative Perchlorate Analysis Testing Results Using Alternate Extraction Methods," January 23, 2007.

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 HPLC/MS WITH FRAGMENTATION^a

HPLC Parameters and Settings			
Autosampler			
Injection Volume:	30 µL		
Analytical Column			
Column Temperature:	30 °C		
HPLC Pump			
Flow Rate:	0.5 mL/min		
Run Time:	13.0-17.0 min ^b		
Mobile Phase:	<u>Isocratic Elution</u> 49.95% CH ₃ CN / 49.95% H ₂ O / 0.1% CH ₃ COOH		
Mass Spectrometer Parameters and Settings			
Ionization Mode	Electrospray		
Polarity	Negative		
SIM Parameters			
<u>SIM Ion</u>	<u>Fragmentor</u>	<u>Gain (EMV)</u>	<u>Actual Dwell</u>
83	160 V or 210 V ^c	1.0 – 3.0 ^d	192 msec
85			192 msec
89			192 msec
Spray Chamber			
<u>Gas Temperature</u>	<u>Drying Gas (N₂)</u>	<u>Nebulizer Pressure</u>	
350 °C	12.0 L/min	50 psig	
Capillary voltage			
<u>Negative</u>			
1500-2000 Vcap			

^aBased on an Agilent 1100 LC/MSD

^bThe run time will vary depending on the column condition and the composition of the mobile phase.

^c160 V for Agilent Models G1946A and G1946B and 210 V for Models G1946D and G1956B

^dIt is recommended that the gain be initially set at 1 EMV.

TABLE 2
EXAMPLE INSTRUMENT SETTINGS FOR HPLC/MS/MS^a

HPLC Parameters and Settings	
Injection Volume	50 µL
Column:	Waters Anion Guard-Pak™ guard column Waters IC-Pak™ Anion HR separator column
Column Heater:	35 °C
Eluent:	100 mM CH ₃ CO ₂ NH ₄ , 50% CH ₃ CN <ul style="list-style-type: none"> • Isocratic • 0.3 mL/min
Mass Spectrometer Parameters and Settings	
ESI Polarity:	Negative
Capillary Voltage:	3.25 kV
Cone Voltage:	50 V
Multiplier Voltage:	650 V
Desolvation Temperature:	350 °C
Source Temperature:	120 °C
N₂ Desolvation Gas Flow:	510 L/hr
N₂ Cone Gas Flow:	60 L/hr
Ar Collision Gas Pressure:	2 x 10 ⁻³ mbar
Collision Energy:	30 eV

^aBased on an Agilent 1100 HPLC and Micromass Quattro Micro triple-stage quadrupole mass spectrometer

TABLE 3

RESULTS OF INTERLABORATORY TESTING FOR PERCHLORATE BY HPLC/MS WITH FRAGMENTATION AND HPLC/MS/MS^a

	Phase I: Initial Demonstration of Proficiency		Phase II: Real-world Matrices							
Matrix	Reagent Water		Salt Water		POTW Waste Water		Soil			
ID	1	2	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	d	d	243 µS/cm	243 µS/cm	3200 µS/cm	d
Aluminum	---	---	d	d	d	d	3700 mg/kg	3700 mg/kg	3700 mg/kg	d
Calcium	---	---	299 g/L	299 g/L	d	d	8900 mg/kg	8900 mg/kg	8900 mg/kg	d
Iron	---	---	d	d	d	d	3120 mg/kg	3120 mg/kg	3120 mg/kg	d
Magnesium	---	---	1050 g/L	1050 g/L	d	d	288 mg/kg	288 mg/kg	288 mg/kg	d
Potassium	---	---	332 g/L	332 g/L	d	d	138 mg/kg	138 mg/kg	138 mg/kg	d
Sodium	< 5 µg/L	< 5 µg/L	9910 g/L	9910 g/L	d	d	e	e	e	d
TOC	< 50 µg/L	< 50 µg/L	d	d	d	d	670 mg/kg	670 mg/kg	670 mg/kg	d
Round Robin Testing Results										
Number of Laboratories	12	12	12	12	1	1	11	11	10	12
Perchlorate True Value	1.75 µg/L	47.0 µg/L	1.70 µg/L	8.30 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	-8.56%	-3.16%	-6.36%	-6.11%	1.18%	3.47%	-13.0%	-12.2%	-7.6%	-14.1%
Repeatability ^f (RSD)	2.99%	4.38%	6.75%	6.09%	4.95%	1.92%	8.00%	4.20%	8.33%	9.1%
Reproducibility ^g (RSD)	6.33%	8.45%	25.9%	12.6%	---	---	16.9%	13.7%	16.0%	19.2%

^aSamples were prepared and analyzed using the conditions described in the test method.

^bSoil and Hazardous Waste QC Standard, Wibby™ Environmental, Inc., Golden, Colorado.

^cFor solids, the conductivity values were based on a 1 g/10 mL extraction solution.

^dNot determined

^eNot detected

^fIntralaboratory precision

^gInterlaboratory precision

Data taken from References 2-4. These data are provided for guidance purposes only.

TABLE 4

COMPARITIVE PERCHLORATE TESTING RESULTS USING REAGENT WATER EXTRACTION
VERSUS 50% ACETONITRILE EXTRACTION^{a-c}

Matrix ID	Soil 1 ^d		Soil 2 ^d		Soil 3 ^d		Soil QC Standard ^{d,e}	
Comparative Testing Results								
Extraction Solvent	Reagent Water	50% CH ₃ CN	Reagent Water	50% CH ₃ CN	Reagent Water	50% CH ₃ CN	Reagent Water	50% CH ₃ CN
Measured Perchlorate Concentration	13.0 mg/kg	12.6 mg/kg	122 mg/kg	117 mg/kg	52.8 mg/kg	50.6 mg/kg	408 mg/kg	440 mg/kg
Repeatability (RSD)	2.13%	2.09%	5.22%	2.05%	4.29%	1.73%	19.1%	f

Matrix ID	Sludge 1		Sludge 2		Sludge 3	
Selected Matrix Characterization Data						
Conductivity ^g	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	Reagent Water	50% CH ₃ CN	Reagent Water	50% CH ₃ CN	Reagent Water	50% CH ₃ CN
Measured Perchlorate Concentration	3.53 mg/kg	20.6 mg/kg	6.46 mg/kg	27.6 mg/kg	41.9 mg/kg	50.5 mg/kg
Repeatability (RSD)	7.18%	5.61%	3.37%	0.788%	8.17%	5.81%

^aReagent water extracts were prepared as described in the test method.

^b50% (v/v) acetonitrile extracts were prepared as described in Ref. 5.

^cAll sample extracts were analyzed by HPLC/MS/MS using a Waters IC-Pak™ Anion HR column with 100 mM CH₃CO₂NH₄, 9.6 M CH₃CN mobile phase.

^dSee Table 3 for soil matrix true values and characterization data.

^eSoil and Hazardous Waste QC Standard, Wibby™ Environmental, Inc., Golden, Colorado.

^fResult based on a single analysis.

^gBased on a 1 g/10 mL extraction solution.

Data taken from Reference 6. These data are provided for guidance purposes only.

FIGURE 1

EXAMPLE SIMULATED GROUND WATER SAMPLE CHROMATOGRAM SPIKED WITH 1 $\mu\text{G/L}$ PERCHLORATE AND OBTAINED USING A K'(PRIME) COLUMN AND HPLC/MS ANALYSIS WITH FRAGMENTATION

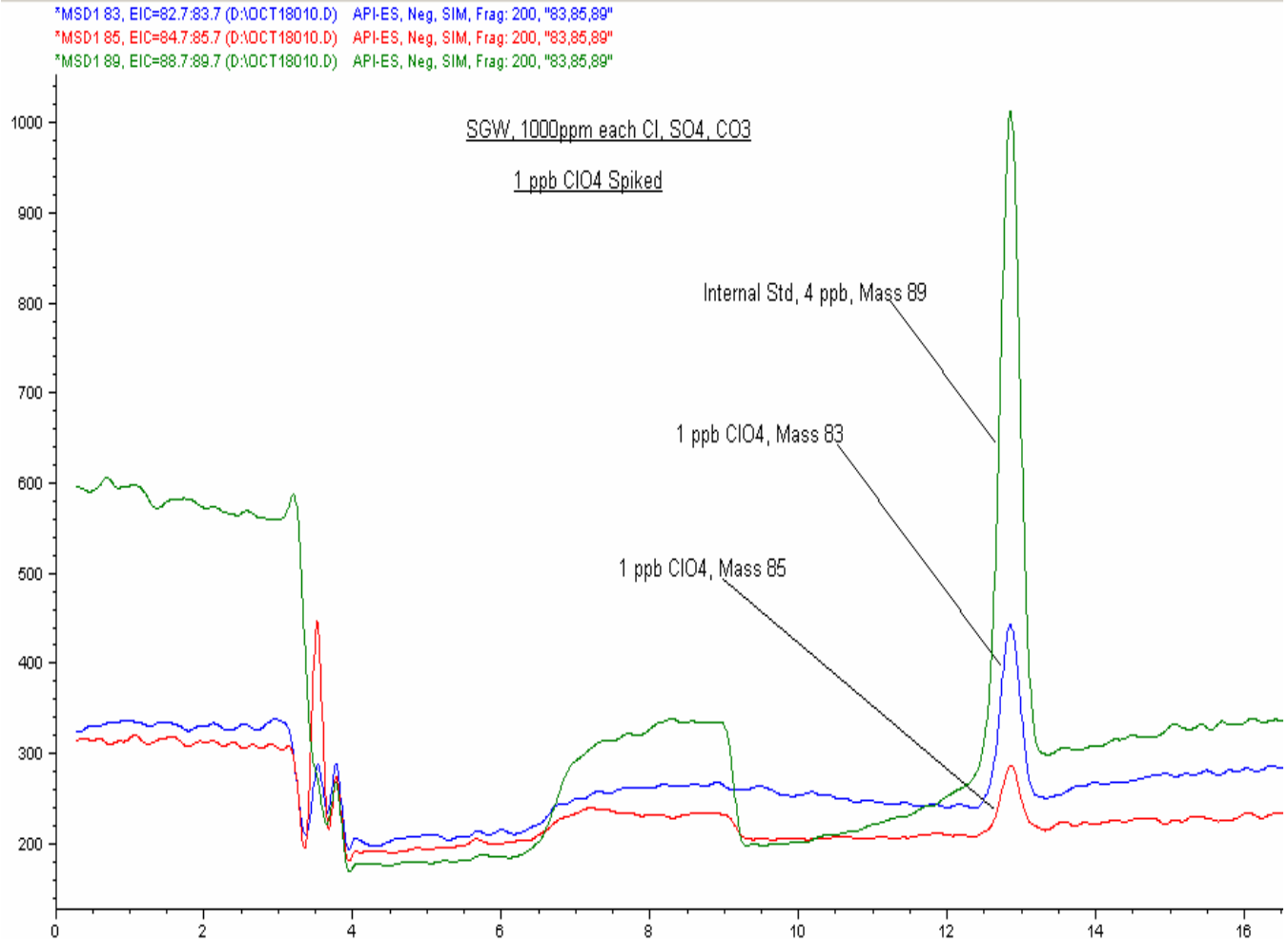


Figure obtained from R. DiRienzo; (801) 266-7700; dirienzo@datachem.com

FIGURE 2

EXAMPLE GREAT SALT LAKE WATER SAMPLE CHROMATOGRAM SPIKED WITH 1 µg/L PERCHLORATE AND OBTAINED USING A K'(PRIME) COLUMN AND HPLC/MS ANALYSIS WITH FRAGMENTATION

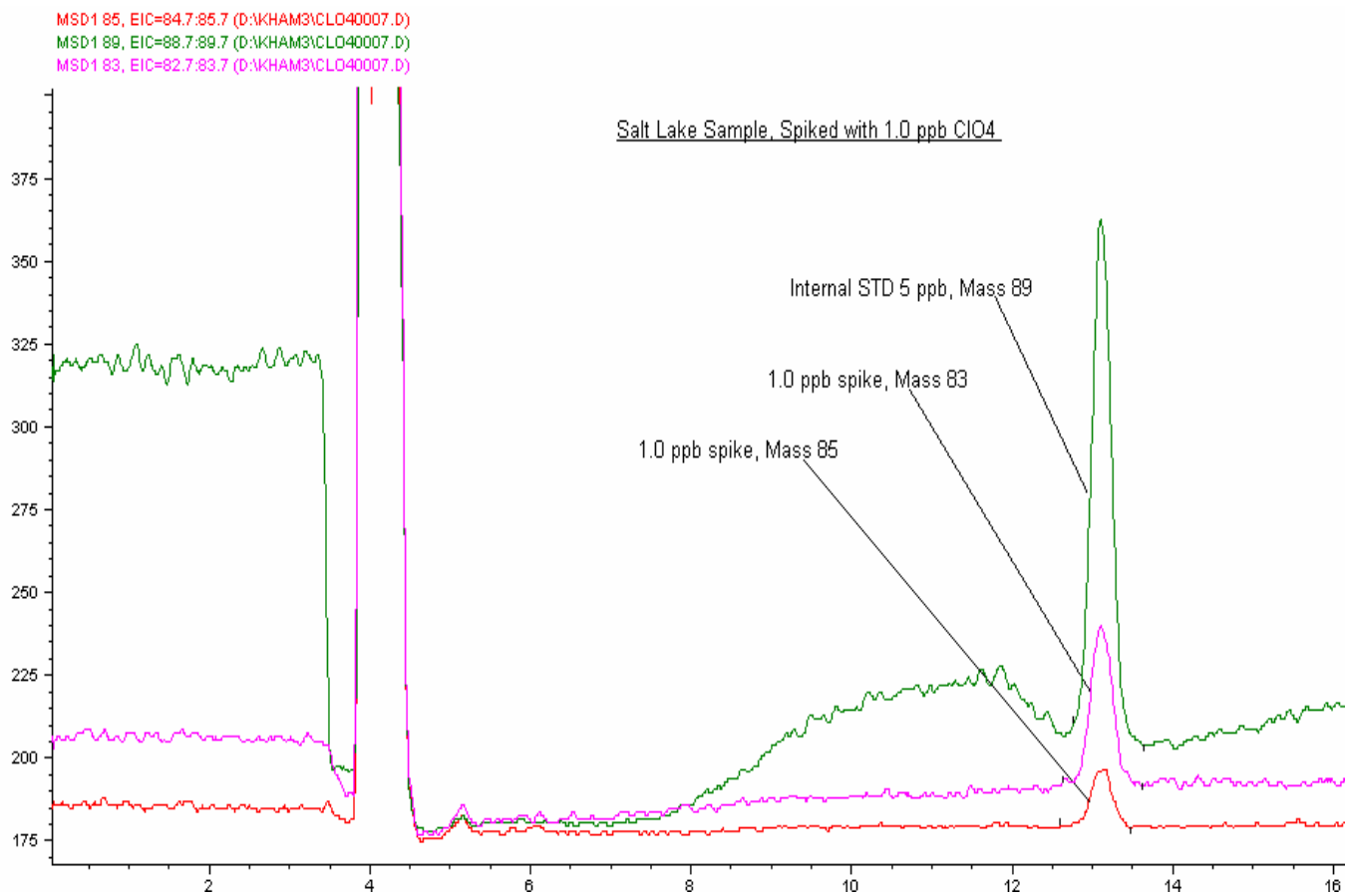


Figure obtained from R. DiRienzo; (801) 266-7700; dirienzo@datachem.com

FIGURE 3

EXAMPLE SOIL EXTRACT CHROMATOGRAM OBTAINED USING A METROHM LCMS COLUMN AND HPLC/MS ANALYSIS WITH FRAGMENTATION

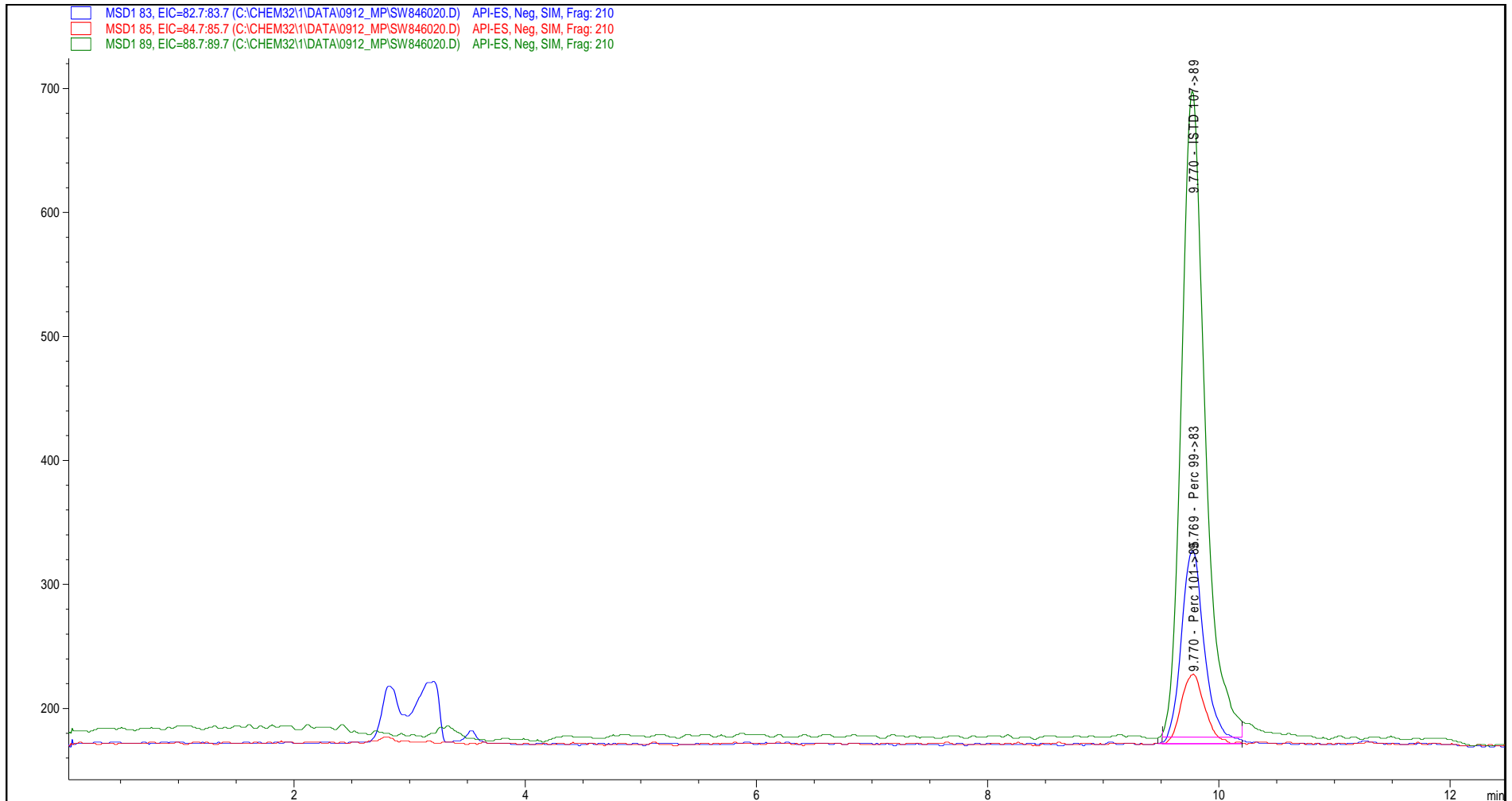


Figure obtained from J. Gandhi; (281) 484-5000; jay@mp-ic.com and J. Mathew; (281) 983-2132; mathew.johnson@usepa.gov

METHOD 6850

