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# METHOD 314.1 DETERMINATION OF PERCHLORATE IN DRINKING WATER USING INLINE COLUMN CONCENTRATION/MATRIX ELIMINATION ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

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# METHOD 314.1

# DETERMINATION OF PERCHLORATE IN DRINKING WATER BY INLINE COLUMN CONCENTRATION/MATRIX ELIMINATION ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

## 1. SCOPE AND APPLICATION

1.1 This is a sample pre-concentration, matrix elimination ion chromatographic (IC) method using suppressed conductivity detection for the determination of perchlorate in raw and finished drinking waters. This method requires the use of a confirmation column to validate all perchlorate concentrations reported at or above the MRL on the primary column. Precision and accuracy data have been generated for perchlorate, with both the primary and confirmation columns, in reagent water, finished groundwater, surface water and a Laboratory Fortified Synthetic Sample Matrix (LFSSM). The single laboratory Lowest Concentration Minimum Reporting Level (LCMRL) has also been determined in reagent water. [1]

| Analyte | Chemical Abstract Services Registry Number (CASRN) |
|---|---|
| Perchlorate | 14797-73-0 |

1.2 The Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method. The single laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall between 50 and 150 percent recovery with 99% confidence. The single laboratory LCRML for perchlorate was 0.140 and 0.130 ug/L for the AS16 and AS20 columns, respectively. The procedure used to determine the LCMRL is described elsewhere. [1]

1.3 Laboratories using this method will not be required to determine the LCMRL, but will need to demonstrate that their laboratory MRL for this method meets the requirements described in Section 9.2.4.

1.4 Detection limit (DL) is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] The DL for perchlorate is dependent on sample matrix, fortification concentration, and instrument performance. Determining the DL for perchlorate in this method is optional (Sect. 9.2.7). The reagent water DL for the perchlorate was calculated to be 0.03 ug/L using 7 replicates of a 0.10 µg/L fortification level with the AS16 columns and 0.03 ug/L for the AS20 columns. These values are also provided in.

1.5 This method is intended for use by analysts skilled in the operation of IC instrumentation, and the interpretation of the associated data.

## 2. SUMMARY OF METHOD

2.1 Water samples are collected in the field using a sterile filtration technique. The sample, without cleanup, is concentrated onto the concentrator/trap column, which is placed in the sample loop position and binds perchlorate more strongly than other matrix anions. The sample matrix anions are rinsed from the concentrator column with 1 mL of 10 mM NaOH. This weak rinse solution allows the concentrator to retain the perchlorate while eluting the majority of the matrix anions, which are directed to waste. The concentrator column is switched in-line and the perchlorate is eluted from the concentrator column with a 0.50 mM NaOH solution. Following elution from the concentrator, the perchlorate is refocused onto the front of the guard column. The eluent strength is then increased to 65 mM NaOH which elutes the perchlorate from the guard column and onto the analytical column where perchlorate is separated from other anions and remaining background interferences. The sample loading and matrix elimination steps must use the same eluent flow direction as the elution and analytical separation steps. Perchlorate is subsequently detected using suppressed conductivity and is quantified using an external standard technique. Confirmation of any perchlorate concentration reported at or above the MRL on the primary column is accomplished with a second analytical column that has a dissimilar separation mechanism.

## 3. DEFINITIONS

3.1 ANALYSIS BATCH – A sequence of field samples, which are analyzed within a 30-hour period and include no more than 20 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. For this method, the required QC samples include:

Laboratory Synthetic Sample Matrix Blank (LSSMB)
Continuing Calibration Check (CCC)
Laboratory Fortified Synthetic Sample Matrix (LFSSM) CCC Standards
Laboratory Fortified Sample Matrix (LFSM)
Laboratory Duplicate (LD) or a Laboratory Fortified Sample Matrix Duplicate (LFSMD).

3.2 ANALYTE FORTIFICATION SOLUTIONS (AFS) – The Analyte Fortification Solutions are prepared by dilution of the Analyte Secondary Dilution Solutions (SDS) and are used to fortify the LFSMs and the LFSMDs with perchlorate. It is recommended that multiple concentrations be prepared so that the fortification levels can be rotated or adjusted to the concentration of target analyte in the native samples.

3.3 CALIBRATION BLANK (CB) – An aliquot of reagent water or other blank matrix that is treated exactly as a CCC. The CB **is not sterile filtered** and is used to determine if the method analyte or other interferences are present in the laboratory environment, the reagents, or the apparatus during the IDC calibration.

3.4 CALIBRATION STANDARD (CAL) – A solution of the target analyte prepared from the Perchlorate Primary Dilution Solution or Perchlorate Stock Standard Solution. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.5 CONTINUING CALIBRATION CHECK STANDARD (CCC) – A calibration check standard containing the method analyte which is analyzed periodically throughout an Analysis Batch, to verify the accuracy of the existing calibration for that analyte.

3.6 DETECTION LIMIT (DL) –The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination (Sect. 9.2.7), and accurate quantitation is not expected at this level. [2]

3.7 LABORATORY DUPLICATES (LDs) – Two sample aliquots ($LD_1$ and $LD_2$), from a single field sample bottle, and analyzed separately with identical procedures. Analyses of $LD_1$ and $LD_2$ indicate precision associated specifically with laboratory procedures by removing variation contributed from sample collection, preservation, and storage procedures.

3.8 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water or other blank matrix to which a known quantity of the method analyte is added. The LFB is analyzed exactly like a sample, including the preservation procedures in Section 8.1. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of a field sample to which a known quantity of the method analyte is added. The LFSM is processed and analyzed exactly like a field sample, and its purpose is to determine whether the field sample matrix contributes bias to the analytical results. The background concentration of the analyte in the field sample matrix must be determined in a separate aliquot and the measured value in the LFSM corrected for native concentrations.

3.10 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A second aliquot of the field sample used to prepare the LFSM, which is fortified and analyzed identically to the LFSM. The LFSMD is used instead of the Laboratory Duplicate to assess method precision and accuracy when the occurrence of the target analyte is infrequent.

3.11 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX (LFSSM) – Aliquots of the LSSM which are fortified with perchlorate (Sect. 7.2.2). These QC samples are used, during an Analysis Batch, to confirm the integrity of the trapping efficiency of the concentrator column and that the analyst has adequate resolution between the common anions and perchlorate in high ionic matrices. The LFSSM samples are treated like the CCCs and are not sterile filtered.

3.12 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all filtration equipment, storage containers and internal standards. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.13 LABORATORY SYNTHETIC SAMPLE MATRIX (LSSM) – An aliquot of reagent water that is fortified with 1000 mg/L of chloride, bicarbonate and sulfate. This solution is representative of a drinking water containing 3000 mg/L of common anions.

3.14 LABORATORY SYNTHETIC SAMPLE MATRIX BLANK (LSSMB) – An aliquot of the LSSM that is processed like a field sample and is used to determine if the method analyte or other interferences are present in the LSSMSS solution. It is also used to determine whether the methodology is in control in terms of low system background.

**NOTE:** The LSSMB is processed through all sample collection steps outlined in Section 8.1. **The LSSMB must be sterile filtered.**

3.15 LABORATORY SYNTHETIC SAMPLE MATRIX FORTIFICATION SOLUTION (LSSMFS) – A dilution of the LSSMSS is prepared to facilitate the addition of sodium to all field samples in an accurate manner without necessitating volume correction (Sect. 7.2.3).

3.16 LABORATORY SYNTHETIC SAMPLE MATRIX STOCK SOLUTION (LSSMSS) – The LSSMSS contains the common anions chloride, sulfate and bicarbonate at 25.0 g/L. This solution is used in the preparation of all CAL and QC samples (Sect. 7.2.2).

3.17 LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single-laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall between 50 and 150 percent recovery with 99% confidence. [1]

3.18 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.19 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported by a laboratory as a quantified value for the target analyte in a sample following analysis. This defined concentration must meet the criteria defined in Section 9.2 and must be no lower than the concentration of the lowest calibration standard for the target analyte.

3.20 PRIMARY DILUTION STANDARD SOLUTION (PDS) – A solution containing the method analyte prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other analyte solutions.

3.21 QUALITY CONTROL SAMPLE (QCS) – A solution containing the method analyte at a known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. The QCS is used to verify the calibration standards/curve integrity.

3.22 REAGENT WATER (RW) – Purified water which does not contain any measurable quantity of the target analyte or interfering compounds at or above 1/3 the MRL.

3.23 SECONDARY DILUTION STANDARD SOLUTION (SDS) – A solution containing the method analyte prepared in the laboratory from the PDS and diluted as needed to prepare calibration solutions and other analyte solutions.

3.24 STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing the method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

## 4. INTERFERENCES

4.1 Interferences can be divided into three different categories: (i) direct chromatographic co-elution, where an interfering analyte response is observed at very nearly the same retention time (RT) as the target analyte; (ii) concentration dependant co-elution, which is observed when the response of higher than typical concentrations of the neighboring peak overlaps into the retention window of the target analyte; and (iii) ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or Total Dissolve Solids) overloading the exchange sites on the column and significantly shortening the target analyte's retention time.

4.1.1 A direct chromatographic co-elution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst must verify that these changes do not induce any negative affects on method performance by repeating and passing all the QC criteria as described in Section 9.2.

4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant co-elution or ionic character displacement, but it must be clarified that sample dilution will alter your MRL by a proportion equivalent to that of the dilution. Therefore, careful consideration of DQOs should be given prior to performing such a dilution.

4.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and /or elevated baselines in the chromatograms. All items such as these must be routinely demonstrated to be free from interferences (less than $^1/_3$ the perchlorate MRL) under the conditions of the analysis by analyzing LRBs and LSSMBs as described in Section 9.2.1. **Subtracting blank values from sample results is not permitted.**

4.3 Matrix interferences may be caused by contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Water samples high in organic carbon or TDS may have elevated baselines or interfering peaks.

4.4 Equipment used for sample collection and storage has the potential to introduce interferences. The potential for interferences from these devices must be investigated during the Initial Demonstration of Capability (Sect. 9.2) by preparing and analyzing a LRB and LSSMB. This procedure should be repeated each time that a new brand or lot of devices are used to ensure that contamination does not hinder analyte identification and quantitation.

4.5 This method utilizes a confirmation column that has a separation mechanism that is sufficiently different for the primary column so that perchlorate may be confirmed. The suggested primary column, the IonPac AS16, has a column chemistry that is based on a low cross-link vinyl aromatic quaternary monomer. It was designed to provide good chromatographic performance for polarizable inorganic anions such as perchlorate with moderate concentration hydroxide eluents. Although less polarizable than inorganic species

such as perchlorate, such aromatic species show enhanced retention due to interaction with the pi electrons of the aromatic backbone. The suggested confirmation column, the IonPac AS20, has a column chemistry that is based on a cross-linked quaternary condensation polymer completely free of any pi electron containing substituents. As such, it exhibits selectivity for polarizable anions which is complementary to the AS16, but because of the absence of any pi electron character, retention of aromatic anionic species is greatly diminished relative to that of the AS16.

4.5.1 One component that has been shown by IC and IC-MS to potentially co-elute with perchlorate on the IonPac AS16 column when using EPA Method 314.0 protocols is 4-chlorobenzenesulfonic acid (4-Cl BSA). [3] As shown in Figure 1, with EPA Method 314.1 protocols, there is some resolution of the two components on the AS16 column and the IonPac AS20 column provides excellent separation of perchlorate and 4-Cl BSA.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. [4-6]

## 6. EQUIPMENT AND SUPPLIES (References to specific brands or catalog numbers are included for illustration only and do not imply endorsement of the product.)

6.1 NON-STERILE SAMPLE CONTAINERS – 125-mL brown Nalgene bottles (Fisher Cat. No. 03-313-3C or equivalent).

6.2 STERILE SAMPLE CONTAINERS – 125-mL sterile high-density polyethylene (HDPE) bottles (I-Chem 125-mL sterile HDPE bottle, Fisher Cat. No. N411-0125 or equivalent).

6.3 SAMPLE FILTERS – Sterile sample filters (Corning 26-mm surfactant free cellulose acetate 0.2-um filter, Fisher Cat. No. 09-754-13 or equivalent). If alternate filters are used they should be certified as having passed a bacterial challenge test. [7] In addition, if alternate filters or different lots of the recommended filters are used, they must be tested using a LSSMB and a LFSSM fortified at the MRL as outlined in Section 9.2 to insure that they do not introduce interferences or retain perchlorate.

6.4 SYRINGES – 20-mL sterile, disposable syringes (Henke Sass Wolf 20 mL Luer lock, Fisher Cat. No. 14-817-33 or equivalent).

6.5 VOLUMETRIC FLASKS – Class A, suggested sizes include 10, 50, 100, 250, 500 and 1000 mL for preparation of standards and eluents.

6.6 GRADUATED CYLINDERS – Suggested sizes include 25 and 1000 mL.

6.7 AUTO PIPETTES – Capable of delivering variable volumes from 1.0 uL to 2500 uL.

6.8 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

6.9 ION CHROMATOGRAPHY SYSTEM WITH SUPPRESSED CONDUCTIVITY DETECTION (IC) – A Dionex model DX500 IC was used to collect the data presented in this method. Alternative IC systems can be used provided all the QC criteria listed in Section 9 are met. The IC system must have a thermostatically controlled column heater and be capable of operating above room temperature (35 ºC) and include an ion chromatographic pump and all required accessories including, analytical, concentrator and guard columns, chromatography module, eluent generator, compressed gasses, autosampler, suppressor, conductivity detector, and a computer-based data acquisition and control system. Additionally, the system must be capable of performing inline sample pre-concentration and matrix elimination steps.

6.9.1 CONCENTRATOR COLUMN – IC column, 4.0 x 35-mm (Dionex Cryptand C1 or equivalent). Any concentrator column that provides effective retention/trapping and eventual release of perchlorate while providing the resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. However, prior to use, the capacity of the concentrator column must be evaluated as per Section 11.4.

6.9.2 PRIMARY GUARD COLUMN – IC column, 2.0 x 50-mm (Dionex IonPac®AG16 or equivalent). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used.

6.9.3 CONFIRMATION GUARD COLUMN – IC column, 2.0 x 50-mm (Dionex IonPac®AG20 or equivalent). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. The separation mechanism for the confirmation guard column must differ from the primary column.

6.9.4 PRIMARY ANALYTICAL COLUMN – IC column, 2.0 x 250-mm (Dionex IonPac®AS16 or equivalent). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used.

6.9.5 CONFIRMATION ANALYTICAL COLUMN – IC column, 2.0 x 250-mm (Dionex IonPac®AS20 or equivalent). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. The separation mechanism for the confirmation analytical column must differ from the primary column.

6.9.6 AUTOSAMPLER – A Dionex AS40 autosampler (or equivalent) is required to perform the sample pre-concentration/matrix elimination steps. The method program must include a timing sequence to allow the autosampler to load two sample vials before the concentrator column is switched in-line to separate and detect perchlorate. The first sample vial contains the sample (2.0 mL) and the second vial contains the rinse solution (1.0 mL of 10 mM NaOH), with the filter cap raised to signify a rinse vial. The method programs for the AS16 and AS20 columns are listed in Table 1A. The method timing sequence for the methods is listed in Table 1B.

6.9.7 ELUENT GENERATOR – An eluent generator (Dionex EG50 or equivalent) with a sodium cartridge (EluGen ® PN 058908 or equivalent) is used to prepare the sodium

hydroxide eluent for this method. An equivalent eluent generator may be used and/or manually prepared eluents may also be used provided that adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) are obtained. Care must be exercised with manually prepared sodium hydroxide eluents to prevent formation of carbonate in the eluent from exposure to the atmosphere, which can dramatically alter the chromatography.

**NOTE:** The Cryptand concentrator columns use manipulation of column capacity as part of the mechanism for separation. The counter ion in the eluent has a strong influence on both the concentrator column capacity and the capacity modification kinetics. In this work, sodium is used to establish the optimal capacity of the Cryptand concentrator column and consequently a **sodium cartridge** (Dionex PN 058908 or equivalent**) rather than a potassium cartridge MUST be used with the EG50.**

6.9.8 ANION SUPPRESSOR DEVICE – The data presented in this method were generated using a Dionex Ultra II Anion Self-Regenerating Suppressor (2-mm ASRS, PN 061562) for electrolytic suppression of the eluent. Equivalent suppressor devices may be utilized providing a comparable conductivity MRL and DL are achieved and adequate baseline stability is attained as measured by a baseline noise of no more than 5 nS per minute over the background conductivity.

**NOTE:** The conductivity suppressor was set to perform electrolytic suppression at a current setting of 100 mA using **the external water mode**. Since unacceptable baseline stability was observed on the conductivity detector using the Ultra II ASRS in recycle mode, **the external water mode must be used**.

6.9.9 CONDUCTIVITY DETECTOR – Conductivity cell (Dionex CD20 or equivalent) capable of providing data as required in Section 9.2.

6.9.10 CHROMATOGRAPHY MODULE – A chromatography module (Dionex LC30 or equivalent) capable of maintaining the columns, suppressor and conductivity cell at 35 °C is required.

6.9.11 DATA SYSTEM – An interfaced data system such as Dionex, Chromeleon Version 6.0 (or equivalent) is required to acquire, store, and output conductivity data. The computer software should have the capability of processing stored conductivity data by recognizing a peak within a given retention time window. The software must allow integration of the peak area of any specific peak between specified time limits. The software must be able to construct a linear regression or quadratic calibration curve, and calculate analyte concentrations.

## 7. REAGENTS AND STANDARDS

7.1 REAGENTS – Reagent grade or better chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided it is first determined that

the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination.

7.1.1 REAGENT WATER (RW) - Purified water which does not contain any measurable quantity of the target analyte or interfering compounds at or above 1/3 the perchlorate MRL. The purity of the water required for this method cannot be overly emphasized. The reagent water used during method development was generated from tap water using a Millipore ELIX-3 followed by a Millipore Gradient A10 system. The water should contain no particles larger than 0.20 microns.

7.1.2 ELUENT SOLUTION – Sodium hydroxide eluent concentrations of 0.50, 65 and 100 mM are automatically prepared using the EG50 eluent generator and/or manually prepared (Sect. 6.9.7).

7.1.3 SODIUM BICARBONATE – ($NaHCO_3$, CASRN 497-19-8) – Fluka Cat. No. 71627 or equivalent.

7.1.4 SODIUM CHLORIDE – (NaCl, CASRN 7647-14-5) – Fisher Cat. No. S-271 or equivalent.

7.1.5 SODIUM SULFATE – ($Na_2SO_4$, CASRN 7757-82-6) – Fluka Cat. No. 71959 or equivalent.

7.2 STANDARD SOLUTIONS – When a compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Solution concentrations listed in this section were used to develop this method and are included as an example. **Even though stability times for standard solutions are suggested in the following sections, laboratories should use standard QC practices to determine when their standards need to be replaced.**

7.2.1 PERCHLORATE STANDARD SOLUTIONS – Obtain the analyte as a solid standard of $NaClO_4$ or as a commercially prepared standard from a reputable standard manufacturer. Prepare the Perchlorate Stock and Dilution Solutions as described below.

7.2.1.1 PERCHLORATE STOCK STANDARD SOLUTION (SSS) (1000 mg/L $ClO_4^-$) – To prepare this solution from a solid $NaClO_4$ standard, weigh out 123.1 mg of $NaClO_4$ into a 100-mL volumetric flask and dilute to volume with reagent water. When stored in opaque, plastic storage bottles, the resulting stock solution may be stable for up to one year.

7.2.1.2 PERCHLORATE PRIMARY DILUTION SOLUTION (PDS) (10.0 mg/L $ClO_4^-$) – Prepare the Perchlorate PDS by adding 1.00 mL of the Perchlorate SSS to a 100-mL volumetric flask and dilute to volume with reagent water. This solution is used to prepare the Secondary Dilution Solution, the Perchlorate Fortification Solutions and the Calibration Solutions below. When stored in opaque, plastic storage bottles, the resulting solution is stable for at least one month.

7.2.1.3 PERCHLORATE SECONDARY DILUTION SOLUTION (SDS) (1.00 mg/L $ClO_4^-$) – Prepare the 1.00 mg/L Perchlorate SDS by adding 10.0 mL of the Perchlorate PDS to a 100-mL volumetric flask and dilute to volume with reagent water. This solution is used to prepare the Perchlorate Fortification Solutions, CAL and CCC Standards listed below. When stored in opaque, plastic storage bottles, the resulting solution is stable for at least one month.

7.2.1.4 PERCHLORATE FORTIFICATION SOLUTIONS (PFS) (50, 200 and 500 µg/L) – The Perchlorate Fortification Solutions are prepared by dilution of the Perchlorate SDS and are used to fortify the Laboratory Fortified Blank (LFB), the Laboratory Fortified Synthetic Sample Matrix (LFSSM), the Laboratory Fortified Sample Matrix (LFSM) and the Laboratory Fortified Sample Matrix Duplicate (LFSMD) with perchlorate. It is recommended that multiple concentrations be prepared so that the fortification levels can be rotated or adjusted to the concentration of target analyte in the native samples. When stored in opaque, plastic storage bottles, the resulting solutions are stable for at least one month. A 20-uL aliquot of each PFS added to a 2.0-mL sample volume yield a perchlorate concentration of 0.50, 2.0 and 5.0 ug/L, respectively.

7.2.2 LABORATORY SYNTHETIC SAMPLE MATRIX STOCK SOLUTION (LSSMSS) – Prepare a LSSMSS that contains the common anions chloride, sulfate and bicarbonate at 25.0 g/L as follows. This solution is used in the preparation of all QC samples. A dilution of the LSSMSS is used to fortify all samples (Sect. 7.2.3).

7.2.2.1 Weigh out 3.44 g of $NaHCO_3$, 3.72 g of $Na_2SO_4$, and 4.00 g of NaCl (Fluka 1627, Fluka 71959, Fisher S-271, respectively or equivalent). Quantitatively transfer these to a 100-mL volumetric flask and dilute to volume using reagent water. This solution is used to add 100 mg/L of the LSSM to all blanks, CALs and CCCs and all field samples.

**NOTE:** EPA Method 314.0 incorporated a synthetic sample matrix containing 1000 mg/L of chloride, carbonate and sulfate that yielded a pH of approximately 10. Method 314.1 uses bicarbonate which yields a pH of approximately 8.6, which more closely resembles a finished drinking water. It should be noted that pH 10 carbonate is a stronger eluent that could cause break-through of perchlorate on the Cryptand concentrator column under conditions listed for this method and should therefore not be used to prepare this solution.

7.2.3 LABORATORY SYNTHETIC SAMPLE MATRIX FORTIFICATION SOLUTION (LSSMFS) – As noted in Sect. 11.4, the capacity of the Cryptand concentrator column is set with sodium. A dilution of the LSSM Stock Solution is prepared to facilitate the addition of sodium to all field samples in an accurate manner yet without necessitating volume correction. Prepare an LSSMFS that contains the common anions chloride, sulfate and bicarbonate at 12.5 g/L as follows.

Add 50.0 mL of the LSSMSS to a 100-mL volumetric flask and dilute to volume using reagent water. The LSSMFS solution is used to add 100 mg/L of the common anions to all field samples (17 µL/2.0 mL of field sample).

7.2.4 CALIBRATION BLANK (CB) – Prepare a CB that contains 100 mg/L of the common anions to ensure effective trapping of the perchlorate by adding 400 µL of the LSSMSS to 100 mL of RW as indicated in the Table below. **The CB is used only during the initial calibration to ensure that no perchlorate or interferences are present in the CAL standards (containing 100 µg/L of the common anions) prior to calibration. The CB is not sterile filtered prior to analysis.**

7.2.5 LABORATORY FORTIFIED BLANK (LFB) – Prepare an LFB that contains 100 mg/L of the common anions by adding 400 µL of the LSSMSS to 100 mL of RW and fortifying the LFB with the appropriate volume of perchlorate PDS or SDS as indicated in the Table below. The LFB must be sterile filtered prior to analysis**.**

7.2.6 LABORATORY SYNTHETIC SAMPLE MATRIX BLANK (LSSMB) – Prepare the LSSMB by adding 4000 µL of LSSMSS to 100 mL of RW as indicated in the Table below. The LSSMB must be sterile filtered prior to analysis**.**

7.3 CALIBRATION STANDARDS (CAL) – Prepare a calibration curve from dilutions of the Perchlorate PDS, the Perchlorate SDS, and the LSSMSS using a minimum of five Calibration Standards, which span the concentration range of interest. The lowest CAL standard must be at or below the MRL. An example of the dilutions used to prepare the CAL standards used to collect the data in Section 17, are shown in the Table below.

**NOTE:** CAL standards are not processed with the sample collection devices or protocols. This step must be omitted for the CALs in order to identify any potential losses associated with the sample filtration or collection protocols.

7.4 CONTINUING CALIBRATION CHECK STANDARDS (CCC) – Prepare the CCC standards from dilutions of the Perchlorate PDS, the Perchlorate SDS, and the LSSMSS. An example of the dilutions used to prepare the CCCs that were used to collect the data in Section 17 are shown in the Table below.

**NOTE:** CCC standards are not processed with the sample collection devices or protocols. This step must be omitted for the CCCs in order to identify any potential losses associated with the sample filtration or collection protocols.

7.5 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CCC STANDARDS -- In order to continually monitor the integrity of the trapping efficiency of the concentrator column throughout an Analysis Batch, the CCCs are also prepared in a 1000 mg/L common anion synthetic matrix. These solutions are termed Laboratory Fortified Synthetic Sample Matrix (LFSSM) CCCs and are analyzed following the normal CCCs during the Analysis Batch. An example of the dilutions used to prepare the LFSSM CCCs that were used to collect the data in Section 17, are shown in the Table below. LFSSM CCCs are processed through all sample collection devices and protocols.

| PREPARATION OF CAL, CCC AND LFSSM CCC STANDARDS | | | | | | |
|---|---|---|---|---|---|---|
| **CAL and CCC Levels** | **Vol. of $ClO_4^-$ PDS (µL)** | **Vol. of $ClO_4^-$ SDS (µL)** | **Vol. of LSSMSS (µL)** | **Final Vol. of Std. (mL)** | **Final Conc. of Common Anions (mg/L)** | **Final Conc. of $ClO_4^-$ (µg/L)** |
| CB | | | 400 | 100 | 100 | 0.0 |
| LSSMB | | | 4000 | 100 | 1000 | 0.0 |
| CAL 1 | | 30 | 400 | 100 | 100 | 0.30 |
| CAL 2 | | 50 | 400 | 100 | 100 | 0.50 |
| CAL 3 | | 100 | 400 | 100 | 100 | 1.00 |
| CAL 4 | 30 | | 400 | 100 | 100 | 3.00 |
| CAL 5 | 50 | | 400 | 100 | 100 | 5.00 |
| CAL 6 | 100 | | 400 | 100 | 100 | 10.0 |
| Low-CCC | | 50 | 400 | 100 | 100 | 0.50 |
| Mid-CCC | 50 | | 400 | 100 | 100 | 5.0 |
| High-CCC | 100 | | 400 | 100 | 100 | 10 |
| Low-LFSSM CCC | | 50 | 4000 | 100 | 1000 | 0.50 |
| Mid-LFSSM CCC | 50 | | 4000 | 100 | 1000 | 5.0 |
| High-LFSSM CCC | 100 | | 4000 | 100 | 1000 | 10 |

## 8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 8.1 SAMPLE COLLECTION

8.1.1 Grab samples must be collected in accordance with conventional sampling practices.[8]

8.1.2 When sampling from a cold water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually approximately 3 to 5 minutes). Collect a representative sample from the flowing system using a beaker of appropriate size. Use this bulk sample to generate individual samples as needed. A volume of at least 20-mL is required for each individual sample.

8.1.3 When sampling from an open body of water, fill a beaker with water sampled from a representative area. Use this bulk sample to generate individual samples as needed. A volume of at least 20-mL of filtered sample is required for each individual sample.

8.1.4 Once representative samples are obtained (at the time of collection), they must be **sterile** filtered (Sect. 8.1.4.1) to remove any native microorganisms. Perchlorate is known to be susceptible to microbiological degradation by anaerobic bacteria.[9] Samples are sterile filtered to remove microbes and stored with headspace to reduce the potential for degradation by any remaining anaerobic organisms.

8.1.4.1 Remove a sterile syringe (Sect. 6.4) from its package and draw up approximately 25 mL of the bulk sample (fill the syringe). Remove a sterile syringe filter (Sect 6.3) from its package without touching the exit Luer connection. Connect the filter to the syringe making sure that no water from the syringe drops on the exterior of the filter.

Depress the syringe plunger gently and discard the first 3-5 mL. Open a sterile sample container (Sect. 6.2) without touching the interior. Using gentle pressure, pass the sample through the filter into the sample container. During this process do not let the syringe or filter make contact with the sample container. Following filtration, seal the sample container tightly, label and prepare the container for shipment. Syringes and filters are single use items and must be discarded after each sample.

8.2 SAMPLE SHIPMENT AND STORAGE – Field samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Field samples should be confirmed to be at or below 10 °C when they are received at the laboratory. Field samples stored in the lab must be held at or below 6 °C until analysis, but should not be frozen.

8.3 SAMPLE HOLDING TIMES – Field samples that are collected and stored as described in Sections 8.1 and 8.2 may be held for 28 days.

## 9. QUALITY CONTROL

9.1. Quality Control requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing field samples. This section describes each QC parameter, their required frequency, and the performance criteria that must be met in order to meet EPA data quality objectives. The QC criteria discussed in the following sections are summarized in Section 17, Tables 5 and 6. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.1.1 METHOD MODIFICATIONS – The analyst is permitted to modify the IC system, columns and separation conditions (Sect. 6.9). However, each time such method modifications are made, the analyst must repeat the procedures of the IDC (Sect. 9.2). In addition, if an alternate concentrator column is used, the procedure outlined in Section 11.4 MUST be completed before the IDC is initiated.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 10.2. Requirements for the IDC are described in the following sections and are summarized in Table 5.

9.2.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze a Laboratory Synthetic Sample Matrix Blank (LSSMB) processed through all sample collection steps outlined in Section 8.1. The LSSMB **must be sterile filtered.** Confirm that the LSSMB is reasonably free of contamination and that the criteria in Section 9.3.1 and 9.3.2 are met.

**NOTE:** It is Good Laboratory Practice to include a blank in the calibration of any instrument. As well, the method should be checked for carry-over by analyzing a LSSMB blank immediately following the highest CAL standard. If this LSSMB sample does not

meet the criteria outlined in Section 9.3.1 then carry-over is present and should be identified and eliminated.

9.2.2 DEMONSTRATION OF PRECISION – Prepare and analyze 7 replicate LFBs and LFSSMs fortified near the midrange of the initial calibration curve. All samples must be fortified and processed using the sample collection protocols described in Section 8.1. The percent relative standard deviation (%RSD) of the results of the replicate analyses must be $\leq$ 20 percent.

$$\%\,\mathrm{RSD} = \frac{\text{Standard Deviation of Measured Concentrations}}{\text{Average Concentration}} \times 100$$

9.2.3 DEMONSTRATION OF ACCURACY – Using the same set of replicate data generated for Section 9.2.2, calculate average recovery. The average recovery of the replicate values must be within ± 25 percent of the true value.

$$\%\,\mathrm{Recovery} = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100$$

9.2.4 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL based on the intended use of the method. Establish an initial calibration following the procedure outlined in Section 10.2. The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm or validate the MRL following the procedure outlined below.

9.2.4.1 Fortify and analyze seven replicate Laboratory Fortified Blanks at the proposed MRL concentration. All samples must be fortified and processed using the sample collection protocols described in Section 8.1. Calculate the mean (*Mean*) and standard deviation (S) for these replicates. Determine the Half Range for the prediction interval of results ($HR_{PIR}$) using the equation below.

$$HR_{PIR} = 3.963S$$

where $S$ is the standard deviation, and 3.963 is a constant value for seven replicates.[1]

9.2.4.2 Confirm that the upper and lower limits for the Prediction Interval of Result ($PIR = Mean \pm HR_{PIR}$) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be $\leq$ 150 percent recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be $\geq$ 50 percent recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100 \geq 50\%$$

9.2.4.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sect. 9.2.4.2). If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

9.2.5 MRL CONFIRMATION IN THE 1000 mg/L LFSSM – Fortify and analyze seven replicate LFSSMs fortified at the proposed MRL concentration. All samples must be fortified and processed using the sample collection protocols described in Section 8.1. Follow the steps outlined in Sections 9.2.4.1 to validate the MRL in the LFSSM. If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

9.2.6 CALIBRATION CONFIRMATION – Analyze a Quality Control Sample as described in Section 9.4.1 to confirm the accuracy of the calibration standards/calibration curve.

9.2.7 DETECTION LIMIT DETERMINATION (optional) -- *While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance monitoring. It is the responsibility of the laboratory to determine if DL determination is required based upon the DQOs.*

Analyses for this procedure should be done over at least 3 days. Prepare at least 7 replicate fortified LFBs using the sample collection protocols described in Section 8.1. Use the solutions described in Section 7.2.1.4 to fortify at a concentration estimated to be near the DL. This fortification concentration may be estimated by selecting a concentration at 2-5 times the noise level. The DLs in Table 2 were calculated from LFBs fortified at 0.10 $\mu$g/L. Analyze the seven replicates through all steps of Section 11.

**NOTE:** If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the DL using the following equation:

$$DL = St_{(n - 1,\ 1 - alpha\ =\ 0.99)}$$

where:

$t_{(n - 1,1 - alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = standard deviation of replicate analyses.

**NOTE: Do not subtract blank values when performing DL calculations**.

9.3 ONGOING QC REQUIREMENTS – This section describes the ongoing QC criteria that must be followed when processing and analyzing field samples. Table 6 summarizes these requirements.

9.3.1 LABORATORY REAGENT BLANK (LRB) – A LRB (Sect. 3.12) is analyzed during the IDC to confirm that potential background contaminants are not interfering with the identification or quantitation of perchlorate. If the LRB produces a peak within the retention time window of perchlorate that would prevent the determination of perchlorate, identify the source of contamination and eliminate the interference before processing field samples. Background from the method analyte or other contaminants that interfere with the measurement of perchlorate must be below $^1/_3$ of the MRL.

9.3.2 LABORATORY SYNTHETIC SAMPLE MATRIX BLANK (LSSMB) – A LSSMB (Sect. 3.14) is required with each Analysis Batch and is used to confirm that potential background contaminants are not in the LFSSM fortification solution and are not interfering with the identification or quantitation of perchlorate. If the LSSMB produces a peak within the retention time window for perchlorate that would prevent the determination of perchlorate, determine the source of contamination and eliminate the interference before processing field samples. The LSSMB must contain the LSSM at the 1000 mg/L concentration and **must be sterile filtered.** Background contamination must be reduced to an acceptable level before proceeding. Background from the method analyte or other contaminants that interfere with the measurement of perchlorate must be below $^1/_3$ of the MRL. Blank contamination may be estimated by extrapolation if the concentration is below the lowest calibration standard. This procedure is not allowed for field sample results as it may not meet the DQOs. If perchlorate is detected in the LSSMB at concentrations equal to or greater than this level, then all data for perchlorate must be considered invalid for all field samples in the Analysis Batch.

9.3.3 CONTINUING CALIBRATION CHECK STANDARDS (CCC) – CCC standards are analyzed at the beginning of each Analysis Batch, after every ten field samples, and at the end of the Analysis Batch. See Section 10.3 and Table 6 for concentration requirements and acceptance criteria.

9.3.4 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CCC STANDARDS – CCC standards are prepared in the LFSSM at the same concentration as the CCC Standards and analyzed at the same frequency as the CCCs. The LFSSM CCCs are used to ensure the integrity of the sample pre-concentration/matrix elimination step and the chromatographic separation of perchlorate from other interfering anionic species in very high ionic matrices. See Section 10.3 and Table 6 for concentration requirements and acceptance criteria.

9.3.5 LABORATORY FORTIFIED BLANK – The LFB is only required during the IDC (Sect. 9.2) and is not required to be included in the Analysis Batch due to the requirement for a LSSMB to be analyzed at the start of each Analysis Batch (Sect. 9.3.2).

9.3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of a field sample to which a known quantity of the method analyte is added. The LFSM is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFSM corrected for background concentrations.

9.3.6.1 Within each Analysis Batch, a minimum of one field sample is fortified as an LFSM for every 20 field samples analyzed. The LFSM is prepared by spiking a field sample with an appropriate amount of the Perchlorate Fortification Solution (Sect. 7.2.1.4). The fortification should be delivered in the smallest volume possible to minimize dilution of the sample. Select a spiking concentration that is equal to or greater than the native concentration, if known. Use historical data and rotate through the designated concentrations when selecting a fortifying concentration.

9.3.6.2 Calculate the percent recovery (%R) for the analyte using the equation.

$$\%R = \frac{(A - B)}{C} \times 100$$

A = measured concentration in the fortified field sample
B = measured concentration in the unfortified field sample
C = fortification concentration.

**NOTE:** If the fortified concentration is below the native concentration, the fortified value is not considered valid. The reported value should be flagged to show that the fortification level was lower than native concentration. However, the fortification frequency requirement for the method will have been met and the analysis batch data considered acceptable.

9.3.6.3 For field samples fortified at or above their native concentration, recoveries should range between 75 and 125 percent, except for low-level fortifications less than or equal to the MRL where 50 to 150 percent recoveries are acceptable. If the accuracy of perchlorate falls outside the designated range, and the laboratory performance for the analyte is shown to be in control in the CCCs and LFSSM CCCs, the recovery is judged to be matrix biased. The result for the analyte in the unfortified field sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.3.6.3.1 Field samples that have an observed positive native perchlorate concentration less than the MRL and are fortified at concentrations at or near the MRL should be corrected for the native levels in order to obtain meaningful percent recovery values. This is the only permitted use of analyte results below the MRL.

9.3.7 LABORATORY DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LD or LFSMD) – Within each Analysis Batch, a minimum of one Laboratory Duplicate (LD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD) must be analyzed. Laboratory Duplicates check the precision associated with laboratory procedures. If target analytes are not routinely observed in field samples, a LFSMD should be analyzed rather than a LD. LFSMDs check the precision associated with laboratory procedures.

9.3.7.1 Calculate the relative percent difference (RPD) for duplicate measurements ($LD_1$ and $LD_2$) using the equation.

$$RPD = \frac{\left|LD_1 - LD_2\right|}{\left(LD_1 + LD_2\right)/2} \times 100$$

9.3.7.2 RPDs for Laboratory Duplicates should be ≤ 25 percent. Greater variability may be observed when Laboratory Duplicates have analyte concentrations that are within a factor of 2 of the MRL. At these concentrations Laboratory Duplicates should have RPDs that are ≤ 50 percent. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and LFSSM CCCs, the recovery is judged to be matrix influenced. The result for that analyte in the unfortified field sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.3.7.3 If a LFSMD is analyzed instead of a Laboratory Duplicate, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation.

$$RPD = \frac{\left|LFSM - LFSMD\right|}{\left(LFSM + LFSMD\right)/2} \times 100$$

9.3.7.4 RPDs for duplicate LFSMs should be ≤ 25 percent. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within a factor of 2 of the MRL. LFSMs fortified at these concentrations should have RPDs that are ≤ 50 percent. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and LFSSM CCCs, the recovery is judged to be matrix influenced. The result for that analyte in the unfortified field sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

## 9.4 QUARTERLY QC REQUIREMENTS

9.4.1 QUALITY CONTROL SAMPLES (QCS) – As part of the IDC (Sect. 9.2), each time a new Analyte PDS (Sect. 7.2.1.2) is prepared, every time the instrument is calibrated and at least quarterly, analyze a QCS sample fortified near the midpoint of the calibration range. The QCS sample should be from a source different than the source of the calibration standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCC. Acceptance criteria for the QCS is identical to the mid- and high-level CCCs; the calculated amount for the analyte must be ± 25 percent of the true value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration for perchlorate is required before any field samples are analyzed. If alternative instrumentation and/or concentrator columns to those listed in this method are used, the procedure outlined in Section 11.4 MUST be completed before the calibration can be initiated. If the initial calibration is successful, continuing calibration check standards are required at the beginning and end of each Analysis Batch, as well as after every tenth field sample.

**NOTE:** CAL solutions and CCC standards are not processed with the sample collection protocols. This step must be omitted for the CALs and CCCs in order to identify any potential losses associated with the sample filtration or collection devices**.**

10.2 INITIAL CALIBRATION – Initial calibration is established during the IDC and may be reestablished prior to analyzing field samples. However, it is permissible to verify the calibration with daily CCCs and LFSSM CCCs. Calibration must be performed using peak areas and the external standard technique. Calibration using peak heights is not permitted.

NOTE: In this method, the CB, LFB, CAL, QCS and CCC standards are prepared in RW fortified with 100 mg/L of the LSSM to ensure optimal trapping of perchlorate. The CB, LFB, LRB, CAL, QCS and CCC standards are not sterile filtered. The CB is used only in the IDC. On the other hand, **the LSSMB represents a drinking water matrix containing 3000 mg/L of common anions and is used in all Analysis Batches and must be sterile filtered**.

10.2.1 INSTRUMENT CONDITIONS – Establish proper operating conditions. Operating conditions used during method development are described in Section 17 Table 1A. Conditions different from those described may be used if the IDC QC criteria in Section 9.2 are met.

10.3 CALIBRATION STANDARDS – Prepare a set of at least five CAL standards as described in Section 7.3. The lowest concentration CAL standard must be at or below the MRL. The MRL must be confirmed using the procedure outlined in Section 9.2.4, after establishing the initial calibration.

10.3.1 CALIBRATION – The conductivity detector is calibrated using the external standard technique. Calibration curves may be generated using the IC data system through the use of a first (linear) or second (quadratic) order calibration curves.

10.3.2 CALIBRATION ACCEPTANCE CRITERIA – The validation of the calibration is determined by calculating the concentration of the analyte from each of the analyses used to generate the calibration curve. Each calibration point, except the lowest (≤ MRL), for the analyte should calculate to be 75 to 125 percent of its true value. The lowest point should calculate to be 50 to 150 percent of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. Corrective action must be taken to reanalyze the calibration standards, restrict the range of calibration, or select an alternate method of calibration.

10.4 CONTINUING CALIBRATION CHECK (CCC) STANDARDS – The CCCs verify the calibration at the beginning and end of each group of analyses, as well as after every 10th field sample during analyses. The LRBs, LFBs, LFSSMs, LFSMs, LFSMDs, CCCs and LFSSM CCCs are not counted as field samples. The beginning CCCs for each Analysis Batch must be at or below the MRL in order to verify instrument sensitivity and the accuracy of the calibration curve prior to the analysis of any field samples. Subsequent CCCs should alternate between a medium and high concentration.

**NOTE:** The analyst may chose to also run a mid-level CCC at the start of an Analysis Batch.

10.4.1 Inject an aliquot of the CCC standards and analyze with the same conditions used during the initial calibration.

10.4.2 Calculate the concentration of the analyte in the CCC standards. The calculated amount for the analyte for medium and high level CCCs must be ± 25 percent of the true value. The calculated amount for the lowest CCC level for the analyte must be within ± 50 percent of the true value. If these conditions do not exist, then all data for the analyte must be considered invalid, and remedial action (Sect. 10.4.4) should be taken which may require recalibration. Any field samples that have been analyzed since the last acceptable calibration verification and are still within holding time should be reanalyzed after adequate calibration has been restored.

10.4.3 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CCC STANDARDS – As noted in Section 9.3.4, LFSSM CCCs Standards are prepared and analyzed to verify the integrity of the concentrator column during the Analysis Batch to ensure that high ionic strength drinking water matrices will not exceed the capacity of the concentrator column. These QC samples are fortified at the same level and run at the same frequency as the CCC Standards and are required to meet the same recovery criteria (Sect. 10.4.2).

10.4.4 REMEDIAL ACTION – Failure to meet CCC or LFSSM CCC QC performance criteria may require remedial action. Maintenance such as confirming the integrity of the trapping efficiency of the concentrator column and matrix elimination step or regenerating or replacing the IC columns will require re-calibration (Sect. 10.2).

## 11. PROCEDURE

11.1 Important aspects of this analytical procedure include proper field sample collection and storage (Sect. 8.1), ensuring that the instrument is properly calibrated (Sect. 10.2) and that all required QC are met (Sect. 9) during the Analysis Batch. This section describes the procedures for field sample preparation and analysis. If alternative instrumentation and/or concentrator columns to those listed in this method are used, the procedure outlined in Section 11.4 MUST be followed prior to analyzing field samples.

11.2 SAMPLE PREPARATION

11.2.1 Collect and store field samples as described in Section 8.1.

11.2.2 Process all LSSMBs, LFSMs and LFSMDs using the sample collection protocols is Section 8.1.

11.2.3 Transfer a 2.0-mL aliquot of each field or QC Sample to an autosampler vial. Add 17 uL of the LSSMFS (Sect. 7.2.3) to all field sample autosampler vials. Place the autosampler vial in the appropriate position.

11.2.4 For each QC standard and field sample to be analyzed, prepare a second autosampler vial containing 1.0 mL of the 10mM NaOH rinse solution with the filter cap raised to signify a rinse vial. Place the rinse vials in the autosampler rack, after every QC standard and field sample.

11.3 SAMPLE ANALYSIS

11.3.1 Establish the instrument operating conditions as described in Table 1A of Section 17. Confirm that the analyte retention times for the calibration standards are stable.

**NOTE:** The ionic strength of the common anion solution used to prepare the LFSSM CCCs will cause these solutions to have shorter retention times (see Sect. 11.3.4.1).

11.3.2 Establish a valid initial calibration following the procedures outlined in Section 10.2 or confirm that the calibration is still valid by running a low-level CCC as described in Section 10.4. If establishing an initial calibration for the first time, complete the IDC as described in Section 9.2.

11.3.3 Analyze field and QC samples at their required frequencies using the same conditions used to collect the initial calibration. Table 7 shows an acceptable analytical sequence that contains all method-required QC samples.

11.3.4 COMPOUND IDENTIFICATION – Establish an appropriate retention time window for perchlorate to identify it in QC and field sample chromatograms.

11.3.4.1 High ionic strength matrices have the potential to cause an increase in background conductivity and severe tailing as other anions elute from the column and cause the perchlorate retention time to decrease.

**NOTE:** As a result of the difference in ionic strength of the 100 and 1000 mg/L common anion matrices, the retention time for perchlorate in the 1000 mg/L matrix is approximately 0.2 minutes shorter than in the 100 mg/L matrix (the higher ionic strength matrix may act as a stronger eluent) using the conditions outlined in Table 1A. Since the ionic strength of drinking water matrices may vary considerably, **the RT window for perchlorate must be set wide enough to account for the variability in the ionic strength of the drinking water matrices and yet exclude any potential interfering peaks.** A window of approximately 0.4 minutes has been found to be acceptable; however setting the window too wide may require additional analyses on the confirmation column.

11.3.4.2 COMPOUND CONFIRMATION – Field samples that have a perchlorate result on the primary column at or above the MRL require confirmation with a second analytical column that has a dissimilar separation mechanism. EPA Methods 331.0 and 332.0 can be used for confirmation of perchlorate results obtained using EPA Method 314.1.

11.3.5 EXCEEDING CALIBRATION RANGE – The analyst must not extrapolate above the established calibration range. If an analyte result exceeds the range of the initial calibration curve, the field sample may be diluted with reagent water and the diluted field sample re-injected (the LSSMFS must be added to the diluted field sample prior to analysis). Incorporate the dilution factor into final concentration calculations. The dilution will also affect the perchlorate MRL.

11.4 CONCENTRATOR COLUMN EVALUATION – This method was developed with a Dionex Cryptand C1 concentrator column. Alternate columns are allowed, but prior to their use, they must be evaluated to optimize sample injection volume, to confirm that the matrix elimination step does not remove perchlorate, and to confirm that the perchlorate is quantitatively transferred to and refocused on the guard column prior to separation on the analytical column. The entire success of this method is totally dependent upon development of column combinations that accomplish the aforementioned protocols. The procedure is challenging and requires very experienced IC chemists to evaluate alternative concentrator column/guard and analytical column combinations using the procedures described below.

11.4.1 CONCENTRATOR COLUMN CAPACITY DETERMINATION – Any concentrator column that provides effective retention/trapping and eventual release of perchlorate while providing the resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. However, prior to use, the capacity of the concentrator column must be evaluated. The analyst must demonstrate the ability to load (or concentrate) at least 2.0 mL of a 5.0 µg/L perchlorate standard in the 1000 mg/L LFSSM (the loading volume required to obtain the data presented in this method) without exceeding more than 80% of the capacity of the concentrator column. This requirement ensures that the addition of the 1000 mg/L of common anions to the field samples will not exceed the capacity of the concentrator column.

11.4.1.1 Prepare 100-mL of the 5.0 µg/L LFSSM CCC according to directions in Table 1. Load increasing volumes of the LFSSM CCC (1.0, 2.0, 3.0, 4.0 and 5.0-mL, smaller increments may be used if desired) using the procedure outlined for sample preparation and analysis sections (Sect. 11.2, 11.3). Observe when perchlorate break-through occurs (i.e., no further increase in observed perchlorate peak area or concentration). Plotting the peak area or concentration versus load volume (as a histogram) will establish the volume at which break-though of the perchlorate becomes evident. At this point, 100% of the capacity of the concentrator column has been exceeded. Ensure that the load volume to be used does not exceed the 80% restriction. It is recommended that this procedure be reproduced at least twice to confirm the break-through point.

11.4.2 EVALUATION OF MATRIX ELIMINATION CONDITIONS – Prior to use of a concentrator column other than the one listed in this method, the matrix elimination protocols must be evaluated in order to ensure that the perchlorate is retained on the concentrator column while the interfering matrix anions are removed (to an acceptable level) and sent to waste.

11.4.2.1 Once the load volume has been established, this can be accomplished by rinsing the concentrated perchlorate (on the concentrator column) with different concentrations and volumes of rinse solution. Prepare several weak NaOH rinse solutions (0.50, 1.0 and 1.5 mM). Prepare several autosampler vials containing the optimized volume of the 5.0 µg/L LFSSM CCC. Prepare several autosampler rinse vials containing different volumes of the NaOH rinse solutions (0.50, 1.0 and 1.5-mL) and analyze using the procedure outlined for sample preparation and analysis sections (Sect. 11.2, 11.3). Choose a concentration and volume that will meet the above criteria. The background conductivity must be less than 1.5 µS when perchlorate elutes in order to obtain data similar to that reported in Tables 2, 3, and 4.

11.4.2.1.1 The rinse solution used to collect this data was 1.0 mL of 10 mM NaOH, prepared from 50% NaOH by diluting 0.8 g of 50% NaOH to 1L with RW. In order to prevent accumulation of carbonate in the rinse solution, the rinse solution is stored, under helium, in a pressurized vessel fitted with a two-way valve on the out line in order to withdraw the rinse solution as required. This rinse solution is prepared fresh weekly.

11.4.3 EVALUATION OF WASH STEP CONDITIONS – Prior to use of a concentrator column other than the one listed in this method, the wash step, which elutes the perchlorate off the concentrator column and refocuses it at the head of the guard column, must be evaluated. The wash step ensures quantitative transfer of the concentrated perchlorate to the guard column head and minimizes band-broadening by ensuring that the perchlorate is efficiently refocused on the guard column before the eluent strength is increased to effect separation and detection of the perchlorate on the analytical column. These steps are critical to method performance and were carefully optimized for the Cryptand concentrator column during method development.

11.4.3.1 Once the load volume and rinse solution concentration and volume have been established, evaluation of the wash step conditions is accomplished by removing the guard and analytical columns from the system and connecting the concentrator column directly to the conductivity detector. Use the EG50 to prepare the wash solutions or use the manually prepared NaOH wash solutions (0.50, 1.0 and 1.5 mM). Using the optimized load volume and rinse solution determined above, use the 5.0 µg/L LFSSM CCC and rinse solution and modify the method to allow different rinse times (10, 12 and 15 minutes) and concentrations of wash solution to be evaluated using the procedure outlined for sample preparation and analysis sections (Sect. 11.2, 11.3). Observe the time at which all the perchlorate has eluted from the concentrator column (baseline returned minimum conductance). The addition of a couple of minutes will ensure complete removal of perchlorate from the concentrator column in all matrices. The 12 minute wash step for this

method provides a non-Gaussian peak that shows when the conductivity baseline has returned to the minimum.

11.4.3.2 After establishing the optimal load volume, rinse solution concentration and volume and wash time, concentration and volume, analyze a low-level CCC and LFSSM CCC to ensure that the optimal conditions chosen provide acceptable chromatography and peak shape and area for perchlorate.

11.4.3.2.1 The EG50 was used to prepare the wash solution (0.50 mM NaOH for 12 minutes) used to collect the data reported in Tables 2, 3, and 4. If the manually prepared wash solution is used, the same precautions to prevent accumulation of carbonate in the wash solution are required. This wash solution is prepared fresh weekly.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify the analyte present in the field and QC samples as described in Section 11.3.4.

**NOTE:** Since the ionic strength of the drinking water matrices can vary dramatically, and perchlorate elutes on the trailing edge of the residual anions present in the sample, the background conductivity is not the same for all injections. Consequently, the slope of the baseline when perchlorate elutes may vary from sample to sample. As a result, it is quite possible that the pre-set, auto- integration parameters may not start and stop peak integration the same for every sample. Therefore, the analyst must thoroughly review all chromatograms and some of the chromatograms may require manual integration of the perchlorate peak.

12.2 Calculate the perchlorate concentrations using the multi-point calibration established in Section 10.2. Quantify only those values that fall between the MRL and the highest calibration standard. Field samples with target analyte responses that exceed the highest calibration standard require dilution and reanalysis (Sect. 11.3.5).

12.2.1 As noted in Section 9.3.2, it may be necessary to extrapolate below the MRL to estimate contaminants in LRBs and LSSMBs and to correct for native levels of perchlorate below the MRL when field samples are fortified at or near the MRL. These are the only permitted use of analyte results below the MRL.

12.3 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

12.4 Prior to reporting data, the laboratory is responsible for assuring that QC requirements have been met or that any appropriate qualifier is documented.

## 13. METHOD PERFORMANCE

13.1 PRECISION, ACCURACY AND DETECTION LIMITS – Tables for these data are presented in Section 17. Instrumental conditions are presented in Table 1A. The LCMRL for perchlorate with both the AS16 and AS20 columns is presented in Table 2 and was calculated

using a procedure described elsewhere.[1] Single laboratory precision and accuracy data are presented in Tables 3 and 4.

13.2 Figure 1 is a representative chromatogram showing the separation of perchlorate from 4-Cl BSA and Figure 2 shows a chromatogram of a surface and a ground water fortified with 1.0 µg/L perchlorate and Figure 3 shows a chromatogram of 3.0 $\mu$g/L $ClO_4^-$ in the 50, 500 and 1000 mg/L LSSM.

## 14. POLLUTION PREVENTION

14.1 For information about pollution prevention that may be applicable to laboratory operations, 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 Street N.W., Washington, D.C., 20036, or on-line at: http://www.ups.edu/community/storeroom/Chemical_Wastes/wastearticles.htm.

## 15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and 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 in Section 14.1, or on-line at: http://www.p2pays.org/ref/01/text/00779/ch15.htm.

## 16. REFERENCES

1. Revisions to the Unregulated Contaminant Monitoring Regulation for Public Water Systems, Proposed Rule, 2004.

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4. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

5. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Blosse, P.T., Boulter, E.M., Sundaram, S., “Diminutive Bacteria Implications for Sterile Filtration”, Pall Corporation, East Hills, NY.

8. ASTM Annual Book of Standards, Part II, Volume 11.01, D3370-82, “Standard Practice for Sampling Water,” American Society for Testing and Materials, Philadelphia, PA, 1986.

9. Xu, J., Y. Song, B. Min, L. Steinberg, and B.E. Logan. 2003. Microbial degradation of perchlorate: principles and applications. Environ. Engin. Sci, 20(5): 405-422.

## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

### TABLE 1.A. INSTRUMENTAL CONDITIONS

**Standard Conditions and Equipment for Primary Analyses [(a)]:**

| | |
|---|---|
| Ion Chromatograph: | Dionex DX500 |
| Pump | GP40, 2-mm microbore |
| Conductivity Suppressor: | Dionex 2-mm Ultra II ASRS external water mode, 100 mA |
| Chromatography Module | Dionex LC30, temperature controlled at 35 °C |
| Detector: | Dionex CD20 suppressed conductivity detector, background conductivity: 1.0 µS |
| Eluent Generator EG50: | 0.50, 65 and 100 mM NaOH (see Table 1B) |
| Autosampler: | Dionex AS40 |
| Columns : | Concentrator column Dionex Cryptand C1, 4 x 35-mm<br>Guard column Dionex AG16, 2 x 50-mm<br>Analytical column Dionex AS16, 2 x 250-mm |
| Sample loop: | Cryptand C1 concentrator column [(b)] |
| Load Volume: | 2.0 mL of sample |
| Rinse Solution: | 1.0 mL of 10 mM NaOH |
| Eluent Flow: | 0.25 mL/min |
| Typical System Back-pressure: | 2350 psi |
| Total analysis time: | 43 minutes |

(a) Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
(b) See Section 11.4

**Standard Conditions and Equipment for Confirmation Analyses [(a)]:**

| | |
|---|---|
| Ion Chromatograph: | Dionex DX500 |
| Pump | GP40, 2-mm microbore |
| Conductivity Suppressor: | Dionex 2-mm Ultra II ASRS external water mode, 100 mA |
| Chromatography Module | Dionex LC30, temperature controlled at 35 °C |
| Detector: | Dionex CD20 suppressed conductivity detector, background conductivity: 1.0 µS |
| Eluent Generator EG50: | 0.50, 65 and 100 mM NaOH (see Table 1B) |
| Autosampler: | Dionex AS40 |
| Columns : | Concentrator column Dionex Cryptand C1, 4 x 35-mm<br>Guard column Dionex AG20, 2 x 50-mm<br>Analytical column Dionex AS20, 2 x 250-mm |
| Sample loop: | Cryptand C1 concentrator column [(b)] |
| Load Volume: | 2.0 mL of sample |
| Rinse Solution: | 1.0 mL of 10 mM NaOH |
| Eluent Flow: | 0.25 mL/min |
| Typical System Back-pressure: | 2350 psi |
| Total analysis time: | 48 minutes |

(a) Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
(b) See Section 11.4

**TABLE 1.B. TIMING SEQUENCE FOR EPA METHOD 314.1 WITH AS16 and AS20 COLUMNS**

| Time | Eluent | Duration | Command | Function |
|---|---|---|---|---|
| -13.60 | 100 mM | 0.01 sec | Pump_Relay_1.Open | Initiates the program |
| -13.599 | 100 mM | 138 sec | Pump_Relay_1.Closed | Starts the AS40 |
| -5.010 | 100 mM | | Start change to 0.50 mM | Change to 0.50 mM |
| -5.000 | 0.50 mM | | Change to 0.50 mM | Establish 0.50 mM in columns |
| 0.000 | 0.50 mM | | ECD.Autozero | Auto-zero the detector |
| | 0.50 mM | | ECD_1.Acqon | Start data collection |
| | 0.50 mM | 1740 sec | Pump_InjectValve.InjectPosition | Switch concentrator column to inject position, elute perchlorate off trap & refocus on AG16 |
| 11.999 | 0.50 mM | | Start change to 65 mM | Change to 65 mM |
| 12.000 | 65 mM | | Change to 65 mM | Separate & detect perchlorate |
| 24.999 | 65 mM | | Start change to 100 mM | Change to 100 mM |
| 24.500 | 100 mM | | Change to 100 mM | Clean columns & establish capacity of trap column |
| 29.000 | 100 mM | | Pump_InjectValve.LoadPosition (1740 sec) | Switch concentrator column to load position |
| 30.000 | 100 mM | | ECD_1.Acqoff | Stop data collection |
| 30.000 | 100 mM | | Wait/end | Eluent Generator ready to start next run |

Minor changes for AS20 columns

Increase the run time to 35 minutes to allow for the fact that perchlorate elutes about 4 minutes later on the AS20 column.

**TABLE 2. LOWEST CONCENTRATION MRL AND DLs FOR PERCHLORATE**

| Analytical Column | Analyte | LCMRL[a] (µg/L) | *DL (µg/L) |
|---|---|---|---|
| AS16 | $ClO_4^-$ | 0.14 | 0.03[b] |
| AS20 | $ClO_4^-$ | 0.13 | 0.03 [b] |

[a]LCMRLs were calculated according to the procedure in reference 1
*The DL was calculated from data acquired on a single day
[b]Replicate fortifications at 0.10 µg/L

**TABLE 3. IC PRECISION AND RECOVERY DATA FOR PERCHLORATE IN VARIOUS MATRICES WITH AS16 COLUMNS (n=7)**

| Matrix | Unfortified Concentration (µg/L) | Fortified Concentration (µg/L) | Mean % Recovery | % RSD |
|---|---|---|---|---|
| *Reagent Water | <0.14** | 0.50 | 102 | 2.6 |
| | <0.14** | 5.0 | 90.0 | 3.2 |
| Chlorinated Surface Water | 0.63 | 1.0 | 82.6 | 2.7 |
| | 0.63 | 5.0 | 85.8 | 2.0 |
| Chloraminated Surface Water | <0.14** | 1.0 | 83.1 | 3.6 |
| | <0.14** | 5.0 | 89.3 | 1.8 |
| Chlorinated Ground Water | <0.14** | 1.0 | 75.9 | 5.4 |
| | <0.14** | 5.0 | 92.4 | 3.3 |
| ***LFSSM | <0.14** | 0.50 | 102 | 2.8 |
| | <0.14** | 5.0 | 80.9 | 1.3 |

* Reagent water containing 100 mg/L LSSM. **The LCMRL = 0.14 ug/L for the AS16 column.
***LFSSM Reagent water containing 1000 mg/L LSSM. Described in Section 3.11 and 3.13.

**TABLE 4. IC PRECISION AND RECOVERY DATA FOR PERCHLORATE IN VARIOUS MATRICES WITH AS20 COLUMNS (n=7)**

| Matrix | Unfortified Concentration (µg/L) | Fortified Concentration (µg/L) | Mean % Recovery | % RSD |
|---|---|---|---|---|
| *Reagent Water | <0.13** | 0.50 | 104 | 5.3 |
| | <0.13** | 5.0 | 94.2 | 1.5 |
| Chloraminated Surface Water | <0.13** | 0.50 | 108 | 2.2 |
| | <0.13** | 5.0 | 97.8 | 2.0 |
| Chlorinated Ground Water | 0.22 | 0.50 | 96.2 | 9.4 |
| | 0.22 | 5.0 | 98.0 | 0.70 |
| **LFSSM | <0.13** | 0.50 | 97.4 | 4.4 |
| | <0.13** | 5.0 | 86.3 | 1.3 |

* Reagent water containing 100 mg/L LSSM. **The LCMRL = 0.13 ug/L for the AS20 column.
**LFSSM Reagent water containing 1000 mg/L LSSM. Described in Section 3.11 and 3.13.

**TABLE 5. INITIAL DEMONSTRATION OF CAPABILITY QUALITY CONTROL REQUIREMENTS**

| Method Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Section 9.2.1 | Demonstration of Low System Background | Analyze a LRB and LFSSMB prior to any other IDC steps. | Demonstrate that perchlorate is below 1/3 of the MRL and that possible interferences from sampling protocols do not prevent the identification and quantification of perchlorate. |
| Section 9.2.4 | Minimum Reporting Limit (MRL) Confirmation | Fortify and analyze 7 replicate LFBs at the proposed MRL concentration. Calculate the mean and the Half Range (HR). Confirm that the Upper PIR and Lower PIR (Sect. 9.2.4) meet the recovery criteria. | Section 9.2.4.2<br><br>Upper PIR ≤ 150%.<br><br>Lower PIR ≥ 50%. |
| Section 9.2.2 | Demonstration of Precision | Analyze 7 replicate LFBs fortified near the mid-point of the calibration curve | %RSD must be ≤ 20%. |
| Section 9.2.3 | Demonstration of Accuracy) | Calculate average recovery for replicates used in Section 9.2.3. | Mean recovery ± 25% of true value. |
| Section 9.2.5 | Validation of MRL in 1000 mg/L LFSSM | Analyze 7 replicate LFSSMs fortified at the MRL. | Section 9.2.4.2<br><br>Upper PIR ≤ 150%.<br><br>Lower PIR ≥ 50%. |
| Section 9.4.1 | Quality Control Sample | During IDC, each time a new analyte PDS is made, every time the instrument is calibrated and at least quarterly. | The result for perchlorate must be 75-125% of the true value. |

**TABLE 6. ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY)**

| Method Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Section 10.2 | Initial Calibration | Use external standard calibration technique to generate a first or second order calibration curve. Use at least 5 standard concentrations.<br>Check the calibration curve as described in Section 10.2.<br><br>Analyze a QCS near the mid-point of the calibration curve. | When each calibration standard is calculated as an unknown using the calibration curve, the result should be:<br><br>Level — Result<br>≤ MRL ± 50% True value<br><br>> MRL ± 25% True value to high CAL<br><br>The result for perchlorate must be 75-125% of the true value.<br><br>Recalibration is recommended if these criteria are not met. |
| Section 9.3.2 | Laboratory Synthetic Sample Matrix Blank (LSSMB) | Daily, or with each Analysis Batch of up to 20 field samples, whichever is more frequent. | Demonstrate that the perchlorate is below $^1/_3$ the MRL, and confirm that possible interferences do not prevent quantification of perchlorate. If the target exceeds $^1/_3$ the MRL, the results for perchlorate in the Analysis Batch are invalid. |
| Section 9.3.3 | Continuing Calibration Check (CCC) Standards | Verify initial calibration by analyzing a low-level CCC at the beginning of each Analysis Batch. Subsequent CCCs are required after every 10 field samples, and after the last field sample in a batch.<br><br>Low CCC – at or below the MRL concentration<br>Mid CCC – near midpoint in calibration curve<br>High CCC – near the highest calibration standard. | For each CCC the result must be<br><br>CCC Level — Result<br>≤ MRL ± 50% True value<br><br>> MRL ± 25% True value to high CAL |

**TABLE 6. (Continued)**

| Method Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Section 9.3.4 | Laboratory Fortified Synthetic Sample Matrix CCCs (LFSSM CCC) | In order to monitor trapping efficiency during an Analysis Batch, the CCC standards, prepared in the LFSSM (Sect. 9.3.3) are also required at the same frequency and concentrations. | For each LFSSM CCC the result must be<br><br>CCC Level — Result<br>≤ MRL — ± 50% True value<br><br>> MRL to high CAL — ± 25% True value |
| Section 9.3.6 | Laboratory Fortified Sample Matrix (LFSM) | Analyze one LFSM per Analysis Batch (20 field samples or less). Fortify the LFSM with perchlorate at a concentration close to but greater than the native concentration (if known). Calculate LFSM recoveries. | Recoveries for the LFSM must be calculated (Sect. 9.3.6.3 ). The result must be<br><br>LFSM Level — Result<br>≤ MRL — ± 50% True value<br><br>> MRL to high CAL — ± 25% True value |
| Section 9.3.7 | Laboratory Duplicate (LD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD) | Analyze at least one LD or LFSMD daily, or with each Analysis Batch (20 samples or less), whichever is more frequent. | Precision must be calculated (Sect. 9.3.7.2). The result must be<br>Level — Result<br>≤ 2 x MRL — ≤ 50% RPD<br><br>2 x MRL to high CAL — ≤ 25% RPD |
| Section 9.4.1 | Quality Control Sample (QCS) | During IDC, each time a new analyte PDS is made, every time the instrument is calibrated and at least quarterly. | Results must be ± 25% of the expected value. |
| Section 8.3 | Sample Holding Time | 28 days when processed and stored according to sections 8.1 and 8.2 with appropriate preservation and storage. | Sample results are valid only if samples are extracted within sample holding time. |

**TABLE 7. SAMPLE ANALYSIS BATCH WITH QC REQUIREMENTS**

| Injection # | Sample Description | Acceptance Criteria |
|---|---|---|
| 1 | **Laboratory Synthetic Sample Matrix Blank (LSSMB)** | ≤ 1/3 MRL |
| 2 | Low-CCC at the MRL (0.5 µg/L) | 0.25 to 0.75 µg/L |
| 3 | Low-Laboratory Fortified Synthetic Sample Matrix CCC (LFSSM CCC @ 0.5 µg/L) | 0.25 to 0.75 µg/L |
| 4 | Sample 1 | sample analysis |
| 5 | Sample 2 | sample analysis |
| 6 | Sample 2 - Laboratory Fortified Sample Matrix (LFSM) | Recovery of 75 - 125% |
| 7 | Sample 2 - Laboratory Fortified Sample Matrix Duplicate (LFSMD) | %RPD = ± 25% |
| 8 | Sample 3 | sample analysis |
| 9 | Sample 4 | sample analysis |
| 10 | Sample 5 | sample analysis |
| 11 | Sample 6 | sample analysis |
| 12 | Sample 7 | sample analysis |
| 13 | Sample 8 | sample analysis |
| 14 | Sample 9 | sample analysis |
| 15 | Sample 10 | sample analysis |
| 16 | Mid-CCC at 5.0 µg/L | 3.75 – 6.5 µg/L |
| 17 | Mid-Laboratory Fortified Synthetic Sample Matrix CCC (LFSSM CCC @ 5.0 µg/L) | 3.75 – 6.5 µg/L |
| 18 | Sample 11 | sample analysis |
| 19 | Sample 12 | sample analysis |

**CONTINUED on NEXT PAGE**

**TABLE 7. (Continued)**

| Injection # | Sample Description | Acceptance Criteria |
|---|---|---|
| 20 | Sample 13 | sample analysis |
| 21 | Sample 14 | sample analysis |
| 22 | Sample 15 | sample analysis |
| 23 | Sample 16 | sample analysis |
| 24 | Sample 17 | sample analysis |
| 25 | Sample 18 | sample analysis |
| 26 | Sample 19 | sample analysis |
| 27 | Sample 20 | sample analysis |
| 28 | High-CCC at 10 μg/L | 7.5 – 12.5 μg/L |
| 29 | High-Laboratory Fortified Synthetic Sample Matrix CCC (LFSSM CCC @ 10 μg/L) | 7.5 – 12.5 μg/L |

**Figure 1**

**EPA METHOD 314.1 CHROMATOGRAM of 5.0 $\mu$g/L $ClO_4^-$ and 300 $\mu$g/L 4-ClBSA WITH IONPAC AS16 AND AS20 COLUMNS**

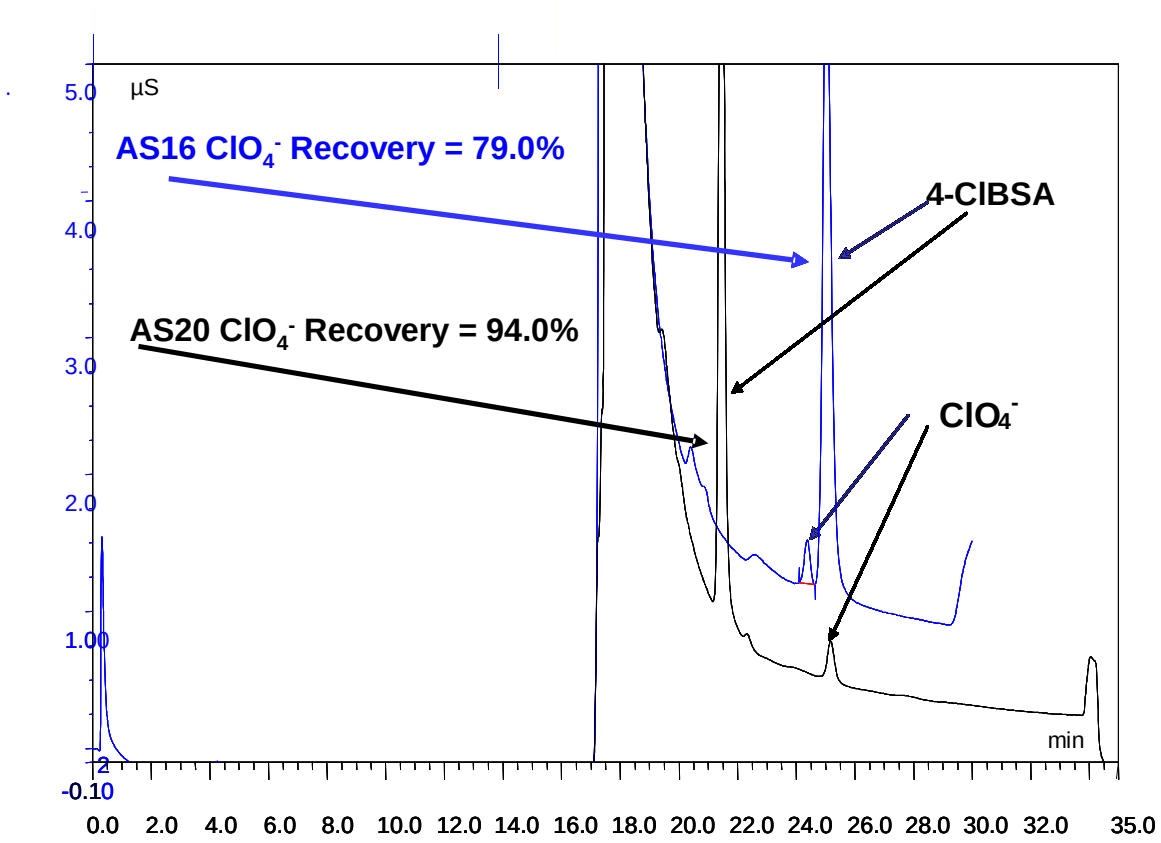

**Figure 2**

**IC CHROMATOGRAM of SURFACE and GROUND WATER FORTIFIED WITH 1.0 µg/L $ClO_4^-$**

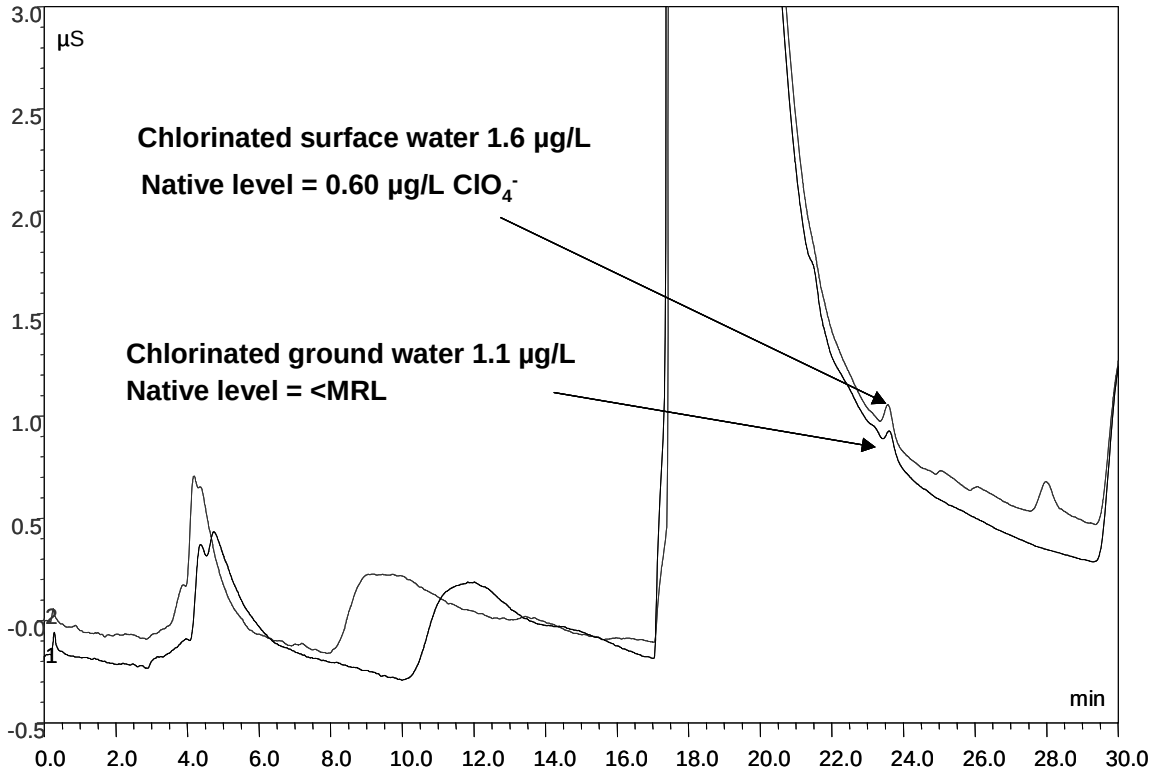

**Figure 3**

**IC CHROMATOGRAM of 3.0 µg/L $ClO_4^-$ in 50, 500 and 1000 mg/L LSSM WITH the IONPAC AS16 COLUMN**