

**Title: DETERMINATION OF PERCHLORATE BY ION  
CHROMATOGRAPHY  
EPA Method 314.0**

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## 1.0 SCOPE AND APPLICATION

1.1 EPA Method 314.0 is used to determine perchlorate in finished drinking water, surface water, reagent water and groundwater.

1.2 The standard reporting limit for perchlorate is 4.0 µg/L. Depending on sample matrix and MDL level, a reporting limit as low as 1.0 µg/L is possible.

1.3 See attached summary for MDL, reporting limit, and QC information (Attachment 1)

1.4 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

## 2.0 SUMMARY OF METHOD

A fixed volume of sample (usually 1000 µL) is introduced into an ion chromatographic system. Perchlorate is separated and measured, using an IonPac AS16 analytical column (or equivalent), and suppressed conductivity detection with an external water mode to quantify perchlorate at low levels.

## 3.0 DEFINITIONS

3.1 **A/H**—Peak Area to Height Ratio. The ratio of the peak area divided by the peak height which is used to monitor analytical performance.

3.2 **ICCS**—Initial Calibration Check Standard. A calibration standard solution at the MRL concentration and used to verify a previously established calibration.

3.3 **IPC-MA**—Instrument Performance Check Solution in Mixed Anion Matrix. A solution containing a specific concentration of primary source perchlorate in a matrix of other test substances (namely chloride, sulfate, carbonate) and used to evaluate instrument performance with respect to a defined set of criteria.

3.4 **MCT**—Matrix Conductivity Threshold. The highest permitted conductance of a sample, which is used to determine when matrix dilution or pretreatment is required.

3.5 **LCS**—Laboratory Control Sample. A solution containing a specific concentration of perchlorate from a same source as the calibration standard.

3.6 **ICV**—Initial Calibration Verification. A solution containing a specific concentration of perchlorate from a source separate from that used for the calibration standards (i.e. second source). ICV=QCS (Quality Control Standard).

3.7 See the laboratory QA manual and EPA Method 314.0 for additional definitions.

## 4.0 INTERFERENCES

4.1 Contaminants in the reagent water, reagents, glassware, or other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms, may cause method interferences.

4.2 Samples that contain particles larger than 0.45 microns require filtration to prevent damage to instrument columns and flow systems.

4.3 Pretreatment cartridges are effective in removing certain matrix interference. An additional pretreated matrix spike/matrix spike duplicate, Laboratory Control Sample, and a Method Blank are analyzed when samples need pretreatment.

4.4 High concentrations of anions interfere with the baseline of perchlorate. All samples must be monitored for conductivity prior to analysis. If the Matrix Conductivity Threshold (MCT) is exceeded, sample dilution and/or pretreatment are necessary.

**4.5** As this method measures perchlorate based only on column retention time and electro-conductivity detection, other analytes sharing these characteristics may be mistakenly identified as perchlorate. If further verification is required, samples may be spiked with a known concentration of perchlorate a retention time noted or they may be analyzed on a method with more rigorous qualitative criteria such as ICMS

**5.0 SAFETY**

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

**5.1 Specific Safety Concerns or Requirements**

Personal Protective Equipment Required: Safety Glasses, Lab coat, Nitrile Gloves

**5.2 Primary Materials Used**

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sodium Hydroxide	Corrosive	2 mg/m <sup>3</sup> - Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Perchlorate	Strong oxidizer	Not Listed	Very hazardous in case of skin contact, of eye contact, of ingestion, of inhalation. Prolonged exposure may result in skin burns. Over-exposure by inhalation may cause respiratory irritation. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

1 – Exposure limit refers to the OSHA regulatory exposure limit.

**6.0 EQUIPMENT AND SUPPLIES**

**6.1 Instrumentation**

- 6.1.1 Dionex DX-500 Ion Chromatograph or equivalent
- 6.1.2 Analytical column: IonPac AS16 Analytical; 4x250 mm (P/N 055346)
- 6.1.3 Guard column: IonPac AG16 Guard; 4x50 mm (P/N 055377)
- 6.1.4 Suppressor column: ASRS, 4mm
- 6.1.5 Conductivity meter

**6.2 Supplies**

- 6.2.1 Analytical balance
- 6.2.2 Pipettes and disposable pipette tips
- 6.2.3 3 ml syringes
- 6.2.4 10 ml syringe
- 6.2.5 50 and 100 ml volumetric flasks
- 6.2.6 15 ml disposable test tubes
- 6.2.7 0.20  $\mu$ m filters
- 6.2.8 Matrix pretreatment cartridges—barium form (Dionex OnGuard-Ba or equiv.)
- 6.2.9 Matrix pretreatment cartridges—silver form (Dionex OnGuard-Ag or equiv.)
- 6.2.10 Matrix pretreatment cartridges—hydrogen form (Dionex OnGuard-H or equiv.)

**7.0 REAGENTS AND STANDARDS****7.1 Reagents**

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

- 7.1.1 Laboratory Reagent Grade Water (De-ionized water, Type II reagent grade, with a resistance of 17.8 M $\Omega$ -cm or better)
- 7.1.2 Sodium Hydroxide (NaOH) 50% w/w
- 7.1.3 Mixed common anion stock solution (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>)
- 7.1.4 Conductivity meter calibration solution (Potassium chloride) ( approximately 10 mS)

**7.2 Standards**

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable) source material.

All prepared standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

- 7.2.1 Sodium Perchlorate 99% ACS reagent grade or better ( NaClO<sub>4</sub>, CASRN 7601-89-0)
- 7.2.2 Perchlorate standard 1000 ppm from Spex or equivalent source

**8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE**

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Glass or plastic bottles	100 mL	Cool >0 to 6°C  Headspace required	28 days	EPA 314.0
Soil	Sleeve or Jar	100 grams	Cool >0 to 6°C	28 days	N/A

**NOTE:** Water samples: The samples may be stored at >0 to 6°C prior to analysis but room temperature storage is all that is required.  
 Notify the project manager immediately if the method holding time has been exceeded.

## 9.0 QUALITY CONTROL

### 9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Unless prohibited by project-specific requirements, each of these QC samples may be re-analyzed once if it doesn't pass, in order to verify the failure wasn't due to a physical or mechanical problem.

#### 9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. The method blank must be free of contamination **and must not be more than ½ the standard reporting limit of 4 ug/L**, or the system must be cleaned and/or recalibrated and samples reanalyzed. (For water samples, the ICB/CCBs are reported as method blanks).

- If the method blank is greater than ½ the standard 4 µg/L reporting limit, but the samples are ND, the results may be reported with a qualifier/NCM.
- If the method blank is greater than ½ the standard 4 µg/L reporting limit, but the samples are greater than 10 times the method blank and 10x the reporting limit, the results may be reported with a qualifier/NCM.
- **For reporting limits below 4 ug/L, the MB is only required to be less than the RL.**

#### 9.1.2 Laboratory Control Sample (LCS) (25ppb)

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within **85 - 115%**. If the LCS is outside of these limits, re-prepare the whole batch and/or re-calibrate the system unless:

- The LCS recovery is above the upper limit and samples are ND. Qualify sample results accordingly.

LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.

For water samples, the LCS may be used as a CCV provided it meet the CCV criteria.

### **9.1.3 Matrix Spike and Matrix Spike Duplicate.**

The sample used for MS/MSD is randomly selected, unless specifically requested by a client.

Prepare and analyze a matrix spike (MS) and a matrix spike (MSD) duplicate for each matrix and with every batch of 20 samples, or less. The recovery must be **80%-120%**, unless there is matrix interference. In the case of matrix interference, qualify the results accordingly. If the problem is not matrix related, fill out a corrective action report and describe the problem and corrective actions taken.

### **9.1.4 Spike Confirmation**

- Unless project requirements specify otherwise, spike confirmations will be performed for **at least 10% of all samples** and/or matrices in which perchlorate is detected at a concentration at or above the laboratory reporting limit, a matrix spike using the target analyte must be performed for qualitative positive identification.
- The spike level will vary with respect to sample concentration but should be at such a level as to be identifiable with respect to the native analyte concentration.
- Confirmation is based on inspection of the spike sample chromatogram. If the spike elutes directly on top of the suspected target analyte peak (i.e same retention time), the detected peak in the unspiked sample is considered confirmed. If there is any difference in retention time between the spike and the analyte peak, the result is not confirmed and the sample result is reported as a non-detect (ND). Spike confirmations are qualitative only and are not evaluated for recovery.

## **9.2 Instrument QC**

### **9.2.1 IPC-MA (25ppb).**

Verify the MCT by analyzing an ICP at MCT on each working day. The following QC criteria must be met by the IPC-MA:

- PD (A/H) between the LCS and the IPC-MA must be less than **25%**.
- The perchlorate concentration in the IPC-MA must be within  $\pm 20\%$  of the true value.
- There is no sudden shift in the RT ( $>5\%$ ) from the previous run and the RT is no less than 80% (20% difference) from the ICAL RT.

If any of conditions are not met for the IPC-MA, the MCT must be repeated or the source of problem must be determined and the IPC-MA reanalyzed.

### **9.2.2 ICCS (4ppb) check standard.**

Recovery must be between **75-125%**.

### **9.2.3 MRL-MA (2ppb)**

The MRL-MA is a 2ppb perchlorate standard prepared in a mixed common anion solution which reflects a conductance near (within  $\pm 10\%$ ) of the MCT. It must be analyzed initially and whenever a column is replaced or there are other major changes to the instrument set-up.

Acceptance criterion:

- Recovery must be between **70-130%**.

If this criterion is not met, analysis must be repeated or the source of problem must be determined and the MLR-MA reanalyzed

#### **9.2.4** Initial Calibration Verification (ICV)

Immediately after the initial calibration, analyze the Secondary source. Verify that that its response is within  $\pm 10\%$  of the true value.

- If not, re-prepare the ICV standard.
- If the ICV is still out of control, re-calibrate the system

#### **9.2.5** Continuing Calibration Verification (CCV)

Analyze a CCV standard after every 10 sample aliquots or less and at the end of the sequence. The recovery must be within  $\pm 15\%$  of the true value. If the CCV is outside recovery limits, re-analyze once. If it is still out the instrument must be recalibrated and samples not bracketed by acceptable CCVs be reanalyzed unless:

- the CCV is out high, any ND samples may be reported with a qualifier.

Follow every CCV with a CCB (calibration blank). The CCB must read less than the method reporting limit. If the CCB is above the reporting limit, re-analyze once. If it is still out, the instrument must be recalibrated and samples not bracketed by acceptable CCBs be reanalyzed unless:

- the CCB is out high, any ND samples may be reported with a qualifier.

#### **9.2.6** Retention Time Shift Check

Check if the daily retention time (RT) is within 5% of the ICV RT when the current calibration was first run by analyzing the daily CCV. If the shift is more than 5 %, investigate before proceeding with analysis. Check if there is improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem.

- Correct the problem and recheck the RT of a fresh CCV.
- If the shift is still more than  $\pm 5\%$ , a new calibration curve must be prepared and analyzed.

#### **9.2.7** Calibration Acceptance Summary

Perform the initial calibration when the method is first set-up, when there is a major change (such as installing a new analytical column) and after that as needed. Changing of the guard column does not require re-calibration.

The lowest spiked calibration standard must be at a concentration at or below the reporting limit. The other concentrations will define the working range of the detector.

The calibration curve consists of a minimum of 5 calibration standards and a blank. The curve is prepared by plotting the response (peak area) of each calibration point against the corresponding concentration using a quadratic (second-order) least squares regression. The resulting correlation coefficient ( $r^2$ ) must be  $> 0.995$ .

**WARNING:** The use of a quadratic calibration model requires great care. Before using any new calibration curve, the calibration plot must be visually inspected to ensure there is no inflection point. The analyst must ensure that a quadratic is not being used to compensate for detector saturation. All chromatograms must be inspected to verify there are no peaks above the calibration

range. All reported results must be verified as real, positive, and within the range of the initial calibration.

Immediately after the initial calibration, analyze the 2<sup>nd</sup> source ICV and verify that its result falls within  $\pm 10\%$  of the stated value.

## 10.0 PROCEDURE

### 10.1 Reagent Preparation

#### 10.1.1 50mM NaOH Eluent

Weigh out 8 grams of NaOH 50% w/w and place in a 2000mL flask. Fill with Laboratory Reagent Grade water to the 2000mL mark. Invert six times to mix. Do not shake vigorously. This will produce a concentration of 50mM NaOH. **Prepare daily.**

**NOTE:** When measuring NaOH, take the aliquot from the middle of the bottle carefully. Do not disturb the surface of the liquid, since carbonate contamination can easily be produced in the NaOH from the outside air.

### 10.2 Standard Preparation

#### 10.2.1 Primary intermediate calibration standard, 10 mg/L.

Prepare this standard by pipetting 500  $\mu\text{L}$  of commercially prepared 1000 mg/L calibration standard stock solution into a 50 mL volumetric flask and bringing up to volume with Laboratory Reagent Grade water. The intermediate standard is stable for three months if stored at  $>0$  to  $6^\circ\text{C}$ .

#### 10.2.2 Working calibration standards

Calibration standards are made by aliquoting the following amounts of the 10 ppm intermediate standard into a 100 mL volumetric flasks and bringing up to 100 mL with Laboratory Reagent Grade water. The diluted working standards should be prepared daily (as needed). The final concentrations are as follows:

Standard	Concentration (ppb)	Amount Added ( $\mu\text{L}$ )
Blank	0	0 $\mu\text{L}/100$ mL
Std 1 <sup>a</sup>	1	10 $\mu\text{L}/100$ mL
Std 2 <sup>b</sup>	2	20 $\mu\text{L}/100$ mL
Std 3	4	40 $\mu\text{L}/100$ mL
Std 4	10	100 $\mu\text{L}/100$ mL
Std 5	25	250 $\mu\text{L}/100$ mL
Std 6	50	500 $\mu\text{L}/100$ mL
Std 7	100	1000 $\mu\text{L}/100$ mL



<sup>a</sup>May be excluded from the curve if reporting limit of 1 ppb is not required.

<sup>b</sup>May be excluded from the curve (along with Std 1) if report limit of 2ppb is not required.

NOTE: Under no circumstances can a calibration point be excluded from the middle of the curve (i.e. between the lowest and highest points used)

### **10.2.3 Working calibration standards--ICV (50 ppb)**

Prepare a 50 ppb ICV by adding 500  $\mu$ L of the 10 ppm intermediate secondary source solution to a 100mL volumetric flask and bringing up to volume with Laboratory Reagent Grade water.

**Prepare daily, as needed.**

### **10.2.4 CCVs (25 and 75 ppb)**

Prepare 25 ppb and 75 ppb CCVs by adding 250  $\mu$ L and 750  $\mu$ L respectively of the 10 ppm intermediate primary solution to a 100 mL volumetric flask and bring up to volume with Laboratory Reagent Grade water. **Prepare daily, as needed.**

### **10.2.5 Mixed Common Anion Stock Solution**

Prepare the Mixed common anions solution by dissolving the following salts in reagent water to the final volume of 25mL: 1.0 g sodium chloride, 0.93 g sodium sulfate, and 1.1 g sodium carbonate. This solution is stable for three months if stored at >0 to 6°C.

### **10.2.6 Mixed Common Anion Intermediate Solution.**

Add approximately 5 mL of Anion Stock Solution to 250 mL of Laboratory Reagent Grade water. This solution is stable for one month if stored at >0 to 6°C. Check and document the conductivity of this solution. This conductivity value must within  $\pm 10\%$  of the MCT. Record the value as a reference on the daily data review checklist.

### **10.2.7 Instrument Performance Check in Mixed Anion Matrix (IPC-MA), (25 ppb)**

Prepare this standard by adding 250  $\mu$ L of the 10 ppm intermediate primary source solution to a 100 mL volumetric flask and bringing up to volume with the Mixed Common Anion Intermediate Solution. **Prepared daily.**

### **10.2.8 LCS, (25 ppb)**

Prepare a 25 ppb LCS by adding 250  $\mu$ L of the 10 ppm intermediate primary solution to a 100 mL volumetric flask and bringing up to volume with Laboratory Reagent Grade water. **Prepared daily.**

### **10.2.9 Initial Calibration Check Standard (ICCS), 4 ppb**

Prepare the 4 ppb ICCS by adding 40 $\mu$ L of the 10ppm intermediate primary source standard into a 100mL volumetric flask. **Prepared daily.**

### **10.2.10 Method Reporting Limit Check in Mixed Anion Matrix (MRL-MA), 2ppb**

Prepare the 2ppb MRL-MA by adding 20  $\mu$ L of the 10 mg/L intermediate solution to a 100 mL volumetric flask and bringing up to volume with the Mixed Common Anion Intermediate Solution. ***Prepared daily, as needed.***

#### **10.2.11 Matrix Spike/Spike duplicate-MS/MSD**

Prepare the MS/MSD by adding 25  $\mu$ L of the 10 ppm intermediate primary solution to 10 mL of source sample.

#### **10.2.12 Second Source Calibration Check Standard, 1000ppm (ICV)**

The second source standard checks solution made from ACS grade Sodium perchlorate dried at 105°C for 30 minutes. Prepare the 1000 ppm standard check solutions by adding 0.3078 g of Sodium Perchlorate (anhydrous) into 250 mL of Laboratory Reagent Grade water. The standard is stable for one year when stored at >0 to 6° C. Alternatively, a purchased second source (from a different vendor than the primary, may be used. Follow vendor storage and shelf life specifications.

#### **10.2.13 Secondary intermediate calibration standard, 10 mg/L**

Prepare a 10 mg/L intermediate second source standard check solution by pipetting 500  $\mu$ L of 1000 ppm standard check into 50 mL volumetric flask and bringing up with Laboratory Reagent Grade water. The intermediate second source standard is stable for three months if stored at >0 to 6°C.

### **10.3 Sample Preparation**

#### **10.3.1 Water samples**

Once the samples have come to room temperature and the conductivity measured, transfer 5 mL of sample into a tube. The sample is ready to be analyzed. (For water samples, filtration is required only if sample contains particles larger than 0.45 microns to prevent damage to instrument columns).

#### **10.3.2 Soil samples**

Add an amount of reagent water equal to ten times the weight of the solid material and mix, for 10 minutes, by either stirring, shaking, or tumbling. Centrifuge and then filter the resulting slurry through a 0.20  $\mu$ m filter. The sample can now be processed as water. Process a Method Blank and LCS, MS and MSDS with the samples including this filtration step.

The 10 ppm intermediate solution is also used to prepare the matrix spike solution. 10 mL of sample is combined with 50  $\mu$ L of the 10 ppm standard. The final concentration is 50 ppb. For samples that require dilution, spike the appropriate amount of 10 ppm standard and perform the appropriate dilution to obtain a final concentration of 50 ppb.

#### **10.3.3 Sample Screening**

Perform a single-point calibration check of the conductivity meter daily using a certified conductivity standard (nominally 10 mS). The conductivity reading must be within  $\pm 10\%$  of the temperature-corrected value certified by the standard manufacturer. Date, analyst initials, standard conductivity reading, standard ID, acceptance criteria and all sample conductivities must be recorded in a controlled logbook.

#### **10.3.4 Sample Pre-treatment**

- Measure the conductivity of the daily IPC-MA.
- Measure the conductivity of all samples prior to analysis.
- If the samples have conductance greater than MCT level, they must be pretreated or diluted with reagent water to lower their conductance before analysis. Dilution is accepted only if it still results in detected perchlorate result. However, any samples maybe pretreated regardless of their conductance (based on experience of the analyst). Any samples that are pre-treated must be accompanied with pre-treated QC samples.
- On a daily basis, the ICP-MA conductivity can be used in lieu of the MCT to determine whether or not a sample must be diluted or pre-treated. The PD (A/H) for the IPC-MA must meet the MCT requirement of <20%. The PD(A/H) value must be documented.
- Pre-treat the samples and associated QC (Blk, LCS, MS/MSD) by stacking the cartridges from top to bottom (Ba/Ag/H). As a rinse, filter 3mL of sample through the cartridges and discard. Filter sample through the stacked cartridges at a rate of 1mL/minute and collect 5-10mL.
- If the conductivity of the sample after pretreatment is below the MCT, then the pretreated sample can be analyzed.
- If the conductivity of the sample is still higher than the MCT, the flow rate through the pretreatment cartridges was too fast, repeat the pretreatment. When done properly, this should yield a 75 to 90% reduction of conductance and acceptable recovery of perchlorate.

#### **10.4 Instrument Initialization**

##### **10.4.1 Instrument Conditions**

- Flow Rate: 1.0 mL/min. (may vary with different suppressors)
- Sample volume: 1000  $\mu$ L
- Detection Suppressed conductivity, ASRS (4mm),
- AutoSuppression external water mode
- System Backpressure: 600-1900 psi
- Background conductance: below 5  $\mu$ S

##### **10.4.2 Instrument start-up**

- Before starting the analysis, make enough fresh eluent to start and run the instrument for the day.
- Place eluent on top of the instrument and screw the cap on.
- Turn on the helium gas then turn knob #1 to approximately 15 psi and knob #2 to approximately 50 Kpa.
- Open the appropriate method file in the Peaknet software. The instrument will turn on and start running. The pressure will rise to 2000 - 2300 psi based on the column used.

##### **10.4.3 Priming the system**

- Change the IP20 isocratic pump from <Remote> to <Local>. Press enter.

- Arrow to the right and change from Method to Direct Control. Press enter.
- Arrow up and change 50 psi to 0 psi. Press enter. Now the pressure limits will read 0 - 2000 psi.
- Open knob, then press Prime. Turn the lever to the left and inject 10 ml of isopropyl alcohol with a 10 ml syringe. Be careful when injecting isopropyl alcohol as to not inject any air bubbles into the system. While still pushing on the syringe handle, turn the lever back to the middle position.
- Allow eluent to rinse through the line for approximately 60 seconds. Then turn off Prime and close knob.
- Change back to 50 psi, Method, and Remote.

Allow the instrument to stabilize for approximately 1 hour.

## 10.5 Calibration

**10.5.1** For a new calibration, load the calibration standards in ascending concentration order of at least 5 standards and a blank. Verify all calibration criteria are met before proceeding.

**10.5.2** Immediately after the initial calibration, verify the calibration curve and the primary calibration standard by analyzing the 2<sup>nd</sup> source ICV standard.

**10.5.3** For a new column, analyze a MRL-MA after ICAL

### 10.5.4 Verification

- On a daily basis, analyze the 4 ppb ICCS.
- On a daily basis, analyze an initial CCV (LCS).
- On a daily basis, analyze the IPC-MA and Calculate the  $PD_{A/H}$
- On a daily basis, check if the retention time (RT) is within 5% of the IPC RT when the current ICAL was first run and no more than 20% different from when the column was first installed.

See Instrument QC for acceptance criteria and corrective actions

## 10.6 Sample Analysis

Analyze samples after the instrument stabilizes. Following is an example of a sequence for samples with conductance less than the MCT:

1. IB ( $\leq \frac{1}{2} RL^*$ )
  2. CCV [LCS] 25ppb ( $\pm 15\%$  recovery)
  3. IPC-MA 25ppb ( $\pm 20\%$  recovery)
  4. ICCS 4 ppb ( $\pm 25\%$  recovery)
  5. ICB [MB] ( $\leq \frac{1}{2} R^*$ )
  6. Sample Runs 1-10; including MS1/MSD1 (20% recovery)
  7. CCV 25ppb ( $\pm 15\%$  recovery)
  8. CCB ( $\leq \frac{1}{2} RL^*$ )
  9. Sample Runs 11-20
  10. CCV -75ppb ( $\pm 15\%$  recovery)
  11. CCB ( $\leq \frac{1}{2} RL^*$ )
- \* for 4ppb RL only; otherwise <RL

For samples with conductance greater than the MCT: dilute and/ or pretreat the samples. If pretreating is needed, a new batch is created with pretreated MB, LCS, sample and MS/MSD.

## 10.7 Preventative Maintenance

- Low pressure: Check for air bubbles and prime the system with isopropyl alcohol to correct for low pressure.
- High pressure: Most likely the column is dirty. Replace the frits and guard discs. Clean the column for two hours with 10x concentrated eluent. Be sure to read Dionex instructions before attempting to clean the column.
- Tailing of peaks: The column is dirty. Replace the frits and guard discs. Clean the column for two hours with 10x concentrated eluent. Be sure to read Dionex instructions before attempting to clean the column.
- High display value: Be sure that the ASRS-II is clean, make sure the eluent is prepared correctly, and that the correct current is being applied to the ASRS-II.
- Noisy baseline/unable to read low end standards: Re-prime the system and/or replace the suppressor. Note: The suppressor flow rate should be 10 mL/min in and 3.5 mL/min out.
- Shifted retention times: Recalibrate the instrument.
- Difficulty in reading the 4.0 ppb standard within  $\pm 25\%$ : Make new eluent using a new bottle of 50% w/w NaOH.
- Record all performed maintenance in the instrument maintenance logbook.
- If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution, and verification of proper operation into the instrument maintenance logbook.

## 11.0 CALCULATIONS / DATA REDUCTION

### 11.1 Determination of Matrix Conductivity Threshold (MCT)

Add 0.0mL, 0.2mL, 0.3mL, 0.4mL, 0.5mL, 0.6mL, 0.8mL, and 1.0mL of the mixed common anion into separate 25mL volumetric flasks. Add 0.0625mL of the perchlorate primary stock solution standard (10ppm) to each flask. There should be eight volumetric flasks each containing 25µg/L perchlorate and ascending levels of the mixed common anion stock solution.

Measure and record the conductivity of each solution.

Analyze each solution and record the peak area to height ratio (A/H) and concentration of perchlorate.

Calculate the A/H ratio percent difference ( $PD_{A/H}$ ) between the A/H ratio for the unspiked solution ( $A/H_{IPC}$ ) and the A/H ratio for each of the eight solutions ( $A/H_{MA}$ ) as follows:

$$PD_{A/H} = \frac{|A/H_{LCS} - A/H_{MA}|}{A/H_{LCS}} \times 100$$

Where  $A/H_{LCS}$  = Area/height ratio for the LCS (without anion mix)  
 $A/H_{MA}$  = Area/height ratio for each Mixed Anion Solution

The MCT is the matrix conductance where the  $PD_{A/H}$  exceeds 20%. To derive the MCT, perform a linear regression by plotting  $PD_{A/H}$  versus the matrix conductance. The resulting regression data should yield an  $r^2$  of >0.95. Record the slope and the y-intercept and calculate the MCT as follows:

$$MCT = (20\%) \times (X\text{-coefficient}) + (\text{constant})$$

The resulting regression data should yield an  $r^2$  value of >0.95

X-coefficient = slope

Constant = intercept value

**NOTE1:** As an alternative, the MCT can be considered as a conductance level of the highest mixed anion solution which yields a PD (A/H) value less than 20%.

**NOTE2:** On a daily basis, the conductivity of the IPC-MA is used for MCT purposes. The daily IPC-MA conductivity must be no higher than the MCT.

After establishing the MCT, confirm the perchlorate MRL in a mixed common anion solution, which reflects a conductance within 10% of the MCT. The recovered perchlorate concentration must be within 70-130% of the MRL

If the MRL recovery fails, the MCT should be lowered 10% and the verification repeated.

Determine the MCT and verify it with a successful recovery of MRL during the Initial Demonstration of Capability or when a significant system change has been made (e.g. a new separator column, a different eluent, a different flow rate, etc). Record the established MCT level and the retention time of perchlorate as a reference for subsequent daily analysis.

## 11.2 Quadratic Calibration

$$y = a'x^2 + b'x + c'$$

Where y is the instrument response (area)

$a'$ ,  $b'$ , and  $c'$  are the quadratic coefficients

x is the concentration

$$C = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Where C is the raw sample concentration (instrument reading)

$$a = 1$$

$$b = b'/a'$$

$$c = (c'-y)/a'$$

### 11.3 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$$

### 11.4 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

### 11.5 Concentration

$$C_{\text{CLO4}} = I \times DF \times PF$$

Where

$C_{\text{CLO4}}$  = final concentration of perchlorate (ug/L or ug/kg)

I = instrument reading, ug/L (calculated from area)

DF = Dilution factor

PF = Prep factor (soils only; nominally 10 L/Kg)

## 12.0 METHOD PERFORMANCE

### 12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An MDL Study should be performed annually or when there is a major system change; e.g. new eluent concentration, different calibration levels. The calculated MDL must be verified annually at a concentration of 1-2 times the MDL.

### 12.2 Retention Time Window

The width of the retention time window used to make identifications of perchlorate is set at  $\pm 5\%$  the retention time of ICV of the most recent initial calibration.

### 12.3 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC can be 1) 4 consecutive LCS samples at 1 to 4 times the RL (prepared from a source different than that used for the ICAL) with an average recovery and RSD within laboratory acceptance limits, or 2) passing results on a blind or PT study. An ongoing DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

#### **12.4 Maximum Conductivity Threshold (MCT)**

Determine the MCT initially and whenever there is a significant change in the instrument configuration.

#### **12.5 Training Requirements**

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

### **13.0 POLLUTION CONTROL**

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

### **14.0 WASTE MANAGEMENT**

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

**Sample/Eluent** – This waste is generated by the IC machines and collected in 3.5 gal carboy satellite containers behind the respectively IC. This waste is disposed of by pouring the liquid waste into the sink, measuring the pH and neutralizing it using soda ash, and then draining the neutralized contents into the sewer system.

**Soil waste** – Generated by analyst/technicians after samples have been prepared and analyzed in the Wetchem area. This waste is stored in 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. The drum is removed from the wetchem area to the main waste storage area by sample archive technicians. Analyst/technicians let the sample archive technicians know when they need to removed this drum.

**Unused standards or reagents** – If the standard or reagent is hazardous and cannot be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).



If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example: buffer solution pH 4).

**15.0 REFERENCES / CROSS-REFERENCES**

- 15.1 EPA Method 314.0 Determination of Perchlorate in Drinking Water Using Ion Chromatography, Revision 1, November 1999.
- 15.2 Dionex Application Note 121 1-13-98 Draft
- 15.3 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition, EPA, January 2005, EPA 815-R-05-004.

**16.0 METHOD MODIFICATIONS**

Item	Method 314.0	Modification
1	Sec. 9.3.1	<i>For Reporting Limits below 4 ug/L, the Method Blank is required to read less than the RL, not ½ the RL. The method has been written for a nominal RL of 4 ug/L and ½ RL levels below this may be below the MDL.</i>
2	Sec. 9.3.2.2	<i>The daily determination of the PD<sub>A/H</sub> is based on the responses of the LCS and IPC-MA run on the same day and not from the LCS in the previous analysis batch.</i>
3	Sec. 4.4	<i>Filtration is required only if sample contains particles that may damage to instrument columns</i>
4	Sec. 7.2.2	<i>Although Section 7.2.2 of the source method specifies de-gassing of the eluent in order to remove microbubbles that may adversely affect instrument response, the laboratory does not de-gas and, as demonstrated by passing PTs, does not experience response problems.</i>

**17.0 ATTACHMENTS**

- 17.1 **Attachment 1:** Analysis Information
- Attachment 2:** Data Review Checklist
- Attachment 3:** ICAL Review Checklist
- Attachment 4:** Data types

**18.0 REVISION HISTORY**

- 18.1 **Revision 0, dated 22 February 2008**
  - Integration for TestAmerica and STL operations
  - This revision supersedes 314\_0.SOP, revision 2 (08/17/07)
- 18.2 **Revision 1, dated 25 September 2009**

- This revision supersedes IR-WET-314.0, revision 0 (02/22/08)
- Section 4.5 – coelution interference
- Addition of Safety sections 5.1, 5.2, and table in 5.2
- Addition of Pollution Control wording
- Addition of Waste Management wording
- Addition of table for method modifications
- Section 9.2.5 - Clarification of when an ICAL needs to be performed
- Method Modifications: De-gassing of the eluent
- Prepared by LH

**18.3 Revision 2, dated 22 October 2010**

- This revision supersedes IR-WET-314.0, revision 1 (09/25/09)
- Revision of Calibration Acceptance Summary Section.
- Revision of MDL Section.
- Addition of MRL-MA
- Revised by LH

**18.4 Revision 3, dated 29 June 2012**

- This revision supersedes IR-WET-314.0, revision 2 (09/22/10)
- Limited daily RT check to  $\pm 5\%$  of the ICV
- Revised Retention Time Window Study.
- Revised by MN and LH

**18.5 Revision 4, dated 02 October 2013**

- This revision supersedes IR-WET-314.0, revision 3 (06/29/12)
- Changed reagent grade water conductivity requirement from 18 to 17.8 M $\Omega$
- Updated Section 14 to use current language for unused standards or reagents
- Revised by CH and DD

**Attachment 1**  
**Analysis Information**

<b>TestAmerica Irvine</b>								
<b>Analytical Method Information</b>								
<b>Analyte</b>	<b>MDL</b>	<b>Reporting Limit</b>	<b>Surrogate %R</b>	<b>Duplicate RPD</b>	<b>Matrix Spike %R</b>	<b>Matrix Spike RPD</b>	<b>Blank Spike / LCS %R</b>	<b>Blank Spike / LCS RPD</b>
<b>Perchlorate 314.0-DEFAULT in Wipe (EPA 314.0 MOD.)</b>								
Preservation:None								
Container:Plastic Bag			Amount Required:1 wipe			Hold Time:28 days		
Perchlorate	0.040	0.16 ug/Wipe			80 - 120	20	85 - 115	15
<b>Perchlorate 314.0-DEFAULT in Water (EPA 314.0)</b>								
Preservation:None								
Container:500 mL Poly			Amount Required:500 ml			Hold Time:28 days		
Perchlorate	0.95	4.0 ug/l			80 - 120	20	85 - 115	15
<b>Perchlorate 314.0-DEFAULT in Soil (EPA 314.0 MOD.)</b>								
Preservation:4 C, Cool								
Container:4 oz Jar/BrassSleeve			Amount Required:100 grams			Hold Time:28 days		
Perchlorate	0.0095	0.040 mg/kg			80 - 120	20	85 - 115	15

**Attachment 2**  
**Data Review Checklist**

**DAILY DATA CHECKLIST**  
 EPA 314.0 – Perchlorate by IC

Analyst: _____	2 <sup>nd</sup> Level Review: _____
Analysis Date: _____	Date: _____
IC #: _____	Calibration file: _____
QC Batches: _____	

**Analyst Rev**    **2<sup>nd</sup> Level Rev**

_____	_____	New sequence file created for each day of analysis
_____	_____	Accepted Matrix Conductivity Threshold (MCT) = _____
_____	_____	<b>IPC-MA</b> (LCS in anion mix at 90-110% of the MCT):
_____	_____	• %REC = 80 - 120
_____	_____	• $PD_{A/H} = \frac{LCS_{A/H} - IPCMA_{A/H}}{LCS_{A/H}} \times 100 =$
_____	_____	• $PD_{(M)} < \pm 25\%$ (relative to LCS);
_____	_____	Retention time shift $\leq 5\%$ from ICAL
_____	_____	If > 5%, check for potential problems: prepared eluent, flow rate...
_____	_____	<b>ICCS/RL</b> (4ppb): %REC = 75 - 125
_____	_____	<b>ICB/CCB</b> : After ICV/CCV: $\leq 1/2$ RL (for 4ppb RL only; otherwise <RL)
_____	_____	<b>Method Blank</b> : Every batch of 20 samples or less; $\leq 1/2$ RL (for 4ppb RL only; otherwise <RL)
_____	_____	<b>CCV</b> : Start, every 10 samples and at end of run; 85 - 115%
_____	_____	<b>LCS</b> : Every batch of 20 samples or less; 85 - 115%
_____	_____	<b>MS/MSD</b> : every batch of 20 samples or less. %REC = 80 - 120
_____	_____	All samples checked for compliant conductance (<MCT)
_____	_____	Samples of high conductance (>MCT) are either diluted or pretreated
_____	_____	Pretreated samples (if any) have associated pretreated MB, LCS and MS/MSD
_____	_____	All samples checked for retention time, integration, linear range, and dilution factor and transcription accuracy.
_____	_____	Comments: _____
_____	_____	_____
_____	_____	_____

**Attachment 3**  
**ICAL Review checklist**

**CALIBRATION CHECKLIST**  
 314.0 – Perchlorate by IC

Analyst: _____ Analysis Date: _____ Instrument #: _____	2 <sup>nd</sup> Level Reviewer: _____ Review Date: _____ Calibration File #: _____
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**Analyst Rev**    **2<sup>nd</sup> Level Rev**

_____	_____	Minimum 5-point calibration, lowest point at or below RL, $r \geq 0.995$ <b>Calibration standard ID:</b> _____
_____	_____	New column retention time: _____
_____	_____	New Calibration retention time: _____
_____	_____	2 <sup>nd</sup> source verification (ICV – 50ppb): %REC = 90 - 110 <b>ICV standard ID:</b> _____
_____	_____	MRL-MA (2ppb, for new column) (conductance within $\pm 10\%$ of the MCT): %REC = 70 – 130%
_____	_____	Calibration date and file checked for completeness and accuracy: <ul style="list-style-type: none"> <li>Correct date, analyst's name and calibration file</li> <li>Calibration points quantitated by peak AREA (not by peak Height)</li> <li>Correct instrument parameters, retention time and window</li> <li>Chromatography peak shape and baseline acceptable</li> <li>Calibration summary and raw data match for calibration levels and are a counts</li> </ul>
_____	_____	Annual MDL study last performed: _____

Comments: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

**Attachment 4**  
**Datatypes**

Method Code	Method Type	Datatype Description	Value to Enter	Units
314.0_LL	Analysis	Initial pH	NA	SU
314.0_LL	Analysis	Final weight/volume of sample	If needed	mL
314.0_LL	Analysis	Filtration (Y/N)	N/A	NONE
314.0_LL	Analysis	Analysis comment	If needed	N/A
314.0_LL	Analysis	Filter Paper Lot Number	NA	NONE
314.0_LL	Analysis	Eluent 1 Lot	[specify]	NONE
314.0_LL	Analysis	Batch Comment	If needed	N/A

Uncontrolled Document