
Appendix V

METHOD 314 FOR DETERMINATION OF
PERCHLORATE IN DRINKING WATER AND
SOIL USING ION CHROMATOGRAPHY



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**United States Army Corps of Engineers
Engineer Research and Development Center
Environmental Laboratory**

Environmental Chemistry Branch
Omaha Facility

**TITLE: DETERMINATION OF PERCHLORATE IN DRINKING WATER AND SOIL
USING ION CHROMATOGRAPHY**

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QA Officer Date

Branch Chief Date

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Current SOP supercedes all previous versions.

Previous Versions of this SOP

SOP Number	Version	Date Issued
M-314.0-ECBO-IA	Initial Draft	NA

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1. Scope and Application

- 1.1. This method is applicable to drinking waters, saline liquids, surface waters, domestic and industrial wastes waters, and solids.

2. Method Summary

- 2.1. The analysis for perchlorate ion (CASRN [14797-73-0]) employs the Dionex DX—120 system in anion exchange chromatography. A fixed volume of sample is introduced into the ion chromatograph. Perchlorate is separated and measured, using a system comprised of an ion chromatograph pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector. The amount of perchlorate in a sample is nominally determined with a typical detection limit of 1 µg/L for water samples and 5 µg/kg for soil samples.

3. Health and Safety

- 3.1 The toxicity or carcinogenicity of each compound or reagent used in this procedure has not been precisely determined. Therefore, all chemicals should be treated as if they pose a health hazard. MSDS sheets are available. The MSDSs are located in room 421.
- 3.2 This method describes a procedure for analyzing samples that may contain organics that may pose a risk through inhalation or skin absorption. Therefore, exposure to these samples should be reduced to the lowest possible level.
- 3.3 The acids used in this method should be handled with care. An acid spill kit should be on hand in the laboratory, and laboratory personnel should be familiar with its location and use. Acid spill clean-up kits are located near the hood in the laboratory.
- 3.4 The following chemicals have the potential to be highly toxic or hazardous. The MSDS for each chemical should be consulted.
 - 3.4.1 Sodium hydroxide
 - 3.4.2 Sulfuric acid
 - 3.4.3 Potassium perchlorate
 - 3.4.4 *p*-Cyanophenol

4. Sample Preservation, Containers, Handling, and Storage

- 4.1. Glass or plastic containers are suitable for collection and storage.
- 4.2. Sample must be stored at 4°C.
- 4.3. Holding times;
 - 4.3.1. Holding time is 28 days for liquid samples.



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4.3.2. Holding time for soils will default to that of liquid samples, 28 days.

5. Interferences and Potential Problems

- 5.1. High levels of anions such as chloride, sulfate, nitrate, nitrite, ortho-phosphate, fluoride or bromide, etc. may cause chromatograph interference through co-elution or obscurity of the perchlorate peak.
- 5.2. Other sources of interference are contaminated water, reagents, glassware and other processing apparatus. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise. Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant co-elution or ionic character displacement, it must be noted that any sample dilution will alter the minimum Sample Reporting Limit (SRL) by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution.
- 5.3. All reagents used by the instrument must be filtered through a 0.20 μm membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Sample filtration must also be employed on every sample prior to analysis. This applies not only to field samples but also to the laboratory method blanks (MB) and the laboratory control sample (LCS, which is a fortified blank sample). The MB and LCS samples function as controls and must be filtered to confirm no bias is attributed to the filtration.

6. Equipment/Apparatus

- 6.1. Analytical balance, weighing accurately to 0.0001g
- 6.2. Glassware, Class A volumetric flasks and pipettes
- 6.3. Dionex DX-120 Ion Chromatography System with Autosampler
- 6.4. Detector: Dionex CD20
- 6.5. Ion Suppressor: Dionex AMMS-III 4mm
- 6.6. Columns
 - 6.6.1. Dionex IonPac AG16 Guard Column (4x50mm)
 - 6.6.2. Dionex IonPac AS16 Analytical Column (4x250mm)
- 6.7. Sample Loop: 1.0mL
- 6.8. Backpressure Loop: 800 μL
- 6.9. Eluent/Flow rates
 - 6.9.1. Eluent: 50mM NaOH J.T. Baker CAT. 3727-01 (50% w/w)



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- 6.9.2. Eluent Flow Rate: 1.25 to 1.50 mL/min.
 - 6.9.3. Regenerant Flow Rate: 8 to 15 ml/min.
 - 6.9.4. Retention Time Perchlorate: 9 to 11 min.
- 6.10. Multi-position (12) wrist sample shaker.

7. Reagents

- 7.1. Prepare all reagents with Type I reagent water in Class A volumetric glassware. Record solution standard preparation in the Standards Log Book. Enter the date, time, and analyst's initials. Also note the stock standard manufacturer, lot number, and date received. The analyst should be familiar with safe laboratory practices and with each MSDS for the following chemicals:
- 7.2. Reagents
 - 7.2.1. Eluent, 50mM NaOH: Degas one liter Type I reagent water. Into a one liter volumetric flask add 3.55ml of 50% NaOH bring up to a final volume with the Type I reagent water and mix. Remake eluent every 3 days or less.
- 7.3. Standards: Stock Standards should be prepared as specified.
 - 7.3.1. Stock Perchlorate Solution 1000ppm: (Spex Certiprep, CAT # AS-CLO49-2Y). Prepare every 12 months.
 - 7.3.2. Intermediate Perchlorate Standard, 1000ppb: Dilute 1mL of the Stock Standard to 1L with Type I reagent water. Prepare weekly.
 - 7.3.3. Working Standards: Dilute Intermediate Standards with Type I reagent water according to the following table. The DX-120 system is calibrated once per week or as needed. Prepare daily.



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Perchlorate Standard	Volume Intermediate Standard	Volumetric Flask	Concentration of Standard
blank*	0.0 mL	100 mL	0 ppb*
Cal STD 1	0.25 mL	100 mL	2.5 ppb
Cal STD 2	0.50 mL	100 mL	5.0 ppb
Cal STD 3	1.00 mL	100 mL	10 ppb
Cal STD 4	2.00 mL	100 mL	20 ppb
Cal STD 5	5.00 mL	100 mL	50 ppb
Cal STD 6	10.0 mL	100 mL	100 ppb
Cal STD 7	12.5 mL	50 mL	250 ppb
Cal STD 8	10.0 mL	25 mL	400 ppb

*The blank is not included in the calibration as a standard

Note: Not all standards are used for every calibration, see section 8.2 for details on which standards to use for analysis.

- 7.4. Stock ICV Perchlorate Solution, 1000 ppm (Environmental Express, CAT# HP1862-A-100). Prepare every 12 months.
- 7.5. Intermediate ICV Standard; 1000 ppb. Dilute 1 mL of the stock ICV solution to 1000 mL with Type I reagent water. Prepare monthly.
- 7.6. Working ICV Standard, 50 ppb: Dilute 5.0 mL of the intermediate ICV standard to 100mL with Type I reagent water. Prepare weekly.
- 7.7. Matrix Spike: 50 ppb. Add 5 mL of perchlorate intermediate stock (1000ppb) with sufficient sample to bring to a total final volumen of 100 mL.
- 7.8. The calibration standard number five (Cal std 5) is used as the LCS and CCV.
- 7.9. Mixed Common Anion Stock Solution; containing the anions chloride, sulfate and carbonate each at 25 mg/mL anion concentration. This solution is used to prepare simulated common anion samples in the determination of the MCT (Section 8.4.1). Dissolve the following salts in reagent water to a final volume of 25.0 mL
 - 7.9.1. 1.0 g sodium chloride (NaCl, CASRN [7647-14-5])
 - 7.9.2. 0.93 g sodium sulfate (Na₂SO₄, CASRN [7757-82-6])
 - 7.9.3. 1.1 g sodium carbonate (Na₂CO₃, CASRN [479-19-8])



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8. Procedure

8.1. Sample Preparation:

- 8.1.1. The sample should be brought to room temperature prior to conducting sample analysis.
- 8.1.2. Soil sample preparation
 - 8.1.2.1. Soil samples are prepared for analysis by placing approximately 5 grams (record mass to nearest 0.001g; record as *mass_of_sample* in equation section 10.2) of sample in 50-ml preparation tube.
 - 8.1.2.2. Add 20 ml (record volume to nearest 0.1ml; record as *prep_volume* in equation section 10.2) of reagent grade water to the soil sample.
 - 8.1.2.3. Place samples with water in wrist shaker and mix for 15 minutes.
 - 8.1.2.4. Allow sample to settle (centrifugation make be necessary) and use clear solution for analysis following the water sample procedures.
- 8.1.3. A Method Blank, Matrix Duplicate, Matrix Spike and Matrix Spike Duplicate and Laboratory Control Sample must be analyzed with each batch at a minimum frequency of once every 20 samples.

8.2. Instrument Calibration

- 8.2.1. Calibrate the instrument at a minimum frequency of once a week following the instrument manufacturer's instructions as listed in Appendix I.
- 8.2.2. The standards to be used for calibration depend on the nature of the analysis. A valid calibration must consist of a minimum of five calibration standards. The type of calibration required for the samples to be analyzed must be known in advance and the type of calibration selected before measuring any standards.
 - 8.2.2.1. For low level work only use standards 1 through 6 (Cal STD 1, Cal STD 2, Cal STD 3, Cal STD 4, Cal STD 5 and Cal STD 6).
 - 8.2.2.2. For high level work only use standards 3 through 8 (Cal STD 3, Cal STD 4, Cal STD 5, Cal STD 6, Cal STD 7 and Cal STD 8).
 - 8.2.2.3. For broad range work use standards 1, 3, and 5-8 (Cal STD 1, Cal STD 3, Cal STD 5, Cal STD 6, Cal STD 7 and Cal STD 8).
- 8.2.3. A second source standard (Initial Calibration Verification (ICV) Standard (see Section 7.6)) must be analyzed following the calibration. Acceptance criteria is listed in Section 11. The ICV standard is to be at a concentration near the mid-point of the calibration range. If acceptance criteria are met, the calibration can be used for sample analysis.

8.3. Calibration verification

- 8.3.1. An initial Continuing Calibration Verification (CCV) Standard (see Section 7.6)) must



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be analyzed at the beginning of an analysis sequence. Acceptance criteria is listed in Section 11. The CCV standard is to be at a concentration near the mid-point of the calibration range. If acceptance criteria are met, the sample analysis may proceed.

- 8.3.2. Continuing calibration Verification (CCV) samples are used to check the validity of the calibration after every 10 samples. The CCV is made according to section 7.3.3 and 7.8. If CCV is within acceptance criteria analysis may continue, see section 11.3.1.
- 8.3.3. A closing Continuing calibration Verification (CCV) sample is to follow the last reportable sample. If the closing CCV is not within acceptance criteria analysis see section 11.3.1 for corrective action.

8.4. Sample Analysis

- 8.4.1. All samples are to be screened prior to analysis using a specific conductance meter refer to SOP No. M-9050-ECBO-GC.

- 8.4.1.1. The highest permitted conductance of an unknown sample matrix, measured prior to conducting analysis, which is used to determine when sample matrix dilution or pretreatment is required is referred to as the Matrix Conductivity Threshold (MCT). The conductance of a sample matrix is proportional to the common anions present in the matrix (which contribute to the level of total dissolved solids (TDS)) which can greatly affect the integrity of this analysis. The value for this threshold is dependent on the conditions, hardware, and state of the hardware employed. Consequently, this threshold is not method defined and must be determined by the individual analytical laboratory during the initial demonstration of capability and confirmed in each analysis batch using the instrument performance check solution (IPC). Matrix conductivity is measured in microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm) which are considered equivalent terms.

- 8.4.1.2. For samples that exceed the MCT matrix dilution may result in a conductance less than MCT. A sample can be analyzed once diluted with reagent water to a conductance below the MCT. The exact magnitude of this dilution will adversely increase the SRL by an equivalent proportion (Section 5.2).

- 8.4.1.2.1. Knowing the matrix conductance exceeds the MCT, estimate the proportion required for the dilution by dividing the measured matrix conductance by the MCT. Round up to the next whole number and dilute the sample by a proportion equivalent to this value. For example, if the established MCT is 6100 uS/cm and a sample reflecting a conductance of 8000 uS/cm was measured, dilute the sample with reagent water by a factor of 2.

- 8.4.1.2.2. Measure the conductance of the diluted sample to confirm it is now below the MCT. Analyze the sample as specified in Section 8.4.2 with the understanding that the SRL (section 5.2) has now been elevated by a proportion equivalent to the dilution.



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8.4.1.2.3. If perchlorate is measured above the elevated SRL, back calculate actual field sample concentration and report. If no perchlorate is measured above the elevated MRL and analysis or project objectives required monitoring below the concentration of the elevated SRL, pretreatment of the matrix may be required, contact Team Leader and QA office.

8.4.2. Samples are analyzed using a Dionex DX-120 system. All samples are to be analyzed and if their response is determined to be greater than the high standard response the sample will need to be diluted and reanalyzed. Repeat the dilution if necessary to bring the measured response is within the calibration limits.

9. Operation Condition

- 9.1. Preparation of Perchlorate Eluent: Add 3.55 mL of (50% w/w) sodium hydroxide solution (J.T. Baker CAT #3727-01) in 1 L volumetric flask. Fill the reservoir being careful to prevent mixing air into the eluent solution. Connect to the sparger line of the regulator to the helium in-line of the reservoir; connect the eluent out-line of the reservoir to the eluent out-line.
 - 9.1.1. Turn the system power on and set the control button on the system panel to local. Turn on the system helium and confirm that the pressure is between 90-110 psi.
 - 9.1.2. Make sure that sufficient volume of eluent in the reservoir is available to sustain extended operation.
 - 9.1.3. Ensure that the pump flow rate adjustment is correct and turn on the pump. (Eluent flow rate 1.25 mL/min.) Set the detection range to the appropriate operating range (Typically 1 μ s) Sample loop volume (already installed)
- 9.2. Priming: After turning the system on, open the waste knob on the transducer (big black knob that is designed to be turned by fingers) by turning it counter clockwise. This opens the waste line. Let it be open for about 30 seconds. This drives eluent from the reservoir to the pump at a rate of about 10 mL/min to help force air bubbles out of the pump. Now close the waste knob on the transducer (clockwise).
- 9.3. Establishing Equilibrium and Monitoring Baseline: Go to the computer terminal and from the PEAKNET main menu, select RUN. Load the Perchlorate method from the FILE/LOAD Method Menu. Select OK. Because the eluent is pumping through the system, the regenerant must be cycling also. You should notice that the conductivity begins to fall on CD20 display. Let the system run until baseline drift is less than 5 mSiemens/min. monitor the stability of the baseline.
- 9.4. Writing and Loading a Schedule
 - 9.4.1. From the PEAKNET Main Menu, select Schedule
 - 9.4.2. Open the calibration schedule from the file menu.
 - 9.4.3. Enter the required data and complete it



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- 9.4.4. Save As –using the naming convention of “mmddy-ss”. Where mm= month, dd=day, yy=year and ss=sequence number of the day. Each sequence is to be saved in its own file directory under the root data level directory and should be named using the “mmddy-ss” convention.
- 9.4.5. Loading Samples for Analysis: Shake all water samples to a homogeneous consistency. Decant the water sample into 5mL vial; fill the vial to the full line. Place a filter cap on to the vial. Use the black insertion tool to properly seat the cap into the vial. Place vials sequentially into load-up trays according to their order in the schedule. Place the tray in front of the compressed pressure plate. Press the RUN/HOLD button to advance the tray into position for sampling the first sample. After the run button is activated, the computer will control the progression of the autosampler henceforth.

10. Calculation

- 10.1. Calculate the percent recovery for MS/MSD and LCS
- 10.2. Calculate the soil sample results using the following equation

$$\text{reported_result, ug / Kg} = \frac{(\text{instrument_result, ug / L}) \times (\text{prep_volume, L})}{(\text{mass_of_Sample, Kg}) \times (\% \text{solids} / 100\%)}$$

11. Quality Control/Quality Assurance

- 11.1. The analyst must demonstrate proficiency in performing the analysis as outlined in SOP No. Q-016-ECBO-QC, Technical Training. Method proficiency must be redemonstrated anytime a major method modification is made, a major software revision is added, or a major instrument modification is made. Demonstration of method proficiency may also be required after major instrument maintenance. This is decided on a case by case basis through discussions with the Team Leader, Laboratory Director, and Laboratory QA Office
- 11.2. QC Criteria
- 11.2.1. The correlation coefficient for the standard curve must be at least 0.995.
- 11.2.2. A matrix duplicate will be analyzed for every 20 samples with a default acceptance limit $RPD \leq 20$ until control charting can be used to establish limits.
- 11.2.3. A matrix spike and matrix spike duplicate will be analyzed for every 20 samples. The default acceptable recovery for matrix spike will be $\pm 20\%$ (80%-120%) of the true value with a $RPD \leq 20$ until control charting can be used to establish limits.
- 11.2.4. A laboratory control sample will be analyzed for every 20 samples The default acceptable recovery for the LCS will be $\pm 20\%$ (80%-120%) of the true value until control charting can be used to establish limits.
- 11.2.5. An Initial Calibration Verification (ICV) sample is to be analyzed each time a new calibration is established. The acceptance limits for the ICV are $\pm 10\%$ (90%-110%) of the true value.



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- 11.2.6. Continuing Calibration Verification (CCV) samples are to be analyzed after every 10 samples and at the end of the analytical sequence. The acceptance limits for the CCV is $\pm 15\%$ (85%-115%) of the true value.
- 11.3. QC Failure: The following summarizes the steps to be taken when QC failure is experienced. The suggestions are listed in the order in which they should be performed. If the first suggestion does not work, then try the second or third etc. If you cannot solve the problem in a reasonable amount of time, inform your supervisor.
- 11.3.1. ICV failure
- 11.3.1.1. If an initial calibration was performed, verify that an initial calibration verification (ICV) was also performed. The ICV must be measured to within $\pm 10\%$ (90%-110%) of the true value. If not, reanalyze the ICV or prepare a new calibration curve as necessary.
- 11.3.2. CCV failure
- 11.3.2.1. Analysis run is to be halted and corrective action taken including but not limited to reanalyzing the CCV or prepare a new calibration curve as necessary – samples are not to be analyzed unless the CCV meets acceptance requirements. Any samples analyzed after the last acceptable CCV and prior to the failing CCV are to be reanalyzed.
- 11.3.3. LCS Fails
- 11.3.3.1. Reanalyze the LCS
- 11.3.3.2. Re-prepare and reanalyze the LCS and associated samples.
- 11.3.4. Spike Fails
- 11.3.4.1. Reanalyze the spike.
- 11.3.4.2. Prepare a new spike and reanalyze
- 11.3.4.3. If the LCS is in control and the matrix spike has failed, then attribute failure to matrix interferences.

12. Waste Disposal

- 12.1. This procedure generates basic waste water. All waste disposal procedures must comply with federal and local regulations. Refer to the Laboratory Waste Management Plan.

13. Reference

- 13.1. Determination of perchlorate in drinking water using ion chromatography, US EPA, Method 314.0, November 1999.
- 13.2. Test Methods for Evaluating Solid Wastes, U.S.EPA, SW-846, proposed update IVb, Method 9058, November 2000.



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13.3. SOP No. Q-008-ECBO-GL, Reagent Water Quality Monitoring.

13.4. SOP No. Q-009-ECBO-QC, Control Chart Generation, Maintenance, and Usage.

End of SOP M-314.0-ECBO-IA