

# RECLAMATION

*Managing Water in the West*

**FOR OFFICIAL USE ONLY**

Technical Memorandum No. MERL-2013-39

## Corrosivity Testing of Waters and Soils



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U.S. Department of the Interior  
Bureau of Reclamation  
Technical Service Center  
Denver, CO

September 2013

## **Mission Statements**

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to Indian Tribes and our commitments to island communities.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

**BUREAU OF RECLAMATION**  
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**Corrosivity Testing of Waters and Soils**

  
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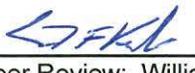
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# Corrosivity Testing of Waters and Soils

## I. Scope

This document outlines procedures for corrosivity testing of soil and water samples. Corrosivity testing, as described here, consists of measuring pH and electrical conductivity (EC) and determining the concentrations of water soluble anions in soil or water samples with primary analytes chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ). Other anions that can be measured include fluoride ( $\text{F}^-$ ), nitrite ( $\text{NO}_2^-$ ), bromide ( $\text{Br}^-$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ).

## II. Summary

The pH and EC of water samples are measured as collected using a meter and probes. To determine the concentration of water soluble inorganic anions in sample waters, the samples are first filtered to remove particulates and then tested using ion chromatography (IC).

For soil samples, the pH and EC are measured from a saturated paste using a meter and probes. To determine the concentration of water soluble inorganic anions in sample soils, ultrapure water is mixed with soil and then agitated to extract water soluble solids. The solution containing the dissolved solids is separated from the soil-water mixture by filtration or centrifugation. The concentration of water soluble inorganic anions is then determined by IC.

## III. Significance and Use

Water soluble minerals may be dissolved and transported in flowing water and in ground water in highly saturated soils. These minerals could cause adverse reactions with buried structures such as corrosion of metals or sulfate attack in concrete. The Bureau of Reclamation recommends corrosivity testing for any structure that comes in contact with water or soil.

This document is not meant to be a training manual. It assumes that the testing will be performed by analysts with at least basic training in chemical analysis and the use of the instrumentation outlined in this document.

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### IV. Reference Documents

#### A. pH

- American Association of State Highway and Transportation Officials (AASHTO) T-289, *Standard Method of Test for Determining pH of Soil for Use in Corrosion Testing* (2004)
- American Society for Testing of Materials (ASTM) D1293, *Standard Test Methods for pH of Water* (2012)
- ASTM D4972, *Standard Test Methods for pH of Soils* (2007)
- ASTM E70, *Standard Test Methods for pH of Aqueous Solutions with the Glass Electrode* (2007)
- *Methods of Soil Analysis, No. 9 - Part 2: Chemical and Microbiological Properties*, American Society of Agronomy, Methods 10-2.3 and 10-3.2 (1982)

#### B. Electrical Conductivity

- ASTM D1125, *Standard Test Methods for Resistivity and Conductivity of Water and Soils* (2009)
- *Methods of Soil Analysis, No. 9 - Part 2: Chemical and Microbiological Properties*, American Society of Agronomy, Methods 10-2.3 and 10-3.3 (1982)

#### C. Water Soluble Anions

- AASHTO T-290, *Standard Method of Test for Determining Water-Soluble Sulfate Ion Content in Soil* (2004)
- AASHTO T-291, *Standard Method of Test for Determining Water-Soluble Chloride Ion Content in Soil* (2004)
- AOAC Official Method 993.30, *Inorganic Anions in Water*, AOAC International (2000)
- ASTM C1580-09, *Standard Test Method for Water-Soluble Sulfate in Soil*

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- ASTM D1193-06, *Standard Specification for Reagent Water*
- ASTM D4327-11, *Standard Test Method for Anions in Water by Suppressed Ion Chromatography*
- EPA Method 300.0, Revision 2.1, *Determination of Inorganic Anions by Ion Chromatography* (1993)
- Standard Methods 4110: *For the Examination of Water and Wastewater*, APHA-AWWA-WEF, 18th edition (1992)
- USBR 5205-89, *Procedure for Preparing Soil Samples by Splitting or Quartering*, USBR Earth Manual- Part 2- Third edition (1990)
- USBR 5450-89, *Procedure for Determining Water Soluble Solids in Soils*, USBR Earth Manual- Part 2- Third edition (1990)
- *USBR Method of Test for Determining the Quantity of Soluble Sulfate in Solid (Soil or Rock) and Water Samples* (1973)

## V. Apparatus

### A. Analytical Balance

The analytical balance should be capable of accurately weighing to the nearest 0.0001 g.

### B. Centrifuge

The centrifuge will be used for separating fine particles from the soil filtrate. It should be capable of maintaining a minimum speed of 4,500 revolutions per minute (rpm) for 10 minutes with a controlled ramp up to and down from maximum speed.

### C. Drying Oven

The drying oven should be capable of maintaining a constant temperature of 60 degrees Celsius ( $^{\circ}\text{C}$ )  $\pm 5$   $^{\circ}\text{C}$ .

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#### D. Ion Chromatograph

The ion chromatograph should have the following components:

- Anion guard column
- Anion analytical column
- Anion suppressor device
- Conductivity detector
- Auto-sampler
- Software capable of generating calibration curves and analyzing test data

#### E. Meter and Probes for pH and Electrical Conductivity

Digital meter should be capable of manual or automatic calibration and manual or automatic temperature correction. Meter and probes should be accurate to 0.01 pH and be capable of reading in the millivolt range for conductivity.

#### F. Pulverizing Apparatus

A mortar and rubber-tipped pestle or other apparatus suitable for breaking up soil aggregates.

#### G. Sample Splitter

A suitable sample splitter capable of obtaining representative portions of the soil samples without loss of fines. Details for obtaining representative samples are outlined in USBR 5205-89, *Earth Manual*.

#### H. Sieves and Filters

Sieves shall be available for sample splitting, including sizes 2.00 millimeter (mm) (No. 10) and 600 micrometer ( $\mu\text{m}$ ) (No. 30). Filtration equipment should also be available, including filter paper and membrane filters down to a filtration size of 0.45  $\mu\text{m}$ .

#### I. Stirring Apparatus

The stirring apparatus could include a variable-speed magnetic stir plate with a polytetrafluoroethylene (PTFE) coated magnetic stir bar or any other apparatus,

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such as a mechanical shaker, capable of maintaining constant and controllable agitation for 1 hour. The stirring apparatus should not cause the sample to increase in temperature.

## VI. Reagents and Materials

### A. Buffer Solutions for pH Calibration

Commercially available buffer solutions of pH 4, 7, and 10 may be used for pH calibration. Alternately, the reference buffer solutions detailed in ASTM D1293 are also acceptable for calibration purposes.

### B. Calibration Solution for Electrical Conductivity

Commercially available solutions for conductivity calibration should be used according to the recommendation of the manufacturer of the EC meter and probe.

### C. Eluent Solution

A mixture of sodium carbonate, concentration 3.2 millimolar (mM), and sodium bicarbonate, concentration 1.0 mM, in reagent water shall be used as eluent solution. Other eluents or eluent concentrations may be used, provided they give sufficient resolution between anion peaks. Eluent shall not be stored for longer than 1 month.

### D. Reagents

Reagent grade chemical shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) grade, where such specifications are available.

### E. Reagent Water

All reagent water used in this method shall be ASTM Type I ultrapure water, 18 megaohm-centimeter ( $M\Omega\cdot cm$ ) resistivity with no particles greater than 0.2  $\mu m$  in size. Freshly purified water should be used to prepare calibration standards and samples.

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#### F. Stock Solutions for Ion Chromatography

A standard stock solution containing all seven anions of interest may be purchased premixed or be prepared from individual anion stock solutions. Instructions for preparing stock solutions containing 1,000 milligrams per liter (mg/L) of the anions of interest can be found in ASTM D4327 and EPA 300.0. The stock solution should be prepared gravimetrically for best accuracy. Calibration solutions must be prepared (gravimetrically) for at least five different anion concentrations ranging from 1.0 to 300 mg/L for chloride and sulfate ions. Table 1 below contains suggested concentrations to be used in instrument calibration. Stock solutions shall also be used to prepare check standards containing 20 mg/L of chloride and sulfate ions.

**Table 1. Suggested concentrations for calibration solutions in mg/L**

Anion	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Cl <sup>-</sup>	1.0	5.0	10	25	50	100	200	300
SO <sub>4</sub> <sup>-2</sup>	1.0	5.0	10	25	50	100	200	300

#### G. Suppressor Rinse and Regeneration Solutions

Reagent water with 0.1 percent (%) methanol, by weight, shall be used as the suppressor rinse solution. The suppressor regenerant solution shall consist of 0.1 molar (M) sulfuric acid.

## VII. Safety Precautions

This procedure may involve the use of hazardous materials. Precautions should be taken for all materials following their material safety data sheet (MSDS) recommendations. A minimum of safety glasses and latex or nitrile gloves shall be worn during all sample and chemical preparations.

Care should be taken when removing hot items from the drying oven. Safety glasses and thermal gloves should be worn for these procedures.

## VIII. Calibration

#### A. pH Meter

Turn on the instrument and allow it to equilibrate per the manufacturer's instruction. Rinse the probe thoroughly with ultrapure water. At least three standard buffer solutions, spanning the range of pH to be measured, should be

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used for calibration. Calibrate using temperature compensation and in accordance with the manufacturer's instruction. Calibrate before initial use and once per hour thereafter.

#### **B. Electrical Conductivity Meter**

Turn on the instrument and allow it to equilibrate per the manufacturer's instruction. Rinse the electrode thoroughly with ultrapure water. Calibrate using temperature compensation and in accordance with the manufacturer's instruction. Calibrate before initial use and once per hour thereafter.

#### **C. Ion Chromatograph**

Turn on the instrument and allow it to equilibrate per the manufacturer's instruction or for a minimum of 1 hour. A blank sample (Type I water) and at least five calibration solutions containing anions of interest shall be analyzed by IC. Retention times for each anion should be compared to the individual analytical column specifications provided by the column manufacturer. Use the IC software to analyze retention time and peak area for each calibration standard and create a calibration curve for each anion. The calibration coefficient shall be greater than or equal to 0.990. Calibrations shall occur quarterly or every 250 samples, whichever occurs first, or if check standards fail.

## **IX. Sample Collection**

#### **A. Water**

When collecting water samples, a clean, 1-liter, high-density polyethylene bottle shall be used. Hands shall be clean or isolated with latex gloves. Before collecting the sample, rinse the bottle three times with sample water. Fill completely and seal the bottle.

#### **B. Soil**

Soil samples should be collected in a clean, 1-quart, resealable plastic bag. Clean hands or latex gloves and a rust-free tool (ideally stainless steel) shall be used to collect the sample. Fill the bag with approximately 1 pound of soil and then seal, evacuating as much air as possible. Wet samples shall be double bagged.

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#### C. General

Label all samples using a permanent marker or a waterproof label with the following information:

1. Sample location (global positioning system [GPS] coordinates, if available) and depth of sample
2. Date and time
3. Name of sample
4. Name of project
5. Field pH, when available

Chloride testing requires no preservatives, but testing should be performed within 28 days of sample collection. Samples that require sulfate testing should be kept cool (< 4.5 °C or 40 degrees Fahrenheit [°F]). Testing should also be performed within 28 days of sample collection.

#### X. Sample Preparation

##### A. Water

Water samples may be tested directly for pH and EC. Samples should be filtered through a minimum 0.45-µm membrane filter or centrifuged at a minimum of 4,500 rpm for 10 minutes before analysis by IC.

##### B. Soil

Soil samples shall be crushed to remove large aggregates, split to obtain a representative sample, and separated by passing through a 2.00-mm sieve. Soil shall then be air dried or dried in an oven at 60 °C for 24 hours. The soil shall be ground to pass a 600-µm sieve using a mortar and rubber-tipped pestle. In the case of wet samples, samples may be air dried or oven dried at a temperature less than 60 °C to achieve a workable state prior to sieving.

For pH and EC testing, weigh 10 g of prepared soil into a 20-mL scintillation vial. Add 10 mL (or equivalent weight) of Type I water to the bottle and mix thoroughly. Agitate the solution using a mechanical shaker for 1 hour before testing. This preparation produces a 1:1 dilution, also known as a saturated paste.

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For anion analysis, water soluble solids shall be extracted by placing 30 g of soil in a 500-mL Erlenmeyer flask. 300 mL (or equivalent mass) of water shall then be added to the flask. Record the mass of soil and mass of water and then calculate the initial dilution factor. The flask should be stoppered and mixed on a magnetic stir plate or other apparatus for 1 hour.

After mixing, measure the EC of the sample and then allow it to settle. At this point, the analyte solution must be filtered through a minimum 0.45- $\mu$ m membrane filter to remove remaining particulates from the solution before analysis by IC. A series of prefilters may be used prior to membrane filtration, if necessary. The solution can then be transferred directly to a properly labeled sample vial for IC analysis. Alternately, the sample may be decanted to a centrifuge vial and centrifuged at a minimum of 4,500 rpm for 10 minutes. Many commercial IC vials are centrifuge compatible.

This preparation produces a 1:10 dilution. Depending on the concentration of anions in the sample, further dilutions may be necessary. Use the EC that was measured after mixing and table 2 to determine the recommended dilution factor. Prepare dilutions gravimetrically and then record mass of initial solution and mass of final solution. Calculate the new dilution factor.

**Table 2. Suggested dilutions for ion chromatography based on EC of 1:10 solution**

Measured EC with 1:10 dilution ( $\mu$ S/cm)	Recommended final dilution	Procedure for 10-mL final volume
< 600	1:10	Use as prepared
600-2500	1:50	Dilute 2.0 mL of 1:10 solution to 10 mL total
2,500-5,000	1:100	Dilute 1.0 mL of 1:10 solution to 10 mL total
5,000-10,000	1:200	Dilute 0.5 mL of 1:10 solution to 10 mL total

Note:  $\mu$ S/cm = microsiemens per centimeter

## XI. Testing Procedures

### A. pH

Determine the pH of the sample using a meter and probe as instructed by the instrument manufacturer. The sample should be measured at room temperature (15 °C to 25 °C) and using temperature correction. Ensure that the electrode bulb is completely submersed in water or inserted partially into the settled portion of

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the soil suspension during measurement. Allow sufficient time for equilibration before recording pH. Rinse the probe thoroughly with water between each sample.

#### **B. Electrical Conductivity**

Determine the EC of the sample using a meter and probe as instructed by the instrument manufacturer. The sample should be measured at room temperature (15 °C to 25 °C) and using temperature correction. Ensure that the electrode portion of the probe is completely submersed in water or inserted partially into the settled portion of the soil suspension during measurement. Allow sufficient time for equilibration before recording conductivity. Rinse the probe thoroughly with water between each sample.

#### **C. Water Soluble Anions (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>)**

Set up the ion chromatograph according to the manufacturer's instructions. Equilibrate the system by pumping eluent through the analytical column and suppressor for a minimum of 1 hour. A stable baseline should be obtained at < 5-µS conductivity. It is recommended that a 0.2-µm membrane filter be placed in-line prior to injection to avoid fouling of the column.

Load the samples into the IC auto-sampler. A blank water sample and a check standard of known chloride and sulfate concentrations should be run at the beginning and end of each batch and after every ten samples. The measured concentration for the check standard should not deviate more than ±10% (e.g., a 20-mg/L check standard will be accepted if the measured value falls between 18-22 mg/L). If the check standard fails, all data following the last accepted check standard will be discarded, the instrument should be recalibrated, and the samples should be retested. If other anions are of interest, they should also be included in the check standard.

Program the instrument software with sample identifications and run as per instrument protocol. Use the software to calculate the peak areas and determine concentrations in the sample based on the calibration curves. Some software will also automatically calculate the concentration of the original solution based on an input dilution factor. To manually account for dilutions, use the following equation to calculate the concentration of the original solution:

$$\text{Anion concentration, mg/L} = \frac{\text{Measured anion concentration, mg/L}}{\text{dilution factor}}$$

## **XII. Report**

The following information shall be reported:

- Project name and location
- Feature name
- Sample identification number
- Date collected
- Date analyzed
- Sample type (soil or water)
- Sample dilution factor
- Measured pH for each sample
- Measured conductivity for each sample
- Calculated concentration for each anion
- Any notes or comments necessary to understand special circumstances or unusual conditions encountered during testing