



Florida Method of Test For Chloride in Soil and Water

Designation: FM 5-552

1. SCOPE

- 1.1. This method covers the determination of chlorides in soil and water using either a screening approach based on a chloride reagent system or an analytical approach as found in the Standard Methods for the Examination of Water and Wastewater, Section 4500-Cl⁻ B or Section 4110 B (SMEWW). This method can also be used for the determination of chloride in coarse aggregate.
- 1.2. Both the screening and analytical approaches use a silver nitrate titration of a sample that is amended with a potassium dichromate. Silver combines first with chloride and then with chromate in a mixture of the two. Both silver chloride and silver chromate are relatively insoluble in water but silver chromate is a brown-red crystal and its appearance in the sample marks the titration endpoint.

2. APPARATUS

- 2.1. Chloride Reagent System: Chloride Low Range Test Kit Model 8-P, 5 to 400 mg/L (Hach catalog #144001) and Chloride High Range Test Kit Model CD-51 (Hach catalog #208601), or equivalent, may be used for chloride determinations. For the Hach Model 8-P test kit, additional glass mixing bottles with a 23-mL mark are needed (for example, Hach catalog #232706). Alternatively, the laboratory instruments referred to in the SMEWW may be used for chloride determination.
- 2.2. Analytical Balance: An analytical balance with a capacity of 2,000 g or greater and a resolution of 0.01 g or better.
- 2.3. Vacuum Filtration System: A vacuum filtration system is required. Such as system includes a vacuum pump, 0.25 in (6 mm) inner diameter flexible vacuum hose, 300-mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.
- 2.4. Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, 0.10-g measuring spoon,



small ceramic dish, a transfer pipette (variable from 0.100 to 1.000 mL, capable of delivering increments of 0.01 mL) and tips, 100-mL graduated cylinder, and disposable nitrile gloves.

3. REAGENTS

- 3.1. Potassium dichromate ($K_2Cr_2O_7$), sodium bicarbonate and silver nitrate ($AgNO_3$) titrant are required for the chloride test kit (Note 1). The potassium dichromate and sodium bicarbonate are supplied as Chloride 2 powder pillows (for example, Hach catalog #105766). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.
- 3.2. Chloride standard solution, 1,000 ppm (mg/L) as Cl^- , NIST-traceable.
- 3.3. Ferric sulfate, hydrated reagent grade (for example, Fisher Scientific catalog #S25322 or #S25322A).
- 3.4. Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Potassium dichromate and silver nitrate are hazardous materials. Refer to the chemical safety data sheets (SDS) regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

4. SAMPLES

- 4.1. Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place 2.4 pounds (1,075 g) \pm 5% of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for a minimum of one hour. This step may be performed in the lab prior to testing.

If the soil sample is obtained from a heap, which has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12" (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the



sample and seal tightly to minimize contact with air.

- 4.2. Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water, such as, lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water, unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating debris, such as leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.
- 4.3. Transporting the samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.
- 4.4. Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per Section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days of collection.

5. SAMPLE PREPARATION

5.1. Preparation of Water:

Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

5.2. Preparation of Soil:

- A. Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hours or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per AASHTO R76 to obtain 425 g ± 5%.
- B. Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, dry in an oven at no higher than 140°F (60°C) for

approximately four hours or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per AASHTO R76 to obtain $425 \text{ g} \pm 5\%$.

5.3. Preparation of Soil Extract:

Place 100 grams of dried soil in a 500 mL Erlenmeyer flask (Note 2). Add 300 mL of dilution water, stopper, and shake vigorously for 20 seconds. Let stand for one hour and repeat agitation. Let stand for a minimum of 12 hours.

- A. Suspended particles (turbidity) or color may interfere with the chloride determination. If the extract is cloudy or colored due to the suspension of fine particles, add ferric sulfate. Dissolve in a small ceramic dish 0.10 g of ferric sulfate into 1 mL of water and pipette the dissolved ferric sulfate into the extract. Allow the sample to stand for three to four hours as the suspended particles settle.
- B. Filter by gravity the soil extract through a Whatman 41 filter (or equivalent) into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.
- C. Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 3) into a clean 1-liter vacuum filtration flask; repeat if necessary to get a clear extract.

5.4. Preparation of Coarse Aggregate:

Split the sample per AASHTO R76 to obtain $1,300 \text{ g} \pm 5\%$ and place aggregate in a suitable container. Add 1,200 mL of dilution water, cover and let stand for 24 hours at room temperature. Collect the leachate using clean equipment to avoid contamination. If leachate contains suspended solids or color, gravity filter the water through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hours of settling both extracts are clear enough to filter, only one of two extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: The MCE membrane filter is white; spacers are blue.



6. TEST PROCEDURE

6.1. Low Range: For the SMEWW analytical approach or an equivalent test kit, follow the kit instructions and include preparation and testing of a blank and 30-ppm check standard. For the Hach Model 8-P chloride test kit (5-400 ppm), follow these instructions:

- A. Check the Reagents: Check that the silver chloride titrant and Chloride 2 Indicator powder pillows have not reached their expiration date.
- B. Prepare a Reagent Blank: Fill one mixing bottle with dilution water to the 23-mL mark. Prepare a blank at least once per day on days in which samples are tested.
- C. Prepare a 30 mg/L (30 ppm) Check Standard: Add to a second mixing bottle 0.690 g of 1,000 mg/L chloride standard solution and fill with dilution water to the 23-mL mark. Prepare a check standard at least once per day on days in which samples are tested.
- D. Prepare a Test Sample (water, soil extract, coarse aggregate leachate): Fill a third mixing bottle with the test sample extract to the 23-mL mark.
- E. Determine the Blank Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the blank. Gently swirl the bottle to achieve a uniform yellow color. Add one drop of 0.0493 N silver nitrate to the blank and gently swirl the bottle to mix. Each drop is equal to 5 mg/L (5 ppm) of chloride (Note 4). With one drop of silver nitrate the color of the blank should turn from yellow to red-brown; this red-brown color will serve as a guide (Note 5). If two or more drops of silver nitrate are necessary to titrate the dilution water to a red-brown color, then either the dilution water is contaminated with chloride or the titrant has gone bad (Note 6).

Sample Calculation: 1 drop x 5 ppm/drop = 5 ppm per blank

- F. Determine the Check Standard Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the check standard. Add one drop at a time of 0.0493 N silver nitrate and gently swirl the bottle to mix. The check standard should turn from yellow to red-brown after the addition of 6 to 8 drops. Record the total number of drops and



subtract from this number one drop for the blank. Multiply the net number of drops by 5 ppm per drop. The check standard concentration should fall between 25 ppm and 35 ppm. If the concentration is less than 25 ppm or greater than 35 ppm the volume of added chloride standard or the drop size of silver nitrate may be off; otherwise the concentrations of either the chloride check standard or the silver nitrate titrant may be off. In either case, prepare a new check standard and re-test.

Sample Calculation: 7 drops x 5 ppm/drop = 35 ppm – 5 ppm blank = 30 ppm for check standard

- G. Determine the Test Sample Chloride Concentration (0-60 ppm): Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the test sample. Gently swirl the bottle to achieve a uniform yellow color. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 5 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. If this result is zero, record that the chloride concentration of the sample as below detection. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample or coarse aggregate but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 5 ppm/drop = 15 ppm – 5 ppm blank = 10 ppm x 3 dilution factor for soil extract = 30 ppm chloride in soil

- H. Determine the Test Sample Chloride Concentration (60-400 ppm): If the test sample has not changed color after the addition of 13 drops (60 ppm), stop the titration. Prepare a new sample extract: fill a clean mixing bottle to the 10-mL mark and add one Chloride 2 Indicator powder pillow. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 20 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample or coarse aggregate but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 20 ppm/drop = 60 ppm – 5 ppm blank = 55



ppm x 3 dilution factor for soil extract = 165 ppm chloride in soil

- 6.2. High Range: If water or soil has a high chloride concentration (for example, seawater has a chloride concentration of 19,000 ppm) use the Hach Model CD-51 chloride test kit (500-100,000) (or equivalent) and follow the kit instructions. For a check standard, fill the measuring tube with a 1000-ppm chloride standard and continue with the test instructions. The standard should be titrated from yellow to red-brown with 1-3 drops of 1.88-N silver nitrate titrant (500 ppm per drop). If more than 3 drops are required to titrate the standard, the titrant may be off.
- 6.3. Sample Dilution: Dilution of the test sample will be necessary if the low range concentration is greater than 400 ppm. To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of test sample and 90 mL of dilution water. The dilution factor for water and coarse aggregate will be 10, for a soil extract, multiply the chloride concentration by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Sample Calculation: 3 drops x 500 ppm/drop = 1500 ppm – 5 ppm blank = 1495 ppm x 30 dilution factor for soil extract = 44850 ppm soil concentration

Note 4: A dropper dispenses more accurately when held in a vertical.

Note 5: White paper serves as a suitable background when observing solution colors.

Note 6: Silver nitrate degrades upon exposure to light and concentrates over time with evaporation. Keep opaque container tightly sealed and away from heat when not in use.

7. PRECISION AND BIAS

- 7.1 Bias: Single-operator, single laboratory bias for this method was evaluated using a Hach Chloride Low Range Test Kit Model 8-P, 5-400 ppm, and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of Chloride 2 indicator. The average bias was -2.5 ppm (-2.5%).

Reproducibility: For a test material (sand, A-3) with an average chloride concentration of 66 ppm, the multi-laboratory standard deviation of a single test result has been found to be 12 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 34 ppm.