FLORIDA DEPARTMENT OF TRANSPORTATION
State Materials Office
5007 NE 39th Avenue
Gainesville, Florida 32609

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Florida Method of Test
for
Chloride in Soil and Water

Designation: FM5-552

1. SCOPE

1.1 This method covers the determination of chloride in soil and water using either a screening approach ***(Method A)*** based on a chloride reagent system or analytical approaches ***(Method B*** *or* ***Method C)*** as found in the ***Standard Methods for the Examination of Water and Wastewater (SMEWW)****,* ***Section 4500-Cl$^-$ B*** or ***Section 4110 B***, respectively. These methods can also be used for the determination of chloride in coarse aggregate.

1.2 Both ***Method A*** and ***Method B*** use 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. Method C involves the use of Ion Chromatography (IC) to separate anions in liquid samples using a column and detector. The conductivity is quantified as the ion elutes from the column and plotted as a peak. Chloride concentration is determined by integrating the peak area or height.

2. APPARATUS

Method A:

2.1 Chloride Reagent System: A test kit that can detect chlorides by drop count titration using silver nitrate. The test kits listed below can detect chloride concentrations from 5 to 100,000 ppm. (Chloride Low Range Test Kit Model 8-P, 5 to 400 ppm Hach catalog #144001 and Chloride High Range Test Kit Model CD-51, 500 to 100,000 ppm Hach catalog #208601). Other kits that use silver nitrate titration may be used if they meet or exceed these ranges. If using the Hach Model 8-P test kit, additional glass mixing bottles with a 23-mL mark are needed (Hach catalog #232706). If using a different test kit, refer to the manufacturer’s instruction manual to determine if additional equipment is needed.

2.2 Analytical Balances:

2.2.1 Analytical balance with a capacity of 2,000 g or greater and a resolution of 0.1 g or better.

2.2.2 Analytical balance with a capacity of 200 g or greater and a resolution of 0.01 g or better is needed for weighing ferric sulfate.

2.3 Vacuum Filtration System: A vacuum filtration system is required. Such a system includes a vacuum pump, 0.25 in (6 mm) inner diameter flexible vacuum hose, 300-mL funnel, a holder for a 47-mm diameter filter, volumetric flask, 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 1 mL transfer pipette and tips, 100-mL, graduated cylinder, and disposable nitrile gloves.

Method B:

Refer to the ***SMEWW Section 4500-Cl$^-$ B***.

Method C:

Refer to the ***SMEWW Section 4110 B***.

3. REAGENTS

Method A:

3.1 Potassium dichromate ($K_2Cr_2O_7$), sodium bicarbonate and silver nitrate ($AgNO_3$) titrant are required ***(Note 1)***. The potassium dichromate and sodium bicarbonate are supplied by Hach as Chloride 2 powder pillows (for example, Hach catalog #105766). Other kits may require using a different form of these reagents, refer to the manufacturer’s instructions.

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 #S25322A) or equivalent.

3.4 Distilled (or higher purity) water with a minimum resistivity of 200,000 ohm-cm (***Note 2***).

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.

Note 2: Distilled (or higher purity) water stored in containers that are not airtight will absorb ions from acidic and basic gases in the atmosphere resulting in lowered resistivity of the water over time.

Method B:

Refer to ***SMEWW Section 4500-Cl⁻ B*** with the following exception:

Use commercially available Potassium Chromate Indicator Solution, 5% w/v.

Method C:

Refer to ***SMEWW Section 4110 B***.

4. SAMPLES

4.1 Sampling and Handling Samples

4.1.1 Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for collecting samples. Excessive moisture should be avoided by sampling from areas that have been allowed to gravity drain. If the soil sample has excess free moisture, place 2.2 lb (1 kg) 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 that has been sitting for a long time, take the sample from a depth below the weathered surface. If sampling from ground level, remove the top 12 in. (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but free-standing water should not be included with the sample. Soil samples should be placed in plastic (watertight) bags. The bag should be squeezed down snugly around the sample and sealed tightly to minimize contact with air.

4.1.2 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 occur in areas conducive to collecting a representative sample. Care should be observed to avoid sampling from stagnant or pooled water unless a structure is placed in such an area.

The water sample container shall be clean, at least 1 qt (1 L) in size and be either glass or plastic with an airtight lid. Rinse the container several times with the water to be collected. When possible, submerge the sample container below the surface of the water to avoid 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.

4.1.3 Transporting Samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.

4.1.4 Storing Samples: Store water and soil samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Analyze samples within seven (7) days of collection.

5. SAMPLE PREPARATION

5.1 Preparation of Water:

5.1.1 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:

5.2.1 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 four hours or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ***AASHTO R 76*** to obtain 425 g ± 5%.

5.2.2 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, or dry in an oven at no higher than 140°F (60°C) for 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 R 76*** to obtain 425 g ± 5%.

5.3 Preparation of Soil Extract:

5.3.1 Place 100 grams of dried soil in a 500-mL Erlenmeyer flask. Add 300 mL of distilled water, stopper, and shake vigorously for 20 seconds. Let stand for one hour and repeat agitation. Let stand for a minimum of 12 hours. If the soil extract is clear enough to gravity filter skip ***Section 5.3.2*** *(**Note 3**)*.

5.3.2 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 0.1 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.

5.3.3 Filter, by gravity, the soil extract through a Whatman 41 filter (or equivalent) into a 500-mL Erlenmeyer flask. Slowly decant into the funnel (containing a filter) the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping. If the extract is clear after gravity filtering, skip ***Section 5.3.4***.

5.3.4 Vacuum filter the soil extract through a 0.45-micron pore size MCE membrane filter *(**Note 3**)* into a clean 1-L vacuum filtration flask; repeat, if necessary, to get a clear extract.

Note 3**:** The soil extract for chloride analysis may also be used for sulfate analysis provided that after 12 hours of settling the extract is clear enough to filter (skipping ***Section 5.3.2***). The same soil extract cannot be used if ***Section 5.3.2*** is performed to remove suspended fines because it would affect sulfate analysis.

5.4 Preparation of Coarse Aggregate:

Split the sample per ***AASHTO R 76*** to obtain 1,300 g ± 5% and place aggregate in a suitable container. Add 1,200 mL of distilled water, cover, and let stand for 24 hours at room temperature. Collect the leachate using clean equipment to avoid contamination.

5.5 Preparation of Coarse Aggregate Leachate:

If the leachate is clear enough to gravity filter skip ***Section 5.5.1*** *(**Note 4**).*

5.5.1 Suspended particles (turbidity) or color may interfere with the chloride determination. If the leachate is cloudy or colored due to the suspension of fine particles, add ferric sulfate. Dissolve in a small ceramic dish 0.1 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 until the suspended particles settle.

5.5.2 Filter, by gravity, the leachate through a Whatman 41 filter or equivalent into a 500-mL Erlenmeyer flask. Slowly decant the water layer into a funnel (containing a filter) followed by any particulate and allow the liquid to drain until it stops dripping. If the extract is clear after gravity filtering, skip ***Section 5.5.3***.

5.5.3 Vacuum filter the leachate through a 0.45-micron pore size MCE membrane filter *(**Note 5**)* into a clean 1-liter vacuum filtration flask; repeat, if necessary, to get a clear extract.

Note 4: The leachate for chloride analysis may also be used for and sulfate analysis provided that after 12 hours of settling the leachate is clear enough to filter (skipping ***Section 5.5.1***). The same leachate cannot be used if ***Section 5.5.1*** is performed to remove suspended fines because it would affect sulfate analysis.

Note 5: The MCE membrane filter is white, the spacers are typically blue.

6. PROCEDURE

Method A:

6.1 Low Range: Follow the instructions included in the kit used. No matter what tests kit is used, a blank and 30-ppm check standard should be prepared for testing. The steps below are for the Hach Model 8-P chloride test kit (for low chloride concentrations 5-400 ppm), follow these instructions:

6.1.1 Check the Reagents: Check that the silver chloride titrant and Chloride 2 Indicator powder pillows have not reached their expiration date.

6.1.2 Prepare a Reagent Blank: Fill one mixing bottle with distilled water to the 23-mL mark. Prepare a blank at least once per day on days in which samples are tested.

6.1.3 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 distilled water to the 23-mL mark. Prepare a check standard at least once per day on days in which samples are tested.

6.1.4 Prepare a Test Sample (water, soil extract, or coarse aggregate leachate): Fill a third mixing bottle with the test sample extract to the 23-mL mark.

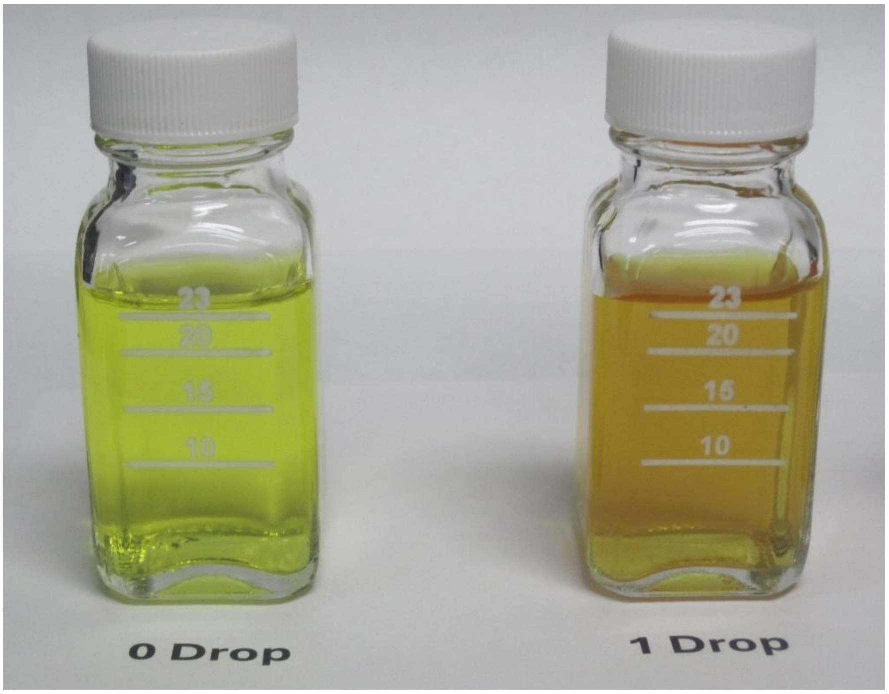
6.1.5 Determine the Reagent Blank Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to the mixing bottle that contains distilled water. Gently swirl the bottle to achieve a uniform yellow color. Add one drop of 0.0493 N silver nitrate to the blank and gently swirl the bottle to mix. Each drop is equal to 5 mg/L (5 ppm) of chloride ***(Note 6)***. The addition of one drop of silver nitrate should produce a slight color change in the blank, indicating the titration end point (***Figure 1*** and ***Note 7***). If two or more drops are required to observe the end point, this suggests either chloride contamination in the distilled water or deterioration of the titrant ***(Note 8)***.

Note 6: A dropper dispenses more accurately when held vertically.

Note 7: White paper serves as a suitable background when observing solution colors.

Note 8: 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.

Figure 1: Comparing a reagent blank with 0 drops of $AgNO_3$ and a completely titrated reagent blank.



6.1.6 Determine the Check Standard Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to the 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. Titration is complete when a color change is first detected. The check standard should reach its end point with the addition of 6 to 8 drops of silver nitrate. 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. 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 concentration 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.

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

6.1.7 Determine the Test Sample Chloride Concentration (0-100 ppm): Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to the mixing bottle that contains the test sample. Gently swirl the bottle to achieve a uniform yellow color. Add 0.0493 N silver nitrate one drop at a time until the first observable color change occurs in the test sample. 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.

Example Calculation for soil sample: 4 drops x 5 ppm/drop – 5 ppm blank = 20 ppm – 5 ppm blank = 15 ppm. Multiply 15 ppm x 3 dilution factor for soil extract = 45 ppm chloride in soil.

6.1.8 Determine the Dilute Test Sample Chloride Concentration (100 – 400 ppm): If the test sample has not changed color after the addition of 21 drops (100 ppm), stop the titration. Prepare a new sample: fill the measuring tube with sample and pour into a clean, dry mixing bottle. Add one Chloride 2 Indicator powder pillow and gently swirl the bottle to achieve a uniform yellow color. Add 0.0493 N silver nitrate one drop at a time until the first observable color change occurs in the test sample. 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. Multiply the chloride concentration by the dilution factor, which may be 1 for a water or coarse aggregate sample 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.

Example Calculation: 3 drops x 20 ppm/drop – 5 ppm blank = 60 ppm – 5 ppm blank = 55 ppm. Multiply 55 ppm x 3 dilution factor for soil extract = 165 ppm chloride in soil.

6.2 High Range:

If the dilute sample (6.1.8) results were greater than 400 ppm, it will be necessary to use a kit that can detect greater concentrations. The Hach Model CD-51 chloride test kit or equivalent test kit can be used. For specific testing procedures, refer to the manufacturer's instructions for the kit being used.

6.2.1 Check the Reagents: Check that the silver chloride titrant and Chloride 2 Indicator powder pillows have not reached their expiration date.

6.2.2 Check Standard and Test Sample: For a check standard, fill the measuring tube with a 1000 ppm chloride standard and pour into a clean, dry mixing bottle. Add one Chloride 2 Indicator Powder Pillow to the mixing bottle. Swirl the bottle to dissolve the reagents and add the silver nitrate one drop at a time. After each drop, tighten the cap and shake vigorously. Record the number of drops required to produce the first detectable color change. The chloride standard should be titrated 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. If the solution is yellow and the precipitate is orange, the sample was not shaken vigorously enough. Start the test again with a new standard check sample.

Example Calculation: 3 drops x 500 ppm/drop – 5 ppm = 1500 ppm

– 5 ppm = 1495 ppm (5 ppm is subtracted for the blank run in 6.1.5)

6.2.3 Determine the Test Sample Chloride Concentration (400-10,000 ppm): Fill the sample tube with the test sample and pour into a mixing bottle. Add one Chloride 2 Indicator Powder Pillow to the mixing bottle. Swirl the bottle to dissolve the reagents and add the silver nitrate one drop at a time. After each drop, tighten the cap and shake vigorously. Record the number of drops required to produce the first detectable color change. If the solution is yellow and the precipitate is orange, the sample was not shaken vigorously enough. Start the test again with a new test sample.

Example Calculation: 3 drops x 500 ppm/drop – 5 ppm = 1500 ppm – 5 ppm = 1495 ppm. Multiply 1495 ppm x 3 dilution factor for soil extract = 4485 ppm chloride in soil (5 ppm is subtracted for the blank).

6.2.4 Sample Dilution: Dilution of the test sample will be necessary if the high range concentration is greater than 10,000 ppm (no color change after the addition of 20 drops). To dilute by a factor of 10, mix in a 100-mL volumetric flask 10 mL of test sample and 90 mL of distilled water ***(Note 9)***. 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). After diluting the sample, follow step 6.2.3.

Note 9: The HACH CD-51 test kit includes a dropper that can be used for testing samples above 10,000 ppm. Follow the directions provided in the kit and do not dilute the sample as indicated in ***Section 6.2.4*** if using the dropper in lieu of the sample tube.

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

Method B:

Refer to the ***SMEWW Section 4500-Cl$^-$ B*** with the following exceptions:

Section 3c

Standard sodium chloride solution. Prepare standard stock solution to 2500 ppm. Weigh 1.0303 g of NaCl (dried at 140°C, 1 hr.) and transfer to 250 mL volumetric flask. Dissolve and dilute to volume with distilled water. Mix well.

Section 3d.1

Use Aluminum Hydroxide suspension for chloride-commercially available.

Section 3d.2

Phenolphthalein Indicator Solution. Phenolphthalein indicator is used to verify pH of sample. Use a pH meter in lieu of the indicator.

Method B Calculations

Water samples: $$Cl^-\left(\frac{mg}{L}\right) = \frac{(A-B)*N*35{,}450}{v} \qquad (1)$$

Soil samples: $$Cl^-\left(\frac{mg}{g}\right) = \frac{(A-B)*N*35{,}450*3}{m} \qquad (2)$$

Where: A = ml of titrant for sample

B= ml of titrant for blank

N = normality of $AgNO_3$

v = mL of sample

m = g of sample

3 = is the dilution factor for a soil sample (100 g/300ml)

Method C:

Refer to the ***SMEWW Section 4110 B***.

Concentration is calculated by the response of the sample against IC standard calibration curve and is determined by instrument software. Dilution factors, if required, are included in the sequence before sample analysis. For soil samples, multiply the result by 3.

7. REPORT

The following information should be reported:

Chloride content of the sample in ppm.

8. PRECISION and BIAS

Method A:

8.1 Precision: 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.

8.2 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%).