Designation: D1411 – 09

Standard Test Methods for
Water-Soluble Chlorides Present as Admixtures in Graded Aggregate Road Mixes[1]

This standard is issued under the fixed designation D1411; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 These test methods are applicable to the determination of water-soluble calcium, magnesium, and sodium chlorides used as admixtures in the preparation of graded aggregate road materials.

1.1.1 *Method A, Total Chlorides*—Add an excess of a standard silver nitrate solution to the filtered sample; back titrate the excess silver with a standard ammonium thiocyanate solution to a red-orange endpoint using Volhard indicator.

1.1.2 *Method B, Calcium Chloride*—Calcium in an alkaline solution is titrated with standard EDTA solution using calcein modified as an indicator. The color change is from green to blue.

1.1.3 *Method C, Magnesium Chloride*—Calcium and magnesium, in a solution buffered to a pH of 10, are titrated with standard EDTA solution using eriochrome black T as an indicator. The color change is from red to blue. Magnesium chloride is calculated by subtracting the EDTA calcium equivalent volume determined in the analysis for calcium chloride from the total EDTA volume used, to obtain the magnesium EDTA equivalent by difference.

1.1.4 *Method D, Alkali Chloride*—Alkali chlorides are calculated from the difference of the total chloride and calcium and magnesium determinations.

NOTE 1—These test methods assume that the aggregate did not contain significant amounts of the water-soluble chlorides in question before the admixture was added. If significant amounts of these chlorides are known or suspected to be present, the aggregate shall be tested for these constituents according to these test methods and the proper corrections made.

1.2 All observed and calculated values shall conform to the guidelines for significant digits and rounding established in Practice D6026.

1.2.1 The method used to specify how data are collected, calculated, or recorded in this standard is not directly related to the accuracy to which the data can be applied in design or other uses, or both. How one applies the results obtained using this standard is beyond its scope.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 This practice offers a set of instructions for performing one or more specific operations. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this practice may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.

1.5 The text of this standard references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of the standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D653 Terminology Relating to Soil, Rock, and Contained Fluids
D1193 Specification for Reagent Water
D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction
D6026 Practice for Using Significant Digits in Geotechnical Data

3. Terminology

3.1 Except as follows in 3.2, all definitions are in accordance with Terminology D653.

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[1] These test methods are under the jurisdiction of Committee D18 on Soil and Rock and are the direct responsibility of Subcommittee D18.15 on Stabilization With Admixtures.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *admixture—in road construction*, a material other than water, aggregates, hydraulic cement, and fiber reinforcement used as an ingredient and added immediately before or during the mixing of road materials.

4. Significance and Use

4.1 The percentage of calcium chloride, magnesium chloride, and alkali chloride (calculated as sodium chloride) in graded aggregate obtained from aggregate roads or aggregate bases under paved roads is of interest to highway departments using calcium chloride or sodium chloride stabilization. The percentages of calcium chloride or sodium chloride obtained in these test methods are compared with the quantities added to determine whether the road material and stabilizing agent were properly mixed, whether leaching of the stabilizing agent occurred, etc.

NOTE 2—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D3740 are generally considered capable of competent and objective testing/sampling/inspection/etc. Users of this standard are cautioned that compliance with Practice D3740 does not in itself assure reliable results. Reliable results depend on many factors; D3740 provides a means of evaluating some of those factors.

5. Purity of Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity conforming to Specification D1193.

6. Preparation of Samples

6.1 Submit samples from the field to the laboratory in sealed containers. For each individual sample, break up any agglomerated particles in a mortar and quarter the sample. Accurately weigh approximately 300 g (dry weight) of a quartered sample and transfer it to a 1-L bottle. Add 479 mL of water, 20 mL of ferric ammonium sulfate (100 g/L) and 1 mL of ammonium hydroxide (sp gr 0.90). Agitate in a shaker overnight or for 12 to 15 h. Filter through fluted filter paper, discarding the first 50 mL and retaining the remainder. Determine calcium, magnesium, and chloride in the clear filtrate.

NOTE 3—The addition of ferric ammonium sulfate and ammonium hydroxide should give complete coagulation of most of the dispersible materials and give clear filtrates.

TOTAL CHLORIDES

7. Summary of Test Method

7.1 Add an excess of a standard silver nitrate solution to the filtered sample; and back titrate the excess silver with a standard ammonium thiocyanate solution to a red-orange endpoint using Volhard indicator.

8. Interferences

8.1 In effect, this method is a "Total Halides" method as it cannot distinguish between chloride and other halides that may be present.

9. Reagents

9.1 *Ammonium Thiocyanate, Standard Solution* (*0.1 N*)—Dissolve 7.6 g of ammonium thiocyanate (NH_4SCN) in water and dilute to 1 L. Standardize against the 0.1 *N* $AgNO_3$ solution.

9.2 *Benzyl Alcohol, Chlorine-Free* .

9.3 *Nitric Acid (sp gr 1.42)*—Concentrated HNO_3.

9.4 *Silver Nitrate, Standard Solution* (*0.1 N*)—Dissolve 17.0 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

9.5 *Volhard Indicator Solution*—Dissolve 10 g of ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) in 100 mL of water and add 1 mL of HNO_3.

10. Procedure

10.1 Acidify a suitable portion of the sample solution (see Section 6) (10-mL aliquot) with 3 to 5 mL of concentrated HNO_3 , add a known volume of the 0.1 *N* $AgNO_3$ solution that is in excess of the amount required to precipitate the chloride, and heat to boiling to coagulate silver chloride (AgCl). Cool to room temperature, add 3 to 5 mL of benzyl alcohol, and shake vigorously. If help is needed to determine the point at which an excess of $AgNO_3$ solution is achieved, add 5 mL of Volhard indicator and 1 mL of 0.1 *N* ammonium thiocyanate prior to the addition of 0.1 *N* $AgNO_3$ solution. The red orange color of Volhard indicator will disappear when excess $AgNO_3$ solution has been added.

10.2 Add Volhard indicator solution to the solution and titrate the excess $AgNO_3$ with 0.1 *N* NH_4SCN solution.

11. Calculation

11.1 Calculate the percentage of total chloride ion as follows:

$$\text{chloride, \%} \; \frac{\left[\left(aN - a'N'\right) \times 0.0355\right]}{bw} \times 100 \qquad (1)$$

where:

a = millilitres of $AgNO_3$ solution added,

a' = millilitres of NH_4SCN solution required for the titration,

N = normality of the $AgNO_3$ solution,

N' = normality of NH_4SCN solution,

b = millilitres of solution in aliquot taken, divided by 500, and

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[3] "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

w = grams of sample used.

CALCIUM CHLORIDE

12. Summary of Test Method

12.1 Calcium in an alkaline solution is titrated with standard EDTA solution using calcein modified as an indicator. The color change is from green to blue.

13. Interferences

13.1 Strontium, and other cations not complexed with cyanide at an alkaline pH will be titrated as calcium.

14. Reagents

14.1 *Calcein Modified Indicator.*

14.2 *Calcium Chloride, Standard Solution*—Place 15.00 g of primary standard calcium carbonate ($CaCO_3$) in 300 mL of water and slowly add concentrated hydrochloric acid (HCl), while stirring continuously. When the calcium carbonate is dissolved, cool and transfer to a 1-L volumetric flask. Dilute to volume with water and mix thoroughly. Pipet a 25-mL aliquot into a 500-mL volumetric flask and dilute to volume with water and mix thoroughly. One millilitre of the second dilution is equivalent to 0.000832 g of calcium chloride.

14.3 *EDTA Standard Solution*—Dissolve 3.792 g of disodium dihydrogen ethylenediaminetetraacetate dihydrate in water in a 1-L volumetric flask and dilute to volume with water. Standardize this solution by titrating 50.0 mL of the dilute calcium chloride standard solution.

14.4 *Hydroxylamine Hydrochloride, 10 % Solution*—Dissolve 10 g of hydroxylamine hydrochloride ($NH_2OH·HCl$) in 90 mL of water.

14.5 *Potassium Cyanide.*

14.6 *Sodium Hydroxide, Standard Solution* (2 *N*)—Dissolve 80 g of sodium hydroxide (NaOH) in 300 mL of water. Transfer to a 1-L volumetric flask and dilute to volume with water.

14.7 *Sugar.*

15. Procedure

15.1 Pipet a suitable aliquot of the solution of the sample (see Section 6) 10.0 mL of the solution, or approximately 6 g of the original sample) into a 500-mL Erlenmeyer flask and dilute to about 200 mL.

15.2 Add 10 mL of the hydroxylamine hydrochloride solution, 1 g of sugar, and swirl to dissolve. Add 40 mL of the 2 *N* NaOH solution and 0.1 g of potassium cyanide and about 0.2 g of the indicator.

15.3 Titrate with standard EDTA solution until the indicator changes from green to purple.

16. Calculation

16.1 Calculate the percentage of calcium chloride ($CaCl_2$) as follows:

$$\text{Let } F = \text{g CaCl}_2/\text{mL EDTA} \quad (2)$$

$$= \frac{50.0 \text{ mL} \times 0.000832 \text{ g CaCl}_2/\text{mL}}{\text{mL of EDTA from standardization}}$$

$$\text{CaCl}_2, \% = (a \times F \times 100)/bw$$

where:

a = millilitres of EDTA solution required for the sample titration,

b = millilitres of solution in the aliquot taken, divided by 500, and

w = grams of sample used.

MAGNESIUM CHLORIDE

17. Summary of Test Method

17.1 Calcium and magnesium, in a solution buffered to a pH of 10, are titrated with standard EDTA solution using eriochrome black T as an indicator. The color change is from red to blue. Magnesium chloride is calculated by subtracting the EDTA calcium equivalent volume determined in the analysis for calcium chloride from the total EDTA volume used, to obtain the magnesium EDTA equivalent by difference.

18. Interferences

18.1 There are no known interferences.

19. Reagents

19.1 *Buffer Solution, Approximately pH 10*—Dissolve 65.5 g of ammonium chloride in 300 mL of water. Add 570 mL of ammonium hydroxide (NH_4OH) (sp gr 0.90) and dilute to 1 L with water.

19.2 *Eriochrome Black T Indicator Solution*—Dissolve 4.5 g of hydroxylamine hydrochloride ($NH_2OH·HCl$) in 100 mL of methanol. Add 0.5 g of Eriochrome Black T and mix.

20. Procedure

20.1 Pipet a suitable aliquot of the solution of the sample (see Section 6) (10.0 mL of the solution, or approximately 6 g of the original sample) into a 500-mL Erlenmeyer flask and dilute to approximately 200 mL.

20.2 Add 10 mL of 10 % hydroxylamine hydrochloride, 20 mL of buffer, 0.1 g potassium cyanide, 5 drops of indicator, and titrate with EDTA to a color change of red to blue.

21. Calculation

21.1 Calculate the percentage of magnesium chloride ($MgCl_2$) as follows:

$$\text{Let } F = \text{g of MgCl}_2/\text{mL EDTA} \quad (3)$$

$$= \frac{50.0 \text{ mL} \times 0.000832 \text{ g CaCl}_2/\text{mL} \times 0.858}{\text{mL of EDTA from standardization}}$$

$$\text{MgCl}_2, \% = [(a' - a) \times F \times 100]/bw$$

where:

a' = millilitres of EDTA solution needed to titrate the aliquot for calcium and magnesium.

a = millilitres of EDTA solution needed to titrate the aliquot for calcium,
b = millilitres in the aliquot of the original sample solution, divided by 500, and
w = grams of sample used.

ALKALI CHLORIDE

22. Procedure

22.1 Alkali chlorides are calculated from the difference of the total chloride and calcium and magnesium determinations.

23. Calculation

23.1 Calculate the percentage of alkali chlorides as follows:

$$\text{Percent alkali chlorides as NaCl} \tag{4}$$

$$= (a \times 1.648) - (b \times 1.053) - (c \times 1.227)$$

where:

a = percent total chlorides,
b = percent calcium chloride, and
c = percent magnesium chloride.

24. Report: Records

24.1 The report shall contain the following:

24.1.1 Specimen identification number, classification, moisture content and other physical data which may be pertinent,

24.1.2 Tests performed and results conforming to the guidelines for significant digits and rounding established in Practice D6026,

24.1.3 Deviation from standards, and

24.1.4 Other observations relevant to the results.

PRECISION AND BIAS

25. Precision and Bias

25.1 *Precision*—A limited interlaboratory round-robin test program has been conducted for the purpose of establishing precision and bias values. Total chlorides were determined by four laboratories with four samples. Table 1 describes the standard deviation (1s) and the 95 % confidence interval (d2s) for the total chloride contents tested. Two tests on similar specimens from the same sample should not differ by more than the amounts indicated in the d2s columns.

TABLE 1 Estimates of Precision

	Single operator		Multi-laboratory	
Material	1s	d2s	1s	d2s
2 % NaCl	0.0082	0.0232	0.0087	0.0246
2.5 % $CaCl_2$	0.0137	0.0387	0.0138	0.0390
3 % NaCl	0.0115	0.0325	0.0120	0.0339
3.5 % $CaCl_2$	0.0128	0.0362	0.0172	0.0486

25.2 The bias for this round-robin test was on the order of minus 35 %. That is, the average results in the four tentative tests were approximately 35 % lower than the actual values which should have been obtained. A more extensive interlaboratory round-robin test series has been proposed to resolve the question of accuracy.[4]

26. Keywords

26.1 admixture; chloride content; soil-stabilization

SUMMARY OF CHANGES

Committee D18 has identified the location of selected changes to this standard since the last issue (D1411–04) that may impact the use of this standard.

(1) 1.1 was modified to summarize each of the test methods.
(2) 1.2, 1.4, and 1.5 were added to reflect caveats required by Committee D18.
(3) Section 2 was modified to include references to D3740 and D6026.
(4) 3.1 was modified to include a delimiting phrase.
(5) Note 2 was added highlighting Practice D3740 as required by Committee D18.
(6) 6.1 was modified to clarify the materials that required grinding.
(7) 7.1 was changed to an active voice.
(8) 14.1 was changed to eliminate an undesirable footnote.
(9) Section 24 “Reports: Records” was added.
(10) Updated Summary of Changes section.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D18-1001.

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