Designation: D 1411 – 04

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

This standard is issued under the fixed designation D 1411; 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.

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 *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.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 653 Terminology Relating to Soil, Rock, and Contained Fluids

D 1193 Specification for Reagent Water

3. Terminology

3.1 Except as follows in 3.2, all definitions are in accordance with Terminology D 653.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *admixture*—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.

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 D 1193.

6. Preparation of Samples

6.1 Submit samples from the field to the laboratory in sealed containers. For each individual sample, break up any large lumps 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

[1] These 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.

[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.

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

and retaining the remainder. Determine calcium, magnesium, and chloride in the clear filtrate.

NOTE 2—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 An excess of a standard silver nitrate solution is added to the filtered sample, and the excess silver is back titrated 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:

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

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
- 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.*[4]

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 ($NH_2OH \cdot HCl$) 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:

[4] A satisfactory indicator is available from G. Frederich Smith Chemical Co., Columbus, OH.