



# Standard Test Methods for Water-Soluble Chlorides Present as Admixtures in Graded Aggregate Road Mixes<sup>1</sup>

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 ( $\epsilon$ ) 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:

D 653 Terminology Relating to Soil, Rock, and Contained Fluids<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

## 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.<sup>4</sup> 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 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.

<sup>1</sup> These methods are under the jurisdiction of Committee D-18 on Soil and Rock and are the direct responsibility of Subcommittee D18.15 on Stabilization with Admixtures.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.08.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> "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.

## TOTAL CHLORIDES

### 7. Reagents

7.1 *Ammonium Thiocyanate, Standard Solution (0.1 N)*—Dissolve 7.6 g of ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) in water and dilute to 1 L. Standardize against the 0.1 N  $\text{AgNO}_3$  solution.

7.2 *Benzyl Alcohol, Chlorine-Free.*

7.3 *Nitric Acid (sp gr 1.42)*—Concentrated  $\text{HNO}_3$ .

7.4 *Silver Nitrate, Standard Solution (0.1 N)*—Dissolve 17.0 g of silver nitrate ( $\text{AgNO}_3$ ) in water and dilute to 1 L. This is a primary standard.

7.5 *Volhard Indicator Solution*—Dissolve 10 g of ferric ammonium sulfate ( $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) in 100 mL of water and add 1 mL of  $\text{HNO}_3$ .

### 8. Procedure

8.1 Acidify a suitable portion of the sample solution (see Section 6) (10-mL aliquot) with 3 to 5 mL of concentrated  $\text{HNO}_3$ , add a known volume of the 0.1 N  $\text{AgNO}_3$  solution that is in excess of the amount required to precipitate the chloride, and heat to boiling to coagulate silver chloride ( $\text{AgCl}$ ). Cool to room temperature, add 3 to 5 mL of benzyl alcohol, and shake vigorously.

8.2 Add Volhard indicator solution to the solution and titrate the excess  $\text{AgNO}_3$  with 0.1 N  $\text{NH}_4\text{SCN}$  solution.

### 9. Calculation

9.1 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  $\text{AgNO}_3$  solution added,

$a'$  = millilitres of  $\text{NH}_4\text{SCN}$  solution required for the titration,

$N$  = normality of the  $\text{AgNO}_3$  solution,

$N'$  = normality of  $\text{NH}_4\text{SCN}$  solution,

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

$w$  = grams of sample used.

## CALCIUM CHLORIDE

### 10. Reagents

10.1 *Calcein Modified Indicator*.<sup>5</sup>

10.2 *Calcium Chloride, Standard Solution*—Place 15.00 g of primary standard calcium carbonate ( $\text{CaCO}_3$ ) in 300 mL of water and slowly add concentrated hydrochloric acid ( $\text{HCl}$ ), 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.

<sup>5</sup> A satisfactory indicator is available from G. Frederick Smith Chemical Co., Columbus, OH.

10.3 *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.

10.4 *Hydroxylamine Hydrochloride, 10 % Solution*—Dissolve 10 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) in 90 mL of water.

10.5 *Potassium Cyanide.*

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

10.7 *Sugar.*

### 11. Procedure

11.1 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.

11.2 Add 10 mL of the hydroxylamine hydrochloride solution, 1 g of sugar, and swirl to dissolve. Add 40 mL of the 2 N  $\text{NaOH}$  solution and 0.1 g of potassium cyanide and about 0.2 g of the indicator.

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

### 12. Calculation

12.1 Calculate the percentage of calcium chloride ( $\text{CaCl}_2$ ) as follows:

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

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

$$\text{CaCl}_2, \% = (a \times F \times 100)/bw \quad (2)$$

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

### 13. Reagents

13.1 *Buffer Solution, Approximately pH 10*—Dissolve 65.5 g of ammonium chloride in 300 mL of water. Add 570 mL of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (sp gr 0.90) and dilute to 1 L with water.

13.2 *Eriochrome Black T Indicator Solution*—Dissolve 4.5 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) in 100 mL of methanol. Add 0.5 g of Eriochrome Black T and mix.

### 14. Procedure

14.1 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.

14.2 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.

## 15. Calculation

15.1 Calculate the percentage of magnesium chloride ( $\text{MgCl}_2$ ) as follows:

$$\begin{aligned} \text{Let } F &= \text{g of MgCl}_2/\text{mL EDTA} & (3) \\ &= \frac{50.0 \text{ mL} \times 0.000832 \text{ g CaCl}_2/\text{mL} \times 0.858}{\text{mL of EDTA from standardization}} & (3) \\ \text{MgCl}_2, \% &= [(a' - a) \times F \times 100]/bw & (3) \end{aligned}$$

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

### 16. Procedure

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

### 17. Calculation

17.1 Calculate the percentage of alkali chlorides as follows:

$$\begin{aligned} \text{Percent alkali chlorides as NaCl} & & (4) \\ = (a \times 1.648) - (b \times 1.053) - (c \times 1.227) & & (4) \end{aligned}$$

where:

- $a$  = percent total chlorides,

- $b$  = percent calcium chloride, and
- $c$  = percent magnesium chloride.

## PRECISION AND BIAS

### 18. Precision and Bias

18.1 *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.

18.2 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.<sup>6</sup>

### 19. Keywords

19.1 admixture; chloride content; soil-stabilization

<sup>6</sup> Details of the precision and bias analysis are on file with ASTM. Request RR: D-18-1001.

**TABLE 1 Estimates of Precision**

Material	Single operator		Multi-laboratory	
	1s	d2s	1s	d2s
2 % NaCl	0.0082	0.0232	0.0087	0.0246
2.5 % $\text{CaCl}_2$	0.0137	0.0387	0.0138	0.0390
3 % NaCl	0.0115	0.0325	0.0120	0.0339
3.5 % $\text{CaCl}_2$	0.0128	0.0362	0.0172	0.0486

## SUMMARY OF CHANGES

This section identifies the location of changes to this test method since the last edition.

- (1) The word “admix” was replaced with “admixture” in the title and paragraph 1.1 because, according to the dictionary, the word “admix” is grammatically incorrect in these circumstances.
- (2) Paragraph 1.2 (safety caveat) was added in accordance with the Form and Style Manual (Blue Book).
- (3) Terminology D 653 was added to Section 2, Referenced Documents.

- (4) Section 3, Terminology, was added to incorporate a new definition. Subsequent sections were renumbered.
- (5) A new definition of “admixture” was added to Section 3, Terminology, because the one found in Terminology D 653 is written for grouts.
- (6) Summary of Changes was added.

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