



# Standard Test Methods for Analysis of Calcium Chloride<sup>1</sup>

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*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 These test methods cover the analysis of calcium chloride and solutions.

1.2 Procedures are given for the determination of calcium chloride, magnesium chloride, potassium chloride, sodium chloride, and calcium hydroxide. The test methods appear in the following order:

	Sections
Calcium Chloride	8 to 16
Magnesium Chloride, Potassium Chloride, and Sodium Chloride	17 to 26
Calcium Hydroxide	27 to 33

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.* Specific hazard statements are given in Section 5.

1.4 Review the current Material Safety Data Sheet (MSDS) for detailed information concerning toxicity, first aid procedures, handling, and safety precautions.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 345 Test Method for Sampling and Testing Calcium Chloride for Roads and Structural Applications<sup>2</sup>

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

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>4</sup>

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis<sup>4</sup>

E 663 Practice for Flame Atomic Absorption Analysis<sup>5</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.02 on Product Standards.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.03.

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

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 15.05.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.06.

## 3. Significance and Use

3.1 Calcium chloride is available in various forms and purities. A major use is the de-icing and dust control of roads. It is also used in the coal industry for dustproofing and freezeproofing, in foods, in electrolytic cells, and in refrigeration brines. The test methods listed in 1.2 provide procedures for analyzing calcium chloride to determine if it is suitable for its intended use.

## 4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, these shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>6</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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

## 5. Hazards

5.1 While calcium chloride is a relatively harmless material, some of the reagents used in these methods present possible safety hazards. Potassium cyanide is extremely hazardous and must be handled with great care. In addition to being poisonous, solutions containing cyanide should never be mixed with acids to preclude the release of poisonous hydrogen cyanide gas. Concentrated hydrochloric acid and sodium hydroxide also are hazardous chemicals which may produce serious burns on contact.

## 6. Atomic Absorption Spectrophotometers

6.1 Photometers and photometric practice used in these methods shall conform to Practice E 663.

<sup>6</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.

## 7. Sampling

7.1 Sampling of calcium chloride is not within the scope of these test methods. See the appropriate sections of Test Method D 345.

7.2 The sample to be analyzed shall be considered to be that sample in a single bottle submitted to the analytical laboratory.

7.3 The size of the sample shall be sufficient to perform all analyses without the reuse of any portion of the sample.

## CALCIUM CHLORIDE

### 8. Scope

8.1 This test method covers the determination of calcium chloride in the range from 0 to 100 %.

### 9. Summary of Test Method

9.1 Calcium in an alkaline solution is titrated with standard ethylenediaminetetraacetate solution, using modified calcein II as an indicator. The color change is from green to purple.  $\alpha$ -hydroxynaphthol blue is also suitable as an indicator, in which case the color change is from red to blue.

### 10. Interferences

10.1 Strontium and other cations not complexed with cyanide at pH of at least 10 will consume ethylenediaminetetraacetate solution and will affect the accuracy of this test method.

### 11. Apparatus

11.1 *Buret*, 50-mL, Class A.

11.2 *Weighing Bottle*, glass-stoppered, 100-mL.

### 12. Reagents

12.1 *Calcium Chloride, Standard Solution* (1 mL = 0.00832 g  $\text{CaCl}_2$ )—Weigh 7.500 g of primary standard calcium carbonate ( $\text{CaCO}_3$ ). Transfer to a 600-mL beaker and add 300 mL of water. Cover with a watch glass and slowly add to the beaker, while stirring, 15 mL of concentrated hydrochloric acid (HCl) delivered from a pipet inserted between the lip of the beaker and the edge of the watch glass. When dissolution of the  $\text{CaCO}_3$  is complete, boil gently to expel  $\text{CO}_2$ . Cool, and transfer to a 1-L volumetric flask. Dilute to volume with water and mix.

12.2 *Ethylenediaminetetraacetate, Standard Solution* (0.1 M)—Dissolve 37.22 g of disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) in water. Transfer to a 1-L volumetric flask, dilute to volume with water, and mix. Standardize as follows: Transfer a 50-mL aliquot of  $\text{CaCl}_2$  standard solution (1 mL = 0.00832 g  $\text{CaCl}_2$ ) to a 500-mL Erlenmeyer flask and dilute to 200 mL with water. Proceed as directed in 13.2. Calculate the  $\text{CaCl}_2$  equivalent of the EDTA solution as follows:

$$\text{Calcium chloride equivalent, g/mL} = 0.416/A \quad (1)$$

where:

A = millilitres of EDTA solution required for the titration of the  $\text{CaCl}_2$  solution.

12.3 *Hydrochloric Acid* (1 + 3)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) and 3 volumes of water.

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

12.5  *$\alpha$ -Hydroxynaphthol Blue*.<sup>7</sup>

12.6 *Modified Calcein Indicator*.<sup>8</sup>

12.7 *Potassium Cyanide* (KCN).

12.8 *Sodium Hydroxide Solution* (80 g/L)—Add slowly 80 g of sodium hydroxide (NaOH) in 300 mL of water stirring constantly. Cool, transfer to a 1-L volumetric flask, dilute to volume with water, and mix.

12.9 *Sugar*, granulated.

### 13. Procedure

13.1 *Solid Samples*—Weigh 100.0 g of sample and wash into a 1000-mL volumetric flask with water. Add 10 mL of HCl (1 + 3) and swirl to dissolve the sample. Cool to room temperature, make to volume with water, and mix. Pipet a 20-mL aliquot into a 500-mL volumetric flask, dilute to volume, and mix. Proceed as in 13.3.

13.2 *Liquid Samples*—Weigh 100.0 g of sample and wash into a 1000-mL volumetric flask with water. Add 10 mL of HCl (1 + 3) and mix. Cool to room temperature, make up to volume with water, and mix. Pipet an aliquot containing about 2 g of  $\text{CaCl}_2$  into a 500-mL volumetric flask, dilute to volume, and mix. Appropriate aliquot volumes are indicated in the table below. Interpolate if necessary.

Expected $\text{CaCl}_2$ Concentration, %	Aliquot Size, mL
10	200
20	100
30	75
40	50
50	40

13.3 Pipet a 100-mL aliquot of the solution prepared in 13.1 or 13.2 into a 500-mL Erlenmeyer flask and dilute to about 200 mL with water. Add in order 10 mL of hydroxylamine hydrochloride solution and 3 g of sugar. Swirl to dissolve. Add 40 mL of NaOH solution (12.8) and swirl to mix. Add 0.1 g of KCN, and swirl to dissolve and mix. Add about 0.2 g of calcein indicator.

13.4 Titrate with 0.1 M EDTA solution until the indicator changes from green to purple.

NOTE 1—If  $\alpha$ -hydroxynaphthol blue indicator is used, 0.4 g should be added and the solution titrated to a blue end point.

### 14. Calculation

14.1 Calculate the calcium chloride concentration as follows:

$$\text{Calcium chloride, \%} = [(A \times B)/C'] \times 100 - D \quad (2)$$

where:

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

B = calcium chloride equivalent of the EDTA solution, g/mL,

C' = mass of sample in the aliquot used, and

<sup>7</sup> Available from Mallinckrodt Inc., Paris, KY.

<sup>8</sup> Available from the G. Frederick Smith Co., Columbus, OH.

$D$  = percent calcium hydroxide expressed as calcium chloride (see 31.1.1).

## 15. Report

15.1 Report the percentage of  $\text{CaCl}_2$  to the nearest 0.1 %. Duplicate determinations that agree within 0.3 % absolute are acceptable for averaging (95 % confidence level).

## 16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (see Note 2).

16.1.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.139 % absolute at 28 degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.4 %.

16.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.229 % absolute at 6 degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.8 % absolute.

NOTE 2—The precision statements are based on an interlaboratory study performed in 1970 on two samples of solid calcium chloride. Eight laboratories participated in the study analyzing each sample in duplicate on each of two days. Practice E 180 was used in developing these precision statements.<sup>9</sup>

16.2 The bias of the test method has not been determined.

## MAGNESIUM CHLORIDE, POTASSIUM CHLORIDE, AND SODIUM CHLORIDE

## 17. Scope

17.1 This test method covers the determination of magnesium chloride, potassium chloride, and sodium chloride in the ranges normally encountered in calcium chloride.

## 18. Summary of Test Method

18.1 A solution of the sample is aspirated into the air-acetylene flame of an atomic absorption spectrometer. The absorption of a resonance line from the spectrum of each cation is measured and compared with the response of the instrument to calibration solutions of the same elements. Recommended lines are: magnesium (2852 Å), potassium (7664 Å), and sodium (5889 Å).

## 19. Concentration Range

19.1 The concentration range for each cation must be selected to correspond with the optimum range of the instrument employed. Higher or lower concentration ranges may be required for different instruments or different source lamps.

## 20. Interferences

20.1 Elements normally present in calcium chloride do not interfere with these determinations.

## 21. Apparatus

21.1 *Atomic Absorption Spectrophotometer*, capable of isolating the resonance line chosen for each cation sufficiently to avoid interference from other elements in the samples being analyzed.

## 22. Reagents

22.1 *Calcium Chloride Solution*—Refer to 12.1.

22.2 *Hydrochloric Acid (1 + 3)*—Refer to 12.3.

22.3 *Magnesium Chloride, Standard Solution* (1 mL = 0.050 mg  $\text{MgCl}_2$ )—Dissolve 0.128 g of 99.9 % magnesium metal in 50 mL of HCl (1 + 3) in a covered 250-mL beaker. Heat gently, if necessary, to complete solution. Cool and transfer to a 1-L volumetric flask. Dilute to volume with water and mix. Pipet 10.0 mL of this solution into a 100-mL volumetric flask. Dilute to volume with water and mix.

22.4 *Potassium Chloride, Standard Solution* (1 mL = 0.300 mg KCl)—Dissolve 0.300 g of potassium chloride (KCl) in water and dilute to 1 L in a volumetric flask.

22.5 *Sodium Chloride, Standard Solution* (1 mL = 0.100 mg NaCl)—Dissolve 1.000 g of sodium chloride (NaCl) in water and dilute to 1 L in a volumetric flask. Pipet 10.0 mL of this solution into a 100-mL volumetric flask. Dilute to volume with water and mix.

## 23. Procedure

23.1 Pipet a 10.0-mL aliquot of the solution prepared in 13.1 or 13.2 into a 100-mL volumetric flask. Dilute to volume with water and mix.

23.2 To five 100-mL volumetric flasks add 2, 4, 6, 8, and 10 mL of each standard solution respectively and 5 mL of  $\text{CaCl}_2$  solution. Dilute to volume with water and mix.

23.3 Prepare a zero calibration solution by adding 5 mL of  $\text{CaCl}_2$  solution to a 100-mL volumetric flask and dilute to volume with water.

23.4 *Instrument Settings:*

23.4.1 Set the instrument parameters to values recommended by the manufacturer.

23.4.2 Select the proper wavelength for the element to be determined and, if appropriate, adjust for maximum response.

23.4.3 Optimize fuel, air, and burner adjustments while aspirating a calibration solution.

23.4.4 When the instrument has operated long enough to attain stability adjust the readout to 100 % transmittance (percent  $T$ ) or 0 absorbance (percent  $A$ ) with water. Aspirate and record the readings of the standard samples with a brief water aspiration after each. Repeat the process with sample, standards, sample and again standards, adjusting the zero between runs if necessary.

## 24. Calculation

24.1 Correct the average of the calibration solution readings by subtracting the average zero calibration solution reading (expressed in absorbance units).

24.2 Prepare a calibration curve by plotting the corrected absorbance values for the calibration solutions versus the micrograms of compound in 100 mL of solution.

24.3 Read the micrograms of compound in the sample solutions from the calibration curve. Calculate the percentage

<sup>9</sup> Supporting data are available from ASTM Headquarters, as RR:E15-1015.

compound as follows:

$$\text{Compound, \%} = A/(B \times 10^4) \quad (3)$$

where:

*A* = micrograms of compound in 100 mL of sample solution,

*B* = grams of sample in 100 mL of sample solution, percent KCl as percent NaCl = percent KCl × 0.7839, and percent alkali chlorides as NaCl = percent NaCl + percent KCl as NaCl.

## 25. Report

25.1 Report the percentage of MgCl<sub>2</sub> to the nearest 0.01 %. Duplicate determinations that agree within 0.01 % absolute are acceptable for averaging (95 % confidence level). See Note 3.

25.2 Report the percentage of KCl to the nearest 0.01 %. Duplicate determinations that agree within 0.12 % absolute are acceptable for averaging (95 % confidence level).

25.3 Report the percentage of NaCl to the nearest 0.01 %. Duplicate determinations that agree within 0.05 % absolute are acceptable for averaging (95 % confidence level).

25.4 Report the percentage of alkali chlorides to the nearest 0.01 %. Duplicate determinations that agree within 0.12 % absolute are acceptable for averaging (95 % confidence level).

## 26. Precision and Bias

26.1 The following criteria should be used for judging the acceptability of results: (See Note 2 and Note 3.)

26.1.1 *Repeatability (Single Analyst)*—Estimates of the standard deviation of results, in percent absolute, (each result the average of duplicates), obtained by the same analyst on different days are shown in Table 1 with the applicable degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than the indicated percent absolute.

26.1.2 *Reproducibility (Multilaboratory)*—Estimates of the standard deviation of results, in percent absolute, (each result the average of duplicates), obtained by analysts in different laboratories are shown in Table 1 with applicable degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than the indicated percent absolute.

NOTE 3—Precision data for magnesium chloride are calculated from results on one sample only. The other, containing 0.0025 % MgCl<sub>2</sub>, was tested but this was too low for calculating a reliable precision estimate. However the data indicate that precision at this level appears to be no poorer than that at the 0.115 % level.

26.2 The bias of this test method has not yet been determined.

## CALCIUM HYDROXIDE

### 27. Scope

27.1 This test method covers the determination of calcium hydroxide in the range from 0.01 to 1.0 %.

### 28. Summary of Test Method

28.1 The sample is dissolved in water and titrated with standard hydrochloric acid to the phenolphthalein end point.

### 29. Reagents

29.1 *Hydrochloric Acid, Standard (0.1 N)*—Prepare and standardize in accordance with Practice E 200.

29.2 *Phenolphthalein Indicator Solution (10 g/L)*—Prepare in accordance with Practice E 200.

### 30. Procedure

30.1 Weigh to ±0.1 g about 10 g of solid sample or an equivalent weight of solution. Dissolve solid samples in 25 mL of water. If necessary dilute liquid samples to 25 to 30 mL. Cool if necessary; add 1 drop of phenolphthalein indicator solution and titrate with 0.1 N HCl solution until the red color nearly disappears.

### 31. Calculation

31.1 Calculate the percent Ca(OH)<sub>2</sub>, *P*, as follows:

$$P = [(M \times H \times 0.03705)/G] \times 100 \quad (4)$$

where:

*M* = millilitres of HCl required for titration of the sample,

*H* = normality of the HCl, and

*G* = grams of sample.

31.1.1 Convert *P* to percent CaCl<sub>2</sub>, *C'*, as follows:

$$C' = P \times 1.4978 \quad (5)$$

where:

*P* = percent calcium hydroxide.

### 32. Report

32.1 Report the percentage of Ca(OH)<sub>2</sub> to the nearest 0.01 %. Duplicate determinations that agree within 0.01 % absolute are acceptable for averaging (95 % confidence level).

### 33. Precision and Bias

33.1 The following criteria should be used for judging the acceptability of results.

33.1.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be

TABLE 1 Repeatability and Reproducibility Values (Atomic Absorption Method)

Determination	Average Weight Percent		Checking Limits for Duplicates	Repeatability			Reproducibility		
	Sample 1	Sample 2		Standard Deviation	Degrees of Freedom	95 % Range Percent Absolute	Standard Deviation	Degrees of Freedom	95 % Range Percent Absolute
MgCl <sub>2</sub>	0.12	...	0.01	0.0029	6	0.010	0.0095	5	0.0346
KCl	1.44	2.71	0.12	0.0546	14	0.165	0.0982	6	0.340
NaCl	0.68	1.39	0.05	0.0331	15	0.100	0.079	7	0.264
Alkali Cl as NaCl	1.91	3.62	0.12	0.0534	16	0.160	0.279	7	0.931

0.005 % absolute at 15 degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.02 % absolute.

33.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.011 % absolute at 7 degrees of freedom. Two such values

should be considered suspect (95 % confidence level) if they differ by more than 0.036 % absolute.

33.2 The bias of this method has not yet been determined.

### **34. Keywords**

34.1 analysis; atomic absorption; calcium chloride; calcium hydroxide; magnesium chloride; potassium chloride

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