**Designation: ~~E449 – 08 (Reapproved 2013)~~ E449 – 18**

# Standard Test Methods for Analysis of Calcium Chloride[1]

This standard is issued under the fixed designation E449; 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.

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

## 1. ~~Scope~~ 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~~ |
| Calcium Chloride | 8 to 17 |
| ~~Magnesium Chloride, Potassium Chloride, and Sodium Chloride~~ | ~~17 to 26~~ |
| Magnesium Chloride, Potassium Chloride, and Sodium Chloride | 18 to 28 |
| ~~Calcium Hydroxide~~ | ~~27 to 33~~ |
| Calcium Hydroxide | 29 to 36 |

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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

1.5 *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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 5.

~~1.5 Review the current Material Safety Data Sheet (MSDS) for detailed information concerning toxicity, first aid procedures, handling, and safety precautions.~~

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D345 Test Method for Sampling and Testing Calcium Chloride for Roads and Structural Applications

D1193 Specification for Reagent Water

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E663 Practice for Flame Atomic Absorption Analysis (Withdrawn 1997)[3]

[1] These test methods are under the jurisdiction of ASTM Committee D16 on ~~Aromatic Hydrocarbons~~ Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.16 on Industrial and Specialty Product Standards.

Current edition approved ~~June 1, 2013~~Feb. 1, 2018. Published ~~June 2013~~April 2018. Originally approved in 1972. Last previous edition approved in ~~2008~~2013 as ~~E449 – 08.~~E449 – 08 (2013). DOI: ~~10.1520/E0449-08R13.~~10.1520/E0449-18.

[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] The last approved version of this historical standard is referenced on www.astm.org.

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

## 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.[4] 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 D1193.

## 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 E663.

## 7. Sampling

7.1 Sampling of calcium chloride is not within the scope of these test methods. See the appropriate sections of Test Method D345.

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 %.~~



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## 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. α -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 $CaCl_2$)—Weigh 7.500 g of primary standard calcium carbonate ($CaCO_3$). Transfer to a 600-mL beaker and add 300 mL of water. Cover with a watch glass and slowly add to the beaker, while

[4] *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.

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 $CaCO_3$ is complete, boil gently to expel $CO_2$. Cool, and transfer to a 1-L volumetric flask. Dilute to volume with water and mix.

12.2 *Ethylenediaminetetraacetate, Standard Solution* (0.1 mol/L (*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 $CaCl_2$ standard solution (1 mL = 0.00832 g $CaCl_2$) to a 500-mL Erlenmeyer flask and dilute to 200 mL with water. Proceed as directed in 13.2. Calculate the $CaCl_2$ 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 $CaCl_2$ 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 ($NH_2OH{\cdot}HCl$) in 90 mL of water.

12.5 *α-Hydroxynaphthol Blue.* [5]

12.6 *Modified Calcein Indicator.* [6]

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 $CaCl_2$ into a 500-mL volumetric flask, dilute to volume, and mix. Appropriate aliquot volumes are indicated in the table below. Interpolate if necessary.

| Expected $CaCl_2$ 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 calcium indicator.

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

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

13.5 Analyze sample in duplicate.

## 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
~~$D$ = percent calcium hydroxide expressed as calcium chloride (see 31.1.1).~~
$D$ = percent calcium hydroxide expressed as calcium chloride (see 33.1.1).

14.2 Average the duplicate results. Duplicate determinations that agree within 0.3 % absolute are acceptable for averaging (95 % confidence level).

## 15. Report

15.1 Report the percentage of $CaCl_2$ to the nearest 0.1 %. ~~Duplicate determinations that agree within 0.3 % absolute are acceptable for averaging (95 % confidence level).~~

## 16. Precision and Bias[5]

16.1 ~~The following criteria should be used~~ An ILS was conducted which included eight laboratories analyzing two samples. Each sample was analyzed in duplicate on two different days. Practice E180 was followed for ~~judging the acceptability of results (see~~the design and analysis of the data; ~~Note 2).~~the details are given is ASTM Research Report RR:E15-1015.

16.1.1 *Intermediate Precision, formerly called 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 then 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 E180 was used in developing these precision statements.[7]~~

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

## 17. Quality Guidelines

17.1 Laboratories shall have a quality control system in place.

17.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

17.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

17.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

17.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.



# 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. Scope

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

## 19. Summary of Test Method

19.1 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).

## 20. Concentration Range

20.1 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.

## 21. Interferences

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

## 22. Apparatus

22.1 *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.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1015. Contact ASTM Customer Service at service@astm.org.