Designation: E291 − 18

Standard Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash (Sodium Hydroxide and Potassium Hydroxide)[1]

This standard is issued under the fixed designation E291; 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*

1.1 These test methods cover only the analyses usually required on the following commercial products:

1.1.1 Caustic soda (sodium hydroxide), 50 and 73 % liquors; anhydrous (solid, flake, ground, or powdered), and

1.1.2 Caustic potash (potassium hydroxide), 45 % liquor; anhydrous (solid, flake, ground, or powdered).

1.2 The analytical procedures appear in the following order:

Alkalinity (Total), Titrimetric (for 50 to 100 % NaOH and 45 to 100 % KOH)	3 to 4
Carbonate, Gas-Volumetric (0.001 g CO_2, min)	4 to 7
Carbonate, Gravimetric (0.001 g CO_2, min)	7 to 10
Chloride, Titrimetric, (0.001 g Cl^-, min)	10 to 11
Chloride, Potentiometric Titration (0.3 to 1.2 %)	11 to 12
Chloride, Ion Selective Electrode (0.6 to 120 µg/g)	12 to 13
Iron, Photometric (0.005 mg Fe, min)	13 to 15
Sulfate, Gravimetric, (0.002 g SO_3, min)	15 to 16
Keywords	16

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard with the exception of inch-pound units for apparatus descriptions.

1.4 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 6.

1.7 *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]

D1193 Specification for Reagent Water

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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

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

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[4]

3. Significance and Use

3.1 Caustic soda and caustic potash are used in a large number of manufacturing processes. The chemicals are available in several grades depending on their intended use. The test

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[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.12 on Caustics and Peroxides.

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

[4] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

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

methods listed in 1.2 provide procedures for analyzing caustic soda and caustic potash to determine if they are suitable for their intended use.

4. Apparatus

4.1 *Photometers and Photometric Practice*—Photometers and photometric practice used in these test methods shall conform to Practice E60.

5. 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.[5] 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 *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.

6. Hazards

6.1 Sodium and potassium hydroxides are caustic alkalies which, in their anhydrous or strong solution form, are hazardous materials. In contact with the skin they produce burns which may be quite serious unless promptly treated. Their action is insidious since they produce no immediate stinging or burning sensation and damage may result before their presence is realized.

6.2 Eyes are particularly vulnerable to severe damage from these alkalies.

6.3 Laboratory workers handling these alkalies should use safety goggles or face shields and rubber gloves and avoid spillage on clothing. These materials rapidly attack wool and leather.

6.4 Spilled caustic should be flushed away with water where possible, or covered with absorbent material (such as sawdust, vermiculite, or baking soda) and swept up and discarded in accordance with all applicable federal, state, and local health and environmental regulations. Last traces may be neutralized with dilute acetic acid and the area washed with water.

6.5 Perchloric acid is toxic, corrosive, and a strong oxidizer. Laboratory workers handling this acid should use safety goggles or face shields and rubber gloves.

7. Sampling

7.1 *General*—The nature of the caustic alkalies is such as to require special care at all points of sampling and preparation for analysis. The following information is included in order that representative samples may be ensured. Additional precautions may be necessary if trace constituents, not covered in these test methods, are to be determined. Instructions for such procedures may be obtained from the publications of most major producers. Sampling techniques must be such as to limit or prevent atmospheric exposure since sodium and potassium hydroxides, both as aqueous solutions and as anhydrous products, rapidly absorb moisture and carbon dioxide (and other acid gases) from the atmosphere. The aqueous solutions are corrosive and sampling devices and sample containers must be selected to avoid contamination with any constituent later to be determined. Strong aqueous solutions of these alkalies are available commercially under the names liquid caustic soda and liquid caustic potash. Liquid caustic potash at a concentration of 45 % remains liquid at temperatures down to −29°C, and freezing or crystallization will only be encountered under severe cold weather. Caustic soda liquors are usually shipped in insulated tank cars at elevated temperatures, and minimum temperatures must be maintained if unloading and sampling problems are to be avoided. Viscosity increases near the freezing point and creates pumping problems. Even partial freezing changes the composition of the remaining liquor and causes sampling and analysis problems. Be sure contents are completely liquid and well mixed before sampling. The following minimum temperatures should be maintained for proper sampling of bulk shipments:

50 % NaOH liquor	20°C
53 % NaOH liquor	30°C
70 to 73 % NaOH liquor	71°C

7.2 *Sample Containers*—The choice of container construction material is important for caustic liquor samples, especially for those to be taken or held at elevated temperatures. Glass can be used except where silica is to be determined. Polyethylene or polypropylene containers which have high-temperature properties may also be used. Nickel is the best practical metal for a metallic sample container for caustic liquors. For the analysis of 73 % caustic soda, the entire sample should be in the liquid state before removing any portion, and such portions must then be used in their entirety to avoid the factor of segregation on freezing. Caustic soda of 73 % concentration may also be "cast" into glass or plastic bottles or tubes, or nickel or silver metallic molds. The molds are later removed and the samples chipped or crushed for analysis. If this is done, the factors of segregation on freezing and atmospheric exposure while crushing must be borne in mind.

7.3 *Sampling Devices and Techniques:*

7.3.1 *Liquid Caustic*—Simple "dipper" or "tap" samples from large quantity shipments or tanks of caustic liquor are inadequate for purchaser and vendor purposes. Numerous specially designed devices are available to procure samples from various levels in tanks. A useful type of such samplers for small tanks has three or five containers mounted on a single rod so that when the device is lowered into a tank and the stoppers are pulled, samples are simultaneously taken at the different levels. These are then combined to provide a representative average sample. Shipments should be sampled at least at the upper, middle, and lower thirds. Samples should never be taken at the surface of the liquid. If it is not necessary to analyze the

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[5] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

liquor before unloading, sampling may be accomplished by a "continuous drip" from a small tap-off with the regulating valve in a vertical section of the unloading line. The "drip" is so timed as to collect the desired amount of sample uniformly during the time of unloading.

7.3.2 *Anhydrous Products:*

7.3.2.1 Commercial anhydrous caustic soda or caustic potash is packaged in drums in solid, flake, ground, or powdered forms. Sampling and handling of these materials must be done with minimum atmospheric exposure.

7.3.2.2 In the case of flake, ground, or powdered sodium or potassium hydroxides, the top 75 or 100 mm of material in a drum should first be removed and a sample then taken from the center part of the drum. The sample should be placed immediately in a suitable wide-mouth container then closed and sealed with taps or wax.

7.3.2.3 Solid caustic shall be packaged by filling metal drums with molten anhydrous product and allowing drums and contents to cool before sealing air tight. On cooling and solidifying, impurities present in the caustic tend to segregate and concentrate in the bottom section. To sample such material properly, the metal drum must be opened at the vertical seam and removed. The solid cake may then be sampled either by drilling at representative levels with a 19-mm auger bit (may cause metal contamination) or by splitting the cake in half vertically with hammer and chisel and chiseling off representative small fragments so that the total sample represents a vertical cross section through the cake. In either case, the sample shall be promptly bottled and sealed in a wide-mouth container. In the laboratory, the lumps shall be reduced to convenient size by enclosing in several thicknesses of clean cloth or kraft paper and pounding with a hammer. The crushed material shall be bottled and thoroughly mixed before analysis.

TOTAL ALKALINITY

8. Scope

8.1 This test method covers the determination of the total alkalinity of 50 and 73 % liquid caustic soda, 45 % liquid caustic potash, and anhydrous caustic soda and caustic potash.

9. Summary of Test Method

9.1 Total alkalinity is determined by titration with standard hydrochloric acid solution using methyl orange indicator solution or modified methyl orange indicator solution.

10. Reagents

10.1 *Hydrochloric (or Sulfuric Acid), Special*(1.0 meq/mL)—Prepare in accordance with Practice E200.

10.2 *Methyl Orange Indicator Solution*—See Practice E200.

10.3 *Modified Methyl Orange Indicator Solution*—See Practice E200.

10.4 *Water, Distilled,* carbon dioxide-free (freshly boiled and cooled).

11. Procedure

11.1 Transfer to a tared, covered weighing bottle a sample of such size as determined from Table 1.

TABLE 1 Sample Size for Total Alkalinity

Sample	Sample Size, g
50 % NaOH	65 to 78
73 % NaOH	45 to 52
Anhydrous NaOH	32 to 40
45 % KOH	100 to 120
Anhydrous KOH	48 to 60

TABLE 2 Sample Size for Carbonate Analysis

Percent Na_2CO_3 or Percent K_2CO_3 Expected	Sample Size, g
0.01 to 0.10	8 to 10
0.10 to 0.50	5 to 7
0.50 to 1.00	2 to 4

11.2 Weigh the sample to the nearest 1 mg and transfer it to a 1-L volumetric flask using several rinses of water to remove all traces of caustic from the weighing bottle. Dilute the solution to about 400 mL with water and cool to room temperature. After cooling, dilute to 1 L and mix thoroughly.

11.3 With a volumetric pipet, transfer 50 mL (see Note 1) of the prepared solution to a 500-mL Erlenmeyer flask and add 2 to 4 drops of modified methyl orange indicator solution (see Note 2). Titrate this solution with standard 1.0 meq/mL acid to a gray end point (see Note 3) and record the volume and temperature of acid used. Correct the acid meq/mL for any difference from the standardization temperature by use of the factor $\Delta N/°C = 0.00035$ between 20 and 30°C adding the correction when temperature of use is below (subtracting when above) the temperature of standardization. (See Practice E200.)

NOTE 1—If a 100-mL buret is to be used for this titration use a 100-mL aliquot.

NOTE 2—If desired, methyl orange indicator solution may be used.

NOTE 3—The analyst should attempt to end the titration at the same shade of color as was used for the end point in the standardization of the acid.

12. Calculation

12.1 Calculate the total alkalinity as % sodium oxide or potassium oxide as follows:

$$\text{Sodium oxide, \% mass} = \frac{A \times B \times 0.030990}{W} \times 100 \quad (1)$$

$$\text{Potassium oxide, \% mass} = \frac{A \times B \times 0.047102}{W} \times 100 \quad (2)$$

where:

A = acid required for titration of the sample, mL

B = corrected meq/mL of the acid, and

W = mass of sample in the aliquot, g.

12.2 Calculate the total alkalinity as the respective hydroxide as follows:

$$\text{Sodium hydroxide, \% mass} = 1.2907 \times \text{\% mass } Na_2O \quad (3)$$

$$\text{Potassium hydroxide, \% mass} = 1.1912 \times \text{\% mass } K_2O \quad (4)$$

12.3 If actual hydroxide content is desired, the carbonate content must be determined separately as described in Sections 16 – 25 or Sections 27 – 35. Then:

$$\text{Sodium hydroxide (actual), \% mass} = A - (B \times 0.755) \quad (5)$$

$$Potassium\ \ hydroxide\ (actual),\ \%\ mass = C - (D \times 0.812) \tag{6}$$

where:

A = % mass NaOH (total alkali),
B = % mass Na_2CO_3,
C = % mass KOH (total alkali), and
D = % mass K_2CO_3.

13. Report

13.1 Report the % mass of sodium oxide or potassium oxide to the nearest 0.01 %.

14. Precision and Bias

14.1 The following criteria should be used in judging the acceptability of results (Note 4):

14.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.057 % absolute at 144 DF. The 95 % limit for the difference between two such runs is 0.16 % absolute.

14.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.17 % absolute at 72 df. The 95 % limit for the difference between two such averages is 0.48 % absolute.

14.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.25 % absolute at 10 df. The 95 % limit for the difference between two such averages is 0.70 % absolute.

NOTE 4—These precision estimates are based on an interlaboratory study on five samples comprising 45 % KOH, 50 % NaOH, 73 % NaOH, anhydrous NaOH, and anhydrous KOH. The number of laboratories analyzing each sample ranged from seven to fifteen with one analyst in each performing duplicate determinations and repeating one day later.[6] Practice E180 was used in developing these precision estimates.

14.2 *Bias*—The bias of this test method has not been determined because of the unavailability of suitable reference materials.

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

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

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

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

15.1.4 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.

SODIUM CARBONATE OR POTASSIUM CARBONATE (GAS-VOLUMETRIC TEST METHOD)

16. Scope

16.1 This test method describes the gas-volumetric determination of sodium carbonate or potassium carbonate in caustic soda or caustic potash respectively. The lower limit of determination is 0.001 g as carbon dioxide.

17. Summary of Test Method

17.1 Carbon dioxide is evolved by acid decomposition of carbonate in the sample. The volume of CO_2 is measured and calculated as sodium carbonate or potassium carbonate.

18. Apparatus

18.1 *Carbon Dioxide Evolution, Measurement, and Absorption Device,* as illustrated in Fig. 1 and consisting of the following special parts:

18.1.1 *Aspirator Bottle, J,* 500-mL, used for leveling.

18.1.2 *Compensator Tube, C,* as shown in Fig. 1 and conforming to details shown in Fig. 2.

18.1.3 *Gas Buret, B,* 100-mL, modified as shown in Fig. 3.

18.1.4 *Gas Pipet, K,* preferably of the bubbler type.

18.1.5 *Glass Condenser with Jacket, L,* 12 in. (305 mm) long and 1¼ in. (32 mm) in outside diameter. The condenser tube shall be of 8-mm outside diameter glass tubing.

18.1.6 *Tubing Assembly, D,* as illustrated in Fig. 4.

19. Reagents

19.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

19.2 *Methyl Orange Indicator Solution* (1 g/L)—See Practice E200.

19.3 *Potassium Hydroxide* (35 % Solution)—Dissolve 350 g of potassium hydroxide (KOH) in 650 mL of water.

19.4 *Sodium Carbonate* (Na_2CO_3), anhydrous.

19.5 *Water, Distilled,* carbon dioxide-free (freshly boiled and cooled).

20. Preparation of Apparatus

20.1 Assemble the apparatus as shown in Fig. 1 after preparing the various parts as follows:

20.1.1 *Compensator Tube, C*—Warm the bulb slightly and place two or three drops of water in the tube. Then add sufficient mercury so that when the tube is at room temperature and normal atmospheric pressure the mercury columns are approximately level and are about 1½ to 2 in. (38 to 51 mm) in length. This is a trial and error operation. Manipulation by alternately warming and cooling the bulb is helpful in making this adjustment.

20.1.2 *Absorption Pipet, K*—Fill this pipet with sufficient caustic potash solution to fill the left bulb completely and to have about 1-in. (25-mm) depth in the right bulb. Protect the solution from the atmosphere with a gas expansion bag, K_2.

20.1.3 *Glass Water Jacket, O*—Bore suitable holes in two No. 12 rubber stoppers, as shown in Fig. 1, to support the buret

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[6] Supporting data have been filed at ASTM International headquarters and may be obtained by requesting RR:E15-1040. Contact ASTM Customer Service at service@astm.org.