Designation: E1787 – 16

Standard Test Method for Anions in Caustic Soda and Caustic Potash (Sodium Hydroxide and Potassium Hydroxide) by Ion Chromatography[1]

This standard is issued under the fixed designation E1787; 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 This test method covers the determination of anionic impurities in 50 % caustic soda (sodium hydroxide) and 50 % caustic potash (potassium hydroxide) solutions using ion chromatography (IC). Anions that can be determined at concentrations of approximately 0.1 to 1000 ug/g (ppm) include: bromide, chlorate, chloride, fluoride, nitrate, phosphate, and sulfate.

1.2 By varying the sample size, this test method can be used for anhydrous caustic soda and caustic potash products, as well as other concentrations of liquid products.

1.3 This test method is not intended to be used to quantify chloride in caustic soda where the sodium chloride concentration is approximately 1 %. For the most accurate determinations, it is recommended that high concentrations of chloride be analyzed using a potentiometric titration procedure, such as the one described in Test Methods E291.

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

1.5 Review the current appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, 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 hazards statements are given in Section 8.

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

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E291 Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash (Sodium Hydroxide and Potassium Hydroxide)

3. Summary of Test Method

3.1 Bromide, chlorate, chloride, fluoride, nitrate, phosphate and sulfate are measured in NaOH or KOH by ion chromatography. The sample solution is diluted and injected onto a sample loop of an automated neutralization module. The sample in the loop is pumped to a suppressor device (electrolytically or chemically regenerated) to neutralize the hydroxide ions. Anionic constituents of the neutralized sample are concentrated on an anion concentrator column. After the concentration they are separated into individual elution bands in the eluent on a separator column. The conductivity of the eluent is reduced with an anion suppression device, and the anions of interest are detected using a conductivity detector. Quantitation of the anions in the sample solution is achieved by calibrating the IC with a series of standards containing known amounts of the anions. These standards are also passed through the neutralization device.

4. Significance and Use

4.1 Anion impurities in caustic soda and caustic potash are monitored by manufacturers and users for quality control of the products. Anions of primary interest are chloride, chlorate, and

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is 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.

*A Summary of Changes section appears at the end of this standard sulfate. This test method has determined precision estimates only for these three impurities.

5. Interferences

5.1 Substances that coelute with the anions of interest will interfere. A high concentration of one anion can interfere with accurate quantitation of another anion if their retention times are close and resolution is affected. For example, caustic soda samples containing large concentrations of chloride can interfere with the quantitation of small amounts of fluoride. Selection of a high capacity anion separator column will minimize this problem.

5.2 Organic acids, surfactants, dyes, metals, etc., can cause fouling of the columns and membranes used in this test method, resulting in interferences and decreased sensitivity. It is very important to follow the manufacturer's recommendations for cleaning and maintaining the various parts of the IC system.

5.3 The anion concentrator column in the neutralization module has a finite capacity for trapping anions. Consult with manufacturer for selection of concentrator column of suitable capacity. Care should be taken not to exceed the capacity of the column. When the capacity of the column is exceeded, the stripping of anions will not be quantitative.

6. Apparatus

6.1 *Ion Chromatograph,* equipped with:

6.1.1 *Conductivity Detector,*

6.1.2 *Anion Separator Column,*

6.1.3 *Guard Column,*

6.1.4 *100-µL Sample Loop,* other sizes are permitted so long as they do not degrade the precision of the method,

6.1.5 *Autoneutralization Device,* capable of neutralizing the caustic sample prior to being directed through the separator column,

6.1.6 *Post-Column Chemical Suppression Device,* capable of reducing background conductivity due to the eluent, and

6.1.7 *Data Acquisition System,* such as an integrator or computer system.

6.2 *100-mL Volumetric Flasks,* for preparing sample solutions.

6.3 *Disposable 10-mL Syringes,* for injecting solution into the IC.

6.3.1 *IC Autosampler* (optional), can be used as an alternative to manually injecting samples.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals should be used in all tests. Unless otherwise indicated, all reagents must 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.

7.2 *Purity of Water*—References to water means Type 1 (18 MΩ-cm deionized water) conforming to Specification D1193.

7.3 *Anion Stock Standards, 1000 ug/g (ppm):*

7.3.1 *Bromide Stock Solution (1.00 mL = 1.00 mg Bromide)*—Dry sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 1.288 g of the dried NaBr in water, dilute to 1 L with water, and mix well.

7.3.2 *Chlorate Stock Solution (1.00 mL = 1.00 mg Chlorate)*—Dissolve 1.275 g of sodium chlorate ($NaClO_3$) in water, dilute to 1 L with water, and mix well.

7.3.3 *Chloride Stock Solution (1.00 mL = 1.00 mg Chloride)*—Dry sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 1.648 g of the dried NaCl in water, dilute to 1 L with water, and mix well.

7.3.4 *Fluoride Stock Solution (1.00 mL = 1.00 mg Fluoride)*—Dry sodium fluoride (NaF) at 105°C for at least 8 h and cool in a desiccator. Dissolve 2.210 g of the dried NaF in 500 mL of water, dilute to 1 L with water, and mix well.

7.3.5 *Nitrate Stock Solution (1.00 mL = 1.00 mg Nitrate)*—Dry sodium nitrate ($NaNO_3$) at 105°C for 48 h and cool in a desiccator. Dissolve 1.371 g of the dried $NaNO_3$ in water, dilute to 1 L with water, and mix well.

7.3.6 *Phosphate Stock Solution (1.00 mL = 1.00 mg Phosphate)*—Dissolve 1.433 g of potassium dihydrogen phosphate (KH_2PO_4) in water, dilute to 1 L with water, and mix well.

7.3.7 *Sulfate Stock Solution (1.00 mL = 1.00 mg Sulfate)*—Dry sodium sulfate (Na_2SO_4) for 1 h at 105°C and cool in a desiccator. Dissolve 1.479 g of the Na_2SO_4 in water, dilute to 1 L with water, and mix well.

7.4 *Eluent*—The eluent used for the anion analysis will depend on the choice of separator column selected. Follow the manufacturer's instructions for preparation of the eluent.

7.4.1 *Eluent Concentrate, 0.27 mol/L (M) Sodium Carbonate/0.03 mol/L (M) Sodium Bicarbonate (100 × Concentrate)*—Dissolve 28.6 g of sodium carbonate and 2.52 g of sodium bicarbonate in a 1-L volumetric flask containing 800 mL of water. Dilute to volume with water and mix. Store in a tightly capped polypropylene bottle.

7.4.2 *Eluent, 2.7 mmol/L (mM) Sodium Carbonate/0.3 mmol/L (mM) Sodium Bicarbonate Eluent*—Pipet 20.0 mL of the eluent concentrate into a 2-L volumetric flask, dilute to the mark with water, and mix.

[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. Pharmacopeial Convention, Inc. (USP), Rockville, MD.

8. Hazards

8.1 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 that 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.

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

8.3 Use safety goggles or face shields and rubber gloves when handling these alkalies, and avoid spillage on clothing. These materials rapidly attack wool and leather.

8.4 Flush away spilled caustic with water where possible, or cover with absorbent material (such as sawdust, vermiculite, or baking soda), and sweep up and discard in accordance with all federal, state, and local health and environmental regulations. Last traces may be neutralized with dilute acetic acid and the area washed with water.

8.5 Consult Safety Data Sheets (SDS) for chemicals listed in this test method for further information.

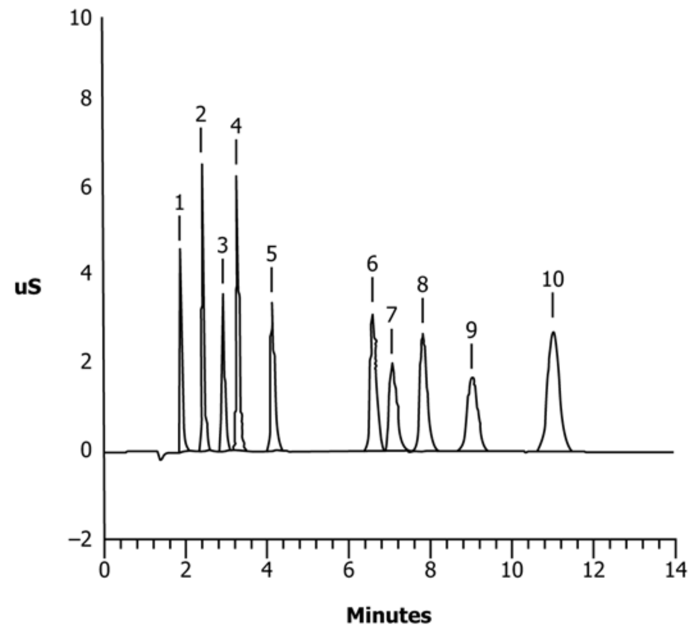
9. Calibration

9.1 The retention time for each anion is determined by injecting a series of standard solutions, each containing only one anion of interest, into the IC and recording the time required for a peak to appear on the chromatogram. Retention times vary with operating conditions. The standards, therefore, must be chromatographed in the same manner as the sample solutions, which includes passing them through the autoneutralization module. Fig. 1 is a typical chromatogram that shows the elution order of various anions separator column using the carbonate/bicarbonate eluent. The elution order may change depending on the column used. See Note 1.

NOTE 1—Other anion separation and guard columns, and eluent may be used so long as the ions of interest are separated and the precision of the method is not degraded.

9.2 Calibrate the ion chromatograph using a series of calibration standards. Each standard should contain all the anions of interest. The concentration of anions in this series of standards should be prepared so they bracket the expected concentration of anions in the diluted sample. After the standards have been analyzed by IC, the "best-fit" straight line is determined for each anion using the concentration versus IC area counts. If the IC is equipped with a computer operated software or an integrator, calibration should be done according to manufacturer's instructions for multi-level external standard calibrations. If an integrator or computer is not used, calibration curves can be created on graph paper by plotting concentration versus peak area for each anion of interest and drawing the "best-fit" straight line through the points.

9.2.1 A typical calibration would include a series of four to five standards containing the anions of interest from 0.1 to 10 µg/mL (ppm).



Peak #	Retention Time (min)	Component
1	1.90	Fluoride
2	2.44	Chlorite
3	2.94	Bromate
4	3.30	Chloride
5	4.15	Nitrite
6	6.61	Bromide
7	7.08	Chlorate
8	7.82	Nitrate
9	9.03	Phosphate
10	11.02	Sulfate

FIG. 1 Typical Chromatogram of Anions Eluting from a AS-12A Separator Column Using $Na_2CO_3/NaHCO_3$ Eluent

10. Procedure

10.1 Set up the ion chromatograph and the automated neutralization device according to the manufacturer's instructions. The IC system can be set up to accommodate the use of an autosampler or manual injection with a syringe. The detector ranges are variable. The range setting required for the analysis will depend on the concentration of anions in the sample and should be chosen accordingly. Table 1 lists typical analytical conditions for the anion analysis by IC.

NOTE 2—Styrene-based strong acid resin in the H^+ form and commercially available neutralization cartridges containing this resin have been used to neutralize caustic samples prior to introduction into an IC. Their use can eliminate the need for sophisticated on-line neutralization devices. Even when rinsed thoroughly, however, they introduce contaminants (especially chloride and sulfate) to the sample solution and are not recommended for determining anions with concentrations less than 50 ug/g (ppm) in caustic soda or caustic potash.

NOTE 3—A chemical suppression device or commercially available

TABLE 1 Ion Chromatograph—Typical Analytical Conditions

Anion separator column:	AS-12A
Guard column:	AG-12A
Eluent:	2.7 mmol/L Na_2CO_3/0.3 mmol/L $NaHCO_3$
Eluent flow rate:	1.5 mL/min
Sample loop:	100 µL
Eluent suppression:	ASRS, recycle mode
Neutralization cycles:	2