Designation: E 1787 – 02

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 E 1787; 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 0.1–1000 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 E 291.

1.4 *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 hazards statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision of ASTM Methods of Analysis and Testing of Industrial Chemicals[3]

E 291 Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash (Sodium Hydroxide and Potassium Hydroxide)[3]

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 suppression device which uses electrolysis to neutralize the hydroxide ions. The sample then is circulated through this device several times until it is completely neutralized. 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 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.[4]

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.

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[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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[2] *Annual Book of ASTM Standards*, Vol 14.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] Ion Pac AS9 HC column, Dionex Corp., Sunnyvale, CA, has been found suitable.

5.3 The anion concentrator column in the neutralization module has a finite capacity for trapping anions, approximately 25 micro-equivalents per 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,*[5]

6.1.3 *Guard Column,*[6]

6.1.4 *100-µL Sample Loop*,

6.1.5 *Autoneutralization Device*, capable of neutralizing the caustic sample prior to being directed through the separator column,[7]

6.1.6 *Post-Column Chemical Suppression Device*, capable of reducing background conductivity due to the eluent,[8] 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.[9] 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 D 1193.

7.3 *Anion Stock Standards, 1000 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. The eluent described below is used with the Dionex AS-12A separator column.

7.4.1 *Eluent Concentrate, 0.27 M Sodium Carbonate/0.03 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 mM Sodium Carbonate/0.3 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.

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 Material Safety Data Sheets (MSDS) 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

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[5] IonPac AS12A column, Dionex Corp., Sunnyvale, CA, has been found to be suitable.

[6] IonPac AG12A column, Dionex Corp., Sunnyvale, CA, has been found to be suitable.

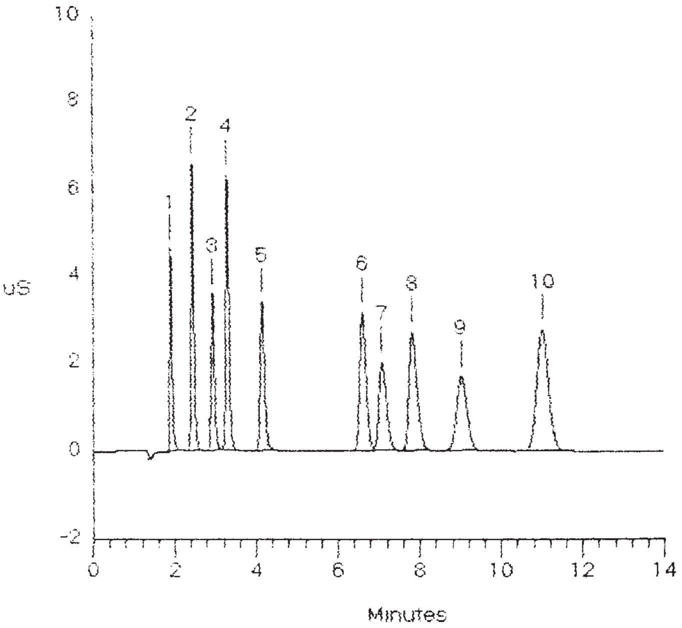
[7] SP10 AutoNeutralization Module, Dionex Corp., has been found to be suitable.

[8] ASRS-Ultra (4 mm), Dionex Corp., Sunnyvale, CA, has been found to be suitable.

[9] *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.

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 from the Dionex AS-12A separator column using the carbonate/bicarbonate eluent.

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.



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

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

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 1—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 ppm in caustic soda or caustic potash.

NOTE 2—An Anion Self-Regenerating Suppressor,[9] installed in the IC system before the separator column, has been successfully used as a replacement for the automated neutralization module to neutralize caustic soda and caustic potash samples. By using this approach, however, the 50 % solutions of caustic soda and caustic potash must be diluted by a ratio of 100:1. The quantitation limits using this modified technique, therefore, are correspondingly higher. Details of the modification are not given in this test method.

10.2 Equilibrate the system by pumping eluent through the columns and the detector until a stable baseline is obtained (approximately 15 to 20 min).

10.3 Sample solutions are prepared by transferring a known weight of sample (weighed to the nearest 0.01 g) to a 100-mL volumetric flask and diluting to volume with water. The amount of dilution is dependent on levels of anions in the sample. In many cases, when both high level and lower levels of anions are to be quantified in the same sample, two or more sample solutions of different dilutions may have to be analyzed. The neutralization module is capable of neutralizing solutions containing 25 % sodium hydroxide when the solution is cycled through the neutralizer at least twice. Sample solutions containing up to 50 g of 50 % product or 25 g of anhydrous, therefore, can be neutralized effectively. Table 2 can be used as a general guideline of sample dilutions based on expected concentrations of individual anions. An IC calibration covering the range of 0.1 to 10 ppm has been assumed.

TABLE 1 Ion Chromatograph—Typical Analytical Conditions

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

TABLE 2 Recommended Sample Amount for IC Analysis

Anion Concentration, µg/mL	Sample Dilution, g/100 mL
<1	50
1–10	20–50
10–100	10–20
100–1000	1–10
>1000	<1

10.4 Inject the sample into the ion chromatograph and record the ion chromatogram of anions in caustic. Fig. 2 shows an IC chromatogram of 45 % caustic potash that was diluted 20 g/100 mL.

11. Calculation

11.1 Calculate the concentration of each anion of interest using the peak area of that anion from the sample chromatogram and response factor derived from "best-fit" linear equation obtained during the calibration procedure.

$$\text{Anion, ppm (wt./wt. basis)} = \frac{A \times R \times B}{G} \qquad (1)$$

where:

A = area of anion peak from the chromatogram of the diluted sample, area counts,

B = final volume of diluted sample, mL,

R = response factor from "best-fit" calibration line, (µg/mL)/area counts, and

G = sample weight, g.

11.2 Concentration of the sodium or potassium salt of the anion can be calculated as follows:

$$\text{Salt concentration} = \text{anion conc.} \times \frac{\text{molecular wt. of anion salt}}{\text{molecular wt. of anion}} \qquad (2)$$

11.3 *Example Calculations*:

$$\text{Cl, ppm} = \frac{20\,000\,000 \times 1 \times 10^{-7} \times 100}{10.00} = 20 \qquad (3)$$

$$\text{NaCl, ppm} = \frac{20 \times 58.44}{35.45} = 33 \qquad (4)$$

where:

20 000 000 = A, area counts of Cl peak from chromatogram,

1×10^{-7} = R, the Cl response factor from calibration, (µg/mL)/area count,

100 = B, final volume of sample solution, mL,

10.00 = G, sample size, g,

58.44 = molecular wt. of NaCl, and

35.45 = molecular wt. of Cl.

12. Report

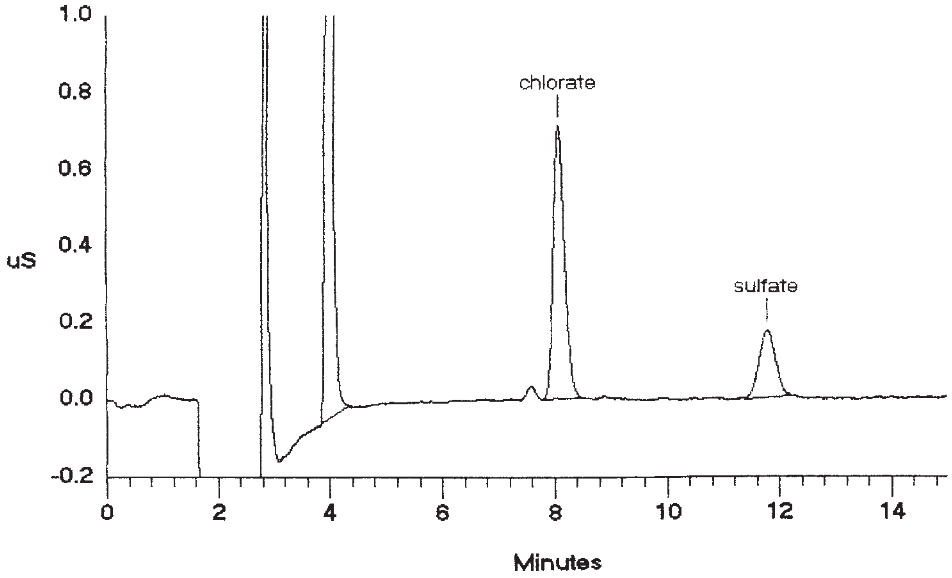
12.1 Report the concentration of each anion of interest in ppm (wt./wt. basis as follows:

Anion, ppm	Report to nearest, ppm
≥10	1
≥1 & <10	0.5
<1	0.1

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (see Note 3).

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value shown in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is given also in the table.



Retention Time, min	Component	Conc., ppm	Area
3.96	Chloride	6.7	38 702 776
8.05	Chlorate	5.3	9 926 832
11.79	Sulfate	0.8	3 537 308

FIG. 2 Typical Chromatogram of 45 % Caustic Potash (Diluted 20 g/100 mL) Using AS-12A Separator Column and 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ Eluent

TABLE 3 Precision for Anions by IC Method

			Repeatability			Laboratory Precision			Reproducibility		
Material	Anion	Average Concentration, ppm	Standard Deviation	Degrees of Freedom	95 % Range ppm, absolute	Standard Deviation	Degrees of Freedom	95 % Range ppm, absolute	Standard Deviation	Degrees of Freedom	95 % Range ppm, absolute
50 % NaOH	Cl	90	1.95	10	5.4	2.33	5	6.5	4.62	4	12.9
	ClO3	11	0.341	12	0.95	0.470	6	1.3	2.02	5	5.6
	SO4	291	3.74	8	10.5	1.79	4	5.0	11	3	30.8
45 % KOH	Cl	7.9	0.254	12	0.71	0.273	6	0.76	1.21	5	3.4
	ClO3	4.9	0.070	12	0.19	0.133	6	0.37	0.862	5	2.4
	SO4	0.8	0.110	8	0.31	0.147	4	0.41	0.30	3	0.84

13.1.2 *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 the value shown in Table 3 at the indicated degrees of freedom. The 95 % limit of the difference between two such averages is given also in the table.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value shown in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is given also in the table.

NOTE 3—The precision estimates are based on an interlaboratory study conducted in 1995 on one sample of 50 % caustic soda and one sample of 45 % caustic potash. The samples were analyzed for chloride, chlorate, and sulfate. One analyst in each of six laboratories performed duplicate determinations on each of two days. Practice E 180 was used in developing these precision estimates.[10]

13.2 *Bias*—The bias of this test method has not been determined because of the lack of acceptable reference material.

14. Keywords

14.1 bromide; caustic potash; caustic soda; chlorate; chloride; chromatography; fluoride; ion chromatography; nitrate; phosphate; potassium hydroxide; sodium hydroxide; sulfate

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[10] Supporting data are available from ASTM International Headquarters. Request RR:E15–1060.