WI 220802.02

T 613

BALLOT NO. 3 SARG

DRAFT NO. 02

DATE 06/01/2023

WORKING GROUP CHAIR Todd Bolton

SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

CAUTION:
This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Analysis of caustic soda

(Proposed RECONFIRMATION of Classical Method T 613 cm-10)

1. Scope

1.1 This method describes a procedure for the analysis of caustic soda (sodium hydroxide). The following determinations comprise the usual complete analysis: alkalinity (total), carbonate, chloride, iron, and sulfate.

1.2 Most of the caustic soda used by the pulp and paper industry is a water solution of approximately 50% or 73% NaOH; it is also available in solid, flake, or ground (powder) form. Commercially, it is quoted on a 76% sodium oxide (Na_2O) basis, approximately equivalent to 98% NaOH.

2. Summary

2.1 *Alkalinity.* Total alkalinity is determined by titrating with hydrochloric acid using methyl orange-xylene cyanole mixed indicator.

2.2 *Carbonate.* Carbon dioxide is evolved by acid decomposition of the carbonate in the specimen and is absorbed on sodium-hydrate-asbestos. The increase in weight is a measure of the carbonate present. The lower limit is 0.001 g of CO_2.

2.3 *Chloride.* The specimen is diluted, acidified, and treated with a small excess of standard $AgNO_3$ solution. The precipitated AgCl is removed by filtration and the excess silver nitrate is titrated with standard ammonium thiocyanate solution using ferric ammonium sulfate indicator (Volhard method). The lower level of determination is 0.0001 g as chloride.

2.4 *Iron.*

2.4.1 Iron is reduced to the ferrous condition where it forms an orange-red complex with 1,10-phenanthroline (orthophenanthroline) in an acetate-buffered solution at pH 5. Intensity of the color so formed is measured at 510 nm in a photometer calibrated with standard iron solutions. The color develops within 15 min, is very stable, and follows Beer's law. The lower limit of determination is 0.1 ppm as Fe.

2.4.2 Impurities normally found in caustic soda do not cause any interference. Copper, if present to the extent of 0.5 mg/100 mL of final solution, changes the hue of the solution but interferes only slightly when excess reagent is present. Zinc, cadmium, and nickel form complexes and consume reagent but do not interfere when sufficient reagent is present.

2.5 *Sulfate.* Sulfate is determined gravimetrically by precipitation as barium sulfate ($BaSO_4$) which is filtered off, washed, ignited, and weighed. The lower limit of determination is 0.002 g as $S0_4$.

3. Apparatus

3.1 *General.* Apparatus needed is described in the following sections in some detail. For sampling, use items in 3.2 and 3.3; for total alkalinity, items in 3.6; for sodium carbonate, items in 3.5; for chloride, items in 3.6; for iron, items in 3.4 and 3.6; for sulfate, items in 3.6.

3.2 *Sample containers*

3.2.1 Container must be of a size to hold the equivalent of at least 200 g NaOH for determinations in duplicate.

3.2.2 The choice of material for the containers is important for liquids taken or held at elevated temperatures. Glass is suitable for 50% NaOH unless silica is to be determined. Glass breakage may be encountered with 73%. Polyethylene or polypropylene may be used with 50% NaOH, polypropylene with 73%. If possible, 73% NaOH should be held in liquid state until tests are complete. However, it may be "cast" into plastic, nickel, or silver containers or molds. The molds are later removed and the samples crushed to prepare the specimens.

3.3 *Sampling device.* A simple “dipper” or “tap” sample taken from a bulk liquid container is inadequate. One satisfactory device has three or five closed containers mounted on a single rod, and when the device is lowered into a tank and stoppers are pulled, samples are taken simultaneously at different levels, which are then combined. "Drip" samples, taken during unloading, may be used if it is not necessary to analyze the caustic before unloading.

3.4 *Colorimeter.* Colorimeter or spectrophotometer with a 5-cm light path and capable of photometric measurement at 510 nm.

3.5 *Carbonate apparatus.* Analytical train for gravimetric determination of carbonate, consisting of the following principal parts (Fig. 1): separatory funnel (C), 100-mL capacity; flask (F), 250-mL extraction; condenser (G), 20-cm modified Liebig; drying tubes (H and J), Schwartz, glass-stoppered, 10-cm; Bubbler bottle (Q), 100-mL capacity; siphon-vacuum bottle, approx. 4000-mL capacity.

3.6 *Other apparatus:* weighing bottle with stopper to hold the equivalent of 20 g of NaOH; seven volumetric flasks, one 1000-mL, one 500-mL, five 100-mL; four burets (two 25-mL and two 50-mL); three pipets, 0.5-, 10- and 50-mL; two graduated cylinders, 10- and 50-mL; two Erlenmeyer flasks, wide-mouth, 250-mL; two beakers, 250-mL; small glass funnel; platinum crucible (or porcelain).

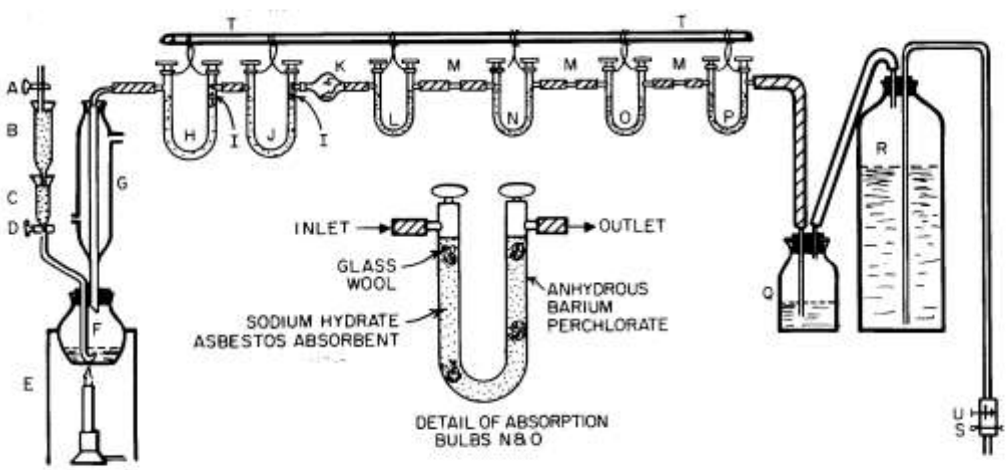

Fig. 1. Carbonate apparatus.

4. Reagents

4.1 *General*

4.1.1 Reagents needed for the several determinations of this method are as follows: for total alkalinity, use items 4.2, 4.6, 4.16, and 4.17; for the carbonate train, use items 4.6 and 4.18 through 4.23; for chloride, use items 4.2, 4.5, 4.6, 4.7, 4.14, and 4.15; for iron, use items 4.2, 4.4, 4.6, 4.8, 4.9, 4.10, 4.12, and 4.13; for sulfate, use items 4.2, 4.3, 4.5, 4.6, 4.16, and 4.17.

4.2 *Hydrochloric acid,* concentrated, 1*N* HCl (see TAPPI T 610 "Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions"). Record the temperature when standardizing for special accuracy.

4.3 *Barium chloride.* Dissolve 120 g of $BaCl_2$ in 1000 mL water.

4.4 *Pure iron wire,* standard solution (1 mL = 0.010 mg Fe). Dissolve 0.1000 g of iron wire, reagent grade, for standardizing, in 10 mL of 1:1 HCl and 1 mL of saturated bromine water. Boil off excess bromine. Add 200 mL of 1:1 HCl and dilute to 1000 mL in a volumetric flask. Dilute 100 mL of this solution to 1000 mL.

4.5 *Silver nitrate,* 0.1*N* $AgNO_3$ (see T 610), also dilute solution (5 g $AgNO_3$ in 100 mL water).

4.6 *Water*, distilled, CO_2-free (freshly boiled and cooled).

4.7 *Ammonium thiocyanate,* 0.1*N* NH_4CNS solution (see T 610).

4.8 *Ammonium hydroxide*, 1:1, mix equal volumes concentrated NH_4OH and water.

4.9 *Ammonium acetate-acetic acid solution.* Dissolve 100 g of ammonium acetate (CH_3 $COONH_4$) in about 600 mL of water, filter, add 200 mL of glacial acetic acid to the filtrate, and dilute to 1000 mL.

4.10 *Congo red indicator paper.*

4.11 *Ferric ammonium sulfate indicator,* saturated solution of ferric ammonium sulfate in water (approximately 40%).

4.12 *1,10-Phenanthroline solution* (3 g per 1000mL). Dissolve 3 g of 1,10-phenanthroline monohydrate in 500 mL of water, add 1 mL of concentrated hydrochloric acid (HCl), mix, filter, and dilute to 1000 mL.

4.13 *Hydroxylamine hydrochloride.* Dissolve 100 g of $NH_2OH \bullet HCl$ in water and dilute to 1000 mL.

4.14 *Nitric acid,* concentrated HNO_3.

4.15 *Volhard indicator,* saturated solution of ferric ammonium sulfate [$NH_4Fe(SO_4)_2 \bullet 12H_2O$] in 100 mL water and acidified with a few drops of HNO_3.

4.16 *Modified methyl orange.* Dissolve 0.1 g of methyl orange and 0.14 g of xylene cyanole dye in 1000 mL of water and filter if necessary.

4.17 *Phenolphthalein* (see T 610).

4.18 *Barium perchlorate* (or magnesium perchlorate), anhydrous, granular.

4.19 *Perchloric acid* (1:2). Mix one volume of 60% $HC1O_4$ with two volumes of water and boil for 10 min in a large Erlenmeyer flask. Cool and bottle.

4.20 *Silver arsenite in sulfuric acid.* Dissolve 2 g of pulverized As_20_3 in the least amount of 10% KOH that will effect solution. Dilute to 250 mL and add dilute H_2SO_4 (1:9) until neutral to litmus. Add 5% $AgNO_3$ as long as a yellow precipitate forms, keeping the solution neutral by adding drops of the 10% KOH when necessary. Stir until coagulated, allow to settle, and wash by decantation. Dissolve the precipitate in an excess of H_2SO_4 (1:9), dilute to 150 mL and filter out any precipitated AgCl.

4.21 *Sodium hydrate,* asbestos absorbent, 12- to 20-mesh.

4.22 *Zinc metal,* mossy, clean.

4.23 *Sulfuric acid,* concentrated (H_2SO_4).

5. Sampling

5.1 *General*

5.1.1 The nature of NaOH is such as to require special care for sampling and preparing specimens for analysis. If trace constituents also are to be determined, additional precautions, such as may be suggested by most major producers, may be desirable. Both aqueous and anhydrous NaOH rapidly absorb moisture and carbon dioxide (and other acid gases) from the atmosphere. The aqueous solutions may be corrosive to sampling devices and may become contaminated.

5.1.2 Caustic soda liquors are usually shipped in insulated tank cars at elevated temperatures and the following minimum temperatures should be maintained for proper sampling:

50% NaOH liquor = 29°C (85°F)

70-73% NaOH liquor = 85°C (185°F)

Partial freezing results in a separation of liquor and solids and causes sampling problems. Each lot is required to be completely liquid and well mixed before sampling.

5.2 *Liquids.* With the sampling device, take samples from at least the upper, middle, and lower thirds of the tank, avoiding the surface.

5.3 *Solids (anhydrous)*

5.3.1 Remove the top (75–100 mm) of material in a drum of flake, ground, or powdered caustic soda and then take a sample from the uncovered middle and immediately enclose and, if necessary, seal it in a container with tape or wax.

5.3.2 When molten solid caustic is packaged in metal drums and cooled to a solid before sealing, any impurities present tend to concentrate near the bottom. Open the metal drum at its vertical seam and with an auger (19 mm) drill out portions at representative levels (may cause metal contamination) or split the cake in half vertically with a hammer and chisel, and chisel off fragments to represent a vertical cross section of the cake. In either case, promptly enclose and seal the materials. Reduce the sample to a convenient size by enclosing in several thicknesses of clean cloth or kraft paper, pounding with a hammer, and mixing and quartering as described in TAPPI T 605 “Reducing a Gross Sample of Granular or Aggregate Material to Testing Size” as quickly as possible, then use immediately.

6. Procedure

6.1 *Total alkalinity determinations*

6.1.1 Transfer duplicate specimens of the following size to weighing bottles which have been tared with their covers, keeping exposure to air to a minimum.

Sample	*Specimen size, g*
50% NaOH	65-78
73% NaOH	45-52
Anhydrous NaOH	32-40

6.1.2 Weigh to the nearest 1 mg and transfer quantitatively to a 1000-mL volumetric flask, using several rinses of water. Dilute to about 400 mL with water and cool to room temperature. Then dilute to 1000 mL and mix. With a volumetric pipet, transfer 50 mL of the prepared solution to a 500-mL Erlenmeyer flask and add 2-4 drops of methyl orange indicator. Titrate with standard 1.0*N* acid to the same color shade end point as for standardizing the acid. Record the volume and temperature of acid used. If necessary, correct the acid normality for temperature between 20 and 30°C by adding 0.00035 per °C if the temperature is below that of standardization, and subtracting when above.

6.1.3 Calculate the total alkalinity from the following:

$$\text{NaOH, \%} = [(A \times B \times 0.030990) / W] \times 100$$

where:

A = normal acid required for titration of the specimen, mL
B = corrected normality of the acid
W = weight of the specimen, g

and

$$\text{NaOH, \%} = 1.2907 \times Na_2O\text{, \%}$$

If the actual hydroxide content is desired, the carbonate content must be determined separately by the gravimetric method described. Then:

$$\text{NaOH (actual), \%} = C - (D \times 0.755)$$

where

C = NaOH (total alkali), %
D = Na_2CO_3, %

6.1.4 Duplicate determinations which agree within 0.16% absolute are acceptable for averaging.

6.1.5 Report the average percentage of Na_2O to the nearest 0.01.

6.1.6 *Precision*

6.1.6.1 Repeatability (within a laboratory) = 0.48% relative.

6.1.6.2 Reproducibility (between laboratories) = 0.80% relative.

6.1.6.3 Comparability = not known.

6.1.6.4 The above estimates are based on an interlaboratory study of five samples comprising 45% KOH, 50% NaOH, 73% NaOH, and anhydrous KOH. The number of laboratories analyzing each sample ranged from 7 to 15 with one analyst in each lab performing duplicate determinations and repeating one day later. The above is in accordance with the definitions of these terms in TAPPI T 1206 “Precision Statement for Test Methods.”

6.2 *Carbonate determination*

6.2.1 The apparatus is assembled as shown in Fig. 1. It consists of a 250-mL extraction flask (F) in which the CO_2 is evolved. Acid is admitted through the stopcock (D) from separatory funnel (C) which should be of at least 80 mL capacity. The acid delivery tube entering F should be bent upwards at the end to prevent the escape of CO_2. To the top of C is attached a similar tube (B) containing sodium-hydrate-asbestos absorbent protected by glass wool, to purify the carrier air which enters at stopcock A. The flask is heated directly by a Bunsen burner and protected from drafts by shield E, either metal or asbestos. The gases escape from F through the water-cooled condenser G. All this part of the apparatus is mounted on one large ring stand, facilities being arranged for removing the flask F and guard tube B for each determination. All stoppers and joints must be absolutely air-tight.

6.2.2 The U-tubes are hung individually from hooks by copper wire loops securely fastened to the necks of the tubes. H is a 15-cm U-tube containing glass beads and a solution of silver arsenite (Ag_3AsO_3) in dilute H_2SO_4. Its function is to remove alkali gases, sulfides, chlorides, chlorine, and other oxidizing gases. I is a plug of glass wool to retain any reagent entrained in the gas. J is a 15-cm U-tube containing H_2SO_4 and glass beads to absorb most of the water from the gas. It is also protected by a plug of glass wool (I) in the outlet tube. K is a bulb containing the mossy zinc which serves to catch any trace of acid carried over from J. L is a 10-cm U-tube containing the anhydrous perchlorate. The tube is prepared in three sections separated by glass wool to eliminate channeling by the gases.

6.2.3 N and O are 10-cm U-tubes for the absorption and weighing of the CO_2, each prepared with two sections of sodium hydrate-asbestos and one of the anhydrous perchlorate separated by glass wool, the desiccant being nearer the outlet end. These tubes are connected to the system and to each other by the short glass tubes M. The tubes are disconnected and weighed with their rubber tubing connections attached.

6.2.4 P is a 10-cm U-tube filled with desiccant to prevent any accidental back draft from containing any weighable moisture. Q is a bubbler bottle containing concentrated H_2SO_4. If the bubbler tube is a 6-mm bore and the tip is placed 1.9 cm below the surface of the acid, one bubbler per second will indicate about 20 mL/min gas flow.

6.2.5 R is a 4000-mL siphon vacuum bottle. It provides sufficient vacuum for the flow required, and its capacity is a good measure of the time required for an analysis. The siphon can be closed by pinchcock S and the rapidity of emptying regulated by screw clamp U.

6.2.6 A freshly prepared train should be conditioned with a 0.2-g sample of Na_2CO_3 carried through the analysis to saturate the reagents with CO_2. Before the train is ready for a series of determinations, successive weighings of the tube N must agree within 0.0002 g before and after the passage of one-half of the volume of air represented by the capacity of R, when no sample is in place. Tube O is used as a precautionary measure. At the indicated gas flow, N will be found to absorb all the CO_2 until its capacity is nearly used up. Tube O should always be weighed as a check for any CO_2 not absorbed in N.

6.2.7 *Procedure.* Weigh to the nearest 0.1 g duplicate specimens sized as below, into tared evolution flasks (F).

Na_2CO_3, %	*Specimen size, g*
0.01-0.10	15-20

0.10-0.50	10-15
0.50-1.00	7-10

6.2.8 Connect the flask F to the analytical train as shown in Fig. 1. Open all stopcocks and adjust screw clamp U for a flow of 60-80 mL/min, corresponding to 3 to 4 bubbles per second when the bubbler Q is built as described. Close stopcock D and pinchcock S. Remove B and add at least 75 mL of the diluted $HClO_4$ into C and replace tube B. Open pinchcock S and then stopcock D carefully to admit the acid. When all the acid has entered, begin heating with a 2.5-cm Bunsen flame. When the heating has progressed to the point where the flow of air through the acid delivery tube seems to stop and the liquid shows a tendency to back up in the tube, close D.

6.2.9 After 5 min of brisk boiling, remove the flame, open stopcock D, and continue drawing air through the train until the water in bottle R has been siphoned off almost entirely. Close S, the last stopcock in P, both stopcocks in O and in N, last stopcock in L, and the first stopcock in H.

6.2.10 Remove tubes N and O and allow them to stand in the balance case for at least 10 min. Open their stopcocks momentarily to attain atmospheric pressure, wipe gently with tissue, and weigh to 0.1 mg.

6.2.11 Calculate the carbonate content as follows:

$$Na_2CO_3, \% = [(A \times 2.4083) / W] \times 100$$

where

A = increase in the weight of U-tubes O and N, g
W = specimen weight, g

6.2.12 Report the average percentages of sodium carbonate to the nearest 0.01%.

6.2.13 Duplicate determinations agreeing within limits shown in the second column of Table 1 are acceptable for averaging.

Table 1. Sodium carbonate method repeatability and reproducibility*

Na_2CO_3 content, %	*Checking limits for duplicates*	*Repeatability, % absolute, one analyst*	*Reproducibility, % absolute, interlaboratory*
0.01-0.02	0.01	0.01	0.02, 0.04-0.08
	0.02	0.02	0.07, 0.12-0.15
	0.03	0.05	0.11
Approx. 0.40	0.05	0.09	0.16

*NOTE: These data are based on results obtained by this method on six samples by one analyst in each of twelve laboratories. Each analyst ran a determination in duplicate, averaged the results, and repeated one day later.

6.2.14 *Precision.* Results of a precision study of this method are shown in Table 1.

6.2.15 Comparability = not known.

6.2.16 The precision statements are in accordance with the definitions of these terms in T 1206.

6.3 *Chloride determination*

6.3.1 *Procedure.* Select a specimen size by means of the following table:

NaCl in sample, %	*Specimen size, g*
1 -2	5
0.5-0.9	10
0.01-0.49	20

6.3.2 If the approximate chloride content is unknown, make a trial determination with a 10-g specimen. If necessary, repeat with the weight of specimen given in the table.

6.3.3 Weigh duplicate specimens in tared and covered weighing bottles, to the nearest 0.001 g for small samples (nearest 0.01 g for larger samples). Transfer the specimen quantitatively to a 500-mL Erlenmeyer flask using about 100 mL of water to effect transfer and solution. Add 1 mL of ferric ammonium sulfate indicator and (slowly) sufficient concentrated HNO_3 to dissolve the reddish-brown precipitate formed with the indicator. Cool to room temperature. Add 0.1*N* $AgNO_3$ in an excess of 5-10 mL over that required to react with the chloride, agitating continuously while adding.

6.3.4 It is sometimes preferred to add 0.5-1.0 mL of 0.1*N* NH_4CNS before adding the $AgNO_3$ to obtain a sharper indicator end point. In this procedure, add $AgNO_3$ in an amount 2-5 mL in excess of that required to cause the disappearance of the brown color. Any NH_4CNS so added must be included in the calculation. The sample is then backtitrated as described below.

6.3.5 Filter off the precipitated silver chloride using semiquantitative paper and only one 5-mL portion of wash water. Leave the filtrate in the receiver flask and backtitrate the excess $AgNO_3$ with 0.1*N* NH_4CNS solution to the first reddish-brown color lasting for a minimum of 15 s. Record the volumes of titrants used to the nearest 0.02 mL.

6.3.6 *Calculation*

$$Chloride,\quad \% = \frac{(A \times N_1) - (B \times N_2) \times 0.035453}{W} \times 100$$

where

A = $AgNO_3$ solution added, mL
B = NH_4CNS solution added, mL
N_1 = normality of $AgNO_3$ solution used
N_2 = normality of NH_4CNS solution used
W = specimen weight, g

6.3.7 If desired, the percentage of chloride may be calculated as sodium chloride as follows:

NaCl, % = % Cl × 1.6485

6.3.8 Report the average percentage of chloride to the nearest 0.01. Duplicate determinations which agree within 0.02% absolute are acceptable for averaging.

6.3.9 Repeatability (within a laboratory) = 0.01% absolute.

6.3.10 Reproducibility (between laboratories) = 0.2% absolute.

6.3.11 Comparability = not known.

6.3.12 The above precision statements are based on an interlaboratory study of four samples containing 0.15–0.8% Cl. One analyst in each of seven laboratories performed duplicate determinations and repeated one day later.

6.3.13 These statements are in accordance with the definitions of these terms in T 1206.

6.4 *Iron determination*

6.4.1 *Preparation of calibration curve.* To a series of 100-mL volumetric flasks, measure 0.5-, 1.0-, 2.0-, 3.0- and 5.0-mL portions of standard iron solution. To each flask add the following reagents in order, mixing after addition of each: 20 mL of water, 5 mL of $NH_2OH \cdot HCl$ solution, and NH_4OH (1:1) as required to bring the pH to 3.5–4.0 (just alkaline to Congo red paper as an external indicator). Add 5 mL of ammonium acetate-acetic acid buffer solution, 5 mL of 1,10-phenanthroline solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min. Prepare a reference solution in another flask with water and the same reagents as indicated above.

6.4.2 Measure the absorbencies of the solutions using an absorption cell with the photometer with a wavelength of 510 nm (or a filter in the range from 500 to 525 nm). Adjust the photometer to read zero absorbency on the reagent blank.

6.4.3 This method has been written for cells having a 5-cm light path. Cells of other dimensions may be used, provided suitable adjustments are made to amounts of specimens and reagents.

6.4.4 Plot on coordinate paper the absorbencies versus milligrams of iron present per 100 mL of solution.

6.4.5 *Procedure.* Into 100-mL beakers, weigh duplicate 10-g specimens to the nearest 0.1 g. Add 100 mL of water and carefully add concentrated HCl in increments until 50 mL have been added if the sample is 50% NaOH, 75 mL if the sample is 73% NaOH, or 100 mL if the sample is anhydrous NaOH.

6.4.6 Cover with a watch glass, heat to boiling, and boil for 1 min (any red residue of Fe_2O_3 should disappear during the boiling period). Cool the solution to room temperature, transfer to a 500-mL volumetric flask, dilute to volume with water, and mix. Pipet an aliquot to contain from 0.005 to 0.050 mg of iron into a 100-mL volumetric flask. Into another 100-mL volumetric flask put 50 mL of water and 1 mL of HCl for a reference solution. To both sample and reference solutions add the reagents as in the preparation of the calibration curve. Dilute to volume, mix thoroughly, and let stand 15 min.

6.4.8 *Calculation.* Convert the photometric reading of the test solution to milligrams of iron by means of the calibration curve.

$$\text{Fe, ppm} = (A \times 100) / B$$

where

A = iron found in 100 mL of solution, mg

B = weight of the specimen, g

6.4.9 Report the average parts per million of iron to the nearest 0.1 ppm.

6.4.10 Duplicate determinations which agree to within 15% relative are acceptable for averaging.

6.4.11 Repeatability (within a laboratory) = 16% relative.

6.4.12 Reproducibility (between laboratories) = 32% relative.

6.4.13 Comparability = not known.

6.4.14 These criteria are based on an interlaboratory study of four samples covering the range of 4-30 ppm Fe in KOH and NaOH. One analyst in each of 15 laboratories performed duplicate determinations and repeated them one day later.

6.4.15 These statements are in accordance with the definitions of these terms in T 1206.

6.5 *Sulfate determination.*

6.5.1 *Procedure.* Select a specimen size according to the following tabulation:

Material	*Specimen size, g*
50% NaOH	45-55
73% NaOH	30-40
Anhydrous NaOH	20-30

6.5.2 Weigh duplicate specimens into 600-mL beakers to the nearest 0.1 g. Add 300 mL of water and mix. Add 2-4 drops of methyl orange and acidify carefully with concentrated HCl adding 3 mL in excess of that required to neutralize the sample. Examine the solution at this point. If it contains any insoluble matter, filter. Return the filtrate to the beaker and heat to boiling. Add slowly, with constant stirring, 25 mL of $BaCl_2$ solution. Digest for 30 min on a steam bath and allow the precipitate to settle overnight at room temperature.

6.5.3 Filter the contents of the beaker on an ashless, fine quantitative paper and transfer the precipitate quantitatively to the paper with a fine stream of hot water from a wash bottle. Wash the precipitate with successive small portions of hot water until the washings are free of chloride on testing with 3-4 drops of $AgNO_3$ solution.

6.5.4 Heat a platinum or porcelain crucible to 850-900°C for 15 min, cool in a desiccator, and weigh to the nearest 0.0001 g. Fold the washed filter paper with precipitate and place it in the tared crucible. Dry and char carefully without flaming. Ignite at 850-900°C for a minimum of 30 min. Remove the crucible from the furnace, allow to cool partially, place in a desiccator, and cool to room temperature. Reweigh to the nearest 0.0001 g.

6.5.5 Calculate the sulfate content as follows:

$$SO_4^{=}, \% = \{[(A \times B) \times 0.41156] / W\} \times 100$$

where

A = weight of crucible and precipitate after ignition
B = weight of empty crucible
W = weight of the specimen, g

6.5.6 Report the average percentage of $SO_4^{=}$ to the nearest 0.001%.

6.5.7 Duplicate determinations should agree within 0.0018% absolute.

6.5.8 *Precision.* Results from a precision study of this method are presented in Table 2.

Table 2. Sulfate method repeatability and reproducibility*

$SO_4^{=}$ content, %	*Approx. repeatability, one analyst, 95% range, % relative*	*Approx. reproducibility, interlaboratory, 95% range, % relative*

0.100	18	33
0.050	27	75
0.010	36	90

*Three samples, with $SO_4^{=}$ content approximately as indicated, were analyzed by one analyst in each of 12 to 15 laboratories. Each analyst ran a determination in duplicate, averaged the results, and repeated one day later.

6.5.9 Comparability = not known.

6.5.10 The above statements are in accordance with the definitions of these terms in T 1200 "Interlaboratory evaluation of test methods to determine TAPPI repeatability and reproducibility."

7. Keywords

Sodium hydroxide, Total alkali, Carbonates, Chlorides, Iron, Sulfates, Alkalinity

8. Additional information

8.1 Effective date of issue: To be assigned.

8.2 This method, formerly T 613 os-77, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superceded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.

8.3 Related method: ASTM-E-291.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■