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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 Material 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

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 SO_4 .

Approved by the Standard Specific Interest Group for this Test Method



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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).

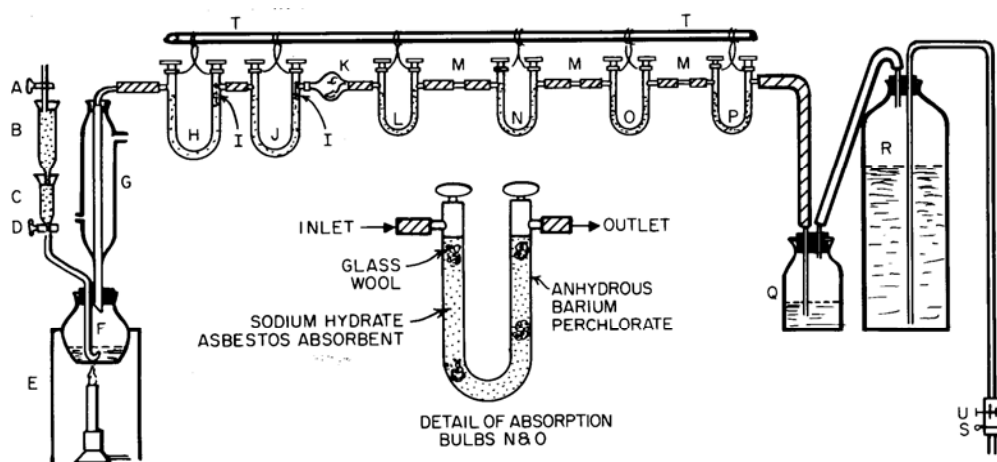


Fig. 1. Carbonate apparatus.

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, 1N 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*, 0.1N 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*, 0.1N 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 ($\text{CH}_3\text{COONH}_4$) 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 $\text{NH}_2\text{OH} \cdot \text{HCl}$ in water and dilute to 1000 mL.
- 4.14 *Nitric acid*, concentrated HNO_3 .
- 4.15 *Volhard indicator*, saturated solution of ferric ammonium sulfate [$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] 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% HClO_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_2O_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