WI 220808.04

T 624

BALLOT NO. 3 SARG

DRAFT NO. 02

DATE 06/01/2023

WORKING GROUP CHAIR To be determined.

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 soda and sulfate white and green liquors

(Proposed Reaffirmation of Classical Method T 624 cm-11)

1. Scope

This method is for an accurate analysis of all the main components of soda or sulfate white or green liquors and may be used as a reference method for establishing quicker or more convenient tests suited to routine control.

2. Apparatus

2.1 *Hydrometer,* 1.0 to 1.1 sp gr, or a pycnometer (specific gravity bottle).

2.2 *Filtering crucible,* 30 mL, porcelain with 3 to 5 µm pores.

2.3 *Kjeldahl flask,* 300 mL (long-necked, round-bottom flask).

2.4 *pH meter,* fitted with platinum and saturated calomel electrodes, plus glass electrode and buffer solutions.

2.5 *Magnetic stirrer,* with 19-mm (3/4-in.) Teflon-covered stirrer bar.

2.6 *Muffle furnace,* electrically heated, with temperature controlled to 1200°C.

2.7 *Other apparatus:* steam bath; Büchner funnel and suction flask, each 250 mL; 100-, 250-, and 500-mL volumetric flasks; 50-mL burets; 1-, 5-, 10-, 25-, and 50-mL pipets; 250- and 500-mL Erlenmeyer flasks; 150-, 250-, and 600-mL beakers; watch glass cover and stirring rod for 250-mL beaker; filter funnel and 5 to 6-cm diameter fine and medium porosity, quantitative filter paper.

2.8 *For ascarite determination of carbonate:*

2.8.1 *CO_2 absorption apparatus,* see Figs. 1 and 2.

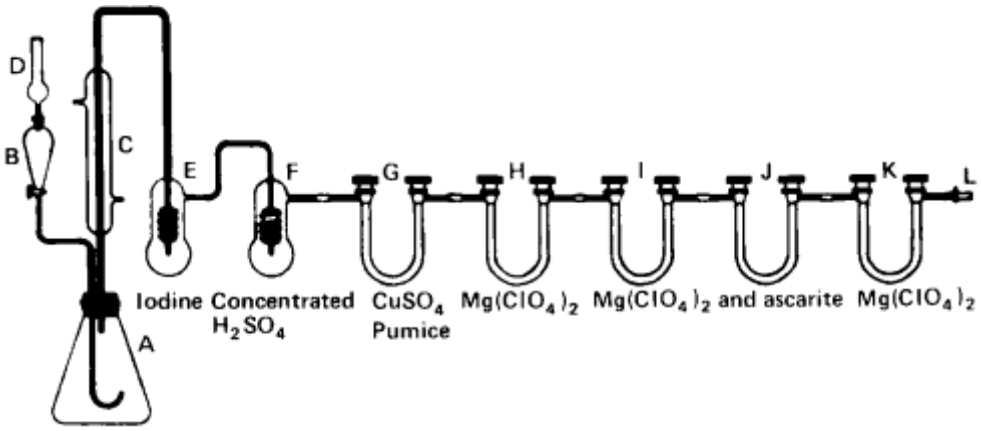

Fig.1. Apparatus for direct determination of carbon dioxide.

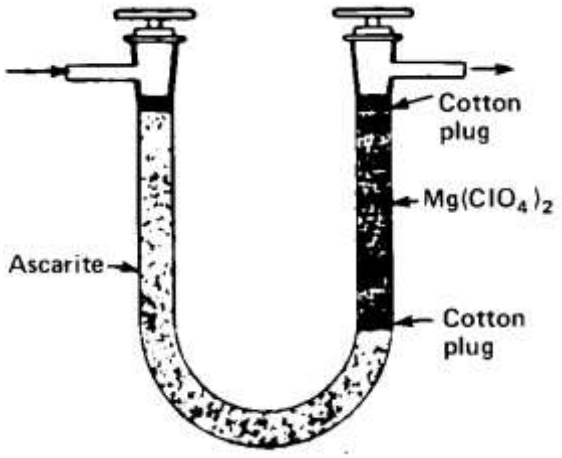

Fig. 2. Absorption tube for carbon dioxide tubes I and J in Fig. 1.

2.9 *For total sulfur, silica, and metals other than sodium:*

2.9.1 *Platinum evaporating dish,* about 100-mL size or larger.

2.9.2 *Platinum crucible and cover,* about 35-mL size or larger.

2.9.3 *Oven,* at 105 and 160 ± 3°C.

3. Reagents

3.1 Use reagent grade chemicals and use dilution water which has been distilled and recently boiled and cooled.

3.1.1 *Sodium thiosulfate,* 0.1*N* $Na_2S_2O_3$, containing 0.1-0.2 g/L Na_2CO_3 (see TAPPI T 610 "Preparation of Indicators and Standard Solutions").

3.1.2 *Iodine,* 0.15-0.2*N.* Dissolve 20 g I_2 in concentrated solution of 60 g KI in water, and dilute to 1 L. Check daily, or before every analysis, by titration with standardized $Na_2S_2O_3$.

3.1.3 *Sulfuric acid,* 20% by volume, also 0.5*N* H_2SO_4 (see T 610).

3.1.4 Hydrochloric acid, dilute HCl 1:20 and 1:100.

3.1.5 Zinc sulfate, 1*M*, $ZnSO_4 \cdot 7H_2O$ (287 g/L).

3.1.6 Sodium carbonate, 1*M* Na_2CO_3 (106 g/L).

3.1.7 Sodium hydroxide, approximately 1*N* and 12*N* NaOH.

3.1.8 Sodium sulfite, Na_2SO_3 (25 g/L).

3.1.9 Barium chloride, $BaCl_2$ (10%).

3.1.10 Ammonium hydroxide, concentrated and approximately 6*N* NH_4OH.

3.1.11 Silver nitrate-ammonia, 2.5% solution $AgNO_3$ to which NH_4OH has been added until brown precipitate just clears.

3.1.12 Methyl orange indicator (see T 610).

3.1.13 Starch indicator (see T 610) or thyodene.

3.1.14 Uranyl zinc acetate reagent (see TAPPI T 623 “Sodium Determination by the Uranyl Zinc Acetate Method”).

3.1.15 Alcohol reagent (see T 623).

3.1.16 Ether.

3.2 *For CO_2 absorption apparatus (for accurate determination of carbonate):*

3.2.1 *Iodine,* 5% solution, dissolved in 1*M* KI.

3.2.2 *Anhydrous magnesium perchlorate,* $Mg(ClO_4)_2$.

3.2.3 *Ascarite,* sodium hydrate asbestos absorbent.

3.2.4 *Copper-sulfate pumice:* soak 4 to 8 mesh pumice stone in saturated $CuSO_4$ and dry at 150 to 180°C. Keep in tightly sealed container.

3.3 *For total sulfur, silica and metals other than sodium:*

3.3.1 *Nitric acid,* concentrated HNO_3 nitrite free (white).

3.3.2 *Ammonium oxalate,* crystals $(NH_4)_2C_2O_4 \cdot H_2O$ and 1% solution.

3.3.3 *Hydrogen peroxide,* 30% H_2O_2.

3.3.4 *Hydrofluoric acid,* concentrated HF.

3.3.5 *Silver nitrate,* 0.1*N* $AgNO_3$ (see T 610).

3.3.6 *Ferric ammonium sulfate,* saturated solution $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$.

3.3.7 *Potassium thiocyanate,* 0.1*N* KSCN (see T 610).

3.3.8 *8-Hydroxyquinoline,* 5% solution in 2*N* acetic acid (60 g CH_3COOH per L).

3.3.9 *Methyl red indicator* (see T 610).

3.3.10 *O-Cresolphthalein indicator,* 0.20% dissolved in alcohol.

3.3.11 *Sodium tauroglycocholate,* surfactant (optional).

4. Sampling

The composition of sulfate liquors tends to change on standing, especially if access to air is permitted. Take a representative sample and store in a completely filled and stoppered alkali-resistant bottle. Perform the analysis as quickly as possible after sampling; state if more than 24 h have elapsed.

5. Procedures

5.1 *Density*

5.1.1 For maximum accuracy, determine the density at 20°C by means of a calibrated pycnometer, weighing the bottle empty, filled with water, and filled with the liquor at the same temperature.

5.1.2 For ordinary purposes use a hydrometer with a range of 1.0 to 1.1 sp gr.

5.2 *Sodium sulfate.* Pipet 25 mL of liquor into a 250-mL beaker and dilute with 50 mL of water. Cover the beaker with a watch glass and add slowly through the beaker's pouring lip 20 mL of concentrated HCl. Boil gently and evaporate on a steam bath to a moist slush. Dissolve the salts in about 50 mL of hot water. Filter the solution through medium porosity quantitative filter paper and wash the residue with about 75 mL of distilled water. Collect the filtrate and washings in a 250-mL beaker and discard the filter paper and the collected solids. Add two or three drops of methyl orange and add concentrated NaOH dropwise until the solution turns from red to yellow. Add 5 mL of concentrated HCl and heat the solution until it just begins to boil. At this point add rather rapidly and with stirring a boiling mixture of 30 mL of 10% $BaCl_2$ and 20 mL of water. Continue stirring for a minute or two, let the precipitate settle for about an hour, and then filter with suction through the tared porcelain filter crucible. Wash the precipitate and the inner wall of the crucible with at least 250 mL of warm water, dry the crucible for a few hours in an oven at 105°C, and then place it in a muffle furnace at 800°C for half-hour intervals until constant weight is attained. Cool the crucible in a desiccator before weighing to obtain the weight of barium sulfate. Convert to sodium sulfate, in grams per liter, by the formula:

$$Na_2SO_4 = \frac{grams\ BaSO_4 \times 1000 \times 142.1}{25 \times 233.4}$$

5.3 *Total reducing compounds* ($Na_2S + Na_2SO_3 + Na_2S_2O_3$) *(1).* Dilute 25 mL of liquor to 100 mL in a volumetric flask. Measure from a buret 25 to 30 mL of the standardized iodine solution into a 250-mL Erlenmeyer flask. Add 5 mL of 20% H_2SO_4 and rinse down the inside of the flask with about 30 mL of water. Add, by pipet, 10 mL of the diluted liquor to the acidified iodine while swirling vigorously the contents of the flask. Titrate the excess iodine with 0.1*N* $Na_2S_2O_3$, adding the starch indicator when the yellow color has nearly disappeared. Calculate the net equivalents of iodine used, and record as total reducing compounds (TRC) expressed in equivalents per liter by the formula:

$$TRC,\ eq/L = \frac{(mL\ I_2 \times N\ I_2) - (mL\ Na_2S_2O_3 \times N\ Na_2S_2O_3)}{2.5}$$

Duplicate titrations should agree within 4 meq/L.

5.4 *Sulfide-free reducing compounds* ($Na_2SO_3 + Na_2S_2O_3$) (*1*, *2*, *3*).

5.4.1 *Removal of sulfide.* Before proceeding with the analysis, remove the sulfides by precipitation and filtration. Make a preliminary test on an aliquot of the liquor to determine the zinc carbonate required for their quantitative precipitation as follows: Pipet 50 mL of the liquor into a 150-mL beaker and add a freshly prepared suspension of $ZnCO_3$ made by mixing 15 mL of 1*M* $ZnSO_4$ with 15 mL of 1*M* Na_2CO_3. Mix the contents of the beaker thoroughly and let it stand until about 13 mm (½ in.) of clear supernatant liquid forms. Add a drop of clear ammoniacal silver nitrate to the beaker. If a black or brown curd or heavy cloud forms *in the supernatant liquid,* precipitation of sulfide is incomplete, and additional $ZnCO_3$ must be added. Prepare this from 5 mL of the $ZnSO_4$ and 5 mL of the Na_2CO_3 solutions, add it to the beaker and test as before. Repeat these additions of the $ZnCO_3$ until the test shows that sulfide ions are absent in the supernatant liquid. Note the total volumes of $ZnSO_4$ and Na_2CO_3 solutions so used, and discard the preliminary test mixture.

5.4.1.1 Pipet 50 mL of liquor into a 250-mL volumetric flask and add the entire amount of $ZnCO_3$ suspension found necessary for the complete removal of the sulfides. Mix thoroughly and dilute to the mark with water. Use no glycerine or other oxidation inhibitors. Filter through a fine quantitative filter paper in a Büchner funnel with mild suction. It may be necessary to pass the filtrate through the pad again to obtain a clear solution. Use this clear filtrate without loss of time for the next two steps.

5.4.2 *Oxidation with iodine.* From a buret, measure 10 to 20 mL of the standardized iodine solution into a 250-mL Erlenmeyer flask and add 5 mL of 20% H_2SO_4. Pipet 25 mL of the clear filtrate obtained as above into the acidified iodine while swirling vigorously the contents of the flask. Titrate the excess iodine with 0.1*N* $Na_2S_2O_3$. Calculate the net equivalents of iodine used, and record as $SFRC_b$ expressed in equivalents per liter, by the formula:

$$SFRC_b,\ eq/L = \frac{(mL\ I_2 \times N\ I_2) - (mL\ Na_2S_2O_3 \times N\ Na_2S_2O_3)}{5}$$

5.4.2.1 Duplicate titrations should agree within 4 meq/L.

5.4.3 *Oxidation with hypoiodite.* Add 50 mL of 12*N* NaOH to a 150-mL beaker containing a Teflon-covered magnetic stirrer bar, and with a pipet add 25 mL of the clear filtrate obtained in 5.4.1. Place the beaker on a magnetic stirrer situated beneath the delivery tip of a 50-mL buret containing 0.15*N* standard iodine solution. Begin the stirring action to mix the sample with the denser 12*N* NaOH solution. The rate of stirring should not create a vortex nor whip air into the liquid. In the homogenized solution, place the tips of a platinum electrode and a saturated calomel electrode which are connected to a pH meter, the calomel electrode connection being the same as for pH measurements. Using the millivolts range of the pH meter, the initial reading should be between -100 and -300. Significantly greater numerical readings indicate the unwanted presence of sulfide ions. If the initial reading is between these two values and drifts towards the numerically greater value, a few minutes waiting (with the stirrer going) will indicate whether or not the numerically greater reading will be exceeded. Begin the titration by adding iodine dropwise. Continue iodine addition until a reading of zero, or a slight (5 mV) positive reading is obtained, and record the volume of iodine used. Calculate the equivalents of iodine used by the formula below and record as $SFRC_c$ expressed in equivalents per liter. Duplicate titrations should agree within 6 meq/L.

$$SFRC_c,\ eq/L = \frac{mL\ I_2 \times N\ I_2}{5}$$

5.5 *Sodium sulfide.* Calculate sodium sulfide in grams per liter by the formula:

$$Na_2S = \frac{(TRC - SFRC_b) \times 78.1}{2}$$

5.6 *Sodium thiosulfate.* Calculate sodium thiosulfate in grams per liter by the formula:

$$Na_2S_2O_3 = \frac{(SFRC_c - SFRC_b) \times 158.1}{7}$$

5.7 *Sodium sulfite.* Calculate sodium sulfite in grams per liter by the formula:

$$Na_2SO_3 = \frac{SFRC_c - \left(\frac{Na_2S_2O_3 \times 8}{158.1}\right) \times 126.1}{2}$$

5.8 *Polysulfide sulfur* (*4*).

5.8.1 The color of the liquor may often be taken as a rough index of the relative amounts of polysulfides present. Very small amounts of polysulfides impart a pale yellow color to the liquor, while liquors rich in polysulfides may appear orange-brown; also, liquors with significant polysulfide content will usually contain only a trace of

Na_2SO_3. With this in mind, the following procedure should be modified accordingly as to sample size or amount of sulfite solution used.

5.8.2 Pipet 50 mL of liquor into a 150-mL beaker and add 20 mL of 25 g/L Na_2SO_3 or the equivalent amount of solid salt. Warm to about 50°C until the yellow color disappears. If the yellow color does not disappear after 15 to 20 min at 50°C, add more sulfite and heat longer until the solution becomes colorless. Cool the solution to room temperature, and transfer it quantitatively to a 250-mL volumetric flask. From this point on, follow the steps in Section 5.4 for the determination of sulfide-free reducing compounds. The object is to determine the difference in thiosulfate content between the liquor treated with sulfite and the untreated liquor. Calculate the polysulfide sulfur in grams per liter by the formula:

$$\text{Polysulfide sulfur} = \frac{s \times u \times 32.1}{158.1}$$

where

s = $Na_2S_2O_3$ found after sulfite treatment

u = $Na_2S_2O_3$ in untreated liquor

NOTE 1: This determination yields a measure of the sulfur, x - 1, in a polysulfide compound generally represented by Na_2S_x. It is not intended to yield results such that a numerical value can be assigned to x, other than an arbitrary average value which depends also upon the sulfide content from 5.5.

5.9 *Total alkali* (Na_2S + NaOH + Na_2CO_3 + Na_2SO_3). Pipet 5 mL of liquor into a 250-mL Erlenmeyer flask, add about 50 mL of water and 1 to 2 drops of methyl orange. Titrate with 0.5*N* H_2SO_4, and record the results in equivalents per liter. If a pH meter is used for the end point, titrate to pH 4.0 in a 150-mL beaker. Duplicate titrations should agree within 3 meq/L. Calculate total alkali (TA) by the formula:

$$\text{TA as } Na_2O \text{ g/L} = (\text{TA, eq/L}) \times 31$$

5.10 *Active alkali* (Na_2S + NaOH).

5.10.1 Pipet 25 mL of white liquor into a 500-mL volumetric flask containing about 200 mL of water, add 25 mL of 10% $BaCl_2$ solution and mix well. (When analyzing green liquor, use a 250-mL volumetric flask containing about 25 mL of water and add 100 mL of the $BaCl_2$ solution.) When the precipitate has partially settled, transfer a drop of the supernatant liquid, by means of a stirring rod, to a test tube containing a few drops of dilute H_2SO_4. If no precipitate forms, add 5 mL of $BaCl_2$ solution to the volumetric flask and test again. Repeat this procedure until a white precipitate is obtained.

5.10.2 Dilute the contents of the volumetric flask to the mark, mix thoroughly, and allow the precipitate to settle until about 200 mL of clear supernatant liquid forms (about 100 mL in the case of green liquor). The contents

of the flask may also be vacuum filtered through general purpose ashless filter paper with medium speed and retention. Pipet 50 mL of this clear liquid into a 250-mL Erlenmeyer flask containing a few drops of methyl orange and titrate with 0.5*N* standard acid. Record the results in equivalents per liter. Titrate to pH 4.0 in a 150-mL beaker if a pH meter is used for the end point. Duplicate titrations should agree within 10 meq/L.

5.10.3 Calculate active alkali (AA) by the formula:

$$\text{AA as } Na_2O, \text{ g/L} = (\text{AA, eq/L}) \times 31$$

5.11 *Sodium hydroxide.* Calculate sodium hydroxide in grams per liter by the formula:

$$NaOH = \left(AA,\ eq/L - \frac{2\ Na_2S}{78.1} \right) \times 40$$

5.11.1 The Na_2CO_3 content of the liquor may be calculated from the data obtained from the difference between the total alkali and the active alkali if the Na_2SO_3 content is known, by the formula:

$$Na_2CO_3,\ g/L = \left[TA,\ eq/L - \left(\frac{NaOH}{40} + \frac{Na_2S \times 2}{78.1} + \frac{Na_2SO_3}{126.1} \right) \right] \times 53$$

5.11.2 The resulting value may be grossly incorrect, however, particularly in the case of white liquor, because among other reasons it depends upon the individual accuracy of four different titrations. The following method for direct determination of Na_2CO_3 as CO_2 gives results of the order of 0.1% accuracy. The volume of the specimen used for each determination should not contain more than about 0.25 g CO_2. The complete apparatus is shown in Fig. 1.

5.11.3 The decomposition vessel A is a 250-mL Erlenmeyer flask having a two-hole rubber stopper fitted with a small condenser C and a dropping funnel B. The upper end of the dropping funnel is closed with a one-hole rubber stopper carrying a drying tube D filled with ascarite resting on a small plug of cotton; the upper end of the drying tube is closed with a plug of cotton. The stem of the dropping funnel reaches nearly to the bottom of the flask and is bent upward at its lower end to prevent the entrance of gases. The upper end of the condenser is connected with the purification train by means of a short section of gum rubber tubing. In this, and other glass-to-glass connections the two ends of the glass tubing should be in contact.

5.11.4 Bottle E is filled with 50 to 75 mL of 5% iodine solution to remove reducing gases such as hydrogen sulfide and sulfur dioxide from the gas. Bottle F contains concentrated H_2SO_4 to remove the bulk of the water vapor not condensed in C. The U-tube G contains the dehydrated $CuSO_4$ on pumice stone, which removes from the gas hydrogen chloride, volatilized iodine, and traces of sulfur dioxide and hydrogen sulfide that may have escaped bottle E. The second U-tube H contains anhydrous magnesium perchlorate to remove the last traces of water vapor from the gas. U-tubes I and J are the CO_2 absorption vessels and are each filled one-third full of anhydrous magnesium

perchlorate and two-thirds full of ascarite as shown in detail in Fig. 2. The ascarite absorbs carbon dioxide and, with the drying agent following, takes up water formed in the reaction:

$$2\ NaOH + CO_2 = Na_2CO_3 + H_2O$$

5.11.5 Ascarite is not a particularly good drying agent, and in each tube it is therefore followed by a better desiccant to take up any water which may pass through. The use of two absorption tubes ensures the complete absorption of CO_2 and gives an indication of when the first tube must be recharged. The last tube K contains magnesium perchlorate and ascarite and serves the purpose of protecting the absorption tubes. From the last U-tube, a rubber tube, provided with a screw-clamp L to regulate the flow, leads to the suction line or aspirator. The U-tubes may be hung by stainless steel or nichrome wire from a horizontal rod or fastened to a panel board with clamps. If bottle F (H_2SO_4) acquires a tinge of lavender color after one determination, because of iodine carryover, a small trap containing a few mL of 0.1*N* $Na_2S_2O_3$ should be placed between E and F.

5.11.6 First test the apparatus for gas leaks as follows: Pour enough water into flask A to cover the lower end of the dropping funnel, replace the stopper and close the top of the tube D tightly with a rubber stopper. Apply gentle suction, gradually open the clamp L until about one bubble per second passes through E and F and keep it open until the bubbles cease (which will occur if the apparatus is free from leaks). Close L tightly and allow the apparatus to stand under the vacuum for about 5 min. Then close the stopcock of B, remove the stopper, gradually open the stopcock of funnel B, and note whether there is an inrush of air as denoted by bubbles in A. If the vacuum has been maintained, it may be assumed that the apparatus is free from significant leaks. If the apparatus has not been found to be gas-tight, examine all the connections carefully, replace any that appear to be defective, wire the tubing to the glass, and again test for leaks. Some analysts may desire to test the apparatus at this point by determining the CO_2 content of a specimen of Na_2CO_3.

5.11.7 When the apparatus has been found to be gas-tight, draw a current of air through it at a rate of about two bubbles per second for about 15 min. Then close the stopcocks of the U-tubes I and J, disconnect the tubes from the train, and weigh them separately against a similar U-tube used as a tare. Allow the tubes to stand inside the balance case for 15 to 20 min before weighing. Open a stopcock of each U-tube for an instant immediately before weighing, to equalize pressure. Replace the U-tubes in the train, and repeat the operation of drawing air through the system until the weight of each tube is constant to 0.5 mg.

5.11.8 When constant weight has been attained, place the specimen in flask A, add 50 mL of CO_2-free water or enough to cover the lower end of the dropping funnel, disconnect the absorption tubes I and J from the train, attach the suction to H, and draw a slow stream of air through the rest of the apparatus for about 5 min to remove any CO_2 introduced when opening flask A to add the specimen. Then connect the absorption tubes I and J, leaving L open and the vacuum source disconnected. Pour 20 mL of 20% H_2SO_4 into funnel B, replace ascarite tube D, and then allow the acid to flow slowly into the flask so that there is a slow evolution of CO_2, corresponding to the passage of about three bubbles per second through E and F. When all the acid has been added and only a slow evolution of gas is taking place, close the stopcock of B, start the water circulating in the condenser C, and gradually heat the contents of the

flask to boiling. Connect the train to the suction line, open the stopcock of B, and regulate L so that the approximately 2 bubbles of gas per second pass through the train. Continue the boiling gently for a few minutes, and then gradually reduce the heat, finally taking away the source of heat altogether. In the meantime regulate the suction so that a constant slow stream of CO_2-free air is being drawn through the system. Continue to draw air through for about 25 min after cessation of heating. Reweigh the absorption tubes against the tare, taking the same precautions as in the first weighing. The gain in weight is the weight of CO_2 in the specimen.

5.11.9 Calculate sodium carbonate, in grams per liter, by the formula:

$$Na_2CO_3 = \frac{grams\ of\ CO_2 \times 1000 \times 106}{44 \times mL\ liquor\ sample}$$

5.12 *Total sodium.* Pipet 5 mL of liquor into a 100-mL beaker, add 20 mL of water, and neutralize to about pH 4 (methyl orange) with HCl. Heat the solution to coagulate the sulfur, and filter into a 100-mL volumetric flask, washing with warm water until the flask is almost full. Discard the filter and add sufficient water to the flask to bring the liquid level to the mark. Mix thoroughly and use 1-mL aliquots of this liquid for determining the sodium according to T 623.

5.13 *Gravimetric determination of total sulfur, silica, aluminum, iron, calcium, and magnesium.* These constituents are determined after oxidation of the liquor with hydrogen peroxide according to the following procedure: Pipet 25 mL of the cooking liquor into the 300-mL Kjeldahl flask and add 50 mL of 30% H_2O_2 and 10 mL of 1*N* NaOH. Clamp the flask by its neck at an angle of about 35° to a ring stand and let it stand overnight. If the mixture tends to heat and foam excessively shortly after the addition of the H_2O_2, immerse the bulb of the flask in cold water. After standing overnight, heat the solution gradually until it boils. Maintain it at the boiling point for about 15 min and cool it to room temperature. Add one drop of methyl orange. If the color gradually fades and disappears, H_2O_2 is still present and more boiling is required. When the color imparted by the addition of one drop of methyl orange is permanent, add concentrated HCl dropwise until the indicator turns red. At this point the solution should be and remain clear. If cloudiness[1] develops, add 10 mL of H_2O_2 and 5 mL of 1*N* NaOH and repeat the oxidation and neutralization procedure. Transfer quantitatively the contents of the Kjeldahl flask to a 250-mL volumetric flask, and dilute to the mark. All sulfur in the original liquor has now been oxidized by the H_2O_2 to sulfates.

5.13.1 *Total sulfur.*

5.13.1.1 Pipet a 25-mL portion from the volumetric flask and determine the sulfate as $BaSO_4$ as described previously in 5.2.

5.13.1.2 Calculate total sulfur, in grams per liter, by the formula:

$$Total\ sulfur = \frac{grams\ of\ BaSO_4 \times 1000 \times 32.1}{233.4 \times 2.5}$$

[1]Cloudiness usually indicates the presence of free sulfur resulting from unoxidized sulfur compounds.

5.13.2 *Silica.*

5.13.2.1 Add 5 mL of concentrated HCl to the contents remaining in the 250-mL flask and evaporate to dryness in the platinum evaporating dish. Heat the solid residue on the steam bath for 1 h; add 5 mL of concentrated HCl. Stir the contents of the dish with a stirring rod so that all the solid is wetted with the acid. Add 75 mL of water, rinsing down the sides of the dish. Stir and heat to dissolve all but the silica. Filter through a small filter paper of medium porosity and collect the filtrate in a beaker. Transfer as much as possible of the silica to the filter paper. Rinse the evaporating dish and filter paper thoroughly with warm dilute HCl (1:20) and finally wash the filter paper once with water. Put the collected filtrate and washings into the platinum evaporating dish and again evaporate to dryness. Heat the residue for an hour at 105°C. Moisten the residue with about 2 mL of concentrated HCl, add 25 mL of water and heat to dissolve all but the silica. Filter through a fresh filter paper and transfer all the silica to the paper. Rinse the dish and the paper with 1:100 cold HCl and collect the filtrate and washings. Remove any silica adhering to the evaporating dish by wiping with small bits of filter paper, using the stirring rod. Place the bits of paper on the filter. Reserve the filtrate and washings for the determination of iron and aluminum.

5.13.2.2 Place the two filter papers and the bits of paper used to wipe out the evaporating dish in the covered platinum crucible. Dry the filter paper and smoke it off at low heat with the cover placed at an angle on the crucible. When the paper has been charred and smoking almost ceases, increase the heat to at least 1000°C and heat at this temperature for one-half hour or more. Place in a desiccator with the crucible lid in place and cool to room temperature. Weigh, remembering that dehydrated silica is hygroscopic, reheat, cool, and weigh again to make sure that it is at constant weight.

5.13.2.3 Carefully moisten the contents of the crucible with about 2 mL of water, adding it from a pipet inserted beneath the cover. Add 4 or 5 drops of 20% H_2SO_4 and then add carefully about 5 mL of concentrated HF. Place the crucible in a hood and heat gently to evaporate the HF without boiling the liquid. Increase the heat to fume off the H_2SO_4. When the contents of the crucible are nearly dry, gradually increase the heat to about 1200°C and bring the crucible to constant weight as before. The loss in weight represents the amount of SiO_2 in the specimen.

5.13.2.4 Calculate silica, in grams per liter, by the formula:

$$SiO_2 = \frac{grams\ of\ SiO_2 \times 1000}{22.5}$$

5.13.3 *Aluminum and iron.*

5.13.3.1 Adjust the volume of filtrate and washings from the silica determination to about 200 mL, add a few drops of methyl red, and heat to the boiling point. Neutralize (yellow color) by adding concentrated NH_4OH dropwise and with stirring, and add 2 or 3 drops more in excess of neutrality. Heat to coagulate the iron and aluminum hydrous oxides. Filter through medium porosity filter paper, and wash the precipitate by decantation three or four times with hot 1% NH_4Cl. It is not necessary to transfer all the precipitate to the filter. Collect and save the filtrate in a 600-mL beaker. Dissolve the precipitate through the filter with about 10 mL of hot 1:1 HCL and receive the solution in the

original beaker containing the remainder of the washed precipitate. Wash the filter paper thoroughly with hot 1:20 HCl. Adjust the volume of the solution to about 200 mL and again precipitate the hydrous oxides as before with ammonia. Filter on a fresh, small, quantitative paper, and catch the filtrate and washings in the 600-mL beaker containing the filtrate and washings from the first precipitation. Transfer all the precipitate to the filter and wash thoroughly with 1% NH_4Cl, then a final wash with water. Ignite at over 1100°C to constant weight. The weight of the precipitate represents essentially the amounts of Fe_2O_3 and Al_2O_3 in the sample.

5.13.3.2 Calculate aluminum and iron, as $Al_2O_3 + Fe_2O_3$, in grams per liter, by the formula:

$$AI_2O_3 + Fe_2O_3 = \frac{grams\ of\ mixed\ oxides \times 1000}{22.5}$$

5.13.3.3 The respective amounts of iron and aluminum present may be determined by analysis of the mixed oxides or colorimetric estimation of iron following fusion in potassium pyrosulfate. Normally the weight of the ash is substantially all Al_2O_3 since iron compounds are sparsely soluble in the original liquor.

5.13.4 *Calcium.*

5.13.4.1 Concentrate the combined filtrates and washings from the $Fe_2O_3 + Al_2O_3$ determination to about 100 mL contained in a 250-mL beaker. Acidify the solution by adding 3 mL of concentrated HCL and add a few drops of methyl red. Add 35 mL of a warm ammonium oxalate solution containing 2 g of $(NH_4)_2C_2O_4 \bullet H_2O$. Heat the solution to about 80°C and add 1:1 NH_4OH dropwise with stirring, until the solution changes color from red to yellow. Let the mixture stand for one hour without further heating and filter through a small, 5 to 6-cm diameter fine quantitative filter paper. Wash the precipitate four or five times with cold 0.1% ammonium oxalate solution. Collect the filtrate and washings in a 600-mL beaker. After washing, place a clean 250-mL beaker under the filter and dissolve the precipitate through the filter by washing the filter with hot 1:1 HCl. Wash the paper thoroughly with hot dilute HCl (1:100), and adjust the volume in the 250-mL beaker to about 100 mL. The filter paper may now be discarded. Add 10 mL of the ammonium oxalate solution to the beaker and heat the solution almost to the boiling point. Precipitate calcium oxalate again by adding 1:1 NH_4OH solution until the methyl red indicator turns yellow. Allow the solution to stand for an hour or two; filter through a tared porcelain filter crucible, and wash the precipitate thoroughly with cold 0.1% ammonium oxalate solution. Collect the filtrate and washings and combine them with the filtrate and washings collected from the first filtration. Dry the crucible in an oven at 105°C for about 2 h, then place it in a cold muffle furnace. Set the temperature regulator on the furnace for about 500°C. The temperature should not vary more than ± 25°C. After about one hour at 500°, remove the crucible from the furnace, cool it in a desiccator, and weigh it. Repeat the heating to constant weight, using 30-min heating periods. The final weight represents the amount of calcium in the sample as $CaCO_3$.

5.13.4.2 Calculate calcium, in grams per liter, by the formula:

$$Ca = \frac{grams\ of\ CaCO_3 \times 1000 \times 40.1}{22.5 \times 100.1}$$

5.13.5 *Magnesium* (*6*).

5.13.5.1 Add 75 mL of concentrated HNO_3 to the combined filtrates and washings from the calcium determination and evaporate to dryness to destroy excess ammonium salts. The beaker should be partially covered with a watch glass when effervescence begins. Add 2 mL of concentrated HCl to the dry salts and 25 mL of warm water and filter the solution into a 250-mL beaker. Adjust the volume of the filtrate to about 100 mL and add 2 g of NH_4Cl, 0.5 mL of 0.02% *o*-cresolphthalein in alcohol, and enough 6*N* NH_4OH so that 2-3 mL is present in excess of that required to give a red-violet color (pH 9.5) to the solution. Heat the solution to almost 80°C and add dropwise and with stirring the 8-hydroxyquinoline solution until a small excess is present as shown by a yellow color in the supernatant liquid. Digest for about a half hour on the steam bath, and filter the hot solution through the tared porcelain filter crucible. A trace of sodium tauroglycocholate in the solution reduces the tendency of the precipitate to stick to the beaker. Wash with about 50 mL of warm water, and dry the precipitate at 160°C to constant weight, first for 1 h and then for ½-h periods. The precipitate dried at this temperature is anhydrous and has the composition $Mg(C_9H_6ON)_2$.

5.13.5.2 Calculate magnesium, in grams per liter, by the formula:

$$Mg = \frac{grams\ of\ Mg(C_9H_6ON)_2 \times 24.3 \times 1000}{312.6 \times 22.5}$$

5.14 *Sodium chloride.*

5.14.1 This is essentially the Volhard method for chloride. Pipet 25 mL of liquor into a 100-mL beaker and cover it with a watch glass. Neutralize the liquor to about pH 4 (methyl orange) with 6*N* HNO_3 and add 5 mL in excess. Heat to coagulate the sulfur and filter through a small quantitative filter paper into a 250-mL beaker. Wash the filter with about 50 mL of water and discard the paper. Cool the filtrate to room temperature and add standard 0.1*N* $AgNO_3$ until about 15 mL in excess of that required for chloride precipitation is present. Filter the coagulated precipitate from the liquid and catch the clear filtrate in a 500-mL Erlenmeyer flask. Wash the precipitate and filter paper with 100 mL of water containing 1 mL of concentrated HNO_3. Discard the filter paper. To the combined filtrate and washings in the 500-mL Erlenmeyer flask add 2 mL of a saturated aqueous solution of ferric ammonium sulfate and titrate with standard 0.1*N* KSCN to a faint, but permanent, red-orange color. The equivalents of $AgNO_3$ used minus those of KSCN used equals the equivalents of chloride ions in the sample. Convert the results to equivalents per liter by multiplying by 40. Duplicate titrations should agree within 0.5 meq/L. If the NaCl concentration in the liquor is found to be below about 10 millimoles per liter, use 0.05*N* solutions of $AgNO_3$ and KSCN.

5.14.2 Calculate sodium chloride in grams per liter by the formula:

NaCl = equivalents per liter × 58.5

6. Report

Report the various constituents in grams per liter to three significant figures.

7. Keywords

Total reducing compounds, Sulfide-free reducing compounds, Polysulfides, Alkalinity, White liquor, Green liquor

8. Additional information

8.1 Effective date of issue: To be assigned.

8.2 Related methods: Canadian CPPA J.12; Scandinavian SCAN-N2:63, N3:63, N4:63, N5:63, N6:63.

8.3 This method, formerly T 624 os-68, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superseded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.

8.4 This method was reaffirmed as classical in 2000. This method was reaffirmed as Classical in 2011 with a revision of the filter paper description.

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