

T 625 cm-14

TENTATIVE STANDARD – 1942

OFFICIAL STANDARD – 1944

TENTATIVE STANDARD – 1963

CORRECTED – 1964

CLASSICAL METHOD – 1985

WITHDRAWN - 1999

REVISED AND REINSTATED AS CLASSICAL METHOD - 2014

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Analysis of soda and sulfate black liquor

1. Scope and summary

This method is for the black or spent liquor separated from the pulp cooked by the soda or sulfate process¹. The black liquor sampled for analysis is usually dilute liquor consisting of the combined liquor from the blow pits, diffusers, and washers.

2. Applicable standards

T 650 “ Solids content of black liquor.”

3. Apparatus

- 3.1 *Hydrometer*, Baumé, accurately calibrated, or a pycnometer (specific gravity bottle).
- 3.2 *Evaporating dish*, platinum, 100 to 150 mL.
- 3.3 *Stirrer*, magnetic or electric with alkali-resistant glass or other alkali-resistant stirring rod for a 250-mL and an 800-mL beaker.
- 3.4 *Potentiometer* or pH meter, with a millivolt scale.
- 3.5 *Electrodes*: (a) silver-silver sulfide indicator electrode; (b) a "high pH" glass reference electrode which has been preconditioned by storing for at least 2 weeks in 1.0N NaOH (it should be kept in that solution); (c) saturated calomel glass electrode.

¹ Corrections have been made in the calculations for active alkali, NaOH, and CaO

Approved by the Standard Specific Interest Group for this Test Method

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3.6 *Conductance bridge*, with 0.5-in. (12-mm) platinum disk electrode mounted on alkali-resistant glass rod to permit variable spacing.

3.7 *Filtering crucible*, porcelain, with 3-5 μm pores, about 30 mL.

3.8 *Buret*, 0 to 50 mL.

3.9 *Muffle furnace*, electrically heated with temperature controller to 1200°C.

3.10 *Other apparatus*: steam bath; 5 to 6 cm diameter Büchner funnel and filtering flask; fine and medium porosity 5 to 6 cm diameter quantitative filter paper; small filter funnel; oven at 105 and 160°C; beakers, 150, 250, 400, 600, and 800 mL; watch glasses for the 250- and 600-mL beakers; pipettes 10, 20, 25, 50, and 100 mL; volumetric flasks, 100, 250, 500, and 1000 mL; graduated cylinder, 100 mL; Erlenmeyer flasks, 250 and 500 mL; hot plate.

NOTE 1: Unless the black liquor to be analyzed is very dilute, the pipettes used for measuring it should be calibrated for the liquor to be tested, using a fixed drainage time before touching the tip to the side of the beaker.

3.11 *For total metals and silica* (excluding sodium, for which see TAPPI T 623 "Sodium Determination by the Uranyl Zinc Acetate Method").

3.11.1 *Kjeldahl flask*, 100 mL.

3.11.2 *Platinum crucible*, about 30 mL, with lid.

3.11.3 *Graduated cylinder*, polyethylene, 0-10 mL.

4. Reagents and materials

CAUTION: This method requires the use of chemicals known to be carcinogens; extreme caution is required in their use and disposal.

4.1 Use reagent grade chemicals and dilution water that has been deionized or distilled and recently boiled to expel oxygen and cooled.

4.2 *Hydrochloric acid*, 0.1N, 0.5N, 1:99 and concentrated HCl.

4.3 *Ammonium hydroxide*, 1:1, 1:99 and concentrated NH_4OH .

4.4 *Sodium hydroxide*, 20% solution NaOH.

4.5 *Silver nitrate*, 0.05 to 0.1N AgNO_3 .

4.6 *Silver nitrate-ammonia*, 2.5% solution of AgNO_3 to which dilute NH_3 has been added until the precipitate just clears.

4.7 *Sulfuric acid*, concentrated, 1:2 (one part of concentrated acid to two of water), and approximately 1.0N H_2SO_4 .

4.8 *Zinc carbonate suspension*. Mix 150 mL each of 1M Na_2CO_3 and 1M ZnSO_4 .

4.9 *Mercuric chloride*, 0.05M HgCl_2 . Accurately weigh 13.58 g HgCl_2 and dilute to 1 L in a volumetric flask.

4.10 *Mercury*, about 20 mL.

4.11 *Formaldehyde*, 40% solution, HCHO.

4.12 *Barium chloride*, 0.5 and 1M BaCl_2 .

4.13 *Acetic acid*, dilute 2:5 CH_3COOH (2 parts of concentrated acid to 5 of water).

4.14 *Nitrogen gas* (cylinder).

4.15 *Glycerin*.

4.16 *Indicators*, methyl orange, phenolphthalein, and methyl red (see TAPPI T 610 "Preparation of Indicators and Standard Solutions").

4.17 For total metals, silica, and sulfur (excluding sodium, for which see T 623).

4.17.1 *Nitric acid*, concentrated HNO_3 .

4.17.2 *Perchloric acid*, concentrated (70 to 72% by weight) HClO_4 .

4.17.3 *Hydrofluoric acid*, concentrated HF.

4.17.4 *Ammonium chloride*, crystals and 0.1% solution NH_4Cl .

4.17.5 *Ammonium oxalate*, crystals and 1% solution $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

4.17.6 *o-Cresolphthalein indicator*, 0.2% dissolved in alcohol.

4.17.7 *8-Hydroxyquinoline* (quinolinol), 5% solution in 2M CH_3COOH .

4.17.8 *Sodium tauroglycocholate surfactant*, optional.

5. Safety

5.1 Caution: this method requires the use of chemicals known to be carcinogens; extreme caution is required in their use and disposal.

5.2 Caution: sections of this standard involve the use of perchloric acid; this chemical can be explosive under certain conditions.. Follow the procedures covered.

6. Sampling

Take a representative sample and store in a completely filled, alkali-resistant bottle. Black liquor is readily oxidized by atmospheric oxygen and will change composition even while stored in a completely filled and tightly sealed container. Accordingly, perform the analyses as soon as possible after sampling and do not allow the sample or specimens to be exposed to the air more than necessary. State if more than 24 h have elapsed between sampling and analysis.

7. Procedures

7.1 Density or specific gravity

7.1.1 For maximum accuracy, determine the specific gravity at 20°C by means of a calibrated pycnometer, weighing the bottle empty, also filled with water and with the liquor, both at the same temperature.

7.1.2 For ordinary purposes, determine the Baumé gravity of the sample at 60°F with the hydrometer. Convert to specific gravity, if desired, by the formula:

$$\text{Sp gr} = 145 / (145 - \text{Baumé})$$

7.2 *Total solids.* The evaluation of the solids content of black liquor requires the use of Ottawa or other spherical-high silica sand to prevent the black liquor from skimming over during the drying procedure and thus never truly reaching dryness. For the evaluation of total solids of black liquor, substitute the procedure specified in T 650 "Solids Content of Black Liquor."

7.3 *Sulfated ash and organic matter.* Starting with a cold muffle furnace, or a very low flame, heat the residue from the total solids determination until the organic material is mostly, but not completely, destroyed. Do not heat excessively. Cool, moisten the residue with water, add a drop of methyl orange, and add concentrated sulfuric acid dropwise until the indicator color turns pink. Evaporate to dryness on a steam bath or on a radiator, then heat at a higher temperature to fume off the excess sulfuric acid. Finally, heat at a dull red or slightly higher heat to completely destroy all organic material. Cool to room temperature in a desiccator and weigh. Moisten with water and add a drop of methyl orange. If a pink color develops, ignite again, repeat until the acid is destroyed, cool, and weigh as before. The residue is arbitrarily assumed to be pure sodium sulfate.

7.4 Sodium sulfide (1, 2)

7.4.1 To an 800-mL beaker, add 100 mL of 20% NaOH solution, 35 mL of 1:99 ammonia, and an aliquot of black liquor containing at least 0.2 g of Na₂S. Adjust the beaker contents to 500 mL with water. Titrate immediately with standard AgNO₃, the concentration of which should be 0.1N or less, corresponding to the relative sulfide concentration in the liquor sample. Use sufficient mechanical or magnetic stirring to cause just the beginning of a vortex. Follow the course of the titration potentiometrically, using a silver-silver sulfide indicator electrode and the high pH glass reference electrode. Add the titrant in fixed increments of volume and record the indicated steady emf after each addition. As the end point approaches, there will be an increase in $\Delta E/\Delta V$, that is, there will be an increase in the change of observed emf per increment of titrant. In the immediate vicinity of the end point, a large and sudden change in the observed emf will occur, to the extent of 100 mV or more. When this happens, add two more increments of the titrant and stop the titration.

7.4.2 Plot the data on linear coordinates with milliequivalents of AgNO₃ as the abscissa and emf as the ordinates to obtain the usual S-shaped titration curve. Determine the exact amount of AgNO₃ used at the end point by projecting the inflection point in the curve to the abscissa.

NOTE 2: An alternate, less time-consuming method to locate the end point is to calculate the zero value of $\Delta E^2/\Delta V^2$, fully described elsewhere (3).