WI	220802.04
T	619
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"

Analysis of salt cake

(Proposed RECONFIRMATION of Classical Method T 619 cm-10)

1.   Scope and significance

1.1   The principal use of salt cake in the pulp and paper industry is in the manufacture of sulfate pulp. Salt cake is an anhydrous sodium sulfate which contains varying amounts of impurities. The principal impurities usually are sulfuric acid, common salt, and sulfates of Fe, Al, Ca, and Mg. "Chrome salt cake," obtained as a by-product in making chromic acid, has a yellow color and contains $Na_2Cr_2O_7$ (and/or Na_2CrO_4).

1.2   A complete analysis of salt cake is somewhat complicated and involves a considerable number of determinations, as outlined below. Since some mills are mainly interested in the acidity and the Na_2SO_4 content, directions for a "short analysis" are also given.

1.3   This method is based on wet chemical analyses of the parameters of interest. If available, other techniques such as AA, ICP or ion chromatography may be employed.

2.   Preparation of sample

Mix the sample thoroughly, breaking down or grinding any lumps; quarter down to about 100 g; grind the quartered portion, if necessary, to about 60-mesh or finer; place in a separate stoppered bottle.

3.   Moisture

Weigh 10 g of the prepared sample in a flat-bottomed dish of porcelain, glass, or platinum and dry to constant weight at $105 \pm 3°C$. (Four hours are usually sufficient.) Let the dish and contents cool in a desiccator before weighing and make the final weighing rapidly. Calculate the loss in weight to percentage and report as moisture.

4.   Insoluble matter

4.1   Weigh 50 g of the prepared sample into a 400- or 500-mL beaker. Add about 250 mL of boiling water and stir well for 5 to 10 min. Filter at once through a filter paper which has been previously dried at $105 \pm 3°C$, cooled, and weighed in a weighing bottle; collect the filtrate in a liter volumetric flask. Wash the residue and the filter paper thoroughly with hot water until a few drops of the washings give no test for sulfates. Place the filter paper and contents in the weighing bottle and dry to constant weight at 100 to 105°C. Calculate the percentage of insoluble matter.

4.2   Cool the filtrate and washings in the liter flask to room temperature, dilute to the mark at 20°C and mix thoroughly. Call this Solution A.

5.   Acidity

Pipet 100 mL of Solution A (equivalent to 5 g of the sample) into a beaker or flask, dilute with an equal volume of water, add about 1 mL of phenolphthalein indicator, and titrate to a pink color with $0.1N$ NaOH. Calculate the titration to percentage of H_2SO_4 and report as acidity, calculated as H_2SO_4.

Calculation: 1 mL 0.1N NaOH = 0.0049 g H_2SO_4.

NOTE 1:   This titration gives the total acidity or alkali-consuming power and includes not only the free H_2SO_4 present in the material but also the acidity due to sulfates of Fe and Al and of any bichromate. The actual free H_2SO_4 may be closely approximated by calculating the amount of H_2SO_4 due to the various impurities and subtracting from the percentage of acidity as H_2SO_4.

Factors: H_2SO_4 equivalent $= Al_2O_3 \times 2.89$

$= FeO \times 1.36$

$= Fe_2O_3 \times 1.84$

$= Na_2Cr_2O_7 \times 0.375$

6.   Chloride

To the solution which has been titrated for acidity add a drop or two of methyl orange or methyl red indicator, make very slightly acid with a few drops of dilute H_2SO_4, and bring back to neutrality by adding about 1 g of powdered $CaCO_3$ and stirring. Set the flask on a white surface or transfer the contents to a porcelain dish; add 10 drops of K_2CrO_4 indicator solution (10%) and titrate with 0.1N $AgNO_3$ until the brick-red coloration due to Ag_2CrO_4 remains just visible after stirring. Calculate the titration to percentages of Cl and NaCl (and also to the equivalent of Na_2O for use in the final calculations).

Calculations: 1 mL 0.1N $AgNO_3$ $= 0.00355$ g Cl

$= 0.00585$ g NaCl

$= 0.00310$ g Na_2O

7.   Ferrous iron

To 5 g of the original prepared sample in an Erlenmeyer flask add 100 mL of warm water and 5 mL of concentrated H_2SO_4. Warm on the steam bath a few minutes, just long enough to dissolve all soluble matter. Cool under a water tap and titrate at once to a pink color with 0.1N $KMnO_4$. Calculate the titration to percentages of FeO and $FeSO_4$ (and also the equivalent of Fe_2O_3).

Calculations: 1 mL 0.1N $KMnO_4$ $= 0.0072$ g FeO

$= 0.0152$ g $FeSO_4$

$= 0.0080$ g Fe_2SO_3

8.   Ferric iron

8.1   Pipet 100 mL of Solution A (equivalent to 5 g of the sample) into a 250-mL beaker, add a few drops of concentrated HNO_3, cover with a watch glass, and boil a few minutes to oxidize the Fe. Add 5 mL of concentrated HCl or about 1 g of NH_4Cl. Then add slowly dilute NH_4OH in slight excess. Boil until the odor of NH_3 is nearly but not quite gone, filter, and wash the residue thoroughly with hot water. Save the filtrate. Place the filter paper in a weighed platinum crucible; dry in an oven; smoke off the filter paper; ignite the residue over a Meker burner to constant weight; and calculate the percentage of $Fe_2O_3 + Al_2O_3$.

8.2   Add about 2 g of $KHSO_4$ to the residue in the crucible and fuse quietly over a gentle heat until the melt is clear. Dissolve the melt in warm water, dilute to about 100 mL, add 5 mL of concentrated H_2SO_4, and pass the hot solution through a Jones reductor to reduce the Fe. Cool the reduced solution and titrate at once with $0.1N$ $KMnO_4$.

Calculate the percentage of total Fe in terms of Fe_2O_3 and subtract the amount of Fe_2O_3 equivalent to the FeO previously determined. The difference is the ferric Fe in terms of Fe_2O_3. Calculate also the equivalent amount of $Fe_2(SO_4)_3$.

Calculations: 1 mL $0.1N$ $KMnO_4$ = 0.008 g Fe_2O_3

$Fe_2O_3 \times 2.50$ = $Fe_2(SO_4)_3$

9.   Alumina

Subtract the percentage of total Fe in terms of Fe_2O_3 from the percentage of mixed oxides, $Fe_2O_3 + Al_2O_3$, and report the difference as alumina. Calculate also the equivalent amount of $Al_2(SO_4)_3$.

Calculation: $Al_2O_3 \times 3.36 = Al_2(SO_4)_3$

10.   Lime

Heat the filtrate from the Fe and Al hydroxides to boiling and add 2 mL of concentrated NH_4OH and 10 mL of 4% $(NH_4)_2C_2O_4$ solution. Let stand 0.5 h or until the precipitate settles clear. Filter and wash thoroughly with hot water. Char off the filter paper in a weighed platinum crucible and finally ignite to constant weight over a Meker burner. Cool in a desiccator and make the final weighing rapidly. Calculate the weight to percentage of CaO. Calculate also the equivalent amount of $CaSO_4$.

Calculation: $CaO \times 2.43 = CaSO_4$.

NOTE 2:   If preferred, instead of igniting the CaC_2O_4 to CaO and weighing, the CaC_2O_4 may be titrated with $0.1N$ $KMnO_4$ as described in TAPPI T 618 "Analysis of Limestone."

11.   Magnesia

Acidify the filtrate from the lime determination with HCl, concentrate to about 150 mL and heat to boiling. Add 10 mL of saturated $NaNH_4HPO_4$ solution and boil for several minutes. Cool to room temperature and add NH_4OH drop by drop with constant stirring until the crystalline precipitate begins to form; then add a moderate excess and continue stirring for several minutes. Let stand in a cool place overnight and filter on a Gooch crucible, previously ignited and weighed. Wash with dilute NH_4OH (1:10) containing a few drops of concentrated HNO_3, ignite in a muffle, cool in a desiccator, and weigh as $Mg_2P_2O_7$. If a muffle is not available, place the Gooch crucible in a larger platinum crucible and ignite directly over a flame. Do not use sufficient heat to fuse or melt the precipitate. Calculate to percentage of MgO. Calculate also the equivalent amount of $MgSO_4$.

Calculations: $Mg_2P_2O_7 \times 0.362$ $\quad = MgO$

$\qquad Mg_2P_2O_7 \times 1.08 \qquad\quad = MgSO_4$

12.   Chromium trioxide

Pipet 100 mL of Solution A (equivalent to 5 g) into an Erlenmeyer flask. Add 5 mL of concentrated HCl and 10 mL of 10% KI solution, and titrate the free iodine with $0.1N$ $Na_2S_2O_3$ solution. When the yellow-brown color has nearly disappeared, add a little starch indicator solution and continue the titration to the disappearance of the blue color. From the titration calculate the percentage of CrO_3 and of $Na_2Cr_2O_7$. Calculate also the equivalent amount of Na_2O.

Calculations: 1 mL $0.1N$ $Na_2S_2O_3$ $\quad = 0.00333$ g CrO_3

$\qquad\qquad\qquad\qquad\qquad\qquad = 0.00437$ g $Na_2Cr_2O_7$

$\qquad\qquad\qquad\qquad\qquad\qquad = 0.00207$ g Na_2O

13.   Total soda

13.1   *Chrome salt cake.*

13.1.1   To 100 mL of Solution A in a 500-mL beaker add 10 mL of alcohol and 10 to 15 mL of concentrated HCl and boil down to half volume to reduce the Cr and remove the bulk of the alcohol. To the hot solution add a slight excess of NH_4OH and 10 mL of 4% $(NH_4)_2C_2O_4$ solution. Boil until the odor of NH_3 is nearly gone; let stand about

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min; filter and wash thoroughly with hot water, collecting the filtrate and washings in a 250-mL volumetric flask. Discard the precipitate which contains the Al, Cr, Fe, and Ca. Cool the solution, dilute to 250 mL at 20°C, and mix thoroughly. Call this Solution B.

13.1.2   Pipet 50 mL of Solution B (equivalent to 1 g of the sample) into a weighed dish, preferably of platinum; evaporate to dryness on the steam bath and ignite carefully to avoid spattering, gradually raising the heat until no more fumes of NH_4 salts or SO_3 come off. After cooling the residue, moisten it with about 2 mL of dilute H_2SO_4 and repeat the evaporation and ignition in order to convert any chloride to sulfate. Cool, moisten the residue with a freshly prepared, nearly saturated solution of $(NH_4)_2CO_3$ in water; again evaporate on the steam bath and ignite strongly over a Meker burner. Cool in a desiccator, weigh, and calculate to percentage.

13.1.2   The residue is Na_2SO_4 + $MgSO_4$. Subtract the percentage of $MgSO_4$, previously determined, and calculate the difference to Na_2O.

$$\textit{Calculation: } Na_2SO_4 \times 0.4364 = Na_2O$$

13.2   *Ordinary salt cake.* In the absence of Cr, omit the preliminary boiling with alcohol. Heat 100 mL of Solution A to boiling; add 10 mL of concentrated HCl, then a slight excess of NH_4OH and 10 mL of 4% $(NH_4)_2C_2O_4$ solution, and proceed as above.

14.   Sulfur trioxide

Pipet 25 mL of Solution B (equivalent to 0.5 g of the sample) into a 400-mL beaker. Add a drop or two of methyl red and then neutralize the solution carefully with very dilute NH_4OH. To the neutral solution add 300 mL of water and 2 mL of dilute HCl (1:18), and heat to boiling. Add to the boiling solution 25 mL of 10% $BaCl_2$ solution, drop by drop from a pipet. Stir well and set aside overnight at room temperature, protected from fumes. Filter and wash with hot water until 25 mL of the filtrate show not more than a slight opalescence with $AgNO_3$ solution. Place the filter and precipitate in a weighed platinum crucible and heat very slowly and carefully over a low flame to char the filter paper without allowing it to catch fire. After completing the charring, ignite until white over an ordinary burner, with the crucible uncovered. Cool and moisten the precipitate with a few drops of dilute H_2SO_4. Heat very carefully to drive off the acid and finally ignite to constant weight, cooling between weighings in a desiccator. Calculate the weight of $BaSO_4$ to percentage of SO_3.

$$\textit{Calculation: } BaSO_4 \times 0.3430 = SO_3$$

15. Final calculations

15.1   From the total Na_2O subtract the Na_2O equivalent to the NaCl and to the $Na_2Cr_2O_7$; calculate and report the remaining Na_2O as Na_2SO_4.

15.2   From the total SO_3 subtract the SO_3 equivalent to the Na_2SO_4, $Al_2(SO_4)_3$, $CaSO_4$, $MgSO_4$, $FeSO_4$ and $Fe_2(SO_4)_3$; calculate and report any excess of SO_3 as free H_2SO_4. (The SO_3 equivalent of each of the sulfates is obtained by subtracting the corresponding oxide percentage from the sulfate percentage; e.g., 1.52% $FeSO_4$ - 0.72% FeO = 0.80% SO_3.)

16. Form of report

It is suggested that the results of a complete analysis be reported in the following form:

	%
Moisture, loss at 100 to 105°C	....
Insoluble in water	....
Acidity, calculated as H_2SO_4	....
Chloride, Cl	....
Ferrous oxide, FeO	....
Ferric oxide, Fe_2O_3	....
Alumina, Al_2O_3	....
Lime, CaO	....
Magnesia, MgO	....
Chromium trioxide, CrO_3	....
Sulfur trioxide, SO_3	....
Combined as follows:	....
Sodium chloride, NaCl	....
Sodium bichromate, $Na_2Cr_2O_7$	....
Aluminum sulfate, $Al_2(SO_4)_3$	....
Ferrous sulfate, $FeSO_4$	....
Ferric sulfate, $Fe_2(SO_4)_3$	....
Calcium sulfate, $CaSO_4$	....
Magnesium sulfate, $MgSO_4$	....
Sodium sulfate, Na_2SO_4	....
Free sulfuric acid, H_2SO_4	....

17.   Short analysis

17.1   Prepare the sample as previously described, except that it may be quartered down to about 25 g before the final grinding.

17.2   *Acidity.* Weigh 5 g into a 300-mL Erlenmeyer flask, add 100 mL of hot water and heat until all soluble matter has dissolved. Cool under a water tap and pour into a 500-mL porcelain dish, using 100 mL of water in small portions to rinse the flask and complete the transfer. Add about 1 mL of phenolphthalein indicator and titrate to a pink color with $0.1N$ NaOH. Calculate the titration to percentage of H_2SO_4 and report as acidity, calculated as H_2SO_4.

Calculation: 1 mL $0.1N$ NaOH = 0.0049 g H_2SO_4.

17.3   *Sodium chloride.* Follow the procedure previously described under chloride. Calculate the titration of percentage of NaCl and also to the equivalent amount of Na_2SO_4.

Calculation: $NaCl \times 1.215 = Na_2SO_4$

17.4   *Sodium bichromate.* If the material contains Cr, warm a 5-g sample with 100 mL of water in a 300-mL Erlenmeyer flask until all soluble matter is dissolved, cool to room temperature and proceed as described previously under chromium trioxide. Calculate the percentage of $Na_2Cr_2O_7$ and also the equivalent percentage of Na_2SO_4.

Calculation: $Na_2Cr_2O_7 \times 0.542 = Na_2SO_4$.

17.5   *Sodium sulfate.* Treat 5 g of the sample in a 500-mL beaker with 100 mL of hot water, 5 mL of concentrated HCl and a few drops of concentrated HNO_3, and stir until all soluble matter is dissolved. Boil a few minutes to oxidize the Fe. If the material contains Cr, add 10 mL of alcohol and boil down to half volume. Then add a slight excess of NH_4OH and 10 mL of 4% $(NH_4)_2C_2O_4$ solution and proceed as previously described under total soda. Calculate the percentage of the final residue, which contains all the Na as Na_2SO_4 and all or part of the Mg as $MgSO_4$. (The latter is usually very small and is disregarded.) Subtract the Na_2SO_4 equivalent of the NaCl and of the $Na_2Cr_2O_7$, and report the difference as sodium sulfate.

18.   Keywords

Moisture, Sodium sulfate, Salt cake, Acidity, Chlorides, Iron, Aluminum oxide, Lime, Magnesium oxide, Chromium oxide, Sulfur trioxide, Sodium oxide, Chlorine, Chromium trioxide, Sodium bicarbonate, Sodium chloride

19.   Additional information

19.1   Effective date of issue: To be assigned.

19.2   This method, formerly T 619 os-53, 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.

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