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WI _____ 220802.03 _____

T _____ 618 _____

DRAFT NO. _____ 01 _____

BALLOT NO. _____ 03 - SARG _____

DATE _____ October 22, 2024 _____

WORKING GROUP

CHAIR _____ Nick Riggs _____

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 limestone

(Proposed WITHDRAWAL of Classical Method T 618 cm-10)

1. Scope

1.1 This method is for the analysis of limestone as used in current sulfite pulping practice.

1.2 Limestone may be in the calcite form (high in calcium) or the dolomite form (approaching the double carbonate of calcium and magnesium). In pieces of various sizes, it is used in the tower system of making bisulfite cooking liquor. As a rule, the combined total of other oxides including silicon, iron, and aluminum should be less than 3%.

2. Apparatus

2.1 *Hammer*, mason's or other type, for sampling large pieces.

2.2 *Jaw crusher*, or other equipment for reducing 2 to 3 cm (1-in.) sample lumps to 60-mesh.

- 2.3 *Testing sieves*, 60 and 100 mesh, and pan.
- 2.4 *Mechanical grinder*, or agate mortar and pestle for reducing 60-mesh material to pass a 100-mesh sieve.
- 2.5 *Glass bottles*, about 175 mL (6 oz) rubber-stoppered, wide mouthed, to contain the sample and protect it from the air.
- 2.6 *Platinum crucible*, 20 to 25 mL, with cover.
- 2.7 *Electric muffle furnace*, for 1000°C and lower, with temperature control and indicator.

NOTE 1: If an electric muffle is not available, a grid-top burner may be used, with less assurance of standard results.

- 2.8 *Casserole*, porcelain, 300-mL.
- 2.9 *Hot plate*, with sand bath, for heating the casserole to 200°C. (A steam bath and an oven for temperatures to 200°C may be substituted.)
- 2.10 *Jones-Reductor*, for KMnO_4 titration of R_2O_3 residue.

NOTE 2: See Scott's *Standard Methods of Chemical Analysis*, 6th Edn., Vol. 1, p. 540 (D. Van Nostrand, 1962).

- 2.11 *Filter paper*, 11-cm diameter.
- 2.12 *Colorimeter* (for colorimetric measurement of Fe_2O_3), with 520 to 580 nm filter, or spectrophotometer capable of accurate measurement of light absorption in the 520-580 nm range. Nessler tubes and visual comparison may be used if a colorimeter or spectrophotometer is not available.
- 2.13 *Other apparatus*: beakers, 250, 400, 600, and 800-mL; volumetric flasks, 100 and 250-mL; burets, 50-mL; graduated cylinder, 25-mL; pipets, 2, 5, and 10-mL; funnels, long-stem, 58 or 60°, 65 mm ID at top; stirring rods.

3. Reagents

- 3.1 *Hydrochloric acid*, 1:1, 1:10, 5% and concentrated HCl.
- 3.2 *Ammonium hydroxide*, 1:3, 5% and concentrated NH_4OH .
- 3.3 *Sulfuric acid*, 1:5, 1:1, and concentrated H_2SO_4 .
- 3.4 *Hydrofluoric acid*, 48% HF (for special SiO_2 determination).
- 3.5 *Oxalic acid*, 10% solution $\text{H}_2\text{C}_2\text{O}_4$.
- 3.6 *Ammonium oxalate*, saturated solution $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
- 3.7 *Diammonium phosphate*, 10% solution $(\text{NH}_4)_2\text{HPO}_4$ (prepared fresh as needed).
- 3.8 *Bromine water* (saturated), or concentrated HNO_3 .
- 3.9 *Ammonium chloride*, 2% solution NH_4Cl .
- 3.10 *Ammonium oxalate-oxalic acid solution*, containing 2% of the former and 1% of the latter.

3.11 *Potassium permanganate*, 0.05N and 0.2N solutions KMnO_4 (see TAPPI T 610 "Preparation of Indicators and Standard Solutions").

3.12 *Methyl red indicator*.

3.13 *Sodium carbonate*, anhydrous Na_2CO_3 .

3.14 *Potassium pyrosulfate* ($\text{K}_2\text{S}_4\text{O}_7$) or potassium bisulfate (KHSO_4).

3.15 *Sodium hydroxide*, 10% solution NaOH .

3.16 *Hydroxylamine hydrochloride*, 10% solution, $\text{NH}_2\text{OH} \cdot \text{HCl}$.

3.17 *Ammonium acetate*, 20% solution $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

3.18 *1, 10 - Phenanthroline* (orthophenanthroline), 0.1% solution.

3.19 *Congo red indicator paper*.

3.20 *Standard iron wire* (A.C.S.) for preparation of standard iron solution.

4. Sampling

4.1 Select material so that it will represent an average of all parts of the pile or car and does not contain a disproportionate share of the top or bottom layers. In view of the usual size of the lumps, it is impractical to take samples with a shovel. It is recommended that samples be taken by breaking small portions with a hammer from approximately 100 lumps situated in various parts of the car or pile. Each piece needs to consist of but an ounce or two, broken so as to pass a 2.5-cm (1-in.) diameter hole.

4.2 Crush the sample as received at the laboratory with a jaw crusher or other means until all of it passes a 60-mesh sieve. Reduce the quantity by quartering (see TAPPI T 605 "Reducing a Gross Sample of Granular or Aggregate Material to Testing Size") to give a minimum of 75 g. Grind this portion, either by a mechanical device or by hand in an agate mortar, until it all passes a 100-mesh sieve. Then thoroughly mix it and place in the widemouth stoppered bottle.

5. Procedures

5.1 *Loss on ignition*. Weigh about a 0.5-g specimen of the prepared sample to the nearest 0.001 g into a clean, previously ignited and weighed, covered platinum crucible. Heat slowly at first to avoid loss by decrepitation, finally to constant weight at 1000°C , in the muffle furnace. (Usually 1 h is sufficient for complete ignition.) Cool in a desiccator and report the loss in weight as the loss on ignition. Save the residue.

5.2 *Silica and insoluble matter*

5.2.1 Transfer the previously-ignited residue quantitatively to a 300-mL porcelain casserole. Carefully slake with about 10 mL of water, and mix to a slurry with a flat-end glass stirring rod. Add 5 to 10 mL of concentrated HCl and digest with gentle heat until solution is complete, carefully breaking up any lumps. Evaporate to dryness and bake the residue on a sand bath or in an oven for 1 h. If the MgO content is high (10% or over on the nonvolatile basis), bake at 120°C ; if below 10% MgO , bake at 200°C . (The high dehydration temperature is efficient for low MgO , but

with high MgO, silica redissolves at temperatures over 120°C). Cool to 40°C or lower, drench with concentrated HCl and allow to stand a few minutes. Then add an equal amount of water, cover the casserole, and heat on the steam or sand bath for about 10 min. Filter through an 11-cm filter paper into a 400-mL beaker. Wash the residue thoroughly with HCl (1:10) and then wash twice with hot (about 60-90°C) water. Pour the filtrate back into the same casserole, evaporate to dryness, treat with HCl and water as before, filter through a second filter paper of the above type and wash twice with hot water. Save the filtrate.

5.2.2 Transfer the wet papers to a previously ignited and weighed platinum crucible, char carefully without allowing the paper to flame, and finally ignite in the muffle furnace to constant weight at 1000°C (30 min is usually sufficient). Cool in a desiccator and weigh.

5.2.3 Report the percentage of residue as silica and insoluble matter.

NOTE 3: Usually the silica is not determined separately, but if it is desired, proceed as follows: Treat the residue in the platinum crucible with about 5 mL 48% HF and one or two drops of concentrated H₂SO₄. Evaporate to dryness, heat for 10 min in the muffle furnace at 1000°C, cool in a desiccator, and reweigh. The loss in weight caused by the HF treatment is SiO₂.

5.2.4 Fuse the residue in the crucible with a little Na₂CO₃ (1 to 2 g), cool the melt, dissolve in 1:1 HCl, and add the solution to the filtrate from silica and insoluble matter.

NOTE 4: A further small quantity of silica may be recovered from the Fe₂O₃ determination below (see titration procedure).

5.2.5 If SiO₂ is not determined, the SiO₂ and insoluble residue may be discarded.

5.3 *Iron oxide and alumina (R₂O₃).*

5.3.1 To the acid filtrate from the silica determination, add a few drops of bromine water or concentrated HNO₃ and boil until all traces of bromine or chlorine are gone. Add enough concentrated HCl so as to have a total volume of 10 to 15 mL of the concentrated acid. Add a few drops of methyl red solution, dilute to 200 to 250 mL, and heat to boiling. Carefully neutralize with concentrated NH₄OH until the color changes to a distinct yellow. Boil for 1 or 2 min, let settle, and filter into a 600-mL beaker. Wash four times with hot 2% NH₄Cl solution. Save the filtrate.

5.3.2 Place the beaker in which the precipitation was made under the funnel containing the precipitate. Dissolve the precipitate on the paper with about 15 mL of 1:1 HCl; wash the paper thoroughly with hot water. Heat, neutralize with NH₄OH, and boil as in the first precipitation. Filter (the same paper may be used) and wash four times with hot 2% NH₄Cl solution. Place the paper in a previously ignited and weighed platinum crucible, char without allowing the paper to take fire, and finally ignite 30 min at 1000°C in the muffle. Cool in a desiccator and weigh as R₂O₃.

NOTE 5: The R₂O₃ as determined can also contain TiO₂, P₂O₅, and Mn₃O₄, but they are usually present in very small amounts and may usually be disregarded.

5.4 *Iron oxide.* If this is desired separately, three alternative methods are suitable, all of which should give the same result. These are: (a) KMnO_4 titration of the iron in the R_2O_3 residue; (b) its colorimetric determination; and (c) KMnO_4 titration of the iron in a separate, larger specimen of the limestone.

5.4.1 *Titration of Fe in R_2O_3 residue.*

5.4.1.1 Fuse the R_2O_3 residue in the platinum crucible at as low a temperature as possible with 3 or 4 g of $\text{K}_2\text{S}_2\text{O}_7$ or KHSO_4 . Cool, transfer the cake to a 250-mL beaker, and rinse any deposit remaining on the crucible into the beaker with water; if the cake sticks to the crucible, put crucible containing cake into beaker. In either case, add 5 mL of concentrated H_2SO_4 in enough water to effect solution on heating. If crucible is in beaker after cake is dissolved, remove it, rinsing with water into beaker. Evaporate solution and finally heat on a hot plate until copious white SO_3 fumes are evolved.

5.4.1.2 Cool, redissolve in water, filter out the small amount of SiO_2 on filter paper, and wash twice with cold water. If the SiO_2 was not determined separately, discard the small amount found here. If SiO_2 was determined separately, ignite the residue in a platinum crucible as in the previous determination of silica and insoluble matter; then determine the SiO_2 using the H_2SO_4 and HF treatment as described above. Add the weight of SiO_2 so found to the previous determination and deduct it from the gross weight of R_2O_3 .

5.4.1.3 Pass the acid filtrate through a Jones reductor and titrate with 0.05N KMnO_4 . Calculate the titration to % Fe_2O_3 .

Calculation: 1 mL 0.05N $\text{KMnO}_4 = 0.0040$ g Fe_2O_3 .

NOTE 6: The zinc in the Jones reductor will also reduce TiO_2 . If this is to be determined and deducted from the Al_2O_3 , then H_2S must be used for reduction, boiling out the H_2S in a stream of CO_2 before titration. Usually the TiO_2 content is negligible.

NOTE 7: If the amount of Fe_2O_3 is too small for an accurate titration on a 0.5-g sample, one of the alternative methods which follow should be used.

5.4.2 *Colorimetric method for Fe_2O_3 .* Fuse the combined oxides of Fe and Al in a platinum crucible at low temperature with 3 to 4 g of $\text{K}_2\text{S}_2\text{O}_7$ or KHSO_4 . Take up the melt with 10 mL of 1:1 HCl and about 100 mL of water and warm to effect solution. Transfer the solution to a 250-mL volumetric flask, dilute to volume, and mix well. Transfer an aliquot containing 0.05-0.20 mg of Fe_2O_3 (25 mL is usually enough) into a 100-mL volumetric flask. Add in this order and mix well after each addition: (1) 2 mL of 10% hydroxylamine hydrochloride, (2) 10 mL of 20% ammonium acetate, (3) 10 mL of 0.1% 1, 10-phenanthroline solution. Add a small piece of Congo red paper to the flask and then 1:3 NH_4OH until the indicator turns red, followed by one drop of the 1:3 NH_4OH in excess. Dilute to 100 mL, mix, and let stand for 20 min. Obtain the colorimetric reading in a colorimeter using a 520 to 580 nm filter or with a spectrophotometer in this wavelength range, and compare the readings against a curve prepared from a set of known quantities of iron similarly treated. Calculate the percentage of Fe_2O_3 by multiplying the weight in grams found on the reference curve by 100 times the dilution factor and dividing by the sample weight in grams.

NOTE 8: If a suitable colorimeter or spectrophotometer is not available, an approximately accurate determination may be made by comparison of the unknown sample with known concentrations of iron in Nessler tubes.

5.4.3 *Volumetric Fe₂O₃ on separate large sample.* Dissolve 2 to 5 g of the specimen in a 600-mL beaker (depending upon the amount of iron present) in concentrated HCl and evaporate rapidly to dryness. Treat the residue with water and HCl, filter off the SiO₂, and wash several times with hot water. Precipitate the iron in a boiling solution with 10% NaOH solution. Let settle, filter, and wash free from chlorides with hot water. Dissolve in 1:5 H₂SO₄. Ignite the insoluble matter from the evaporated HCl solution in a platinum crucible. Treat with H₂SO₄ and HF and heat until SO₃ fumes appear. Dissolve the residue with a few drops of H₂SO₄ and combine the solution with the main iron solution. Reduce this through the Jones reductor and titrate with KMnO₄.

5.5 *Alumina.* Subtract the Fe₂O₃ from the weight of the Fe₂O₃ + Al₂O₃ and calculate the remainder to percentage of Al₂O₃.

NOTE 9: The Al₂O₃ thus determined will include P₂O₅ and certain other impurities. These are usually neglected.

5.6 *Calcium oxide*

5.6.1 Combine the two filtrates from the iron oxide plus alumina determination. Make just acid to methyl red with concentrated HCl, then add 2 mL of the acid in excess. Evaporate to 350 mL, add 20 mL of 10% oxalic acid and boil. To the boiling solution add 1:3 NH₄OH dropwise from a pipet until a precipitate begins to form. Now add the NH₄OH still more slowly, allowing most of the precipitate to form between each addition. Continue until the methyl red just turns yellow. Add 25 mL saturated ammonium oxalate and stir. Let the solution stand and cool for 1 h.

5.6.2 If the MgO content of the limestone is below about 8%, a single precipitation as above is satisfactory. For higher MgO contents, however, a double oxalate precipitation should be made. Alternative procedures for high and low MgO contents follow.

5.6.3 *Low MgO content.* Filter the calcium oxalate precipitate into a 600-mL beaker, washing the original beaker twice. Wash the precipitate 12 times with cold water to remove all traces of oxalate salts. Reserve the filtrate for MgO. Transfer the precipitate back into the original beaker in which the precipitation was done, spreading the paper out against the upper inside surface of the beaker. Wash the precipitate off the paper with a jet of hot water, fold the paper and leave it adhering to the upper portion of the beaker. Wash funnel with 100 mL of hot 1:10 H₂SO₄, allowing the washings to run into the beaker. Rinse funnel into beaker with distilled water, cover the beaker, and heat to 80-90°C, but do not boil. Titrate with 0.2N KMnO₄ to a persistent pink. Drop the folded filter paper into the solution and stir to break up the paper. Finish titrating dropwise to the pink end point.

Calculation:

$$\text{CaO, \%} = \frac{(\text{mL KMnO}_4) \times (\text{normality}) \times 2.804}{\text{Weight of sample}}$$

(weight of sample in grams)

5.6.4 *High MgO content.* Filter the precipitate into an 800-mL beaker and wash four times with a 2% ammonium oxalate, 1% oxalic acid solution. Save the filtrate. Place a clean 400-mL beaker under the funnel containing the precipitate. Dissolve the precipitate from the paper by pouring 40 mL of hot 1:4 HCl through it. Wash the paper free of acid with hot water, collecting the washings with the acid calcium solution in the 400-mL beaker. Dilute the filtrate to about 150 mL, add 5 mL of 10% oxalic acid, and heat to boiling. Add two drops of methyl red indicator and precipitate with 1:3 NH₄OH as in the first precipitation. Add 10 mL saturated ammonium oxalate solution, stir to coagulate, and allow to cool for 1 h. Filter through the same paper into the 800-mL beaker containing the filtrate from the first precipitation. Wash thoroughly (10 to 12 times) with cold water until free of oxalate. Save combined filtrate for MgO determination. Dissolve the precipitate in H₂SO₄, titrate with KMnO₄, and calculate the percentage of CaO as in the above procedure for limestone with a low MgO content.

5.7 *Magnesium oxide*

5.7.1 Acidify the filtrate from the calcium oxalate precipitation and evaporate to about 450 mL. Cool to room temperature. Add 30 mL of a freshly prepared 10% solution of (NH₄)₂HPO₄. Add a few drops of methyl red, stir vigorously, and add concentrated NH₄OH slowly—especially while the precipitate is still forming—until the solution is alkaline to the methyl red. Now add 10 mL of concentrated NH₄OH for each 100 mL of solution. Stir vigorously a few times at about 15-min intervals. Let settle overnight.

5.7.2 Filter through filter paper to which some paper pulp has been added. Wash with 5% NH₄OH and discard the filtrate. Wash the bulk of precipitate back into the precipitation beaker, add 10 mL of 1:1 HCl and heat to boiling. Place a clean 250-mL beaker under the funnel. Pour acidified solution through the filter, then wash the filter six times with hot 5% HCl and discard the filter paper. Dilute the filtrate to 150 mL, add 3 mL of freshly prepared 10% (NH₄)₂HPO₄ solution and then add 1:3 NH₄OH very slowly with constant stirring until it is just alkaline to methyl red, and the crystalline precipitate has been well formed. At this point, add about 5 mL concentrated NH₄OH for each 100 mL of solution and stir well. Allow the solution to stand 4 h, preferably overnight.

5.7.3 Filter through a tared Gooch crucible, transferring all the precipitate to the crucible with the aid of a rubber policeman. Wash with cool 5% NH₄OH. Ignite in a muffle furnace, starting at 300°C, gradually increasing the heat to 1000°C. Hold at 1000°C for 1 h.

5.7.4 Cool in a desiccator and weigh as Mg₂P₂O₇. Calculate the MgO as follows:

$$\text{MgO, \%} = \frac{\text{weight of Mg}_2\text{P}_2\text{O}_7 \times 36.21}{\text{weight of specimen}}$$

NOTE 10: If the limestone contains Mn, most of it will come down with the Mg₂P₂O₇. Usually this is neglected.

6. Precision

The data in Table 1 indicate the degree of reproducibility that may be obtained. While the methods used for obtaining these results differed somewhat from those described herein, these differences are not considered such as to affect reproducibility. The data were obtained under carefully controlled conditions by three different laboratories of the same company; they represent quadruplicate analyses for five constituents of two samples.

7. Keywords

Limestone, Loss on ignition, Silica, Iron Oxide, Aluminum oxide, Iron, Calcium oxide, Magnesium oxide, Solubility

7. Additional information

7.1 Effective date of issue: **To be assigned.**

7.2 This method, formerly T 618 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.

7.3 Related method: ASTM C-25. (Refer to this method for a more detailed analysis including CO₂, S, and P.)

Table 1. Reproducibility: percent by weight of indicated constituent

Lab no.	CaO			MgO			SiO ₂ + Insol.			R ₂ O ₃			Fe ₂ O ₃		
	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
High Ca limestone															
1	54.00	53.46	53.85	0.88	0.85	0.87	1.36	1.28	1.32	0.36	0.32	0.34	0.21	0.20	0.21
2	53.83	53.74	53.78	0.85	0.84	0.84	1.32	1.31	1.32	0.36	0.33	0.35	0.23	0.19	0.21
3	54.00	53.80	53.87	0.88	0.86	0.87	1.36	1.35	1.36	0.33	0.31	0.32	0.21	0.21	0.21
Dolomite															
1	30.15	30.12	30.14	21.21	21.12	21.16	1.26	1.14	1.18	0.30	0.24	0.27	0.17	0.10	0.13
2	30.35	30.03	30.33	21.08	21.00	21.04	1.18	1.17	1.18	0.26	0.26	0.26	0.11	0.11	0.11
3	30.18	30.18	30.18	21.10	21.10	21.10	1.24	1.20	1.22	0.28	0.26	0.28	0.11	0.11	0.11

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