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CHEMICAL CONTROL OF THE KRAFT PROCESS

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CHEMICAL CONTROL OF THE KRAFT PROCESS

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COMPLETE METHOD OF ANALYSIS OF WHITE LIQUOR

The following complete method of analysis includes a determination of sulphites and thiosulphates that are ordinarily neglected in the analysis of white liquor but which play an important part in the cook. This is especially true of thiosulphate, which in the presence of caustic soda, acts to a large extent similarly to sodium sulphide. This method has been worked out and checked by Sidney E. Lunak, of the Forest Products Laboratory, Madison, Wis., and found to be accurate except in the presence of polysulphide, where an error is introduced into the iodine titration. For all ordinary work, this error is not serious enough to be appreciable.

(a) Total Alkali Expressed in Terms of Na_2O

Two Cc. of the solution are withdrawn with a pipette and titrated with half normal acid, using methyl orange as an indicator. The number of Cc. of acid used represents the alkali existing in the solution as Na_2CO_3 , NaOH , Na_2S , and $1/2 \text{Na}_2\text{SO}_3$.

(b) Soda as $\text{NaOH} + \text{Na}_2\text{S}$

To 2 Cc. of the solution contained in a 100 Cc. graduated flask add 20 Cc. of a 10-percent solution of barium chloride and make up to mark with boiling distilled water; shake for a few minutes and allow to settle; cool and draw off 50 Cc. of the clear liquid and titrate with half normal acid, using methyl orange as an indicator. The number of Cc. indicates the amount of acid necessary to neutralize the NaOH and Na_2S in the sample. The difference between this titration and the previous titration represents the number of Cc. it takes to neutralize the Na_2CO_3 and $1/2 \text{Na}_2\text{SO}_3$, barium sulphite being practically insoluble in a large volume of water.

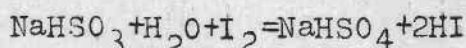
¹Report of committee of the Technical Association of the Pulp and Paper Industry on standardization of methods of chemical control of the Kraft process, George S. Holmes, Joseph E. Hedin and Otto Kress.

(c) Sodium Sulphide+Na₂SO₃+Na₂SO₃

This is determined by adding the sulphide solution to an amount of iodine within half a Cc. of the end point, which can be found by trial. Two Cc. of this solution is added to this amount of iodine in about 200 Cc. of distilled oxygen-free water and acidified with an excess of acetic acid. The titration is then completed, using starch as an indicator. One Cc. of a decinormal iodine solution is equal to .003908 Gm. of Na₂S and .003105 Gm. of Na₂O. This titration indicates the amount of Na₂S, Na₂S, Na₂S₂O₃ and Na₂SO₃ in the sample.

(d) Sodium Thiosulphate and Sodium Sulphite

To 5 Cc. of the solution in a graduated 250 Cc. flask add an excess of an alkaline solution of zinc chloride; make up to mark, shake for a few minutes and allow to settle; draw off 50 Cc. of the clear solution with a pipette and neutralize with normal sulphuric acid, using methyl orange as indicator. This converts the sulphites present to acid sulphites. When acid sulphites are titrated with iodine solution the following reaction takes place:



Thus one molecule of acid sulphite on titration with iodine solution liberates acid equivalent to three molecules of sodium hydroxide.

The solution is then titrated with tenth normal iodine solution, using starch as an indicator. It is then decolorized with one drop of sodium thiosulphate solution and titrated to neutral with tenth normal sodium hydroxide solution. The number of Cc. multiplied by .0042 gives the amount of Na₂SO₃ in the sample, and this figure divided by .0063 gives the iodine value of the sodium sulphite. Subtract this from the iodine titration previously obtained, which will give the iodine equivalent to the sodium thiosulphate present.

CALCULATION OF RESULTS

c-d gives the Cc. of iodine for sodium sulphide.
a-b gives the number of Cc. for Na₂CO₃ and 1/2

Na₂SO₃.

1 Cc. second normal (N/10) H₂SO₄ = .0265 Gm. of Na₂CO₃ = .0155 Gm. of Na₂O.

The titration in (b) expressed in Na_2O , minus the sodium sulphide as Na_2O , gives the Na_2O as NaOH .

1.29 $\text{Na}_2\text{O} = \text{NaOH}$.

1 Cc. tenth normal iodine = .0158 Gm. of $\text{Na}_2\text{S}_2\text{O}_3$.

BLACK LIQUOR¹

The examination of black liquor is conducted as follows:

(1) A 50 Cc. portion of black liquor is evaporated to dryness in a platinum dish. The residue is ashed over a bunsen burner and the soluble salts are leached out with hot distilled water. The entire solution obtained is titrated with normal sulphuric acid, using methyl orange as an indicator. The number of cubic centimeters of acid required to produce the end point multiplied by 0.62 gives the grammes per liter of total sodium oxide (Na_2O) in the black liquor.

(2) A 100 Cc. portion of the same black liquor is mixed with 50 Cc. of 10 per cent barium chloride solution in a 500 Cc. calibrated flask. The mixture is then diluted to 500 Cc. with neutralized or freshly distilled water, free from carbon dioxide and thoroughly agitated. After settling, 50 Cc. of the clear supernatant liquor is titrated with tenth normal hydrochloric acid, using phenolphthalein as indicator. The number of cubic centimeters of acid required for the end point multiplied by 0.401 gives the number of grammes per liter of free caustic soda (NaOH) in the black liquor.²

¹Taken from Bulletin of the U. S. Department of Agriculture No. 80, (Professional Paper), "Effects of Varying Certain Cooking Conditions in Producing Soda Pulp from Aspen," by Henry E. Surface, Engineer in Forest Products, Forest Products Laboratory, Madison, Wisconsin.

²This result must be corrected if Na_2S is found to be present in the black liquor, which can be determined by the method given. Na_2S , on titration with acid, using phenolphthalein as indicator, turns, when half of it is neutralized, to NaSH .

(3) The causticity of the black liquor was calculated from the following equation:

$$\frac{A (0.775) 100}{B} = \text{percent causticity.}$$

In which:

A=the number of grammes per liter concentration of caustic soda (NaOH). (Correct for Na₂S if present.)

B=the number of grammes per liter concentration of total sodium oxide (Na₂O).

Sulphide, if present in black liquor may be determined as follows:

DETERMINATION OF Na₂S₄ (VOLUMETRIC METHOD)¹

(a) Standard Zinc Solution: (301.44 Gm. for 18 L: 1 Cc.=.02 Gm. Na₂S.)

16.746 grammes of C. P. powdered (30-mesh) zinc are dissolved in a small excess of nitric acid; ammonia is then added until the precipitate formed is completely redissolved. The solution is diluted to 2,000 Cc. Enough ammonia must be present to just keep the zinc from precipitating when diluted to this volume.

1 Cc.=.010 Gm. Na₂S.

(b) Ammoniacal NiSO₄ indicator:

Nickel ammonium sulphate made alkaline with ammonia.

(c) Manipulation:

50 Cc. black liquor is diluted to 1,000 Cc., and 20 Cc. (equivalent to 1 Cc. original black liquor) is diluted to about 100 Cc. with distilled water and the standard zinc solution run in from a burette. The end reaction is determined by noting whether a precipitate of black NiS is formed when a little of the solution being titrated is added to three drops of ammoniacal NiSO₄ indicator on a spot plate or white waxed surface.

¹This method has been carefully checked by G. C. McNaughton of the Forest Products Laboratory and found to give good results.

RAPID METHOD OF ANALYSIS FOR CONTROL OF WHITE LIQUOR

(1) Take 5 Cc. of the liquor and dilute to 100 Cc. with water. Of this diluted liquor take 20 Cc. and titrate it with N/4 HCl, using methyl orange as an indicator. This titration indicates the number of Cc. of N/4 acid required to neutralize all the alkali present.

(2) Then take 5 Cc. liquor and precipitate with BaCl_2 adding enough water to make 100 Cc. After precipitation, take 20 Cc. and titrate with N/4 HCl, using phenolphthalein as an indicator. After the color changes add methyl orange indicator and titrate again.

Suppose amount of acid used with phenolphthalein indicator to be represented by "A", and the total acid for both titrations by "B", then

$A = \text{Cc. N/4 HCl equivalent to NaOH plus } 1/2 \text{Na}_2\text{S.}$

$B = \text{Cc. N/4 HCl equivalent to NaOH plus Na}_2\text{S.}$

$A - (B - A) = \text{Cc. N/4 HCl equivalent to NaOH.}$

$2 (B - A) = \text{Cc. N/4 HCl equivalent to Na}_2\text{S.}$

Total alkali = Cc. N/4 HCl equivalent to Na_2CO_3 plus Na_2S plus NaOH.

Total alkali - $(A - (B - A) - 2 (B - A)) = \text{Cc. N/4 HCl equivalent to Na}_2\text{CO}_3.$

Total alkali - B = Cc. N/4 HCl equivalent to $\text{Na}_2\text{CO}_3.$

Example:

Suppose total alkali = 12.4 Cc.

Suppose A = 7.7 Cc.

Suppose B = 9.1 Cc.

NaOH =

$A - (B - A)$

$7.7 - (9.1 - 7.7) = 6.3 \text{ Cc. N/4 HCl}$

$6.3 \times 0.04 / 4 \times 1000 = 63 \text{ grammes per litre.}$

$\text{Na}_2\text{S} =$

$2 (B - A)$

$2 (9.1 - 7.7) = 2.8 \text{ Cc. N/4 HCl}$

$2.8 \times 0.039 / 4 \times 1000 = 27.3 \text{ grammes per litre}$

$\text{Na}_2\text{CO}_3 =$

Total alkali - B

$12.4 - 9.1 = 3.3 \text{ Cc. N/4 HCl}$

$3.3 \times 0.053 / 4 \times 1000 = 43.725 \text{ grammes per litre.}$

CAUSTIC LIQUOR

As a matter of every day work to secure a sufficiently accurate knowledge of the causticity of the liquor, take first, 5 Cc. of the liquor, dilute to 100 Cc. with water and titrate, using methyl orange as indicator.

Place 50 Cc. of the liquor in a 500 Cc. flask, add about 50 Cc. distilled water and precipitate by BaCl_2 , dilute to mark, mix and settle. Withdraw 50 Cc. of the clear liquor, or filter and titrate with $\text{N}/4$ HCl , using methyl orange as indicator.

Suppose first titration to have used 12.4 Cc. of $\text{N}/4$ HCl and the second 10.5 Cc. $\text{N}/4$ HCl . To get causticity divide 10.5 by 12.4 or 84 plus percent caustic.