Na_2S Solution.

A 50 c.c. sample of liquor is pipetted into a 500 c.c. volumetric flask, 50 c.c. of 10-per-cent. $BaCl_2$ solution added, the mixture made up to 500 c.c., thoroughly shaken, and allowed to settle.

A 10 c.c. portion is added to a slight excess of 0·1N iodine previously acidified with 10 c.c. of concentrated acetic acid. The excess iodine is then titrated with 0·1N sodium-thiosulphate solution, using starch as an indicator.

A = c.c. of 0·1N iodine solution ; B = c.c. of 0·1N thiosulphate solution.

$(A - B) \times 3{\cdot}9 = Na_2S$ in grammes per litre.

Black Liquor : Ratio of Combined to Total Alkali.

Free Alkali.

A 100 c.c. sample of black liquor is pipetted into a 1,000 c.c. volumetric flask, 100 c.c. of 10-per-cent. $BaCl_2$ solution added, made up to 1,000 c.c., thoroughly shaken, and allowed to settle. A 100 c.c. portion of the clear solution is titrated with 0·1N HCl to phenolphthalein end point.

Total Alkali.

A 100 c.c. sample of black liquor is pipetted into a Duriron dish, evaporated to dryness, and ashed. The ash is dissolved with distilled water and made up to 1,000 c.c. in a volumetric flask. A 100 c.c. portion is titrated with 0·1N HCl to methyl-orange end point.

x = c.c. 0·1N acid for free alkali ; y = c.c. 0·1N acid for total alkali.

$\left(100 - 100\,\frac{x}{y}\right)$ = per cent. ratio of combined to total alkali.

APPENDIX IX. — METHODS OF ANALYSIS OF COOKING-LIQUORS FOR SEMI-KRAFT PROCESS.

NaOH and Na_2S Solution.

A 50 c.c. sample of liquor is pipetted into a 500 c.c. volumetric flask, made up to the mark with distilled water, and thoroughly agitated. 50 c.c. of 10-per-cent. $BaCl_2$ solution is added to precipitate carbonates. Allow to settle. Pipette off a 10 c.c. sample of the clear liquor and add it to an excess of 0·1N iodine solution, previously acidified with acetic acid. Enough glacial acetic should be used to neutralize all the alkali and render the solution acid. The liquor containing the Na_2S must be added to the 0·1N iodine, and not *vice versa*, or low results will be obtained. Titrate the excess iodine with 0·1N thiosulphate solution, using starch as an indicator. A new 10 c.c. sample is titrated with 0·1N acid to methyl orange.

Calculations :—

Let c.c. 0·1N iodine = A ; let c.c. 0·1N thiosulphate = B ; let c.c. 0·1N acid = C.

$(A - B) \times 3{\cdot}9 = Na_2S$ in g.p.l.

$\{C - (A - B)\} \times 4{\cdot}0 = NaOH$ in g.p.l.

For analysis of black liquor see procedure under soda and kraft process.

APPENDIX X. — METHODS OF ANALYSIS OF COOKING-LIQUORS FOR SEMI-CHEMICAL PROCESS.

Semi-chemical Process.

Na_2SO_3 and $NaHCO_3$ Solution.

A 2·0 c.c. sample is titrated with 0·1N iodine, using starch as an indicator. An air-condenser is attached to the Erlenmeyer flask and the solution is boiled gently until all CO_2 is expelled. Each cubic centimetre of 0·1N iodine forms 1 c.c. of 0·1N acid, according to the equation—

$$Na_2SO_3 + 2I + H_2O = Na_2SO_4 + 2HI.$$

The acid thus liberated reacts with the $NaHCO_3$. Care must be taken that sufficient 0·1N acid is present, however, to decompose all of the $NaHCO_3$. If the original liquor is low in sulphite, sufficient 0·1N acid should be added by means of a burette before the boiling. After all the CO_2 is expelled the flask is cooled under the water-tap. An excess of 0·1N NaOH solution, which contains a small amount of $BaCl_2$, is added by either a burette or pipette. The excess NaOH is then titrated with 0·1N acid, using phenophthalein as indicator. The $NaHCO_3$ is calculated as Na_2CO_3.

Calculations :—

Let c.c. 0·1N iodine = A ; let c.c. 0·1N acid = B ; let c.c. 0·1N NaOH = C.

$A \times 3{\cdot}15 = Na_2SO_3$ in g.p.l.

$\{(A + B) - C\} \times 2{\cdot}65 = Na_2CO_3$ in g.p.l.