Free SO_2.

This is obtained by difference between the per cent. total and per cent. combined SO_2.

Loosely combined SO_2.

A portion of the SO_2 combined with the dissolved ligneous materials in sulphite liquor is but very loosely combined, presumably with aldehyde groups, and may be hydrolyzed off with NaOH. This is the basis of the quantitative estimation of SO_2 in this form. The method follows: After the titration of sulphite liquor for total SO_2 by iodine, the blue colour is destroyed by a drop of N/16 $Na_2S_2O_3$ (sodium thiosulphate). An excess, 10 c.c. of 15-per-cent. NaOH is added, and the solution allowed to stand for twenty minutes, the solution then being made slightly acid with HCl, and again titrated with N/16 iodine. This titration gives the per cent. SO_2 present as loosely combined SO_2, each cubic centimetre of iodine being equivalent to 0·1 per cent. SO_2.

Determination of Total SO_2.

A method for the determination of SO_2 in all forms, or the total SO_2 content of sulphite cooking-liquor, as worked out by Miller and Swanson, Forest Products Laboratory, is as follows: A 2 c.c. sample of the liquor is run into a 1 c.c. portion of 15-per-cent. NaOH in a 35 mm. porcelain crucible. This is then absorbed in about 4 grm. Eschka mixture, and the crucible and contents dried at 105° C. The crucible is then placed in a Shimer crucible and heated in a stream of oxygen, at a dull red for one hour. The oxygen and sulphur gases pass through a ret-hot zone in the silica tube attached to the Shimer crucible, and out through an outlet-tube into a Drexel flask containing 5 c.c. of 15-per-cent. NaOH and 10 c.c. saturated bromine water in 100 c.c. distilled water. After the combustion the porcelain crucible and contents are placed in a 600 c.c. beaker and allowed to cool. Then the contents of the Drexel flask are added, the flask being washed with hot water three times, the washings being added to the beaker-contents. The beaker is placed on a hotplate, and allowed to digest for half an hour. Then the contents are filtered into a 600 c.c. beaker, the residue and crucible being washed six times with hot water. The filtrate, about 400 c.c., is made slightly acid with HCl, the excess bromine boiled off, and 10 c.c. of 10-per-cent. $BaCl_2$ solution pipetted into the solution. The $BaSO_4$, precipitated, after digestion for one hour on a water bath, is separated by filtration into a weighed Gooch. After washing the precipitate several times with hot water the crucible and contents are dried and ignited, cooled, and weighed. From the weight of $BaSO_4$ obtained, the per cent. SO_2 is found thus:—

$$\text{Wt. } BaSO_4 \times 0{\cdot}27443 \times 50 = \text{per cent. } SO_2.$$

or $$\text{Wt. } BaSO_4 \times 0{\cdot}1372 = \text{per cent. } SO_2.$$

Soluble Sulphates in Sulphite Liquor.

In 250 c.c. Soxhlet flasks are placed about 55 c.c. of distilled water and 25 c.c. of 25-per-cent. hydrochloric acid (approximately equivalent to 16 c.c. of ordinary concentrated acid). The flasks are clamped in position under the condensers, and 25 c.c. of waste sulphite liquor, or raw sulphite acid, as the case may be, are pipetted into the two Soxhlet flasks, the second being corked immediately and connected to the generator. The condenser-stoppers are coated with collodion in order to ensure tight connections. The flasks containing the iodine solution and standard sodium thiosulphate are connected to the condenser-outlet. Carbon dioxide is then passed through for about five minutes until all the air is displaced from the apparatus, thus obtaining an atmosphere of carbon dioxide in which very little or no oxidation of SO_2 to SO_3 takes place. At this stage the solutions in the Soxhlet flasks are slowly heated until they boil gently, and the boiling is continued until the experiment is finished. Any liquor vapourizing during heating is condensed back into the flask, thus maintaining almost constant concentration of the solution. The SO_2 evolved is swept out by the carbon dioxide, is cooled on escaping, and is finally absorbed in the iodine solution. At the end of the experiment the excess iodine is titrated with sodium thiosulphate of equivalent strength, using starch solution as an indicator. From the amount of iodine reduced by the evolved SO_2 the quantity of the latter is calculated. The end point of the reaction occurs when the iodine solution is no longer decolorized, or, better still, by bubbling the escaping gas through a very weak iodine solution in a pill-plate in case the amount of SO_2 given off is not being determined. Ordinarily it takes from forty-five minutes to one hour to completely remove the SO_2, this time varying according to the amount of SO_2 present, the rate at which the CO_2 is passed through the solution, and also according to the rate of heating of the latter. When all the SO_2 is expelled the Soxhlet flasks are disconnected, and the sulphate-free precipitate formed is filtered off. The filter is thoroughly washed with hot water, and the clear filtrate is neutralized with NH_4OH and made slightly acid with HCl. It is diluted to approximately 400 c.c., brought to a boil, and 10 c.c. of N/2 $BaCl_2$ are very slowly added. Boiling is continued until the $BaSO_4$ precipitated becomes granular, and is then kept hot for from four to six hours longer. The $BaSO_4$ is then filtered and thoroughly washed with hot water until free from chloride. It is carefully ignited, allowed to cool, and then weighed.

Lime as CaO in Sulphite Liquor.

A 10 c.c. sample of the liquor* is pipetted into a 250 c.c. beaker, and is treated with 5 c.c. concentrated H_2SO_4 and 10 c.c. concentrated HNO_3, and heated until sulphur trioxide (white) fumes appear. If the organic matter is not destroyed, more HNO_3 is added, and heat applied, until the solution appears clear. Then the solution is allowed to cool, is diluted to 150 c.c. and treated with

* Raw or finished acid may be treated as follows: Heat 10 c.c. in 250 c.c. beaker as above, but add 10 c.c. concentrated HCl instead of HNO_3 and H_2SO_4; boil to expel SO_2, and proceed as above.