

The Sulphur Dioxide Content of Natal Sugars

By D. J. COGHILL.

Mr. D. J. Coghill read the following paper:—

The report deals with the results of the examination of over one hundred different samples of, mostly raw sugars, obtained from fifteen factories during the 1929 crushing season.

Methods of Investigation:

Three methods in general use for the estimation of the sulphur dioxide content of sugars are:—

- (1) Sulphide stain method,
- (2) The iodine titration method, and
- (3) The distillation method.

(1) Sulphide Stain Method.

The sulphide stain method developed by Mann and described by Ogilvie (1926) depends on the reduction of sulphur dioxide to hydrogen sulphide by means of nascent hydrogen generated from zinc and hydrochloric acid. The method is employed in the laboratories of Messrs. Tate & Lyle, London. According to details supplied by Mr. L. Blacklock, of Hulett's Refineries, the procedure is as follows:

Standard stains are made covering a range of 10 to 25 parts per million of sulphur dioxide. The standards are prepared from "pure anhydrous sodium sulphite" and involve the use of "unblued (1) triple washed, granulated sugar, free from sulphur dioxide and other reducing substances." A relatively small amount of the sample is used, 5 gms. or less, should the stain procured prove darker than the standard stain for 20 parts per million sulphur dioxide.

For refined sugars and for cargo sugars containing small amounts of sulphur dioxide, the method is suitable and accurate; however, in the case of sugar containing considerable amounts of sulphur dioxide, the quantity of sample to be taken would necessarily be small, and the error due to non-uniformity of sample large.

I have found that even using 100 gms. portions of certain samples for determination of sulphur dioxide by the distillation method, differences in results could be traced to this difficulty.

Samples of raw sugars have been found to contain scales of calcium sulphite. Clearly, with a moist coarse-grained raw sugar it is practically impossible

to mix the sample so thoroughly as to obtain a uniform sample. Largely owing to limitations of this kind the method has not been employed in this laboratory for the estimation of sulphur dioxide in raw sugars.

(2) Iodine Titration Method:

The iodine titration method was introduced by Ripper (1892) for the estimation of sulphur dioxide in white wines.

The method now finds almost universal application for the estimation of sulphur dioxide as a routine procedure covering a large variety of materials.

An excellent resumé of methods for the estimation of sulphur dioxide appears in a paper compiled by Monier-Williams (1927), and it contains useful discussion on the iodine titration method. Monier-Williams states, *inter alii*: "It would appear, therefore, that direct iodine titration is subject, in a greater or lesser degree, to a number of errors, some of which will compensate each other, and that although apparently accurate results may often be obtained—these must be regarded as being due, in many cases, to a balancing of errors." Farnsteiner (1904), de Sornay (1911), Ogilvie (1926) and Hurst (1927) have used the method for sugars, and consider the results sufficiently accurate enough for works purposes, and Mestre (1927) for beet sugars. Hurst, *loc. cit.*, reports the presence of less than 70 parts per million, and of frequently less than 25 parts per million of sulphur dioxide for Trinidad yellow crystal sugar. The iodine titration method is used in this laboratory as a routine method and the procedure adopted is as follows:—

Iodine Titration Method as used at the Sugar Experiment Station:—50 grams. of the sample are dissolved in 150 cc. of distilled water and solution of sugar hastened by warming on the water bath, taking care to avoid overheating.

The solution is then cooled to room temperature and a further 100 cc. of distilled water added. The sulphur dioxide, possibly in combination with the sugar and other "unknown" bodies, is liberated by the addition of 20 cc. of 5 per cent. caustic soda

until the dark coloured alkaline solution becomes light and clears, then add 10 cc. of the sulphuric acid in excess. Immediately add from 10 to 20 ccs. of approximately 0.032 N/iodine solution depending on the amount of sulphur dioxide in the sample under test. It is desirable to have up to 5 cc. or more of the iodine solution in excess. Titrate at once the excess iodine, using approximately 0.032 normal/sodium thiosulphate. Starch is used as an indicator³. The actual iodine value of the sodium thiosulphate used is found by titrating 10 cc. of the iodine solution employed. The iodine solution is to be standardised against 0.032 N. arsenious oxide.

The calculation is made as follows:—

Example: Used 20 cc. of 0.036 N/iodine solution and found that 10 cc. of this iodine requires 9.32 cc. of thiosulphate. Then 1 cc. Thio = $10/9.32 = 1.07$ cc. iodine solution. Therefore, $9.32 \times 1.07 = 9.97$ cc. iodine solution used in excess, and $20 - 9.97 \times 0.036 \times 20,000 =$ parts per million of sulphur dioxide.

Baissac (1927) reports good agreement between iodine titration results compared with a gravimetric distillation method (using phosphoric acid, carbon dioxide, and absorbing sulphur dioxide into bromine water and with estimation of the sulphate formed)

for direct consumption white Mauritius sugars, and Jensen (1928) finds good agreement of white Mauritius sugars, but for a raw sugar a difference of over 40 per cent.

It was found in the case of a Natal cargo sugar made by the carbonation process that considerable differences were obtained for the sulphur dioxide content determined by the iodine titration as compared with the distillation method. The average of six results by the iodine titration method gave 13.3 parts per million of sulphur dioxide and for four results by the distillation method 5.5 parts per million of sulphur dioxide; approximately 58 per cent. lower.

Some iodine reducing substance is present, and this was demonstrated by absorbing the products of distillation by the Monier-Williams method, q.v., into (a) two absorbing vessels each containing hydrogen peroxide, and (b) one vessel containing iodine solution and arranged in the order as mentioned. One distillation was conducted, using considerably more hydrochloric than usual for the method, and for the second distillation concentrated phosphoric acid was used.

The results are shown in the table below:

RESULTS OF PARTS PER MILLION OF SULPHUR DIOXIDE.

Treatment.	First Hour (a)		Second Hour (a)		Third Hour (a)	
	H ₂ O ₂	I ₂	H ₂ O ₂	I ₂	H ₂ O ₂	I ₂
Hydrochloric Acid, 100 c.c. of 1 : 1.	5.5	4.0	—	2.4	—	0.4
Phosphoric Acid, 30 c.c., 1.75 sp. gr.	3.7	3.0	2.2	1.1	—	—

(a) Period of distillation.

The sulphur-dioxide gas absorbed in the hydrogen peroxide receivers is, of course, oxidised to sulphate, and the sulphuric acid determined both volumetrically and gravimetrically. The figures in the table refer to gravimetric results. The excess iodine (0.032 N/iodine used) in the iodine receiving vessel was titrated with sodium thiosulphate in the usual way, and the results calculated as sulphur dioxide appear as such in the table above. It was found, however, that no sulphate could be detected in the iodine receivers, consequently the iodine reducing substances could not have been sulphur dioxide.

(3) Distillation Method.

The distillation method for sulphur dioxide as used in this laboratory is due (with slight modifications) to Monier-Williams (1927).

It consists of liberating the sulphur dioxide from the sample by means of a strong acid (hydrochloric acid) and absorbing the sulphur dioxide evolved into hydrogen peroxide and titrating the sulphuric acid formed as a result of the oxidation of sulphur dioxide to sulphate. The distillation is effected in a current of carbon dioxide gas and a reflux condenser used to prevent acid of any kind (except, of course, sulphurous acid dissociated as free sulphur dioxide) i. 2, hydrochloric, etc. Special apparatus is used and is catalogued in Baird & Tatlock's 1928 Chemical Apparatus List (4).

It is possible, however, to assemble suitable apparatus using the ordinary lines of equipment common to a chemical laboratory.

The apparatus found suitable and in use in this laboratory consists of a 2.5 litre Kjeldahl shape distillation flask (2) and fitted with a rubber stop-

per bored with three holes. The stopper carries a 5—6 mm. diameter glass tube reaching to very nearly the bottom of the long-necked distillation flask, and serves for passing in the carbon dioxide gas used before and during distillation; a second tube of about 12—15 mm. bore and bent at an angle for connecting the reflux condenser and a 150 cc. tap funnel. The reflux condenser used is a four bulb Allihn's type, and is set sloping towards the distillation flask. The reflux is connected to the absorption train by means of a length of 4—6 mm. bore glass tubing. The train consists of two 250 cc. ordinary shape Erlenmeyer flasks, rubber stoppers, suitably bored, being used for connection. A Kipps apparatus is used for supplying carbon dioxide gas, but, no doubt, carbon dioxide cylinders (such as are used in the aerated water trade) would be more suitable in respect of getting a regular and steady means of supply and control of gas.

Distillation Method as used at the Sugar Experiment Station.—The sample is thoroughly mixed and 100 gm. charge or more used for the determination.

The quantity taken is dissolved in 100 cc. of recently boiled and cooled distilled tap water and warmed on the water bath to expedite solution, care being taken to avoid overheating. In the distillation flask place 500 cc. of recently boiled and cooled distilled or good quality tap water, add 10 cc. pure concentrated hydrochloric acid, connect up, pass in carbon dioxide (5) boil for at least 5 minutes. In each of the two absorption flasks place 10 cc. of 20 volume hydrogen peroxide and connect up

apparatus, making certain that all joints, etc., are gas tight.

The sugar solution is added per the tap funnel at such a rate that it is all passed during one half-hour. Wash the beaker, including any residue (which may be sulphite of lime), into the tap funnel and run into distillation flask. Turn off the water supply to the condenser and continue boiling until the bend at the top of the reflux condenser is unpleasantly warm to touch. This is necessary in order to evaporate off any traces of sulphurous acid left in the condenser. Stop gas, wash down the tube connecting the absorption flasks and transfer the contents of both to a 600 cc. beaker and titrate with 0.1 N/caustic soda, using brom phenol indicator, until a decided blue colour is reached. Place a sheet of white paper under the beaker during titration. Titrate 20 cc. of the hydrogen peroxide used in order to ascertain the value of the blank (7).

Calculation of Results:

Example: Say 100 gm. of raw sugar used, found blank requires 0.82 cc. of 0.112 N/caustic soda solution and sample 17.6 cc. of the same. Then $17.6 - 0.82 \times 0.112 \times 0.032 = 601$ parts per million of SO_2 .

The Monier-Williams method has recently been critically examined by Fitelson (1929) and the accuracy of the method fully established.

Sulphur Dioxide Content of Natal Sugars.—The results of analyses of one hundred and four samples of sugars secured during the 1929 season appear in the tables below:—

TABLE No. 1.

Sample No.	Factory No.	Quality.	SO_2 in parts per million. Iodine Titration.				SO_2 in parts per million. Distillation Method.			
			1.	2.	3.	4.	1.	2.	3.	4.
—	20	Cargo.. ..	31.6	31.6	—	—	40.5	42.3	—	—
—	"	Treacle	126.8	114.8	—	—	114.0	116.0	—	—
—	"	Export	125.2	129.9	127.8	—	113.3	118.7	105.7	—
1	21	Raw	83.0	—	—	—	—	—	—	—
—	"	White	83.2	—	—	—	72.4	—	—	—
—	"	Cargo	87.2	—	—	—	68.7	—	—	—
—	"	"A"	12.0	—	—	—	—	—	—	—
—	"	"B"	34.0	—	—	—	—	—	—	—
—	"	"C"	38.0	—	—	—	—	—	—	—
—	"	Cargo.. ..	13.6	12.6	—	—	3.7	3.7	—	—
—	"	"	13.6	12.0	—	—	3.7	3.7	—	—
—	"	"	15.3	13.8	—	—	—	—	—	—
—	"	"	13.7	12.7	—	—	—	—	—	—
5	7	Export	33.0	—	—	—	—	—	—	—
6	18	Cargo.. ..	33.0	—	—	—	—	—	—	—
—	"	"	41.2	—	—	—	28.0	27.8	—	—
7	8	Cargo.. ..	65.8	—	—	—	—	—	—	—
1	"	"	63.4	—	—	—	—	—	—	—
2	"	"	96.0	—	—	—	—	—	—	—
3	"	"	88.8	—	—	—	—	—	—	—
1	"	"	32.0	—	—	—	29.7	—	—	—

TABLE No. 1.—*continued.*

Sample No.	Factory No.	Quality.	SO ₂ in parts per million. Iodine Titration.				SO ₂ in parts per million. Distillation Method.			
			1.	2.	3.	4.	1.	2.	3.	4.
2	8	Cargo	32.0	—	—	—	33.4	—	—	—
8	22	Raw	37.6	—	—	—	—	—	—	—
9	3	Raw	15.8	—	—	—	—	—	—	—
—	12	"A"	73.0	—	—	—	—	—	—	—
—	"	"B"	157.0	—	—	—	—	—	—	—
—	"	"A"	75.6	—	—	—	79.8	79.8	—	—
—	"	"B"	45.8	45.8	—	—	46.4	—	—	—
—	"	Raw	29.1	25.1	—	—	22.3	22.3	—	—
—	"	"	42.9	39.6	—	—	33.4	33.4	—	—
—	"	"	61.2	56.6	—	—	51.0	57.5	—	—
—	14	Export	44.0	—	—	—	—	—	—	—
1	"	"	42.6	39.4	—	—	12.9	—	—	—
2	"	"	58.6	—	—	—	33.1	—	—	—
3	"	"	38.4	—	—	—	33.0	—	—	—
4	"	"	40.2	—	—	—	34.9	—	—	—
5	"	"	50.2	—	—	—	48.2	—	—	—
6	"	"	59.3	46.2	—	—	41.7	42.7	—	—
7	"	"	48.2	48.2	46.2	—	33.5	—	—	—
8	"	"	—	—	—	—	29.0	—	—	—
9	"	"	—	—	—	—	66.7	42.6	—	—
10	"	"	—	—	—	—	52.0	—	—	—
11	"	"	—	—	—	—	65.0	—	—	—
12	"	"	—	—	—	—	48.2	—	—	—
13	"	"	48.0	—	—	—	55.6	—	—	—
14	"	"	—	—	—	—	57.5	—	—	—
15	"	"	—	—	—	—	50.1	—	—	—
16	"	"	—	—	—	—	50.1	—	—	—
17	"	Refinery	41.6	—	—	—	35.9	—	—	—
18	"	Export	45.6	—	—	—	27.8	—	—	—
19	"	Refinery	47.5	—	—	—	38.0	—	—	—
20	"	"	57.4	51.4	—	—	37.1	35.3	—	—
21	"	"	—	—	—	—	45.3	—	—	—
22	"	"	—	—	—	—	45.3	—	—	—
23	"	"	58.4	—	—	—	45.6	52.2	—	—
24	"	"	67.0	—	—	—	51.5	53.4	—	—
25	"	Export	65.8	—	—	—	—	—	—	—
26	"	"	70.0	—	—	—	—	—	—	—
27	"	"	62.6	62.6	—	—	46.0	46.0	—	—
28	"	Refinery	49.6	—	—	—	—	—	—	—
29	"	"	48.4	—	—	—	—	—	—	—
30	"	"	53.4	—	—	—	44.2	47.8	—	—
1	15	Raw	228.0	227.7	228.2	—	238.8	238.9	—	—
2	"	"	86.0	87.0	—	—	72.4	70.5	—	—
3	"	"	488.0	486.0	—	—	370.0	—	—	—
2	"	"	124.0	127.0	—	—	130.6	—	—	—
1	5	Raw	—	—	—	—	52.0	48.3	—	—
2	"	"	—	—	—	—	81.6	89.0	—	—
1	4	Cargo	44.4	—	—	—	—	—	—	—
3	"	"	77.6	—	—	—	—	—	—	—
8	"	"	73.6	—	—	—	—	—	—	—
11	"	"	58.4	—	—	—	—	—	—	—
14	"	"	77.6	—	—	—	—	—	—	—
15	"	"	78.8	—	—	—	—	—	—	—
16	"	"	94.0	—	—	—	—	—	—	—
19	"	"	114.4	—	—	—	—	—	—	—
22	"	"	77.6	—	—	—	—	—	—	—
23	"	"	77.6	—	—	—	—	—	—	—

TABLE No. 1.—*continued.*

Sample No.	Factory No.	Quality.	SO ₂ in parts per million. Iodine Titration.				SO ₂ in parts per million. Distillation Method.			
			1.	2.	3.	4.	1.	2.	3.	4.
24	4	Cargo..	83.8	—	—	—	—	—	—	—
25	"	"	57.2	—	—	—	—	—	—	—
26	"	"	61.4	—	—	—	—	—	—	—
27	"	"	61.4	—	—	—	64.3	—	—	—
28	"	"	51.2	—	—	—	—	57.0	—	—
29	"	"	45.0	—	—	—	45.9	—	—	—
30	"	"	51.2	—	—	—	47.8	—	—	—
31	"	"	51.2	—	—	—	68.0	—	—	—
32	"	"	55.2	—	—	—	—	—	—	—
33	"	"	43.0	—	—	—	31.3	—	—	—
34	"	"	45.0	—	—	—	40.5	—	—	—
35	"	"	55.2	—	—	—	—	—	—	—
1	"	"	20.4	19.7	—	—	18.4	16.6	16.6	12.9
2	"	"	20.4	—	—	—	12.9	12.7	5.5	9.2
3	"	"	30.2	28.6	—	—	18.4	16.6	—	—
1	6	Raw ..	38.4	—	—	—	—	—	—	—
2	"	"	58.6	—	—	—	—	—	—	—
3	"	"	83.0	—	—	—	—	—	—	—
4	"	"	36.4	—	—	—	—	—	—	—
5	"	"	34.4	—	—	—	—	—	—	—
6	"	"	60.8	—	—	—	—	—	—	—
7	"	"	87.0	—	—	—	—	—	—	—
—	0	Cargo..	29.5	35.9	—	—	14.8	11.1	13.0	—
—	"	"	47.6	50.8	—	—	20.4	20.4	—	—
—	"	"	100.8	97.8	—	—	57.0	55.2	58.9	—

The results for the iodine titration method range from 14 to 488 parts per million of sulphur dioxide, and for the distillation method from 4 to 370 parts per million of sulphur dioxide. For sixty samples examined by the distillation method 15 per cent. of them contain over 70 parts per million of sulphur dioxide (SO₂).

The average results calculated for the different samples received from the various factories submitting two or more samples appears in the table below:—

TABLE II.
SHOWING THE MEAN SULPHUR DIOXIDE CONTENT OF NATAL SUGARS.

Factory Number.	Quality.	Number of Samples examined.	SO ₂ in p.p.m. by Distillation Method.	Number of Samples.	SO ₂ in p.p.m. by Iodine Titration.	Difference % between Titration and Distillation Method.
8	Cargo..	2	31.5	6	63.0	100.0
12	Raw ..	3	36.6	3	42.4	15.8
4	Cargo..	9	37.6	25	60.2	60.1
10	"	3	30.2	3	60.4	100.0
15	Raw ..	4	202.7	2	231.7	14.3
5	"	2	67.7	—	—	—
14	Refinery ..	6	42.2	7	51.2	21.3
"	Export ..	—	—	3	51.8	—
"	All Sugars..	25	42.8	21	51.9	21.2
18	Cargo..	—	—	2	37.1	—
6	Raw ..	—	—	7	57.0	—

Effects of Storage:

It was considered desirable to ascertain whether the sulphur dioxide content of sugar diminishes on storage.

For this purpose several samples were analysed immediately on receipt of sample, and again at intervals later. The samples were kept in tightly screwed down "Mason" jars and in a room free altogether of sulphur dioxide. The results are shown in the table below:—

TABLE III.
SHOWING THE EFFECTS OF STORAGE ON THE SULPHUR DIOXIDE CONTENT OF NATAL SUGARS.

Factory Number.	Quality.	Days in Storage.	Iodine Titration in p.p.m. SO ₂ mean.	Per cent. Loss.	Distillation Method, p.p.m. SO ₂ mean.	Per cent. Loss of Sulphur Dioxide.
20	Cargo	—	31.6	—	41.4	—
20	"	8	34.3	Gain	—	—
20	"	36	—	—	35.3	14.7
20	"	47	—	—	32.0	22.7
20	Treacle	1	120.8	—	115.0	—
"	"	7	141.7	Gain	—	—
"	"	35	—	—	131.7	Gain
"	"	54	—	—	127.1	Gain
"	"	75	—	—	126.2	Gain
20	Export	2	—	—	111.9	—
"	"	—	3	—	114.1	—
"	"	4	127.3	—	—	—
"	"	11	—	—	101.9	8.9
"	"	12	93.2	26.7	—	—
"	"	33	—	—	74.2	33.6
"	"	52	—	—	57.5	48.6
"	"	53	—	—	63.1	43.6
"	"	72	—	—	64.0	42.8
"	"	163	32.6	74.3	33.1	66.2
15	Raw	—	227.9	—	238.9	—
"	"	68	144.3	36.6	143.5	39.9
"	"	74	131.2	42.4	—	—
"	"	—	86.5	—	71.4	—
"	"	68	57.4	33.6	61.6	13.7
"	"	—	—	—	367.0	—
"	"	19	—	—	412.0	Gain
"	"	—	—	—	130.6	—
"	"	19	—	—	112.2	14.0

The effects of storage results in a loss of sulphur dioxide.

Results obtained for a treacle sugar from Factory No. 20 seem to indicate increase of sulphur dioxide on storage but, as the maximum increase amounts

to 15 per cent. on the 35th day of storage, but 10 per cent. after 75 days, and it proved impossible to secure a representative portion as used for the analysis, little or no significance can be attached to the apparent increase of sulphur dioxide.

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LIST OF FOOT-NOTES TO SULPHUR DIOXIDE REPORT.

- (1) Ultramarine is a mineral and is isomorphous with hauynite, lazurite, and sodalite. It contains sodium, aluminium, silicon, sulphur and oxygen. Ultramarine blue analyses indicate from 11 to 16 per cent. of sulphur. Spengler & Brendel, cited in the *Intern. Sugar Journ.*, 29, 372 (1927), found that a very strongly blued sugar increased the sulphur dioxide content of a sample they examined by 16 parts per million.
- (2) May be obtained from local suppliers in Durban.
- (3) A suitable starch indicator will be found described by Nichols, *Journ. Indust. Eng., Chem. (Analyt. Edit.)* 1, 215 (1929).
- (4) Baird & Tatlock's catalogue, 1928 edition, Item No. C4204.
- (5) At the rate of about one bubble of gas per second. A wash bottle, containing water, should be used.
- (6) Bromphenol blue (Clark—Lubs indicator), 0.1 % solution in alcohol. Colour change is yellow in acid to blue in alkaline solution, and is unaffected by weak acids, i.e., carbonic acid, etc.
- (7) Hydrogen peroxide, made by Allen & Hanbury, 20 volume is found suitable. Blank for this peroxide usually runs about 0.85 cc. of 0.1 N/caustic soda against brom-phenol-blue.

Natal Sugar Experiment Station,

South African Sugar Association,
MOUNT EDGECOMBE.

31st January, 1930.

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Mr. BLACKLOCK: I would like to congratulate Mr. Coghill on his excellent paper; it is very interesting, and I am sure it represents a great deal of hard work and time. Our experience of the various methods enumerated substantially confirms Mr. Coghill's work. We have found higher results from the titration method, but not to the extent set forth in Mr. Coghill's paper. Roughly, our distillations showed a 10 per cent. lower figure than the titration. This, with say 80 parts per million, only gave a difference of 8 to 10 parts, and I think this difference is not material when we are dealing with parts

per million. The lead sulphide stain method which is used by Tate & Lyle—particulars of which I supplied to the Association and the various mills last year—is only applicable to sugars and products containing up to say 25 parts per million. It is worked generally on a 5 gramme sample, and any higher proportion of S.O.₂ than this proportionately less of the sample is taken for experiment. Small portions like this increase the risk due to non-uniformity of sample and poor representation. The preparation of standard stains from the various sugar solutions enumerated is somewhat involved and tedious, and it is difficult to obtain zinc and reagents of the requisite purity readily. The result at the finish is a process of colour matching, and dependent greatly on the human element. I regard the distillation method as being more reliable when accurate work is required; but it is tedious and somewhat lengthy and requires a good deal of special apparatus and room when looked upon in the light of a routine test involving 10 to 20 estimations per day. We have not had any experience of the use of strong hydrochloric acid in this connection, however, and rather fear a possibility of oxidation of some S.O.₂ in the flask and accordingly lower results. We used phosphoric acid and conducted the distillation on the lines given in the official method adopted by the Association of Official Agricultural Chemists of America. Messrs. Lane & Eynon, Consulting Chemists, London, use this method. 300/400 c.c. of distilled water and 5 c.c. syrupy pho. acid are placed in an 800 c.c. distilling flask and boiled for 15 minutes, passing C.O.₂ from a cylinder or Kipps. The C.O.₂ is passed through a Woolff's bottle, which serves to regulate the stream of gas. Two bubbles per second is the maximum allowable. Fifty grams of the sugar dissolved in a small quantity of lukewarm water are added gradually through a funnel after connecting up the delivery tube with a condenser and finally with an absorption flask containing Bromine water. The distillation is considered complete when some 150 c.c. have distilled over. Bromine is expelled by boiling in the presence of HCl and the sulphate precipitated by Barium chloride and weighed in the usual way. The method which we have used ordinarily in routine work is also based on the official method used by the Association of Agricultural Chemists. Concordant results can only be obtained by standardising all conditions of analyses, but once this is done there is very little difficulty. Slightly higher results—(according to the paper very much higher in some instances apparently)—are given than with the distillation method, but the figures are on the safe side from the Industry's point of view, and at any rate the results are comparative. This method is given in full in the methods set forth by the Committee on Standardisation of Chemical Control. We have to choose the best method under the circumstances; any variation or change of method which will give increased accuracy without sacrificing rapidity will be welcome. Practically I agree with Mr. Coghill's

paper and the results he has obtained. We have not had any experience of driving off the SO₂ by strong acid nor of absorbing the gas in peroxide and titrating the sulphuric acid formed.

CHAIRMAN: It is very satisfactory to find that Mr. Blacklock's work corroborates ours at the Experiment Station. It is interesting to compare the results between the iodine titration method and the distillation method as is done in one of these tables. Usually the results by the iodine method under our conditions are much greater. That is probably all on the safe side, as regards factory control work, but it would be interesting to know why that is so. Undoubtedly iodine is a very reactive substance and will combine with a good many other substances than SO₂. In the experiments Mr. Coghill describes where something in the distillation product passes on after all the SO₂ has been absorbed, which will react with iodine is a very interesting chemical point which should be further studied. It is not a very simple matter to study because we are dealing with such very small quantities of material when we are dealing in parts per million. In some countries I believe they find the converse is the case—in Java and the West Indies—and the results by the iodine method are

less than those obtained from direct distillation. That has been explained by the fact that under certain conditions the SO₂ can enter into forms of combination that don't readily react with iodine, but that does not seem to be the case under our conditions, since our iodine tests are almost invariably higher than the distillation method. With regard to the time taken by the distillation method we rather funk'd this method at first because on paper it seemed rather a cumbersome one, but once the apparatus is set up it is remarkably little trouble to do the test, and they can be done very accurately and rapidly, which is by no means the case, as Mr. Blacklock has pointed out, with the sulphide stain method. It would be very interesting to know what Mr. Coghill's ideas are regarding the volatile substance which is evidently not SO₂, but which still reacts with iodine.

Mr. BLACKLOCK: Is Mr. Coghill satisfied that no oxidation is going on when strong acid is used to drive out the SO₂?

Mr. COGHILL: That may be possible, but it is avoided by the process of distillation we used in the laboratory inasmuch as we added the sugar solution slowly to the boiling acid.