

Rapid Determination of Sulphur Dioxide in Foods

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A rapid method for sulphur dioxide estimation in foods is described. The method uses a compact, semi-automatic distillation apparatus normally used for nitrogen estimation, and gives a much reduced analysis time compared with those of conventional methods, whilst the apparatus design reduces operator attention and error. Typical analysis times are 3 min for jams and soft-drinks, and 12 min for sausages.

Introduction

Sulphur dioxide (SO_2) is used extensively as a preservative in the food industry to prevent and control microbial spoilage.

It is used in its gaseous or liquid form, or dissolved in water to form sulphurous acid, or in the form of its acid or neutral salts—the sulphites, bisulphites and metabisulphites. In addition to its anti-microbial role, sulphur dioxide will also inhibit non-enzymic and enzymic browning and help in the preservative action of ascorbic acid; but adversely it causes cleavage of thiamine and may give rise to “off” flavours and odours, and cause bleaching in high concentrations.

Sulphur dioxide inhibits the growth of all three main groups of food spoilage micro-organisms—bacteria, yeasts and moulds—and lactic and acetic acid bacteria are particularly sensitive to the chemical. The undissociated free sulphur dioxide is generally regarded as being the inhibiting agent for most micro-organisms and the preservative is most effective in lower pH foods.

The maximum permitted levels of sulphur dioxide in foods are subject to periodic revisions and at present, in the United Kingdom, range from zero to several thousand parts per million (p.p.m.) or mg/kg, in different foods. Sulphur dioxide is perhaps most associated with soft-drinks, sausages and jams (as a residue), where it is permitted in maximum concentrations of 350, 450 and 100 p.p.m., respectively, and is often determined by either Shipton's modification of the Monier-Williams method¹ or by the Rapid Committee method². Both methods suffer from the disadvantages that they are lengthy and the design of the apparatus can lead to leakage and loss of sulphur dioxide.

It is the object of this paper to present details of a simple, rapid distillation method from which some of these disadvantages have been eliminated.

Experimental

MATERIALS

Sodium metabisulphite was used as the source of sulphur dioxide. This and all other reagents were obtained either from BDH Chemicals Ltd, Poole,

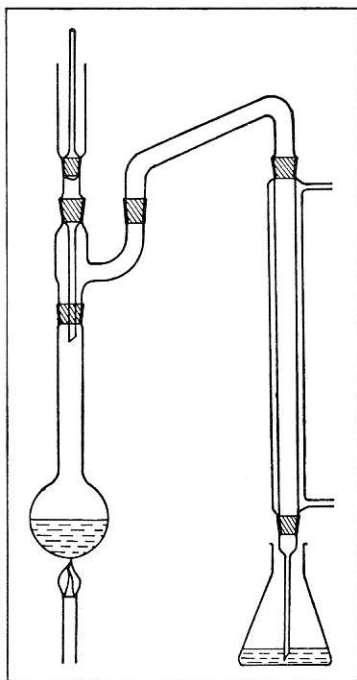


Fig. 1. The modified Lucke and Geidel apparatus.

Dorset, England or Sigma Chemical Co. Ltd, Poole, Dorset, England, and were analytical grade where possible.

Food samples were obtained through local suppliers.

EQUIPMENT

Shipton's apparatus and the Committee apparatus (Fig. 1) were used in the reference methods. A commercial, semi-automatic distillation unit normally used for nitrogen determination (Fig. 2) was used in the new method. This

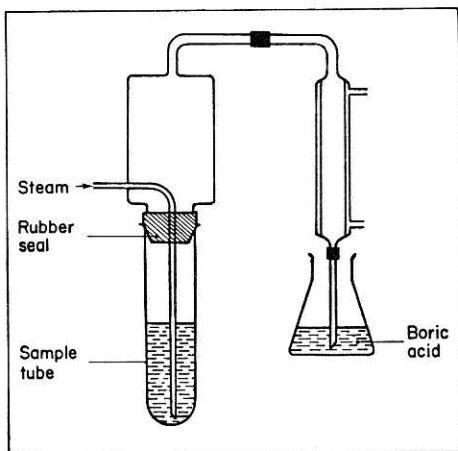


Fig. 2. The new Buchi apparatus.

was manufactured by Buchi Ltd, Switzerland, and involved direct steam injection of the sample to facilitate distillation of sulphur dioxide.

METHOD

Sulphur dioxide is determined for reference where required by using either the Shipton method or the Committee method as described in the literature.

The method using the Buchi unit is as follows. Place a measured excess of 0.05 M iodine and 50 cm³ distilled water into a 500 cm³ conical flask (receiver) and place under the collection outlet of the apparatus. Place 50 g of sample, 20 cm³ of concentrated hydrochloric acid and 50 cm³ of distilled water in the special Buchi tube and place the tube in the apparatus. Switch on and allow the sample to distil for the requisite time. The sulphur dioxide distilled over is collected in the iodine. After switching off, titrate the excess iodine in the receiver with standardised sodium thiosulphate using starch indicator, and calculate the amount of iodine reacted with sulphur dioxide and hence the sulphur dioxide content of the sample.

Sample size is fixed at 50 g as this represents a convenient amount to handle and facilitates calculation of results.

Results and Discussion

Sulphur dioxide recovery was found to be independent of the volume of water added to the sample, sample size and volume of excess iodine added to the receiver. However, to avoid waste of iodine where the expected concentration of sulphur dioxide is low, Table I gives recommended values for iodine volumes based on the expected sulphur dioxide content of the sample.

TABLE I
RECOMMENDED VOLUME OF IODINE (0.05 M) ADDED TO RECEIVER
IN SULPHUR DIOXIDE DETERMINATIONS

Maximum expected level of sulphur dioxide (p.p.m.)	Volume of 0.05 M iodine (ml)
100	2
200	4
300	5
400	7
500	8
1000	16
2000	32
3000	50

Recovery was found to be dependent on distillation time, and a series of experiments was carried out to determine the optimum time based on the recovery of known concentrations of sulphur dioxide from various systems.

(1). *Recovery of SO₂ from standard aqueous solutions of sodium metabisulphite.* The results are given in Table II for different concentrations equivalent to 100–2000 p.p.m. of sulphur dioxide in 50 cm³ of sample solution and different distillation times. In each case the percentage recovery and concentration of sulphur dioxide are given, and these figures represent the means of duplicate determinations.

In addition to the new method, the Shipton's and Committee methods were also examined to assess their efficiency of recovery with standard solutions, and these distillations were carried out for the recommended times of 40 and 13 min, respectively. The recoveries obtained with the Buchi apparatus compare favourably with those obtained by the standard methods and with standard solutions, optimum distillation time with the new method being about 3 min.

Whilst this study is important, it does not represent an authentic system where other food components might perhaps interfere with the determination. The work was therefore repeated, but adding known concentrations of sulphur dioxide to selected foods.

TABLE II
RECOVERY OF SULPHUR DIOXIDE FROM STANDARD AQUEOUS SOLUTIONS

Time of distillation (min.)	Sulphur dioxide concentration (p.p.m.)									
	100		200		500		1000		2000	
	Recovery (per cent.)	(p.p.m.)	Recovery (per cent.)	(p.p.m.)	Recovery (per cent.)	(p.p.m.)	Recovery (per cent.)	(p.p.m.)	Recovery (per cent.)	(p.p.m.)
Buchi method										
1.0	81.0	(81)	86.1	(172)	77.7	(389)	82.3	(823)	87.0	(1740)
1.5	90.6	(91)	91.7	(183)	91.1	(456)	91.3	(913)	90.6	(1812)
2.0	93.8	(94)	93.5	(187)	93.0	(465)	91.3	(913)	92.3	(1846)
3.0	95.0	(95)	95.4	(191)	95.4	(477)	92.5	(925)	95.5	(1910)
4.0	94.8	(95)	95.4	(191)	94.8	(474)	92.6	(926)	94.9	(1898)
5.0	94.8	(95)	95.1	(190)	96.0	(480)	91.6	(916)	96.0	(1920)
10.0	95.1	(95)	93.3	(187)	94.6	(473)	92.8	(928)	95.4	(1908)
Shipton's method										
40.0	96.0	(96)	98.4	(197)	90.4	(452)	96.6	(966)	96.1	(1917)
Committee method										
13.0	91.2	(91)	92.8	(186)	87.4	(437)	95.5	(955)	91.9	(1838)

(2). *Recovery of SO₂ standards from foods.* A concentrated orange drink and freshly prepared sausages were used as typical food samples. Neither contained any added sulphur dioxide. Different levels of sulphur dioxide (as an aqueous solution of sodium metabisulphite) were added to the soft-drink, and recovery of the preservative was determined using the Buchi apparatus, Shipton's method and the Committee method, in each case the method being operated for the recommended time. The results are given in Table III, each result being the mean of duplicate determinations.

For the sausage samples, only one concentration of sulphur dioxide was used (500 p.p.m.) and the results for its recovery are given in Table IV, where each result represents the mean of duplicate determinations. The results from one of the standard method (Shipton's) run for 40 min are also shown.

The results obtained using the new method with the orange juice show some anomalies. After 10 min distillation time with either 100 or 200 p.p.m. of SO₂ added, the percentage recovery exceeded the theoretical maximum, indicating distillation of iodine-reducing substances in the orange drink itself in

TABLE III
RECOVERY OF SULPHUR DIOXIDE FROM SOFT DRINKS

		Sulphur dioxide concentration (<i>p.p.m.</i>)							
		100		200		500		1000	
Time (<i>min</i>)		Recovery (<i>per cent.</i>)	(<i>p.p.m.</i>)	Recovery (<i>per cent.</i>)	(<i>p.p.m.</i>)	Recovery (<i>per cent.</i>)	(<i>p.p.m.</i>)	Recovery (<i>per cent.</i>)	(<i>p.p.m.</i>)
Buchi method									
1.0	74.5	(75)		79.0	(158)	80.0	(400)	80.6	(806)
1.5	92.5	(93)		92.0	(184)	90.8	(454)	91.2	(912)
2.0	96.6	(97)		94.5	(189)	95.3	(477)	91.7	(917)
3.0	97.8	(98)		97.0	(194)	97.9	(490)	93.5	(935)
4.0	96.8	(97)		97.5	(195)	97.7	(489)	93.5	(935)
5.0	100.5	(101)		97.0	(194)	97.5	(488)	93.9	(939)
10.0	115.5	(116)		103.5	(207)	98.5	(493)	93.4	(934)
Committee method									
13.0	94.4	(94)		93.5	(187)	95.0	(475)	90.7	(907)
Shipton's method									
40.0	96.8	(97)		95.0	(190)	95.2	(476)	96.4	(964)

TABLE IV
RECOVERY OF SULPHUR DIOXIDE FROM SAUSAGES

Sulphur dioxide recovered from 500 <i>p.p.m.</i> added initially (<i>per cent.</i>)		
Buchi method		
1	22.7	(114 <i>p.p.m.</i>)
3	46.0	(230 <i>p.p.m.</i>)
5	60.7	(304 <i>p.p.m.</i>)
8	66.7	(334 <i>p.p.m.</i>)
10	73.4	(367 <i>p.p.m.</i>)
12	80.0	(400 <i>p.p.m.</i>)
15	80.3	(402 <i>p.p.m.</i>)
20	81.9	(410 <i>p.p.m.</i>)
Shipton's method		
40	80.0	(400 <i>p.p.m.</i>)

addition to any sulphur dioxide present. At higher concentrations of sulphur dioxide, no such problems were evident, although this does not necessarily indicate that they did not occur. No excessive recoveries were obtained with the sausage samples using the Buchi apparatus. It was considered essential to carry out blank determinations on the food samples alone, with no sulphur dioxide added, and these results are given in Table V. Each result represents the mean of duplicate determinations.

No iodine-reducing substances were detected in the soft drink or sausage samples using the standard methods (in contrast to the original Committee report). Using the Buchi apparatus, however, appreciable concentrations were detected. For the orange drink, after 5 min of distillation, the 15 *p.p.m.* reducing substances (calculated as SO₂) represents about 4 per cent. of the maximum 350 *p.p.m.* permitted. For lower concentrations of added sulphur dioxide,

TABLE V
RECOVERY OF REDUCING SUBSTANCES IN FOOD SAMPLES

Distillation time (min)	Iodine-reducing substances (calculated as <i>p.p.m.</i> of sulphur dioxide)	
	Orange juice	Sausages
Buchi method		
1	2	11
2	4	ND*
3	5	16
4	8	ND*
5	15	16
10	28	38
12	ND*	40
15	ND*	50
Shipton's method		
40	0	0
Committee method		
13	0	ND*

* ND = Not determined.

TABLE VI
COMPARATIVE DETERMINATION OF SULPHUR DIOXIDE IN SAUSAGES

Sample number	Sulphur dioxide content (<i>p.p.m.</i>)	
	Buchi method (12 min)	Shipton's method (40 min)
1	279	296
2	223	215
3	370	367
4	298	282

No significant difference was established between the results obtained by the two methods.

TABLE VII
COMPARATIVE DETERMINATION OF SULPHUR DIOXIDE IN JAMS

Sample number	Sulphur dioxide content (<i>p.p.m.</i>)		
	Buchi method (3 min)	Shipton's method (40 min)	Committee method (13 min)
1	21	3	19
2	28	12	34
3	40	22	34

No significant difference was established between the results obtained by the Buchi and Committee methods. The Shipton's method gave significantly lower results ($P \leq 0.01$) than the Buchi method.

the error would, of course, be proportionately greater. After 3 min of distillation, the majority of the sulphur dioxide has been recovered with no excessive production of other iodine-reducing substances (about 5 p.p.m.). Three minutes therefore represents the optimum distillation time for this method.

For the sausage samples, there is a good correlation between the results obtained with the new method after 12 min and those obtained with Shipton's method after 40 min. Reducing substances in the sausages (other than SO_2) after 12 min of distillation, amount to about 40 p.p.m. as SO_2 , representing an amount equivalent to just less than 10 per cent. of the total permitted sulphur dioxide in sausages.

Figure 3 shows the results for sulphur dioxide determination in soft drinks

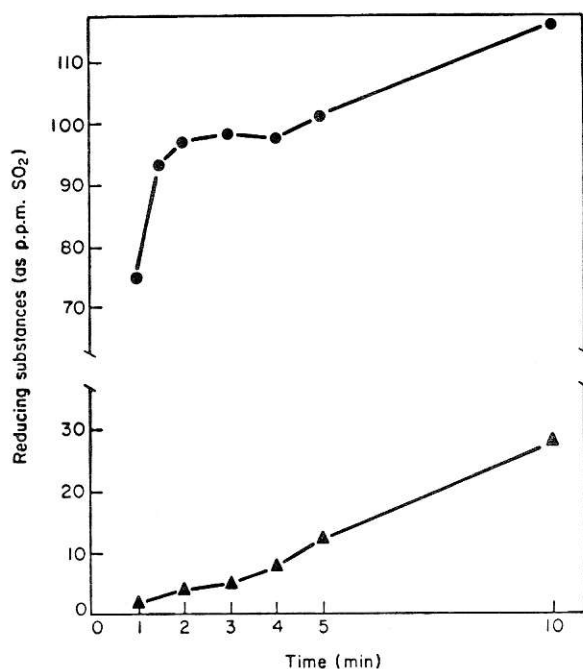


Fig. 3. Sulphur dioxide determination in soft drinks with and without added SO_2 . ●—●, Orange drink with 100 p.p.m. SO_2 ; ▲—▲, orange drink with no added SO_2 .

with and without added sulphur dioxide. It is interesting to note the shapes of the curves and the fact that an increase in iodine-reducing substances occurs at the point when most of the sulphur dioxide has been evolved. Thus it appears that, providing distillation is carried out for the correct time, these iodine-reducing substances will not significantly affect the results for sulphur dioxide estimation.

The very low recovery of sulphur dioxide from sausages, about 80 per cent., was not unexpected, as sausages are known to lose sulphur dioxide rapidly after addition of the preservative, especially in unsealed packs.

(3). *Analysis of food samples for sulphur dioxide.* Commercial samples of sausages, jams and soft drinks were analysed for sulphur dioxide content using the new method and the standard methods, and the results were subjected to statistical analysis. The results are given in Tables VI, VII and VIII, and each result is the mean of duplicate determinations.

The results indicate that the new method, using the Buchi apparatus, is directly comparable with Shipton's method for analysis of sausages for sulphur dioxide, and with the Committee method for analysis of soft drinks and jam. The method has the advantages of a short distillation time and improved design to eliminate leakage of sulphur dioxide during the determination. Whilst Shipton's method was used in the analysis of soft drinks and jam samples, this was only for the purposes of comparison, the Committee method being preferred for these samples.

TABLE VIII
COMPARATIVE DETERMINATION OF SULPHUR DIOXIDE IN SOFT DRINKS

Sample number	Sulphur dioxide content (<i>p.p.m.</i>)		
	Buchi Method (3 min)	Shipton's method (40 min)	Committee method (13 min)
1	336	304	329
2	314	298	319
3	327	325	322
4	321	210	320

No significant difference was established between the results obtained by the three methods.

Conclusions

Use of the Buchi distillation apparatus for sulphur dioxide determination in foods results in reduced analytical time and the apparatus design should lead to reduced operator error. Although other iodine-reducing substances in addition to sulphur dioxide are produced by the new method if the distillation time is prolonged, the results obtained for food samples compare favourably with those using conventional methods if the recommended procedures are followed.

References

1. Shipton, J., *Food Preserv. Q.*, 1954, **14**, 54.
2. Knapp, A. W., and Campbell, L. E. *Analyst, Lond.*, 1928, **53**, 118.