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THE DETERMINATION OF SULPHUR DIOXIDE IN FOODS

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PREFATORY NOTE BY THE CHIEF MEDICAL OFFICER.

To the Right Hon. NEVILLE CHAMBERLAIN, M.P.,
Minister of Health.

SIR,

I beg to present the following report by Dr. G. W. Monier-Williams, who is in charge of the Chemical Laboratory of the Ministry, on the determination of sulphur dioxide in foods. Under the Public Health (Preservatives, etc., in Food) Regulations, the main provisions of which came into force on January 1st, 1927, the use of sulphur dioxide and benzoic acid as preservatives is permitted in certain scheduled foods, provided that the amount present does not exceed certain specified limits. The exact analytical determination of the amount of preservative present in a sample of food is therefore of prime importance in connection with the administration of the Regulations, and it has been considered that a comprehensive review of the literature, such as Dr. Monier-Williams has prepared, will be of assistance to Public Analysts in enabling them to select those methods best suited to the class of foodstuff under examination.

In Report No. 39 of this series, recently published, the methods available for the determination of benzoic acid have been reviewed, and in the present report Dr. Monier-Williams deals with sulphur dioxide on similar lines. The work already carried out on this analytical problem is fully discussed, and a detailed description is given of a practical method, recently worked out in the Ministry's laboratory.

The preparation and publication of this report has not been undertaken with the view of prescribing or imposing any special methods of analysis or testing under the Regulations, but of providing information which it is hoped may be useful and timely to Public Analysts, chemical advisers of industrial concerns, and others charged with duties or responsibilities in this matter.

I have the honour to be,
Sir,
Your obedient servant,
GEORGE NEWMAN.

May, 1927.

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THE DETERMINATION OF SULPHUR DIOXIDE IN FOODS.

Introduction.

Under the Public Health (Preservatives, etc., in Food) Regulations, 1925, the main provisions of which take effect from January 1st, 1927, the only preservatives permitted to be used in foods and drinks are sulphur dioxide and benzoic acid. The first Schedule to the Regulations specifies the articles of food to which preservative may be added and the maximum quantity allowable.

For many reasons it has not been considered desirable that anything in the nature of a definite technique should be laid down for the determination of the permitted preservatives. It is left to the analyst to adopt those methods which experience has shewn to be the most reliable for the purpose. In view, however, of the fact that much of the published work on this subject is scattered in various journals, not always readily accessible, it is considered that a review of the existing literature, with references to papers and abstracts, will be of value to Public Analysts and others who may have to undertake this work.

The determination of benzoic acid has already been fully dealt with in Report No. 39 of this series, and the present Report deals on similar lines with sulphur dioxide. The term "sulphurous acid" is used throughout the Report to designate sulphur dioxide in solution, the latter term being used for the gas itself, or in cases where there is an actual or implied reference to the terms of the Regulations.

In general, the determination of the total amount of sulphur dioxide in a food, in the quantities in which it is usually present as a preservative, does not present the same difficulties as are met with in the case of benzoic acid. The method originally given by Haas in 1882 has been adopted, with unimportant modifications, by almost every worker, and found to be satisfactory. Much of the work carried out since the publication of Haas' paper has been concerned with the difficult problem of differentiating between "free" and "combined" sulphurous acid, it having been stated by many authorities that the acid, when combined with aldehydic or ketonic groups, is much less active physiologically than when in the free state. In the present Regulations no distinction has been made between free and combined sulphur dioxide, so that the problem of its determination is greatly simplified. It is chiefly in the case of foods containing

small amounts of sulphur dioxide, of the order of 5 to 50 parts per million, that difficulties may arise, owing to uncertainty as to whether the analytical figures really represent sulphur dioxide or are due in some measure to volatile sulphur compounds of a different character, originating from the food itself. A further problem, which, however, is chiefly administrative, is the progressive and variable loss of sulphur dioxide which occurs through oxidation and volatilization, a loss which may in many cases lead to discrepancies in the results obtained on the same sample by different analysts.

The usual method employed, which depends on distillation in a current of carbon dioxide into bromine or iodine solution followed by gravimetric determination as barium sulphate, is somewhat tedious, and many analysts have tried to find a quicker and equally accurate method. The work already done in this direction is reviewed in this Report, and a method is suggested (p. 41) which, while obviating to a great extent the errors due to volatile sulphur compounds, permits of direct titration of the distillate.

1. Free and combined sulphurous acid.

As already mentioned, the Schedule to the Regulations specifies the total amount of sulphur dioxide permissible in various foods, and makes no distinction between "free" and "combined" sulphurous acid. It is, however, important that the nature and extent of the combination which occurs between sulphurous acid and certain constituents of food should be appreciated, since the presence of the comparatively stable "hydroxy-sulphonic acids" of aldehydes, sugars, &c., may, unless the necessary precautions be taken, affect to a considerable extent the determination of total sulphur dioxide in the food.

A. *Nature of the compounds formed with aldehydes and ketones.*

The fact that sulphurous acid combines with the acetaldehyde present in wine, to form a compound which cannot be titrated direct with iodine, was first pointed out by Ripper (1892). He found that direct titration of white wines with iodine shewed only a small proportion of the sulphur dioxide known to be present, but that if the aldehyde-sulphurous acid compound was first decomposed by treatment with alkali, and the liquid then acidified and titrated quickly with iodine, correct results were obtained. Rocques (1898) came to the conclusion that sulphurous acid could also enter into combination with the sugars in wine, but that this reaction took place more slowly and incompletely than that with acetaldehyde, which was practically quantitative. He also pointed out that combined sulphurous acid is very resistant to atmospheric oxidation.

According to Rocques the greater part of the sulphurous acid in Sauterne wines is combined with glucose and fructose, the amount of acetaldehyde present being insufficient to account for more than a small proportion of the combined acid. On the other hand Kerp (1904, 2) was of opinion that it is rare to find wines in which sulphurous acid is in excess of the aldehyde present, and is free to enter into combination with sugars. Acetaldehyde, if present, removes sulphurous acid from combination with glucose. Possibly there is a considerable difference in this respect between sweet and dry wines. Jalowetz (1902) concluded that about 30 per cent. of the sulphurous acid usually present in beer was combined with aldehyde, and the occurrence of combined sulphurous acid in beer was confirmed later by Baker and Day (1911), who, however, attributed it to the presence of sugars and dextrins rather than acetaldehyde.

In 1902 Beythien and Bohrisch discovered that practically all the dried fruit imported into Germany from America was heavily sulphured. This observation was followed by the publication of numerous papers in which the admissibility of sulphur dioxide as a preservative was actively debated. The discussion centred chiefly on the question as to the amounts of free and combined sulphurous acid in the fruit, and their relative physiological significance. Widely different figures were obtained according to the methods of analysis employed. Beythien and Bohrisch (1902) by distilling the fruit in a current of carbon dioxide, with and without the addition of phosphoric acid, obtained results which indicated that by far the greater part of the sulphurous acid was in the free state. Farnsteiner (1902) and Fresenius and Grünhut (1903), using Ripper's direct titration method (p. 12), found that practically all of it was in the combined state. Differences of opinion also arose as to the rate at which sulphur dioxide disappears from dried fruit when stored or when exposed to the air, and as to the proportion retained when the fruit is made into "compôte."

In 1904 the whole question was subjected to a thorough investigation by Kerp, Schmidt and others in the laboratories of the German Public Health Department, and the results, both chemical and physiological, were published in a long series of papers in the "Arbeiten aus dem Kaiserlichen Gesundheitsamte." References to these papers, omitting those of purely physiological interest, are given at the end of this Report.

Kerp started by proving definitely the existence of acetaldehyde in wine by converting it, through the agency of an alkaline solution of diazo-benzene, into benzol-azo-formazyl, a reaction discovered by Bamberger and von Pechmann. He then prepared pure specimens of the sodium bisulphite compounds of formaldehyde, acetaldehyde, acetone, benzaldehyde, and glucose, and studied their stability, dissociation in solution, and general properties under various conditions. The relative degree of molecular dissociation of the sodium salts of these "hydroxy-sulphonic acids" is shewn in the following table.

Compound.	Formula.	Percentage of total salt present dissociated.		
		$\frac{N}{1}$ solution	$\frac{N}{10}$ solution	$\frac{N}{30}$ solution
Formaldehyde sodium bisulphite	$H.CH(OH)SO_3Na$.	0·034	0·097	0·155
Acetaldehyde sodium bisulphite	$CH_3·CH(OH)SO_3Na$.	0·17	0·45	0·71
Benzaldehyde sodium bisulphite	$C_6H_5·CH(OH)SO_3Na$.	2·07	2·98	4·90
Acetone sodium bisulphite	$(CH_3)_2C(OH)SO_3Na$.	5·73	14·58	23·67
Glucose sodium bisulphite	$C_5H_{11}O_5·CH(OH)SO_3Na$	42·32	74·61	81·89

Thus it appears that while solutions of acetaldehyde sodium bisulphite contain hardly any free bisulphite titratable with iodine, glucose sodium bisulphite is highly dissociated, especially in dilute solutions.

B. *Dissociation of combined sulphurous acid.*

When neutral or acid solutions of these compounds are titrated with iodine, it is only the free sulphurous acid present which reacts with the iodine. The equilibrium is, however, upset by the oxidation and removal of the free sulphurous acid and further dissociation of the aldehyde compound takes place. Thus, if the solution be titrated with iodine in the presence of starch until a blue colour is obtained, and the liquid allowed to stand for a short time, it becomes colourless and requires a further quantity of iodine to reproduce the blue colour. This progressive increase in the amount of iodine required continues until no more combined sulphurous acid remains in solution. The attainment of the final end-point under these conditions is, however, a very slow process, lasting several days.

Normal sodium sulphite, Na_2SO_3, does not combine with aldehydes and ketones and the hydroxy-sulphonic acids are immediately decomposed on treatment with alkali. Upon this depends Ripper's method of determining total sulphur dioxide in wine by direct iodine titration (p. 12).

Sodium bisulphite, when combined with aldehyde, is extremely resistant to atmospheric oxidation. Kerp (1904, 3) found that when a current of air was drawn through a 0·03 per cent. ($\frac{N}{500}$) solution of acetaldehyde sodium bisulphite for 14 hours, 99·91 per cent. of the compound remained unoxidized. In a similar experiment with glucose sodium bisulphite 79·4 per cent. remained unoxidized.

The extent to which these compounds and the free hydroxy-sulphonic acids are decomposed in solution into free aldehyde or sugar and sodium bisulphite or free sulphurous acid follows in the main the ordinary laws of dissociation and mass action. The amount of dissociation is increased by dilution and by a rise of temperature, and is diminished in presence of an excess of either of the reacting substances. The effect of adding acid to the solution, with production of the free hydroxy-sulphonic acids, is to increase the actual extent of dissociation when equilibrium is reached, although the immediate effect is to reduce the rate at which dissociation takes place. This is shewn by the following figures which Kerp and Baur (1907, 1) obtained by the iodine titration of (i) 1·48 grm. of acetaldehyde sodium bisulphite in 300 c.c. of water ($\frac{N}{30}$ solution) and (ii) the same quantity of aldehyde bisulphite in 300 c.c. of $\frac{N}{30}$ hydrochloric acid, the solutions being allowed to stand for different lengths of time before titration :—

Aqueous solution.		Acid solution.	
Time.	Per cent. of salt dissociated.	Time.	Per cent. of salt dissociated.
4 minutes	0·59	4 minutes	0·095
30 ,,	0·87	20 ,,	0·244
24 hours	0·90	20 hours	1·43

The extent of dissociation of the acetaldehyde compound becomes greater on increasing the degree of acidity and is also very sensitive to increase of temperature. At 37·5° C. the amount dissociated in $\frac{N}{30}$ hydrochloric acid solution is more than double that at 20° C. Although, therefore, the amount of free sulphurous acid or bisulphite present in neutral or slightly acid liquids containing much aldehyde is almost negligible, yet by strongly acidifying the liquid and raising the temperature sufficiently, the whole of the aldehyde compound is eventually decomposed and the sulphur dioxide carried over into the distillate. The greater the dilution the more readily will this decomposition take place.

In the case of glucose sulphurous acid the degree of dissociation in acid solution is not much greater than in neutral solution. In $\frac{N}{10}$ solutions, both acid and neutral, the proportion dissociated is approximately 74 per cent. This is not appreciably affected by rise of temperature. On the other hand, the rate of dissociation is greatly delayed by the presence of acid. Kerp and Baur (1907, 3) found that a $\frac{N}{10}$ solution of sodium glucose bisulphite in $\frac{N}{30}$ hydrochloric acid had not attained complete equilibrium in 120 hours, whereas in neutral solution equilibrium was complete in 48 hours. At the end of the first 15 minutes the extent of dissociation in neutral solution was 17·6 per cent., but in acid solution only 1·4 per cent. Farnsteiner and others have found that in materials such as dried fruits, containing much glucose and comparatively little water, the combined sulphurous acid is very insensitive to the removal of free sulphur dioxide by atmospheric oxidation, and that after an initial rapid loss of sulphur dioxide, the rate of oxidation of the remainder is slow (p. 37). The inhibiting effect of acid on this decomposition may have some significance in the determination of total sulphur dioxide by Haas' method in dried fruits, molasses and carbohydrate foods generally, although Kerp and Baur's observations did not extend to the behaviour of glucose sulphurous acid when boiled in acid solution.

C. *Rate of combination of sulphurous acid with acetaldehyde and glucose.*

When acetaldehyde and sulphurous acid are brought together in aqueous solution they rapidly combine. In $\frac{N}{2}$ solutions 91 per cent. of the reactants have combined in 2 minutes. In $\frac{N}{100}$ solutions the amount of combination in 2 minutes is 52 per cent. and in 30 minutes 87 per cent. The more dilute the solution the slower and the less complete is the reaction. In the case of glucose and sulphurous acid the rate of combination is much slower and not nearly so complete. Presumably, although Kerp does not give definite figures on the point, the presence of excess of acid exercises the same delaying effect on the union of sulphurous acid and acetaldehyde as it does upon the dissociation of the compound when formed. Otherwise, on acidification of white wine after alkali treatment as in Ripper's titration method, recombination would take place so quickly as to introduce a much greater error than is actually the case (p. 13). Farnsteiner (1904) found that the union of sulphurous acid with glucose takes a long time to arrive at a state of equilibrium in presence of much acid, but that equilibrium is reached much more rapidly if the acidity be kept low.

The influence of a large excess of one of the reactants is well shewn in Farnsteiner's experiments on glucose. In 100 c.c. of a 40 per cent. solution of glucose containing 113 mgm. of total sulphur dioxide, 82 mgm. of the latter had combined with glucose after a period of four months.

D. *Union of sulphur dioxide with various constituents of foods.*

The hydroxy-sulphonic acids of acetaldehyde and glucose are typical of a number of compounds of this nature. Of the sugars, arabinose has the strongest affinity for sulphurous acid (Farnsteiner, 1904) followed by the hexoses mannose, galactose and glucose, the disaccharides maltose and lactose, and the trisaccharide raffinose. The last named has very little affinity for sulphurous acid, as has also the ketone sugar fructose. Saccharose, if free from traces of invert sugar, shews no tendency at all to combine with sulphurous acid.

The optical activity of sugars is appreciably affected in the presence of sulphurous acid. According to Kerp and Baur (1907, 2) sodium bisulphite combines with glucose to give two optically active stereo-isomers. The solid salt, which can be prepared in a pure state, is laevo-rotatory, and on solution in water is partially changed into the other isomer, the initial laevo-rotation becoming a slight dextro-rotation. The rotation then gradually increases during the partial dissociation of the salt into glucose and sodium bisulphite until equilibrium is reached. The possible effect of sulphur dioxide on the polarimetric determination of sugars appears to have received very little attention.

Sulphurous acid is found in the combined state in foods containing no aldehydes or sugars, and appears to be able to combine with dextrins (Baker and Day, 1912), and with cellulose and proteins (Schmidt, 1904). It does not combine with citric, malic or tannic acids, pure glycerine (Farnsteiner, 1904) or alcohol (Ripper, 1892), but according to Farnsteiner some commercial "pure" glycerines can combine with considerable amounts, as can also commercial alcohol (Baker and Day, 1912), no doubt owing to the presence of traces of aldehyde. With commercial peptone slight combination can take place (Farnsteiner, 1904). Pectins do not exhibit any affinity for sulphurous acid, but if apples are allowed to rot, substances are formed by oxidation which can combine with considerable amounts of sulphurous acid (Warcollier and Le Moal, 1922). These are possibly of aldehydic or ketonic nature.

The compounds formed by sodium bisulphite with unsaturated aldehydes are of interest in that the SO_3Na group may be attached either to the aldehyde group or at the point of the double bond, or at both positions simultaneously, giving rise to disulphonates. Thus citronellal may form the following three compounds (Kerp and Wöhler 1909, 1).

(i) $(CH_3)_2\cdot C:CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH(OH).\ SO_3Na.$
(ii) $(CH_3)_2\cdot C(SO_3Na).\ CH_2\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CHO.$
(iii) $(CH_3)_2\cdot C(SO_3Na)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH(OH).\ SO_3Na.$

The first of these compounds is partially dissociated in dilute solution to citronellal and sodium bisulphite. The latter then combines with unchanged citronellal sodium bisulphite to give the third compound, which is only slightly dissociated in solution. The second compound is very stable in solution and is not appreciably dissociated. No sulphur dioxide could be obtained on heating it with dilute mineral acids.

Furfural sulphurous acid is contained in the waste liquor resulting from the manufacture of cellulose from wood. Although an unsaturated compound, it does not combine with a second molecule of sulphurous acid at the point of the double bond. In the extent to which it dissociates in solution it occupies a position between the corresponding benzaldehyde and acetone compounds (p. 4). Sulphite pulp liquor also contains lignin sulphonic acids, in which part of the sulphur dioxide is firmly bound and is given off only with extreme slowness on distillation with strong acids (Stutzer, 1910).

In the case of gelatine there appears to be some doubt as to whether the sulphurous acid is in the combined condition. According to Buttenberg and Stüber (1906) and Padé (1908) it is all combined, and no appreciable quantity of sulphur dioxide is evolved on heating gelatine solutions unless they are strongly acidified. Lange (1909) found that pure gelatine when treated with sulphur dioxide gave up the whole of it on subsequent exposure to air but that commercial gelatines did not, neither was the sulphur dioxide oxidized on exposure. Commercial gelatine does not give up all its sulphur dioxide on boiling with water alone, and the presence of acid is necessary, but at the same time the sulphurous acid in the solution can all be titrated direct with iodine, which indicates that it is in the free state. Lange thinks that it may possibly be present either in the form of an alkali sulphite or else absorbed by the protein. Gutbier, Sauer and Brintzinger (1921) also found that the sulphur dioxide in commercial gelatine could be titrated direct with iodine.

According to Korczynski and Glebocka (1920), sulphur dioxide forms unstable addition compounds with primary, secondary and tertiary amines, and with certain alkaloids. These compounds lose sulphur dioxide when kept in a desiccator.

Incidentally it may be noted that sulphurous acid, when combined with aldehydes or sugars, exercises practically no antiseptic action (Hailer, 1911, Müller-Thurgau, 1914, Laborde, 1916).

E. *Determination of free and combined sulphurous acid.*

It is evident from the above that determinations of free and combined sulphurous acid in foods are not likely to give reliable results unless the conditions under which the analysis is conducted are such that no appreciable alteration of equilibrium can occur during the determination. Even acetaldehyde sodium bisulphite decomposes to some extent when distilled in neutral solution (Schmidt, 1904), and in presence of organic fruit acids the decomposition is almost complete. Mensio (1907), in criticising the Italian official method of determining free and combined sulphur dioxide in wine, points out that aldehyde sodium bisulphite gives up 30–35 per cent. of its sulphur dioxide on boiling with water alone, and 90–95 per cent. when boiled with wine. Distillation of a food with water alone, therefore, as carried out by Beythien and Bohrisch, gives no indication of the amount of free sulphurous acid actually present.

With liquids such as wine, direct titration with iodine solution gives fairly accurate results for free sulphurous acid, since during the short time taken for the titration, and the slight change in the volume of the liquid, the alteration of equilibrium is hardly appreciable. Details of Ripper's titration method for free and total sulphurous acid in wines are given on page 12. According to several authors accurate results may be obtained by first oxidizing the free sulphurous acid present in wine by the addition of a very slight excess of iodine. The free iodine is then removed with sodium arsenite solution, and the combined sulphurous acid determined by the usual distillation method with phosphoric acid. A second distillation of a portion of the original sample without the addition of iodine gives the total sulphur dioxide, from which the amount present in the free state can be calculated. In the case of red wines the quantity of iodine to be added is ascertained by a preliminary titration using starch as an outside indicator (Amberger, 1924).

2. Tests for the presence of sulphur dioxide.

Wartha in 1880 suggested the use of silver nitrate as a test for sulphur dioxide in the distillate from foods. He distilled off 2 c.c. into a test-tube and added a few drops of neutral silver nitrate. In the presence of sulphurous acid a white opalescence or precipitate of silver sulphite is obtained, which is distinguished from silver chloride by its solubility in hot dilute nitric acid. According to Haas (1882), this test is not specific for sulphurous acid unless a fairly heavy precipitate is obtained. Hackl (1923) gives the limit of sensitiveness as 0·1 mgm. of sulphur dioxide in 10 c.c.

The best known test for sulphur dioxide, and the one that is official in Germany for meat products, depends on the blue colour given with potassium iodate-starch paper. According to Schumacher and Feder (1905, 1), the reaction between sulphur dioxide and potassium iodate is as follows :—

$$2\ KIO_3 + 5SO_2 + 4H_2O = K_2SO_4 + 4H_2SO_4 + 2I.$$

Although the presence of moisture is thus necessary to the reaction, the sensitiveness of the test is impaired if the paper be allowed to get wet (Lange, 1909). The test is usually carried out on 1 to 50 grms. of the food, according to the amount of sulphur dioxide present, with a little dilute sulphuric or phosphoric acid, in a small flask closed by a cork to which the test paper is attached. If the reaction is not given at once, the mixture may be slightly warmed on the steam-bath. Under these conditions Schmidt (1904) obtained a blue colour in 2 minutes with 1 grm. of dried apricots containing 1·5 mgm. of sulphur dioxide, but the test was uncertain with 10 grm. of prunes containing the same quantity of sulphur dioxide. For less highly sulphured foods Schmidt recommends that 50 grm. be taken. It would seem, therefore, that this test is not very sensitive. Under the most favourable circumstances it will only detect quantities of the order of 1 mgm. of sulphur dioxide. Lange claims to have increased its sensitiveness by placing the paper at the upper end of a glass tube 20 cm. in length, which serves as a reflux condenser and thus permits of the flask contents being strongly heated without the paper becoming wet. He states that in this way 0·2 mgm. of sulphur dioxide can be detected.

A rapid method of applying this test to meat for rough sorting purposes is given by Meyer (1903). A small piece of the meat is placed on potassium iodate-starch paper and moistened with dilute sulphuric acid. In presence of sulphur dioxide a deep blue ring appears on the paper round the piece of meat. Unsulphured meat gives only a faint blue colour at the point of contact of the meat with the paper. Obviously, however, the test can be relied on only for negative indications. A positive result must be confirmed in other ways.

A more delicate test than potassium iodate and starch is the decolorization by sulphur dioxide of a very dilute starch-iodine solution. This was used by Schmidt (1904), and has been greatly improved by Parkes (1921, 1926). Parkes uses a small conical flask closed by a rubber stopper in which is fitted a small thistle tube containing two or three drops of 0·01N iodine solution, and a small quantity of barium chloride. Apparently the starch is omitted. The flask contains 10 grm. of the food mixed with 10 c.c. of water and the same quantity of dilute hydrochloric acid. On adding a few pieces of marble and immediately replacing the stopper carrying the thistle funnel, the escaping carbon dioxide bubbles through the iodine solution. After the evolution of carbon dioxide has moderated, the contents of the flask are heated carefully to boiling. The presence of sulphur dioxide in the food is shewn by the decolorization of the iodine and the formation of a white opalescence or precipitate of barium sulphate. By filtering off the barium sulphate on black paper and comparing it with standards the process can be made approximately quantitative. The limit of sensitiveness of the test as originally described is 0·25 mgm. of sulphur dioxide in 10 grm. of the sample, and the later modification as given above is possibly even more delicate. Decolorization of the iodine in this test is not necessarily due to sulphur dioxide. It may be caused by other volatile substances, but according to Parkes the formation of barium sulphate affords a definite indication of the presence of sulphur dioxide. In the case of foods liable to give off traces of hydrogen sulphide a small quantity of copper sulphate is added to the flask. It should be borne in mind, however, that some foods, notably onions, yield traces of volatile organic sulphur compounds which may be oxidized to sulphuric acid by iodine (p. 32).

According to Schmidt (1904) freshly prepared potassium ferricyanide paper can be used as a test for sulphur dioxide. This paper, when touched with a drop of a solution of a ferric salt, gives a brown colour, but after reduction of the ferricyanide to ferrocyanide by sulphur dioxide, the ferric salt gives a blue colour. The test is capable of detecting 1·5 mgm. of sulphur dioxide in 1 grm. of dried fruit.

An ingenious test for sulphur dioxide in wine is given by Mathieu (1910, 2). To 20 c.c. of wine is added 1 grm. of a mixture consisting of 4 grm. of crystallized barium chloride, 20 grm. of citric acid, and 100 grm. of barium sulphate. This results in the precipitation of all the sulphates in the wine. The barium sulphate serves apparently as a nucleus for the precipitation of traces of sulphates. The clear filtrate is treated with iodine solution, and if free sulphurous acid be present, the iodine will be decolorized and barium sulphate precipitated. If the sulphurous acid be in the combined state it is necessary to warm the liquid to obtain this reaction. It is claimed that this test will indicate 2 mgm. of sulphur dioxide in one litre of wine. If this be so, it is a remarkably delicate test, but an element of doubt is introduced in the case of foods, such as onions, containing soluble sulphur compounds oxidizable by iodine to sulphuric acid. It would perhaps be preferable to add hydrogen peroxide to the filtrate in place of iodine (cf. p. 33).

Another test frequently used depends on the reduction of sulphur dioxide to hydrogen sulphide by zinc and hydrochloric acid, and recognition of the hydrogen sulphide by its action on lead acetate paper. This test is, however, of value only for foods which contain no sulphur compounds capable of being reduced to hydrogen sulphide by zinc and acid, a condition which is but rarely fulfilled. Strauss (1905) states that the test is quite unreliable with products containing onions, and Kühn and Rühle (1910), make the same observation in respect of foods flavoured with garlic. According to Reinke (1910), unsulphured malt gives a positive reaction in this test, although giving no sulphur dioxide on distillation. On the other hand, the test has been found valuable in the case of pure materials containing no sulphur compounds, such as highly refined sugar, and has been developed by J. S. Mann into a quantitative process (Ogilvie, 1926). In this method five grm. of the sample are dissolved in water and introduced into a 400 c.c. flask containing 50 grm. of pure zinc and 100 c.c. of dilute (1 in 2) hydrochloric acid. The gas evolved is made to pass through a disc of filter paper impregnated with lead acetate solution, and the depth of the brown colour produced is compared with standards. The method is stated to be extremely sensitive and accurate for pure sugars, but the number of foods to which it could be applied would appear to be strictly limited to those containing no organic sulphur of any kind. Full details of the method are given in Ogilvie's paper.

3. Direct titration with iodine: Ripper's method.

The determination of sulphur dioxide in white wines by direct titration with iodine was worked out by Ripper (1892), and recommended by him as being much quicker and easier than Haas' distillation method. The details, as given by Ripper, are as follows :—

Free sulphurous acid.—A flask of 100 c.c. capacity is filled with carbon dioxide, and 50 c.c. of wine are introduced, followed by 5 c.c. of dilute sulphuric acid (1 : 3), and a few drops of starch solution. The wine is then titrated rapidly with $\frac{N}{50}$ iodine solution till the blue colour persists for an appreciable time, or as Ripper expresses it, after four or five "umschwenken." It is not permissible to titrate back with thiosulphate solution if the end-point be overshot.

Total sulphurous acid.—Twenty-five c.c. of $\frac{N}{1}$ potassium hydroxide solution are introduced into a 200 c.c. flask. Fifty c.c. of wine are then pipetted in, the point of the pipette being under the surface of the liquid, and the mixture allowed to stand for 10–15 minutes. Ten c.c. of dilute sulphuric acid (1 : 3) are then added and a few drops of starch solution, and the liquid titrated rapidly with iodine as above. One c.c. of $\frac{N}{50}$ iodine solution = 0·0006 grm. of sulphur dioxide.

Ripper gives the following results to shew the accuracy of the method, the figures being compared with those obtained by Haas' method on the same samples :—

Sulphur dioxide by titration after treatment with KOH, grm. per 100 c.c.	Sulphur dioxide by Haas' distillation method, grm. per 100 c.c.	Difference, grm. per 100 c.c.
0·00426	0·00420	+ 0·00006
0·00114	0·00114	± 0
0·01435	0·01393	+ 0·00042
0·01048	0·01101	– 0·00053
0·00729	0·00769	– 0·00040
0·00411	0·00398	+ 0·00013
0·00617	0·00617	± 0
0·00086	0·00079	+ 0·00007
0·01514	0·01488	+ 0·00026
0·00903	0·00943	– 0·00040

Ripper's method, as applied to white wines, would thus appear to be capable of yielding extremely accurate results, but it is highly questionable whether this apparent accuracy may not be due in great measure to a fortuitous combination of errors.

A. *Causes of high results.*

The most obvious of these possible errors, leading to high results, is the action of iodine on substances other than sulphur dioxide. It is well known that many constituents of foods are more or less easily oxidized by iodine and, according to Farnsteiner, this takes place more readily after treatment with alkali and subsequent acidification. He puts the error from this cause as high as 10 mgm. of sulphur dioxide per 100 c.c. in some cases. The relative error is naturally greater when small amounts of sulphur dioxide are in question (Schmidt, 1904). It may be minimized by rapid titration and by taking as the end-point the first appreciable persistence of the blue colour with starch. Traces of ferrous salts, if present, are liable to introduce a high positive error (Farnsteiner, 1902).

This action of iodine on organic substances no doubt accounts for the fact that most workers who have used Ripper's method have obtained high results. According to Barth (1894) it always shews from 1 to 4 mgm. too much sulphur dioxide per 100 c.c. of wine and Mathieu (1910, 1) suggests that the positive error to be allowed for is 2 mgm. per 100 c.c. De Sornay (1911) while recommending the method for routine control of cane sugar products, states that the results shew from 1 to 3 mgm. too much sulphur dioxide in 50 grm. of syrup (20 to 60 parts per million) as compared with Haas' method. Ogilvie (1926) says that Ripper's method is satisfactory for the routine examination of cane syrups but not for beet syrups. Farnsteiner (1904) found that it gave accurate results in pure cane sugar solutions and that with lemon juice cordials the results were in fairly close agreement with those given by Haas' method. Baker and Day (1911) obtained somewhat high results for beer, but state that in general the agreement between the two methods is fairly good. In pure gelatine, sulphur dioxide can be accurately determined by direct iodine titration (Lange, 1909), but commercial gelatines contain substances which are acted upon by iodine and the end-point is indefinite. Gutbier, Sauer, and Brintzinger (1921) take 10 grm. of gelatine and dissolve it in distilled water in a 250 c.c. flask after first allowing it to soak in the water for 12 to 24 hours. Twenty-five c.c. of the solution, corresponding to 1 grm. of gelatine, are diluted to 50 c.c. and titrated with standard iodine solution and starch in a porcelain dish with stirring. The authors state that this method gives fairly accurate results for bone gelatine but is inadmissible for glues obtained from leather waste.

B. *Causes of low results.*

There are several factors on the other hand which may tend to produce low results in Ripper's method. Kerp (1904, 2) points out that if acetaldehyde or formaldehyde be present, rapid recombination of these with sulphurous acid will take place on acidification of the solution prior to titration, and that this may result in an under-estimation of sulphur dioxide present by as much as 10 per cent. even in $\frac{N}{1,000}$ solution. In sugar solutions recombination would not occur to an appreciable extent owing to the slowness with which glucose reacts with sulphurous acid. Low results may also be obtained in presence of substances which can liberate iodine from hydrogen iodide. This may occur in foods containing traces of iron or manganese oxides, caramel, and tannin. Farnsteiner (1904) states that tannin develops oxidizing properties when its solutions are treated with alkali and subsequently acidified with mineral acids. The use of organic acids for acidification renders the end-point indefinite.

In applying the iodine titration method to aqueous extracts from solid foods, such as dried fruits, it is not always easy to extract the whole of the sulphurous acid from the food. Beythien and Bohrisch (1903) found that even after treatment with dilute potassium hydroxide for a quarter of an hour the amount of sulphurous acid in the extract was considerably less than that obtained by distillation of the whole sample. Schmidt (1904) found that when 100 grm. of dried fruit were extracted several times in succession with 200 c.c. of water, sulphurous acid was present in the sixth extraction, and a small amount still remained in the fruit. Even when an alkaline solution was used for extraction the results were rather low, but Schmidt was of opinion that alkaline extraction might be made to yield correct results if sufficiently prolonged. These remarks, of course, apply also to the determination of sulphur dioxide by distillation, in aqueous or alkaline extracts of foods.

Another possible cause of low results in Ripper's method is the readiness with which sulphurous acid is oxidized in alkaline solution, and the slight loss due to the so-called "neutralization effect" when the solution is acidified (cf. p. 39).

In the ordinary method of determining sulphur dioxide by means of iodine, the former is run into an excess of standard iodine solution. Under these conditions oxidation to sulphuric acid is complete (Giles and Shearer, 1884). Bunsen found that if iodine solution was run into sulphurous acid the oxidation of the latter to sulphuric acid was incomplete unless the concentration of the sulphurous acid was not greater than 0·04 per cent. Volhard considered that this was due to the interaction of sulphur dioxide and hydriodic acid, giving free iodine and sulphur.

$$SO_2 + 4HI = 2I_2 + 2H_2O + S.$$

Raschig (1904), on the other hand, could find no evidence of separation of sulphur and considered that when iodine is run into sulphurous acid the errors observed are due solely to the escape of sulphur dioxide from the liquid during titration. The more dilute the solution the less likelihood is there that sulphur dioxide will escape. Berg (1902) found that the reaction between sulphur dioxide and hydriodic acid took place very slowly, the solution becoming cloudy, owing to separation of sulphur, only after standing for four or five days. He considered that the errors observed were due to oxidation and volatilization of sulphur dioxide. In the titration of foods, however, it is only in few cases that the concentration of sulphurous acid will greatly exceed 0·04 per cent. (400 parts per million), so that errors from incomplete oxidation by iodine are not likely to arise. Possibly also Brown's observation that in presence of glycerine iodine may be run into sulphurous acid solutions with accurate results (p. 39) may apply to wines, since according to Mensio (1917) wines may contain from 6 to 8 parts or more of glycerine per 100 parts of alcohol.

It would appear, therefore, that direct iodine titration is subject, in greater or less degree, to a number of errors, some of which will compensate each other, and that although apparently accurate results may often be obtained, e.g., those already quoted as given by Ripper, these must be regarded as being due, in many cases, to a balancing of errors.

4. Direct precipitation as barium sulphate.

Blarez and Tourrou (1899) estimated sulphur dioxide in wine from the difference between two barium sulphate determinations, the first being carried out on the wine itself, and the second on another portion of the sample after treatment with bromine. This method is criticized by Kerp (1904, 2), who says that it is liable to give high results owing to the oxidation of protein sulphur by bromine. Buttenberg and Stüber (1906) determine sulphur dioxide in gelatine by precipitation as barium sulphate after oxidation with a large excess of iodine solution, a blank determination being made on the gelatine without iodine. Lévy (1913) adds 2 grm. of barium peroxide to 50 c.c. of wine and allows the mixture to stand overnight in a well-stoppered or corked vessel. Hydrochloric acid is carefully added until there is no further effervescence, then ammonium chloride, and the liquid is boiled. The precipitate of barium sulphate is filtered off, washed with dilute ammonium chloride, and weighed. A blank determination is carried out on 50 c.c. of wine by precipitation with barium chloride in the usual way. Lévy states that the results agree well with those obtained by Haas' and Ripper's methods. Cazenave (1910) says that the results obtained by double precipitation of barium sulphate in wine before and after oxidation are accurate, but objects to the necessity of carrying out two gravimetric determinations. Possibly Mathieu's test, already referred to (p. 11) might be made quantitative. If so, this would involve only one gravimetric determination.

5. Distillation.

It is generally agreed that distillation is the most reliable method of determining sulphur dioxide in foods, but opinions differ considerably as to the way in which the distillation should be carried out, and as to the best method of determining the sulphur dioxide in the distillate. Some authors favour distillation in steam, others under reduced pressure, while the majority, following Haas, distil in carbon dioxide or in some other inert gas. The sulphur dioxide in the distillate may be oxidized to sulphuric acid by bromine, iodine, hydrogen peroxide or possibly other oxidizing agents, and determined either volumetrically or gravimetrically. In this and the following sections the relative advantages and disadvantages of the numerous methods which have been proposed are discussed, and some indications are given of the precautions which must be taken to ensure satisfactory results.

A. *Use of carbon dioxide.*

Haas (1882) distilled wine in a current of carbon dioxide, the distillate being received in iodine solution contained in a Peligot tube immersed in water and no condenser being used. He stated that fairly good, although slightly low, results could be obtained by omitting the carbon dioxide, but that trouble was then experienced on account of the iodine solution being sucked back into the delivery tube. Both Cazenave (1910) and Claassen (1911) considered that the use of carbon dioxide was unnecessary, and the latter said that equally good results could be obtained with glucose syrups by ordinary distillation after acidification.

A few other authors claim to have obtained satisfactory results without carbon dioxide. Froboese (1920) is of opinion that an atmosphere of carbon dioxide is not so important as the use of air-free water in the distilling flask. He points out that sulphur dioxide is not readily oxidized in pure water or in steam, but only when heated in presence of minute amounts of catalysts, such as are contained in foods, or even in ordinary distilled water. Any oxidation which occurs during the progress of the distillation takes place in the liquid which is being distilled, being caused by dissolved oxygen under the influence of catalysts, and no sulphuric acid is formed in the vapour or in the condenser, even when air is present. A current of carbon dioxide has very little effect in preventing this oxidation, but at the same time it is of value in promoting the expulsion of sulphur dioxide from the liquid, and in carrying it over into the receiver.

Järvinen, on the other hand, gives figures which indicate that the omission of carbon dioxide results in a definite loss of sulphur dioxide. He distilled several samples of dried fruit (apricots, peaches, pears, etc.) containing from 0·065 to 0·244 per cent. of sulphur dioxide, with and without carbon dioxide, and found that in absence of carbon dioxide the results were from 0·013 to 0·018 per cent. lower, except in one case where the figures for the two distillations were the same. In the case of beer, Baker and Day (1911) point out that the amount of oxygen present in solution is only 0·7 parts per million, so that the possible loss of sulphur dioxide from oxidation is only three parts per million, an amount outside the limits of error of the method. It is probably difficult to prevent oxidation altogether, even by the use of well-boiled water and carbon dioxide, since, as Giles and Shearer (1884), and also Adeney, have shown, water absorbs oxygen rapidly when exposed even for a short time to air. The oxidation of sulphurous acid under various conditions is dealt with more fully on p. 37.

Carbon dioxide, as generated from the ordinary Kipp apparatus, using marble and hydrochloric acid, is usually impure. Marble may contain traces of metallic sulphides (Ripper, 1892, Beythien and Bohrisch, 1902). Franz and Sonntag (1908) pass the gas through two wash-bottles containing copper sulphate solution. Pure hydrochloric acid should be used, since, as Poetschke (1913) points out, commercial hydrochloric acid frequently contains chlorine which is not removed by washing the gas with copper sulphate. Ripper (1892) washed his carbon dioxide with potassium permanganate and chromous chloride, the object of the latter being to remove traces of oxygen occluded in the marble. Chaston Chapman (1926), in the standard method proposed for the determination of sulphur dioxide in beer, washes the carbon dioxide with dilute sodium carbonate solution.

It is undoubtedly more satisfactory, and cheaper in the long run, to use a cylinder of liquid carbon dioxide. Cylinders containing 28 lbs. of the gas can be obtained in London at a cost of 10s., the cylinder itself being on loan without charge for one month, and at about 2s. 6d. a month for periods up to three months. It is necessary to use a fine-adjustment valve, costing 10s. 6d., which permits of a steady flow of gas being obtained at any desired speed. These valves are supplied by the manufacturers of carbon dioxide with the necessary screw fitting for the standard cylinder nozzle, this being of a type different from those used on oxygen and hydrogen cylinders.

Instead of using carbon dioxide from a separate generator, some analysts prefer to add a small quantity of marble or sodium carbonate to the liquid in the distilling flask, and to use hydrochloric acid in place of phosphoric acid for acidifying the liquid. (Baker and Day, 1911, Järvinen, 1925.) Järvinen considers that sulphur dioxide is driven off from solution more quickly and completely by this means than by distillation with phosphoric acid in a current of carbon dioxide from a separate generator, especially in the case of dried fruit, where the diffusion from solid to liquid is rather slow. In eight comparative experiments he obtained from 0·002 to 0·029 per cent. more sulphur dioxide, using marble and hydrochloric acid in the liquid, than by the ordinary distillation process, but in two other experiments the results were 0·004 and 0·014 per cent. lower. In one experiment the results were the same by both processes. The use of marble in the flask, has, of course, the disadvantage that the gas is not washed, and traces of volatile sulphur compounds evolved from the marble may affect the results. I am informed, however, by Dr. Percy May that when using this method for dried fruits, he has never obtained any appreciable amount of barium sulphate in blank experiments, so that this source of error has possibly been exaggerated. At the same time, Dr. May's results with dried fruit are in many cases higher than those obtained on the same samples by other analysts using the ordinary method, which is probably to be attributed to the use of hydrochloric acid in place of phosphoric (p. 48).

B. *Use of other inert gases.*

Ripper (1892) tried distillation in hydrogen instead of carbon dioxide, the distillate being collected in $\frac{N}{1}$ potassium hydroxide solution. The latter was then acidified and titrated with iodine. The distilling flask was not heated above 80° C. in order to prevent the distillation of volatile organic compounds which would affect the iodine titration. The results agreed well with those obtained by Haas' method. Franz and Sonntag (1908) also used hydrogen in some experiments, but found that the results obtained were not more accurate than with carbon dioxide. If compressed nitrogen be available, it may perhaps be used in place of carbon dioxide. I am informed by the manufacturers that compressed nitrogen normally contains about 0·5 per cent. of oxygen, whereas in cylinders of liquid carbon dioxide the proportion of air is about 0·3 to 0·6 per cent., corresponding to 0·06–0·12 per cent. of oxygen (by volume). Whether these small amounts of oxygen are capable of affecting the results is a moot point. In cylinders of the same size the amount of hydrogen or nitrogen is much less than the amount of carbon dioxide. The only possible advantage of these gases is that they admit of the use of caustic alkalies in the receiver.

Järvinen (1925) carried out two experiments with hydrogen evolved from zinc in the distilling flask. This presumably would result in some of the sulphur dioxide being reduced to hydrogen sulphide, but if bromine were used in the receiver this would be oxidized to sulphuric acid. The results were slightly lower in one case and higher in the other as compared with those found by distillation in carbon dioxide.

C. *Connections.*

As to whether corks or rubber stoppers should be used for connections, it is advisable not to use vulcanized rubber where contact with bromine or iodine vapour may occur (Zerban and Naquin, 1908).

Many analysts prefer to use corks throughout, but it is not so easy to obtain gas-tight joints with corks. When distilling with carbon dioxide into a receiver consisting of two Peligot tubes or similar absorption vessels, the atmosphere in the flask, condenser and delivery tube is under slight pressure, equivalent to a column of one to three inches of water according to the type of receiver used. Even this slight pressure greatly increases the risk of leakage of gas through imperfect corks, and it is always advisable to ensure that the apparatus is perfectly gas tight under pressure before commencing to distil. In the ordinary method of distilling in a current of carbon dioxide into bromine water, with the end of an adapter dipping just below the surface of the liquid, the pressure is negligible until some considerable amount of distillate has been collected.

When using hydrogen peroxide in the receiver (p. 42) rubber stoppers may be used with advantage. Ferguson (1917) refers to the possibility of errors occurring in gas analysis owing to the absorption of sulphur dioxide by rubber, but I have not found that any loss occurs from this cause in the distillation of sulphur dioxide from foods.

D. *Use of acid in distilling flask.*

Most authors have used phosphoric acid for acidifying the food prior to distillation. The amount of acid used by different workers varies considerably. In the standard method proposed for beer (Chaston Chapman, 1926), 5 c.c. of glacial phosphoric acid are mixed with 100 c.c. of water, and after expulsion of air from the flask, 250 c.c. of beer added. Froboese (1920) used 50 c.c. of 25 per cent. phosphoric acid to 400 c.c. of water, while Mentzel (1906) used 15 c.c. of phosphoric acid (presumably the concentrated acid) to 350 c.c. of water.

Several workers have found that sulphur dioxide is evolved from certain foods very slowly on distillation with phosphoric acid. Thus Zerban and Naquin (1908) found it extremely difficult to distil off all the sulphur dioxide from molasses. Fifty grammes of molasses were mixed with 400 c.c. of water and 5 c.c. of phosphoric acid, and 200 c.c. distilled off. A further 200 c.c. of water were added to the contents of the distilling flask, and the same amount distilled off. It was necessary to repeat this four times to ensure that the whole of the sulphur dioxide was driven over. The fourth distillate still contained traces of sulphur dioxide. Järvinen (1925) found that dried fruits gave up sulphur dioxide slowly and incompletely on distillation with dilute phosphoric acid, and that better results were obtained with hydrochloric acid and marble in the distilling flask. He attributed this to the slow diffusion of sulphurous acid from solid to liquid, but it was more probably due to the effect of the stronger acid in promoting dissociation of combined sulphurous acid.

Many analysts submit carbohydrate foods, such as cornflour, to a preliminary treatment with alkali, with the object of decomposing combined sulphurous acid prior to acidification and distillation, and state that the results so obtained are from 10 to 20 parts per million higher than those given by direct acid distillation. In the German official method for sulphur dioxide in foods a small quantity of sodium carbonate is added to the contents of the flask before acidification with phosphoric acid. It would seem, however, from the experiments recorded on p. 47, that the effect of alkali treatment is negligible compared with that produced by using a stronger acid such as hydrochloric acid. With dried fruits especially, it is difficult to ensure the expulsion of all the sulphur dioxide present when using phosphoric acid. Prolonged boiling with hydrochloric acid invariably gives higher results. In the method described in Section 12, I have used 20 c.c. of concentrated hydrochloric acid in 500 c.c. of water, and even then one hour's boiling was hardly sufficient in the case of dried apricots. This may be due to the slowness with which glucose sulphurous acid is dissociated in solution and to the comparatively small effect of heat in hastening this dissociation (p. 5). It is more probable that in dried fruit part of the sulphurous acid is present in some other form of combination, possibly akin to lignin sulphonic acid. Stutzer (1910) found that the evolution of sulphur dioxide from the lignin sulphonic acids present in sulphite pulp liquor depended on the amount of phosphoric acid used, being greater in presence of a large amount of acid.

A relatively large proportion of acid has also the advantage that it hastens hydrolysis of the food constituents and reduces frothing, but with protein foods there is perhaps the danger that excessive acidity may favour the production of volatile sulphur compounds from the protein.

A series of comparative experiments using phosphoric and hydrochloric acids, with and without previous treatment of the food with alkali, are given on page 47. When using methods involving preliminary treatment with alkali, it should be noted that sulphurous acid is much more readily oxidized in alkaline than in acid solution, and care should be taken to exclude air.

Franz and Sonntag (1908) used acetic or tartaric acid in place of phosphoric in cases where it was desired to evaporate the residue in the flask for the purposes of an ash determination. Stutzer (1910), however, found that acetaldehyde sulphurous acid was not completely decomposed when heated with dilute acetic acid, so that it would not be safe to rely upon this method in the case of wines containing acetaldehyde.

With gelatine, in which the sulphurous acid, according to Lange (p. 8) is all in the free state, the whole of it comes over on distillation in 20 minutes (Trotman and Sutton, 1924). The tendency of gelatine solutions to froth on distillation may be obviated by the addition of 2–3 grm. of tannin for every 10 grm. of gelatine (Lange 1909). This forms a flocculent precipitate on the surface of the liquid, which dissolves slowly on subsequent heating. Kühn and Rühle (1910) use liquid paraffin to prevent frothing when dealing with meat products.

6. Titration of the distillate.

A. *Iodine and sodium thiosulphate.*

Distillation of sulphur dioxide from foods into standard iodine solution and titration of the excess of iodine was originally suggested by Wartha (1880), and the method has been used with modifications by several chemists. It is satisfactory only in the absence of volatile organic compounds capable of reducing iodine, and also when the necessary precautions are taken to avoid loss of iodine by volatilization in the current of carbon dioxide. Unfortunately, a great many foods yield, on distillation, volatile products which affect iodine titration. Schmidt (1904) found that hops, which contained 0·015 per cent. of sulphur dioxide, shewed as much as 0·099 per cent. when this method was used. Dried apricots, on the other hand, gave an accurate result, indicating the absence of volatile compounds capable of reducing iodine. Padé (1908), Poetschke (1913) and Trotman and Sutton (1924) state that iodine titration of the distillate is inapplicable to gelatine. Baker and Day (1911) used this method for beer and found that it gave only 5 or 6 parts of sulphur dioxide per million in excess of that found by the gravimetric method. With very acid beers, however, containing more than 1 per cent. of acetic acid it was not trustworthy. Chaston Chapman (1926) gives the method as an alternative, for control purposes only, to the standard gravimetric process suggested for beer. Gudeman (1909) states that if the distillation of foods be carried out in a current of steam, so that the contents of the flask are progressively diluted instead of becoming more concentrated during the progress of the distillation, the errors due to volatile organic compounds may be largely avoided, but he gives no figures to support this contention. Ripper (1892) when distilling wine in a current of hydrogen, with potassium hydroxide solution in the receiver (p. 18) heated the wine only to 80°C. in order to avoid the volatilization of other substances. His results agreed well with those obtained by Haas' method. Ferré (1914) eliminated volatile organic compounds by distilling from a flask fitted with a reflux condenser. This is effective in most cases and I have adopted it in the method described on pp. 41–48. Low results may be obtained, owing to retention of small quantities of sulphur dioxide in the moisture which clings to the walls of the condenser and the delivery tube, unless these are steamed through for a few moments at the end of the distillation.

Loss of iodine from the receiver by volatilization in the current of carbon dioxide is, according to Schmidt (1904), difficult to prevent. He found it necessary to use at least two extra absorption vessels containing potassium iodide solution, to retain all the iodine vapour. Chaston Chapman (1926) finds that one additional absorption flask containing potassium iodide solution is sufficient, but does not recommend the titration method for accurate work. Veterre (1907), Ferré (1914) and Coppetti (1921) use a guard tube containing a measured quantity of standard thiosulphate solution, which is added to the iodine solution in the receiver before titration and included in the titration figure. Veterre (1907) and Monimart (1912) use a mixture of standard dichromate, potassium iodide and hydrochloric acid in the receiver. They claim that this obviates the necessity of making up iodine solution, and has the advantage that standard dichromate remains unaltered in strength on keeping. Paturel (1902) avoids loss of iodine by carrying out the titration continuously during the distillation. As the sulphur dioxide comes over it is titrated with successive small quantities of iodine, so that the latter is never in large excess, and is not carried off by the current of carbon dioxide.

B. *Alternative methods of titrating the distillate.*

A number of alternative methods have been tried at various times for the titration of sulphur dioxide in the distillate. Several of them are open to the same objections as have been noted above for iodine, while others have given satisfactory results with certain foods, but are not capable of general application.

(i) *Use of potassium iodate or bromate.*

The reduction of iodic acid to iodine by sulphur dioxide, already referred to on page 9 as furnishing a useful test for the presence of the gas, was used by Schwicker (1891) for the determination of sulphurous acid and sulphites in solution. A solution of potassium iodate was acidified and titrated with sodium thiosulphate. To another portion of the iodate solution was added a measured quantity of the sulphite solution, and the excess of iodic acid, together with the free iodine formed, again titrated with thiosulphate. The amount of sulphur dioxide was arrived at from the difference between the two titrations, but the calculation is somewhat complicated. Schumacher and Feder (1905, 2) found that this method, while accurate enough with pure sulphite solutions, could not be used with foods owing to the action of the free iodine upon other volatile constituents of the food.

A variant of the method is to boil off the free iodine which is formed in the reaction, or the bromine when bromic acid is used (Feit and Kubierschky, 1891), and to determine the unreduced iodic or bromic acid remaining. This method was used by Schumacher and Feder. They standardized their iodate solution by adding to it an excess of potassium iodide, acidifying with sulphuric acid, and titrating the free iodine produced with thiosulphate. On distilling sulphur dioxide into a known amount of this standard potassium iodate, the following reaction occurs (cf. p. 9)

$$2KIO_3 + 5SO_2 + 4H_2O = K_2SO_4 + 4H_2SO_4 + 2I.$$

Sulphur dioxide is not oxidized by the iodine as long as a sufficient excess of potassium iodate is present, oxidation being effected solely through the agency of the iodate. After the distillation is finished the iodine is boiled off and the residual iodate determined by adding potassium iodide, acidifying with sulphuric acid and titrating with thiosulphate. Reducing substances other than sulphur dioxide, if present, are partly oxidized by the iodine set free in the reaction and partly driven off during the subsequent boiling of the liquid. On testing this method with unsulphured dried fruit to which known amounts of sodium sulphite had been added, the results obtained were very accurate. In eleven experiments with amounts of sulphur dioxide varying from 32 to 432 mgm. the errors were never more than 1 mgm. and in most cases much less. With minced meat, also, the difference between the amount of sulphur dioxide added and that found was never more than 0·7 mgm. Schumacher and Feder state that great care was taken in the distillation to use only well-boiled water and pure carbon dioxide from a cylinder. With wine, however, the method cannot be used, owing to oxidation of volatile compounds by iodine. Järvinen (1925) tested this method with dried fruit, and found that it gave high results, since some of the potassium iodate is reduced by volatile compounds other than sulphur dioxide. In two experiments carried out by halving the distillate and doing one half by titration and the other gravimetrically he got the following results :—

Titration.	Gravimetric.
0·192 per cent. SO_2	0·178 per cent. SO_2.
0·209 ,, ,, ,,	0·161 ,, ,, ,,

Another method, in which iodic acid is used in a solution made strongly acid with hydrochloric acid, was suggested by Andrews in 1903 and elaborated by Jamieson (1914). It was used by Haller (1919) in determining sulphur dioxide in the gases used for the catalytic production of sulphuric acid. In this method the iodine first formed by reduction of iodic acid is converted into iodine monochloride in presence of excess of iodic and hydrochloric acids, and the end-point is the sudden disappearance of the iodine colour in a globule of chloroform when shaken up with the liquid. Several advantages are claimed for this method, but it has not yet been tested with foods. Haller's paper is readily accessible, and need not be considered here in detail.

According to Hendrixson (1925) bromic acid does not oxidize sulphur dioxide completely to sulphuric acid unless a small amount of potassium iodide is also present in the solution.

(ii) *Use of potassium permanganate and dichromate.*

Potassium permanganate solution is not satisfactory for the determination of sulphur dioxide, owing to the formation of some dithionic acid. The titration figure gives only $\frac{9}{10}$ths of the quantity of sulphur dioxide actually present (Dymond and Hughes. 1897). This was confirmed by Milbauer (1909), who, however, found that fairly good results could be obtained when the permanganate solution was used in ten-fold excess, and contained at least 20 per cent. by volume of sulphuric acid. The sulphur dioxide solution must not be stronger than 1 mgm. of SO_2 per c.c. The excess of permanganate is determined with standard oxalic acid, hydrogen peroxide or ferrous sulphate. Traces of iodine or bromine are of assistance in acting as catalysts in the reaction. Hendrixson (1925) draws attention to the effect of potassium iodide in promoting the oxidation of sulphur dioxide by permanganate and dichromate, but states that it must be present in amount equal to half the equivalent of the permanganate. Kolthoff (1924), on the other hand, states that the oxidation of sulphur dioxide to sulphuric acid is complete only in strongly alkaline solution with excess of permanganate.

The use of permanganate, whether acid or alkaline, for determining sulphur dioxide in distillates from foods would probably be impracticable owing to the readiness with which it reacts with other volatile organic substances. For this reason Craig's method (1919) of determining sulphurous acid by oxidation with hydrogen peroxide and titration of the excess of hydrogen peroxide with permanganate is not applicable to foods. The same objection applies to Peacock's method (1923) of determining sulphur dioxide in cattle cake by distilling with phosphoric acid into a solution of ferric ammonium sulphate (iron alum), and titrating the resulting ferrous salt by permanganate. He found that the method gave high results owing to volatile reducing substances which affected the permanganate. In various cattle cakes this error amounted, in terms of sulphur dioxide, to 0·006-0·019 per cent.

Martini and Nourrisson (1922) distil wine with phosphoric acid under reduced pressure into a neutral solution of potassium dichromate containing 4·906 grm. per litre $\left(\frac{N}{60}\right)$. They state that when the wine is boiled on a steam bath in a good vacuum all the sulphur dioxide passes over in five minutes. The dichromate solution is boiled to remove alcohol, acidified with hydrochloric acid, cooled, and titrated with thiosulphate after addition of potassium iodide in the usual way. No details are given as to the accuracy of the method.

Knecht and Hibbert (1915) determine sulphur dioxide in commercial bisulphites, etc., by allowing the solution to run into excess of alkaline potassium dichromate solution. On gradual acidification with sulphuric acid the sulphite is oxidized, and the excess of chromic acid determined by means of titanous chloride. This is one of the many applications of the titanous chloride titration methods worked out by these authors, but it has not, apparently, been applied to foods. The same objections would probably apply to the use of dichromate as have been noted above for permanganate.

(iii) *Neutral hydrogen peroxide.*

Franz and Sonntag (1908) distilled in carbon dioxide and collected the sulphur dioxide in a small quantity of 3 per cent. ("10 volume") hydrogen peroxide, which oxidizes it quantitatively to sulphuric acid. The sulphuric acid was titrated in the distillate after boiling off the carbon dioxide and the titration checked, where necessary, by a gravimetric determination as barium sulphate. They draw attention to the fact that commercial hydrogen peroxide frequently contains sulphuric acid and must, therefore, be tested before use. The results given for experiments on pure solutions of sodium sulphite shew a high degree of accuracy. The method was used by them for the determination of sulphur dioxide in urine in connection with physiological work. It cannot be used for wine or for foods containing volatile acids which may distil over and affect the titration. Even with urine, traces of volatile sulphur compounds were produced which were partially oxidized to sulphuric acid on boiling the hydrogen peroxide prior to titration, leading to high results. Lange (1909) and Froboese (1920) found that this method was not accurate for gelatine, owing to the distillation of volatile fatty acids.

Gutbier, Sauer and Brintzinger (1921), with a view to preventing the distillation of volatile acids from gelatine, used a reflux condenser, so that only carbon dioxide and sulphur dioxide passed over into the receiver. Their results were fairly accurate, but not so concordant as those obtained by direct iodine titration of gelatine. A reflux condenser had previously been used by Ferré (1915) when distilling into iodine solution (p. 21) and probably the discrepancies observed were due to retention of sulphur dioxide by condensed moisture in the delivery tube. Partial refluxing is also a feature of Froboese's method described below (p. 26).

I have adopted the principle of a reflux condenser with distillation into pure hydrogen peroxide in the method described on pp. 41–48, which has given accurate and concordant results with a number of different foods.

(iv) *Distillation into alkali.*

Several methods have been proposed which depend on the use of alkaline solutions for absorbing sulphur dioxide. Ripper (1892) distilled in hydrogen with $\frac{N}{1}$ potassium hydroxide in the receiver, and titrated the sulphur dioxide with iodine after acidification. This method gave results for wine which compared well with those got by Haas' method. Blarez and Chelle (1909) distilled wine under reduced pressure into dilute sodium hydroxide solution, and titrated with iodine after acidification. Their results shewed excellent agreement both with the figures obtained by precipitation of the titrated distillate with barium chloride, and with those obtained by Haas' method. Gudeman (1909) distilled in a current of steam into weak alkali and titrated with iodine after acidification.

It is not possible to employ caustic alkalies in conjunction with iodine titration when carbon dioxide is used, since as Haller (1919) pointed out, the alkali would be converted into bicarbonate, and on subsequent acidification the escaping carbon dioxide would carry with it sulphur dioxide.* Sulphur dioxide can be absorbed in sodium bicarbonate, normal sodium sulphite being formed, and according to Froboese (1920) the absorption is quantitative. Direct titration of the solution with iodine does not give accurate results (Ruff and Jeroch, 1905), but if the sodium sulphite be converted into sulphate by adding hydrogen peroxide

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* The possibility of loss of sulphur dioxide in this way on opening bottles containing effervescent drinks should be noted.

the excess of bicarbonate can be titrated with standard acid and methyl orange. Upon this depends Froboese's method of determining sulphur dioxide in foods.

In this method the food, made up to 400 c.c. with water containing 50 c.c. of 25 per cent. phosphoric acid, is distilled from a 750 c.c. flask, in a current of carbon dioxide, through a vertical tube 40 cm. in height, which, by acting as a partial reflux condenser, keeps back volatile acids to a great extent. At the top of the tube is a splash-bulb. The distillate is then taken down through a condenser to the receiver. The latter contains a known quantity of $\frac{N}{10}$ sodium bicarbonate solution, 40 c.c. of which are sufficient for the absorption of 80 to 90 mgm. of sulphur dioxide. The rate of distillation is such that 200 c.c. are distilled off in 1¼ hours. Sulphur dioxide reacts with the bicarbonate and is converted into normal sodium sulphite. When the distillation is finished, hydrogen peroxide (preferably 30 per cent. strength), is added to the bicarbonate solution in amount sufficient to oxidize the sulphite to sulphate. The solution is then boiled for about three minutes until there is no further evolution of carbon dioxide or oxygen on shaking, and titrated with $\frac{N}{10}$ hydrochloric acid and methyl orange. The advantage of using hydrochloric acid here is that it allows of a subsequent gravimetric determination of the sulphuric acid present, if desired. It is claimed that traces of hydrogen sulphide do not affect the accuracy of the method, being largely swept out of the receiver by the current of carbon dioxide. The presence of acetic acid in amount up to 0·3 grm. in the 400 c.c. of liquid distilled does not affect the results. Most of the acetic acid is held back by the reflux condensing tube and the small amount that goes over does not affect the methyl orange titration. The following results were obtained in test analyses with acetic acid.

Acetic acid added to flask contents.	SO_2 added to flask (by iodine titration.)	SO_2 by titration of distillate.	SO_2 in distillate (gravimetric).
mgm.	mgm.	mgm.	mgm.
90	90	90·8	87
90	90	89·9	86
300	84	88·6	89
300	84	87	85·6

These results are fairly satisfactory, but it is not clear why the gravimetric determination in No. 3 should be nearly 6 per cent. too high. With wine and dried fruit good agreement was obtained between the volumetric and gravimetric figures, and also with gelatine. In a sample of gelatine, Froboese's method shewed

400 parts per million volumetrically and 388 parts gravimetrically. The same sample examined by Haas' method shewed 480 parts per million, which indicates that Froboese's method obviates to some extent the errors due to volatile sulphur compounds. Very small amounts of sulphur dioxide are best determined gravimetrically, titration being liable to give rather high results.

Froboese's method has not been criticised by subsequent workers and would seem to be sound in principle, although the boiling of the distillate before titration is open to objection (cf. p. 33). Possibly brom-phenol blue would be a better indicator to use than methyl orange, as the colour change is sharper. I am informed by a firm of cornflour manufacturers that they have used a modification of this process for determining small amounts of sulphur dioxide in cornflour with excellent results. In this method 25 grm. of the cornflour are mixed with 500 c.c. of well-boiled water and 25 c.c. of 3N hydrochloric acid. A small quantity of calomel is added to retain any hydrogen sulphide which may possibly be present. The mixture is distilled in a current of carbon dioxide from a Kipp apparatus and the distillate (100 c.c.) collected in 20 c.c. of $\frac{N}{125}$ sodium hydroxide containing 10 c.c. of pure hydrogen peroxide (10 volume). The distillate is heated to boiling point and the residual alkali titrated with $\frac{N}{125}$ nitric acid, using brom-thymol blue. One c.c. of $\frac{N}{125}$ solution corresponds to 10 parts of sulphur dioxide per million when 25 grm. of cornflour are taken. The titration figure can be checked by precipitation, the liquid being acidified with nitric acid and precipitated with barium nitrate. One mgm. of barium sulphate corresponds approximately to 10 parts of sulphur dioxide per million when 25 grm. of cornflour are taken.

7. Gravimetric determination of sulphur dioxide in the distillate.

The errors due to volatile organic compounds, with the exception of those containing sulphur, can be avoided if the sulphur dioxide in the distillate is determined by oxidation to sulphuric acid and precipitation as barium sulphate. Haas (1882), who was the first to use this method, distilled into iodine solution, and most analysts have adopted this method. As alternatives bromine and hydrogen peroxide may be used, both of which convert sulphur dioxide completely into sulphuric acid. Peacock (1923) quotes Kühn and Rühle (1910) as stating that sulphur dioxide is not completely oxidized to sulphuric acid by iodine, but I have been unable to trace this statement in the paper referred to. Solutions of iodine and hydrogen peroxide containing barium chloride both give, even when cold, an immediate precipitate or turbidity of barium sulphate with the smallest quantities of sulphur dioxide. With hydrogen peroxide a fair excess of the oxidizing agent must be present. Comparative determinations carried out with iodine or hydrogen peroxide on pure sulphurous acid solutions always agree with the results obtained when bromine is used. Bromine is more irritating to work with than iodine, but it does not exhibit the same tendency to form resinous precipitates with volatile organic compounds from which the solution must be filtered before precipitation with barium chloride. Also it has perhaps the advantage that bromine vapour is present in the atmosphere of the receiver above the liquid and may serve to oxidize traces of sulphur dioxide which might otherwise be carried off by the escaping carbon dioxide. The main difference between these three oxidizing agents lies in their action upon the volatile sulphur compounds which are produced in small amounts in the distillation of certain foods, and which may introduce an element of uncertainty into the results obtained, especially when small quantities of sulphur dioxide are in question.

A. *Volatile sulphur compounds from foods.*

The presence of volatile sulphur compounds in the distillates from unsulphured foods of various kinds has been noted by several writers. Niemann and Rubner (1893) detected the presence of hydrogen sulphide and mercaptans in the distillates from vegetables, and Schmidt (1904) also found that fresh fruits and vegetables yielded traces of volatile sulphur compounds. More recently König (1926) has investigated the volatile substances from several foods and has found that egg albumen on being heated to 100° C. in a current of nitrogen yields 28 parts of hydrogen sulphide per million, while cauliflowers give 5·6 parts of hydrogen sulphide and 2·6 parts of methyl mercaptan per million. Mentzel (1906) found that unsulphured meat gave from 5 to 8 mgm. of barium sulphate per 100 grm. when distilled into iodine solution, and that the addition of onions to the meat resulted in a large increase in the amount of "apparent" sulphur dioxide found. By distilling onions alone into iodine solution he obtained as much as 0·006 per cent. (60 parts per million) of "apparent" sulphur dioxide. Mentzel considered that in the case of meat it is not safe to infer the presence of sulphur dioxide unless the amount indicated is greater than 0·004 per cent. (40 parts per million), or 0·005 per cent. from meat products containing onions.

According to Alexander (1907) and Lange (1909) gelatine may give traces of volatile sulphur bodies, but Poetschke (1913) and Trotman and Sutton (1924) obtained no volatile sulphur from pure gelatine on distillation with steam into iodine and bromine respectively.

Horne (1907), in determining sulphur dioxide in sugar products, passed the steam from the distilling flask through a small vessel containing neutral 2 per cent. solution of cadmium chloride, the object being to precipitate hydrogen sulphide. Winton and Bailey (1907) used 1 per cent. copper sulphate solution. These reagents retain hydrogen sulphide but not volatile organic sulphur compounds, such as ethyl sulphide and methyl mercaptan, which are among the cleavage products of sugar cane protein (Zerban and Naquin, 1908). Winton and Bailey examined samples of beef, mutton, veal and pork both when fresh and after keeping for various periods up to 23 days, and determined the amounts of hydrogen sulphide from the weight of copper sulphide formed, and also the volatile organic sulphur ("apparent" sulphur dioxide) from the amount of sulphuric acid in the distillate after oxidation with bromine water. The meat was distilled with dilute phosphoric acid. The amount of "apparent" sulphur dioxide in fresh meat was almost negligible, of the order of 4 parts per million, while no hydrogen sulphide could be detected. On keeping veal for nine days the apparent sulphur dioxide went up to 48 parts per million and the hydrogen sulphide to 72 parts. Mutton after nine days gave 84 parts per million of apparent sulphur dioxide and 6 parts of hydrogen sulphide. Beef and pork on being kept for the same time did not give so much volatile sulphur. Winton and Bailey give a table showing the results obtained up to a period of 23 days, but the figures are very irregular. They suggest that sulphites may be formed in decomposing meat as intermediate products of the oxidation of sulphides to sulphates, but it is more likely that the apparent sulphur dioxide is due to volatile organic sulphur compounds.

Some analysts recommend the addition of copper sulphate to the distilling flask for the purpose of retaining hydrogen sulphide, but the possible effect of the copper in promoting the oxidation of sulphur dioxide catalytically should be borne in mind (p. 39).

Kühn and Rühle, in view of the fact that iodine solution does not oxidize hydrogen sulphide to sulphuric acid, but only to sulphur, are inclined to discount altogether the possibility of error being caused by volatile sulphur bodies when iodine is used in the receiver. They consider that the small amounts of barium sulphate obtained are due entirely to sulphur dioxide absorbed from the products of combustion of coal gas during the process of boiling off iodine prior to precipitation with barium chloride. This contention is dealt with more fully on page 34.

It is frequently argued that hydrogen sulphide, if present in foods, or if formed during distillation, cannot exist in the vapour or in the distillate in presence of sulphur dioxide, since the two will react to produce free sulphur and pentathionic acid.

$$SO_2 + 2H_2S = 3S + 2H_2O.$$
$$5SO_2 + 5H_2S = H_2S_5O_6 + 5S + 4H_2O.$$

These reactions take place, however, comparatively slowly when the two gases are in dilute solution or mixed with a large volume of inert gas. Lunge (1890) says :—

> "In the Chance-Claus sulphur recovery process a gaseous mixture escapes containing small quantities of both SO_2 and H_2S, together amounting to about 30–50 grm. of sulphur per cubic metre. Owing to the enormous amount of foreign

gases, chiefly nitrogen, in spite of the presence of moisture, no reaction ensues between SO_2 and H_2S."

Heinze (1919) found that sulphurous acid and hydrogen sulphide could exist together in very dilute aqueous solution. Under these conditions interaction between the two, with the production of sulphur, is a slow process. The rate at which it takes place depends on the concentration.

B. *Action of different oxidizing agents on volatile sulphur compounds.*

Hydrogen sulphide is oxidized completely to sulphuric acid by bromine, but with iodine solution free sulphur is formed :—

$$H_2S + 2I = 2HI + S.$$

Lührig and Wiedmann (1903) found that the precipitated sulphur is not oxidized to sulphuric acid even on boiling with excess of iodine solution, and this was confirmed by Poetschke (1913), who says that when iodine is used in the receiver it is not necessary to pass the steam from the distilling flask through copper sulphate solution.

Hydrogen peroxide, according to Lunge (1890), also oxidizes hydrogen sulphide to sulphur, but I have found that when a weak solution of hydrogen sulphide is added to hydrogen peroxide containing barium chloride the liquid remains clear and no sulphur separates. On heating, barium sulphate is precipitated. In presence of hydrochloric acid the solution still remains clear when cold, but barium sulphate is formed somewhat more readily on heating. Only a small part, however, of the hydrogen sulphide is oxidized to sulphuric acid by hydrogen peroxide under these conditions, as is shewn by the following experiment. Three solutions were taken (i) 150 c.c. of saturated bromine water, (ii) 50 c.c. of $\frac{N}{10}$ iodine solution diluted to 150 c.c., and (iii) 150 c.c. of a solution containing 1·2 per cent. of hydrogen peroxide, 0·15 per cent. of hydrogen chloride, and 2 per cent. of barium chloride (cryst.). To each of these solutions was added 10 c.c. of half-saturated solution of hydrogen sulphide. The bromine and iodine solutions were boiled to remove excess of the oxidizing agent and precipitated with barium chloride in the usual manner after addition of a few drops of hydrochloric acid. The experiment with hydrogen peroxide was done in duplicate, one being boiled and the other filtered cold. The weights of barium sulphate were as follows, after subtraction of the small amounts found in blank tests on the solutions :—

Bromine	118·9	mgm.	$BaSO_4$
Iodine	2·0	,,	,,
Hydrogen peroxide (hot)	32·3	,,	,,
,, ,, (cold)	1·0	,,	,,

The hydrogen peroxide was heated for the same length of time as the bromine and iodine solutions, in a conical flask covered with a watch glass. In another experiment with hydrogen peroxide, heated in an open dish on the steam bath for a quarter of an hour, 12·0 mgm. of barium sulphate were obtained.

It is evident, therefore, that hydrogen sulphide yields practically no sulphuric acid when oxidized by iodine. Partial oxidation to sulphuric acid occurs with hydrogen peroxide, but only on heating.

Hydrogen sulphide, however, is only one of the many volatile sulphur compounds produced in the distillation of various foods. Judging from the approximate estimations given below, it appears to form roughly one-third to one-half of the total volatile sulphur in the distillate from fresh eggs and yellow mustard seed, and about ⅛th of the volatile sulphur from onions. With the object of ascertaining the effect of different oxidizing agents on a distillate containing a varied assortment of volatile sulphur compounds a mixture of 170 grm. of yellow mustard seed, ground up in the laboratory, 150 grm. of onions, and 165 grm. of minced hard-boiled eggs was mixed with water, acidified with phosphoric acid and distilled in steam until 500 c.c. had been collected. Hard-boiled eggs, as is well known, smell strongly of hydrogen sulphide when minced, and readily blacken metallic silver. Yellow mustard seed does not yield appreciable amounts of volatile isothiocyanates, but the brown variety was not available at the time. Fifty c.c. of the distillate were oxidized by bromine, iodine, and hydrogen peroxide in the same way as given above for hydrogen sulphide. The hydrogen peroxide solution used in all these experiments contained 20 grm. of barium chloride, 4 c.c. of concentrated hydrochloric acid, and 400 c.c. of ten-volume (3 per cent.) hydrogen peroxide in one litre, and was filtered clear before use. The weights of barium sulphate obtained were as follows, corrected for blank tests.

Bromine	5·2	mgm.	$BaSO_4$
Iodine	4·0	„	„
Hydrogen peroxide (hot)	4·3	„	„
„ „ (cold)	1·1	„	„

The experiment was repeated with larger quantities of material, one pound of each of the ingredients being taken and 2,000 c.c. distilled off, of which 200 c.c. were taken for oxidation. The bromine and iodine were boiled off in conical flasks on electric hot plates with watch glasses on the flasks to avoid possible errors due to sulphur fumes from coal gas. The results, corrected for blanks, were as follows :—

Bromine	19·7	mgm.	$BaSO_4$
Iodine	17·2	„	„
Hydrogen peroxide (hot)	15·9	„	„
„ „ (cold)	1·7	„	„

Obviously, therefore, with this particular mixture of volatile sulphur compounds, there is little to choose between bromine, iodine and hydrogen peroxide, if the last-named is heated in the usual way before precipitation, but hardly any barium sulphate is obtained with hydrogen peroxide if precipitation and filtration are carried out without heating.

The experiments were then repeated on the separate ingredients. One dozen hard-boiled eggs were taken, and 700 c.c. distilled off in steam, 200 c.c of the distillate being taken for oxidation. The two hydrogen peroxide experiments were done on the same portion, the barium sulphate being first filtered cold, and the amount thus found added to that obtained on heating the filtrate.

The results were as follows:—

Bromine	2·8	mgm.	BaSO$_4$
Iodine	2·9	,,	,,
Hydrogen peroxide (hot)	3·5	,,	,,
,, ,, (cold)	1·6	,,	,,

A similar distillation of one pound of yellow mustard seed gave

Bromine	39·7	mgm.	BaSO$_4$
Iodine	5·8	,,	,,
Hydrogen peroxide (hot)	8·4	,,	,,
,, ,, (cold)	4·6	,,	,,

The cold hydrogen peroxide in this case was allowed to stand overnight before being filtered.

One pound of onions distilled in the same way gave

Bromine	20·9	mgm.	BaSO$_4$
Iodine	20·9	,,	,,
Hydrogen peroxide (hot)	13·8	,,	,,
,, ,, (cold)	0·9	,,	,,

A rough colorimetric estimation of the amount of hydrogen sulphide in the three distillates, using lead acetate, gave the following figures expressed as mgm. of H$_2$S per 200 c.c. of distillate.

Eggs	0·15	mgm.	H$_2$S	corresponding	to	1·0	mgm.	BaSO$_4$
Yellow mustard seed	2·42	,,	,,	,,	,,	16·6	,,	,,
Onions	0·35	,,	,,	,,	,,	2·4	,,	,,

A brown colour with lead acetate is not, of course, conclusive evidence of the presence of hydrogen sulphide, as other volatile sulphur bodies may conceivably give a similar reaction.

A sample of brown mustard seed was then obtained and one pound of the ground seed distilled in steam after acidification with phosphoric acid. 800 c.c. were distilled off and filtered and 200 c.c. taken for oxidation. The results were as follows:—

Bromine	412·4	mgm.	BaSO$_4$
Iodine	66·5	,,	,,
Hydrogen peroxide (hot)	185·9	,,	,,
,, ,, (cold)	6·4	,,	,,

The distillate when fresh contained a small quantity of hydrogen sulphide, which disappeared completely after keeping for 24 hours. The iodine solution contained much insoluble resinous matter, possibly sulphur, from which it was filtered before precipitation.

Experiments were then carried out on saturated aqueous solutions of pure allyl isothiocyanate and pure allyl sulphide. The oils were shaken with water and the solutions filtered.

100 c.c. of each solution were taken for oxidation and gave the following results :—

(i) Allyl isothiocyanate, "mustard oil."

Bromine	288·9	mgm. $BaSO_4$
Iodine	24·3	,, ,,
Hydrogen peroxide (hot)	24·4	,, ,,
,, ,, (cold)	0·9	,, ,,

On heating for 1¼ hours hydrogen peroxide gave 43·1 mgm. $BaSO_4$. The iodine solution contained much insoluble resinous matter, possibly sulphur, from which it was filtered before precipitation.

(ii) Allyl sulphide.

Bromine	1·5	mgm. $BaSO_4$
Iodine	3·2	,, ,,
Hydrogen peroxide (hot)	30·5	,, ,,
,, ,, (cold)	Nil.	,, ,,

The results with allyl sulphide are in accordance with the well-known behaviour of organic sulphides, which form addition compounds with bromine and iodine and are not oxidized to sulphuric acid. The action of hot hydrogen peroxide solution on allyl sulphide was somewhat unexpected.

The following are the main conclusions to be drawn from these experiments :—

(i) Hydrogen peroxide, when cold, does not oxidize appreciable amounts of hydrogen sulphide or volatile organic sulphur to sulphuric acid, but if the solution be heated in the usual manner before precipitation with barium chloride, considerable oxidation takes place and the results may be practically the same as when iodine is used.

(ii) Only in the case of mustard, both yellow and brown, was any considerable difference observed between bromine and iodine in the amount of barium sulphate obtained. This difference is probably due to the formation of hydrogen sulphide as a product of hydrolysis, and its oxidation to sulphur by iodine.

(iii) The distillate from onions consists chiefly of volatile sulphur compounds other than allyl sulphide and hydrogen sulphide. These compounds are oxidized to sulphuric acid with equal facility both by bromine and iodine.

C. *Use of hydrogen peroxide.*

It would appear, therefore, that in the determination of sulphur dioxide in foods containing volatile sulphur compounds, hydrogen peroxide will give the most reliable results, provided that precipitation and filtration of barium sulphate are carried out at room temperature. Chaston Chapman (1922) recommended the use of hydrogen peroxide for this purpose, but does not state whether the distillate was heated or not before precipitation. He found that with mustard flour and onions the merest trace of barium sulphate was obtained when hydrogen peroxide was used, while mustard flour distilled into bromine gave as much as 0·16 per cent. of "apparent" sulphur dioxide. He distilled in a current of carbon dioxide, whereas in the experiments recorded above steam distillation was used, so that the conditions were somewhat different. Hydrogen sulphide and probably other volatile sulphur bodies might be largely swept out of the receiver by the current of gas, and thus removed before the hydrogen peroxide is heated for precipitation.

Franz and Sonntag (1908) in determining sulphur dioxide in urine in connection with physiological investigations, distilled into hydrogen peroxide. They found that even when cadmium and copper salts had been added to the urine to retain hydrogen sulphide, volatile sulphur compounds came over which were oxidized to sulphuric acid by hydrogen peroxide when heated and precipitated in the usual way.

The determination of sulphuric acid by precipitation with barium chloride at room temperature is perhaps open to the objection that the precipitate may be more or less contaminated with barium chloride, which when once thrown down with barium sulphate is not readily removed by washing. If, however, the precipitate be allowed to settle, the supernatant liquid poured off through a filter, and the barium sulphate remaining in the beaker boiled three times with water before being brought on to the filter, the error is practically negligible.

8. Errors due to sulphur in coal gas.

Von Meyer (1890) found that if distilled water was evaporated for six or more hours over a gas flame, sulphur dioxide was absorbed in considerable amount from the products of combustion of the gas, and was oxidized to sulphuric acid in the water. On precipitating the residue with barium chloride he obtained as much as 30 to 40 mgm. of barium sulphate. Beythien (1903) drew attention to the possibility of errors arising from the absorption of sulphur dioxide from coal gas during the boiling off of iodine and bromine, and considered that the amount of sulphur dioxide thus absorbed might be as much as 10 mgm. Other authors also have drawn attention to this source of error, and Kühn and Rühle (1910) carried out a number of experiments to find out how much it amounted to under various conditions. On distilling 30 grm. of meat, free from sulphur dioxide, into iodine solution in the usual way, they found that when the iodine was boiled off rapidly over a gas flame in beakers covered with clock glasses, the amount of barium sulphate obtained corresponded to 0·0005–0·0023 per cent. of "apparent" sulphur dioxide. When the iodine was evaporated off on a steam bath in an open beaker the apparent sulphur dioxide rose to 0·007–0·010 per cent. On keeping the meat for 16 days until it was definitely bad, it still gave only 0·0005 to 0·0018 per cent. of apparent sulphur dioxide. Minced meat when fresh gave 0·0023 and 0·0027 per cent. and when rotten

0·0013 and 0·0023 per cent. of apparent sulphur dioxide, when the iodine was rapidly boiled off in ¼–½ hour in a beaker covered with a clock glass. It made hardly any difference if three times the amount of meat was taken for distillation ; the amount of barium sulphate obtained was approximately the same. By boiling off the iodine over a spirit lamp in a room with no gas flames the sulphur dioxide was reduced to a negligible amount (0·0006–0·0005 per cent).

Kühn and Rühle then carried out experiments with pure iodine solutions, the iodine being evaporated off in various ways. They got the following results :—

	$BaSO_4$ grm.
(i) 5 minutes rapid boiling over Bunsen flame with clock glass	0·0002
(ii) 30 minutes rapid boiling over Bunsen flame with clock glass	0·0033
(iii) 30 minutes boiling in open beaker	0·0042
(iv) 4 hours on steam bath in beaker with clock glass ..	0·0040
(v) 3 hours on steam bath in open beaker	0·0163
(vi) 14 hours on steam bath in open beaker	0·0265
(vii) Iodine distilled off in flask in a current of carbon dioxide	0·0010
(viii) 30 minutes boiling in distilling flask without carbon dioxide	0·0022

The difference between the amounts obtained by boiling over a gas flame and heating on the steam bath was due, in their opinion, to the fact that in the first case the solution was actively boiling and in the second the surface of the liquid was quiescent and therefore more readily accessible to gas fumes. From their results Kühn and Rühle concluded that, contrary to Winton and Bailey's findings, meat, even when rotten, does not produce volatile sulphur compounds on distillation and that the barium sulphate obtained is due solely to sulphur dioxide from coal gas.

Kühn and Rühle worked at Stettin and give no figures as to the amount of sulphur in the gas supply there. Beythien in 1903 worked at Dresden, where the gas contained 0·75 grm. of sulphur per cubic metre. This corresponds to 33 grains per 100 cubic feet or approximately the same as some London gas.

Schmidt (1904) working in Berlin, where the gas supply contained only half as much sulphur, found that the error from this cause was negligible. Schumacher and Feder (1905) working at Aachen with coal gas containing 0·4 grm. of sulphur per cubic metre found that 50 c.c. of $\frac{N}{10}$ iodine solution, heated on a steam bath till all the iodine had been driven off, gave 4·5 mgm. of barium sulphate.

According to my own experiments with bromine, iodine and hydrogen peroxide, it would seem that the effect of coal gas has been greatly exaggerated. Portions of the distillate from the mixture of eggs, onions, and mustard referred to on page 31 were oxidized with bromine, iodine and hydrogen peroxide, the last named being treated with barium chloride and filtered before use. The mixtures were heated each in three ways, (i) in conical flasks covered with watch glasses on electric hot plates; (ii) in open beakers over a gas flame and (iii) in open porcelain dishes on a steam bath heated by gas, the heating being continued until the bromine and iodine had been driven off. All the operations were carried out in a fume cupboard with a good draught. Blank tests were done on the same quantities of bromine and iodine solutions at the same time. The following were the weights of barium sulphate obtained:—

—	On electric hot plates. mgm.	In open beakers. mgm.	On steam bath. mgm.
Distillate + bromine	20·4	20·7	21·0
Bromine alone	0·7	0·7	1·0
Distillate + iodine	18·5	18·1	15·6
Iodine alone	1·3	1·7	1·5
Distillate + hydrogen peroxide ..	15·9	14·9	7·1

The low results when iodine and hydrogen peroxide solutions were heated on the steam bath in open dishes were no doubt due to the partial escape of volatile sulphur bodies before oxidation was complete.

100 c.c. of $\frac{N}{10}$ iodine solution were then heated in an open porcelain dish on a steam bath in a closed fume cupboard with no draught for one hour, and three other Bunsen flames were kept fully burning at the same time in the fume cupboard. All the iodine had been driven off in one hour, and on precipitation with barium chloride 16·4 mgm. of barium sulphate were obtained. This last experiment was purposely carried out under the most adverse conditions possible, and merely indicates that large errors may occur unless the usual precautions be taken. With ordinary care the absorption of sulphur dioxide from coal gas in boiling off bromine or iodine would appear to be negligible.

9. Thiosulphates.

Arnold and Mentzel (1903) drew attention to the occasional use of sodium thiosulphate ("hyposulphite") to preserve the red colour of meat products. Its use in this country has not been noted. On treatment of thiosulphates with mineral acids a variable amount of sulphur dioxide is given off and sulphur is precipitated (Vaubel, 1889). Arnold and Mentzel find that while zinc and hydrochloric acid reduce both sulphites and thiosulphates to hydrogen sulphide, sodium amalgam reduces only thiosulphates, sulphites being unaffected. Two or three c.c. of the solution are reduced with one to two c.c. of liquid sodium amalgam, containing 0·5 per cent. of sodium, and after ten minutes the solution is poured off from the excess of amalgam. Two or three drops of a 2 per cent. solution of sodium nitroprusside are then added. If thiosulphate was originally present, a red colour will be produced owing to the presence of alkali sulphide, while if only sulphite was present the solution remains yellow, unless sulphite was present to the extent of over 3 per cent. which never occurs in practice. Alcohol increases the sensitiveness of the reaction and may therefore be used to obtain a clear extract of the meat. The test will indicate one part of sodium thiosulphate in 12,500 parts of water.

Pittarelli (1924) gives two tests for thiosulphates which depend (i) on the yellow colour produced with p-amino-phenol and ferric chloride and (ii) on the decolorization of aurine in strongly acid solution. Hydrogen sulphide must be removed in both cases. Commercial bisulphites may apparently contain small amounts of thiosulphates. Von Possanner and Dittrich (1912) say that when calcium bisulphite solution is prepared by passing air containing 6 to 8 per cent. of sulphur dioxide through milk of lime, some thiosulphate is always formed.

10. The oxidation of sulphur dioxide and sulphites under various conditions.

A. *Disappearance of sulphur dioxide from foods on keeping.*

As already mentioned (p. 4) sulphur dioxide in combination with aldehydes and sugars is not readily oxidized. When foods containing these compounds are exposed to air, an initial rapid loss of sulphur dioxide occurs owing to volatilization and oxidation of the free sulphur dioxide present, but the rate of loss then becomes much slower, and some foods may retain a large proportion of their original content of sulphur dioxide even after exposure to air for several months.

Schmidt (1904) gives the following results and compares them with similar figures given by Beythien:—

Schmidt's experiments. Finely divided dried apricots exposed to air on glass plates.		Beythien's experiments. Different kinds of dried fruit in loose open paper bags.			
Length of exposure in days.	SO_2 mgm. per 100 grm.	Fruit.	Time kept in months.	Original SO_2 mgm. per100grm.	SO_2 after keeping. mgm. per100grm.
0	190	Apricots	14½	294·1	205·4
4	162	Pears	14½	60·9	51·6
8	157	Apricots	8	159·6	130·1
12	155	,,	8	163·2	123·4
16	151	Peaches	8	246·3	210·5
21	147	Apricots	8	184·0	123·4
30	145	,,	8	181·0	104·6
53	125	Peaches	8	140·0	140·3
100	114	Apricots	7	361·9	190·4
198	28	,,	5	347·0	305·3

On the other hand, Marpmann's results, quoted by Schmidt, shewed a much greater loss of sulphur dioxide on keeping dried apricots for as little as eight days.

In another series of experiments, Schmidt found that dried apricots containing 2,670 parts of sulphur dioxide per million, when kept in a paper bag for several weeks still contained 2,470 parts per million, and another sample containing 1,950 parts shewed 1,810 parts after the same period. Apricots which originally contained 1,670 parts per million were cut into small pieces and exposed freely for 10 days. They still contained 1,410 parts per million. This is in accordance with Farnsteiner's observation (p. 6) that the compound of glucose and sulphurous acid dissociates only slowly on removal of the free sulphur dioxide. The rate of loss of sulphur dioxide will depend largely on the water content of the fruit.

The rate of disappearance of sodium sulphite added to meat which was then kept in glass-stoppered bottles hermetically sealed with paraffin wax, has been studied by Campbell (1924). His results were as follows :—

Time kept.	Sulphur dioxide, parts per million.		
	Kept at room temperature.		Kept in refrigerator.
	Sample A.	Sample B.	Sample A.
As prepared	346	790	360
7 days	301	770	313
14 ,, ...	310	—	—
28 ,, ...	304	—	—
42 ,, ...	—	750	313

The slow rate of oxidation after the first seven days is perhaps to be attributed here to the absence of air, rather than to the union of sulphur dioxide with constituents of the meat.

B. "*Positive*" *and* "*negative*" *catalysis.*

Apart altogether from the resistance to oxidation shewn by sulphurous acid in the combined state, we have the curious effect of "positive" and "negative" catalysts in promoting or retarding the oxidation of free sulphurous acid. Bigelow (1898) investigated the retarding action of various organic compounds and found that benzyl alcohol had the greatest effect, followed by butyl and allyl alcohols, both of which were more effective than benzaldehyde. Mannitol and glycerine were fairly effective in retarding oxidation. Succinic acid on the other hand appeared to lessen the retarding effect of the above compounds. Titoff

(1903) found that the oxidation of sodium sulphite in aqueous solution could be either accelerated or retarded according to the nature of the catalyst present. In complete absence of catalysts oxidation is very slow, or even non-existent. Traces of salts of the heavy metals, especially copper, accelerate oxidation, and the effect of as little as one part of copper in 16 million parts of water can just be measured. Mannitol is a negative catalyst in that it counteracts the accelerating effect of the copper, but 1,800 molecules of mannitol are required to neutralize the effect of one molecule of copper. Among inorganic negative catalysts are stannic and stannous chlorides, which are by far the most effective, potassium cyanide, which is more effective than mannitol, ammonia and its salts, and sodium nitrite, the last named being less effective than mannitol. Acetone, in $\frac{N}{1000}$ solution, produces no retarding action, which indicates that the effect is not due to the formation of a ketone bisulphite compound.

Saillard (1913) found that cane sugar is also a negative catalyst, although, as Farnsteiner shewed, it does not combine with sulphur dioxide. One per cent. of sulphur dioxide in a 50 per cent. cane sugar solution remains practically unoxidized when air is passed through it at 70° C. for four hours. Saillard also found that this effect was exhibited to some extent by asparagin, aspartic acid, glutamic acid and lactic acid, and concluded that in molasses there are many substances which inhibit the oxidation of sulphur dioxide.

Glycerine is also a negative catalyst and has been used by several workers to prevent oxidation of sulphur dioxide during titration. Brown (1910) found that when 5 per cent. of glycerine was added to a solution containing 3·8 per cent. of sulphur dioxide and the solution kept in a stoppered bottle only half full, the amount of sulphur dioxide at the end of 12 months was 3·1 per cent., whereas without glycerine it had fallen to 1·5 per cent. He states, moreover, that in presence of glycerine sulphur dioxide can be titrated direct with iodine with accurate results. It is not necessary to add the sulphurous acid solution to an excess of iodine (cf. p. 14). Five per cent. of glycerine was also used by Haller (1919) and Waterman (1920) to prevent premature oxidation in the determination of sulphur dioxide and sulphites.

Sulphur dioxide is more readily oxidized in alkaline than in acid solution. Waterman (1920) found that the addition of excess of alkali to sodium sulphite solution accelerated the formation of sodium sulphate.

C. *Neutralization effect.*

Another somewhat obscure reaction is the so-called "neutralization effect." Raschig (1904) found that when normal sodium sulphite is converted into bisulphite, or conversely when bisulphite or sulphurous acid is converted into normal sulphite, there is always a loss due to oxidation. He says: "Sulphur dioxide is very insensitive to oxygen; it shews, however, extreme affinity for oxygen at the moment when it passes into a salt, or is set free from one of its salts."

Baker and Day (1912) also found that the addition of alkali followed by acid seems to promote oxidation of the sulphur dioxide. According to Haller (1919) it is prevented by glycerine. This neutralization effect may be akin to the reaction noted by Bennett (1922). He found that sulphurous acid liberated in solution from its salts at temperatures of 100°–120° C. or lower may undergo instantaneous auto-reduction with production of hydrogen sulphide and sulphuric acid.

$$4H_2SO_3 = H_2S + 3H_2SO_4.$$

According to Bennett the high reducing power of the sulphurous acid under these conditions may be due to the momentary existence of an acid of the unsymmetrical formula $H.SO_2OH$.

The possible error due to the neutralization effect should be borne in mind when adding alkali to foods with the object of decomposing combined sulphurous acid prior to acidification and distillation.

11. Alleged natural occurrence of sulphur dioxide.

Several authors (Pfeifer, 1889, Seifert, 1893, and others) have asserted that traces of sulphur dioxide may be produced during the fermentation of beer worts and wine musts. Pfeifer found 11 parts of sulphur dioxide per million in beer, whereas the hopped wort contained only traces. The same amount of sulphur dioxide was also produced in sugar solutions containing ammonium sulphate, when fermented with yeast. Seifert (1893) found 8 parts per million in wine fermented in the laboratory from unsulphured grape juice, and Schmidt (1904) quotes J. Schuch as saying that wines which have never been sulphured may contain as much as 57 parts per million.

In view of the work which has been done on volatile sulphur compounds since these papers were published, little importance can be attached to these findings. Jalowetz (1902) could find no evidence that sulphur dioxide is formed in appreciable amount during the fermentation of beer worts, and Schmidt (1904) suggested that the results of earlier workers may have been due to traces of hydrogen sulphide, which is sometimes present in beer.

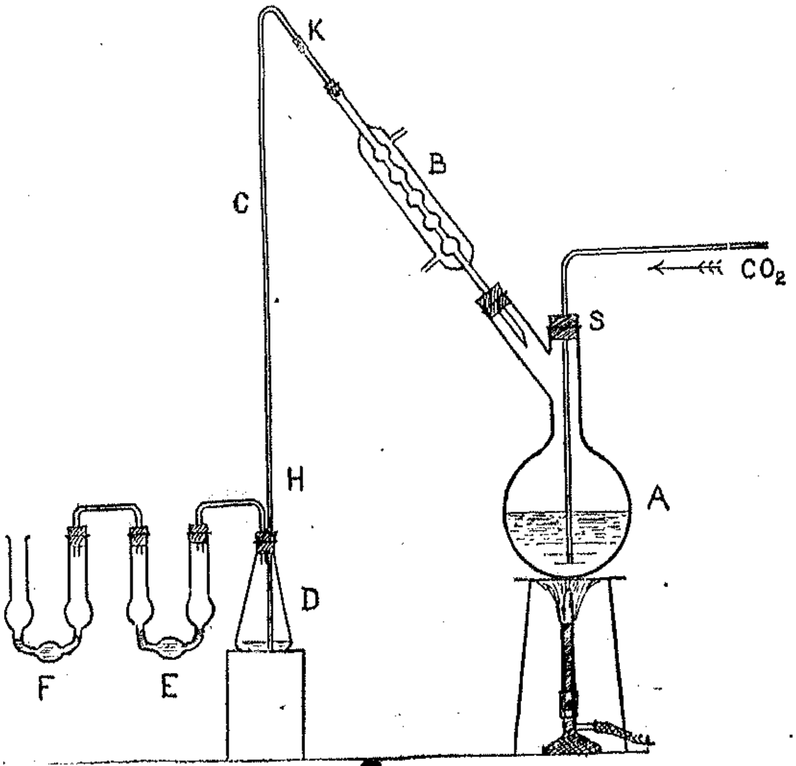
The possible absorption of sulphur dioxide from the atmosphere has been referred to by Kickton (1905, 1906) in the case of meat, and by Poetschke (1913) in the case of gelatine. Kickton could find no evidence that meat as ordinarily exposed to air takes up appreciable quantities of sulphur dioxide, but if the meat was hung in heavily sulphured store rooms, as is sometimes the practice in abattoirs, it took up an appreciable quantity. Poetschke states that gelatine prepared from materials free from sulphur dioxide may take up as much as 200 parts per million on being dried in an air current, but this would seem highly improbable, unless the air be contaminated with combustion products from fuel containing sulphur. It has been suggested that cornflour and similar foods will absorb sulphur dioxide from the air of towns, but no definite figures have been published. On the evidence available it may be concluded that the traces of sulphur dioxide which can find their way into food by natural agency are infinitesimal, and have no significance in connection with analyses of samples under the Regulations.

12. A general method for the determination of sulphur dioxide in foods.

From the foregoing review of the literature on this subject it is apparent that the determination of sulphur dioxide in most foods, in the amounts in which it is usually present as a preservative, does not present any special difficulties. When simple titration methods, either direct or after distillation, cannot be applied, distillation into bromine, iodine, or hydrogen peroxide solution, followed by gravimetric determination as barium sulphate, will always give accurate results, provided that certain precautions are taken. The most important points are (i) to ensure that the whole of the sulphur dioxide has been separated from combination with aldehydes, sugars, etc., and has been driven over into the distillate, (ii) to prevent oxidation of sulphur dioxide during distillation, and (iii) to correct the results for volatile sulphur compounds oxidized to sulphuric acid in the distillate.

With many foods the whole of the sulphur dioxide is readily separated by distillation from an acid solution, and also the errors due to volatile sulphur compounds are negligible. With others, in particular dried fruits, traces of sulphur dioxide are sometimes obstinately retained by the food, even when strongly acid, and it may be necessary [illegible] continue the distillation for several hours. Again, if much protein be present, or volatile products containing sulphur, the correction to be applied to the results may be rather large. Unless a sample of the same food, unsulphured, be available, the analyst will not know what correction to apply. In any case the gravimetric method takes a good deal of time and is not well suited for use in a commercial laboratory, where many samples have to be dealt with in a short time.

I have, therefore, endeavoured to find some method of general application which, while eliminating as far as possible the sources of error above referred to, will permit of an accurate determination of the sulphur dioxide in the distillate by titration. The method described below has been evolved from those already used by Franz and Sonntag (1908), Ferré (1914), Froboese (1920), Gutbier, Sauer and Brintzinger (1921) and Chaston Chapman (1922). It consists essentially of distillation in a current of carbon dioxide through a reflux condenser into pure neutral hydrogen peroxide, and titration of the sulphuric acid formed. The advantages of this method are that (i) errors due to hydrogen sulphide and volatile organic sulphur compounds are eliminated, the sulphuric acid found being due to sulphur dioxide alone, (ii) volatile acids do not pass over into the distillate and interfere with the titration, and (iii) it is not necessary to carry out a gravimetric determination, except when very small quantities of sulphur dioxide are in question.



A round-bottomed flask of 1,500 c.c. capacity (A), preferably provided with two necks, is connected as shewn in the figure with a sloping reflux condenser (B). An ordinary distilling flask with one neck may be used, but a two necked flask is far more convenient for general work. The lower end of the condenser should be cut off at an angle to facilitate a steady return flow of the condensate. The upper end of the condenser is connected by a vertical tube (C), about 4 to 4·5 mm. internal diameter, to a 200 c.c. conical flask (D) followed by two Peligot tubes (E and F). The delivery tube reaches to the bottom of the receiver. Rubber stoppers are used throughout. The conical flask (D) contains 10 c.c. of pure ten-volume (3 per cent.) hydrogen peroxide, free from sulphuric acid. The first Peligot tube (E) also contains 10 c.c. of hydrogen peroxide, and the second (F) contains 5 c.c. of a mixture of hydrogen peroxide and barium chloride acidified with hydrochloric acid. The solution used in the experiments recorded below was of the composition given on p. 31, but the exact strength is immaterial. The object of this guard tube is merely to serve as a check on the complete absorption of sulphur dioxide in the first two vessels, since the slightest trace of escaping gas will give a turbidity of barium sulphate. In no case was this observed in these experiments. After the apparatus has been connected up, 500 c.c. of distilled water are introduced into the flask together with 20 c.c. of pure concentrated hydrochloric acid. This solution is boiled for a short time in a current of pure carbon dioxide in order to remove air (for remarks as to carbon dioxide, *see* p. 16). If the food to be tested is liquid, it can now be introduced through a tap funnel (not shewn in the figure). 100 grm. is a convenient quantity in most cases. If the food is solid, the flask contents are first cooled by gradual immersion in a saucepan of water, the current of carbon dioxide being continued during cooling, and the food introduced by momentarily removing the stopper (S). The mixture is then boiled for one hour in a slow current of carbon dioxide. With some foods, such as cornflour, it may be necessary to heat at first in a saucepan of boiling water so as to avoid cracking the flask. No trouble from frothing has been experienced with any of the foods so far examined. It is possible that distillation for a shorter time than one hour would be enough in many cases (cf. Trotman and Sutton, 1924), but with dried fruits a full hour, or even longer, is necessary (p. 48).

Just before the end of the distillation the flow of water in the condenser is stopped. This causes the condenser and delivery tube gradually to become hot, and any sulphur dioxide retained by condensed moisture in the tube is driven over into the receiver. The receiver (D) may be kept cold during this operation by means of a small vessel of water. Directly the vertical tube just above its point of entry into the receiver at (H) is hot to the touch, it is disconnected at (K). The tube is washed down into the receiver with a small quantity of water, and the contents of the Peligot tube (E) transferred to ([illegible]). The liquid, which will measure with washings about 40 to 50 c.c., is titrated at room temperature with $\frac{N}{10}$ sodium hydroxide solution, using brom-phenol blue or methyl orange as indicator. Brom-phenol blue is in some respects more satisfactory than methyl orange for this purpose, since the colour change from yellow to blue, through an intermediate grey tint, is sharper. This indicator changes colour between 2·8 and 4·6 on the p_H scale, and is quite unaffected by carbon dioxide and by the slight traces of volatile organic acids which may reach the receiver during the final operation of steaming out the condenser. The $\frac{N}{10}$ sodium hydroxide used should of course be standardized against sulphuric acid with the same indicator. In artificial light the apparent end-point is shifted slightly towards the acid side. If desired the titration figure may be checked by a gravimetric determination, the precipitation of the barium sulphate being carried out at room temperature (p. 33). The precipitate is allowed to settle, and the supernatant liquid poured off through a filter. The residual barium sulphate is then washed three times by decantation with boiling water, before being brought on to the filter. In the test analyses given below a gravimetric determination has been carried out in every case, but this would not usually be necessary.

The method was first tested on pure solutions of sulphurous acid, prepared by passing the gas from a syphon into boiled and cooled distilled water until saturated, and diluting this solution as required. A measured quantity of the diluted solution was added to 500 c.c. of water in the distilling flask, previously boiled and cooled in a current of carbon dioxide and containing 20 c.c. of concentrated phosphoric acid. Phosphoric acid was used in these experiments in place of hydrochloric, as it was not until the method had been applied to foods that the advantages of the stronger acid became evident. The exact amount of sulphur dioxide introduced was determined on a separate portion by iodine titration, and also by titration with $\frac{N}{10}$ sodium hydroxide after oxidation with hydrogen peroxide. The latter titration includes, of course, any traces of sulphuric acid which may have been formed by oxidation while the solution was being prepared. The distillate was titrated with $\frac{N}{10}$ sodium hydroxide and bromphenol blue, and then acidified with hydrochloric acid and precipitated with barium chloride. The following were the results obtained:—

Sulphur dioxide added.		Sulphur dioxide found.			
		By titration.		Gravimetric.	
By iodine titration. mgm.	By titration with $\frac{N}{10}$ NaOH after oxidation with H_2O_2. mgm.	c.c. $\frac{N}{10}$ NaOH	SO_2 mgm.	$BaSO_4$ mgm.	SO_2 mgm.
101·3	102·2	31·2	99·8	362·5	99·5
46·2	47·4	14·3	45·8	169·4	46·5
33·3	33·0	9·9	31·7	118·6	32·5
20·4	20·2	6·1	19·5	71·1	19·5
11·9	11·9	3·7	11·8	41·7	11·4
6·2	6·4	1·95	6·2	22·3	6·1
2·1	2·1	0·6	1·9	7·1	1·95

The dilute phosphoric acid remaining in the flask after distillation was titrated with $\frac{N}{100}$ iodine solution and starch, and in no case could any residual sulphur dioxide be detected. On evaporating the flask contents and adding barium chloride a slight precipitate of barium sulphate was obtained, but this was due in great part to traces of sulphuric acid in the phosphoric acid used. Indications, were, however, obtained that very slight oxidation had occurred during distillation, which might account for the slightly low results in some of the experiments.

Tests were then carried out to determine the effect, if any, of acetaldehyde and volatile acids. The addition of excess of acetaldehyde to a solution of sulphurous acid prevents almost completely its oxidation by iodine and hydrogen peroxide, and interferes to a great extent with its oxidation by bromine, unless the bromine solution be heated. The question was whether acetaldehyde or volatile acids could pass through the reflux condenser into the receiver in amount sufficient to affect either the oxidation of the sulphur dioxide or the titration figure. The experiments were carried out in the same way as above described. In the first experiment 100 mgm. of acetaldehyde were added to the sulphurous acid solution before distillation, this amount of acetaldehyde being considerably more than would normally be present in 100 c.c. of wine. The amount of sulphur dioxide added was 70·1 mgm. and the amount found was 70·2 mgm. by titration and 68·2 mgm. gravimetrically. Acetaldehyde, therefore, in the amounts in which it may normally be present, does not affect the accuracy of the results. Acetaldehyde is not appreciably oxidized to acetic acid by hydrogen peroxide. In the second experiment 5 c.c. of glacial acetic acid, and 0·2 grm. each of benzoic, salicylic and cinnamic acids were added to the flask contents and distilled without any sulphur dioxide. The titration figure was 0·15 c.c., which indicates that practically no volatile acid passes over into the distillate. No benzoic or salicylic acid could be detected in the distillate.

The method was then tried with a number of foods of various kinds. Most of these were done in duplicate, one portion being distilled direct with phosphoric or hydrochloric acid, and the other after treatment with sodium bicarbonate solution. The object of this preliminary treatment with bicarbonate was to decompose combined sulphurous acid, it having been stated that several foods, such as cornflour, give a higher result when so treated than by direct distillation with acid. Eight grammes of sodium bicarbonate in 500 c.c. of water (approx. $\frac{N}{5}$ solution) were boiled in a current of carbon dioxide and cooled, and the food then introduced and allowed to remain in contact with the alkaline solution, with occasional agitation, for 10 to 15 minutes, or until thoroughly disintegrated. With dried fruits this may take half-an-hour or longer. Sodium hydroxide or carbonate may be substituted for bicarbonate, but the net result is the same, since the solution, after boiling and cooling in a slow current of carbon dioxide, will contain a mixture of carbonate and bicarbonate, either of which will effect the decomposition of aldehyde sulphurous acid on standing for a short time. In sample No. 1 (p. 47) sodium hydroxide was in fact used instead of bicarbonate. It will be seen from the analyses given below that alkali treatment does not make any appreciable difference to the results. The small differences observed in some cases are of the same order as the limit of experimental error. In sample No. 9 the higher result obtained was undoubtedly due to the use of hydrochloric acid in place of phosphoric, and not to the effect of alkali. It would appear that when hydrochloric acid, which is a much stronger acid than phosphoric, is used, treatment with alkali is not necessary with any of the foods examined.

The determinations in which hydrochloric acid was used are marked with an asterisk in the table. The other determinations were done with phosphoric acid. Previous tests with pure dilute hydrochloric acid had shown that none of the acid passes over into the receiver under the conditions of the experiment.

500 c.c. of water and 20 c.c. of either concentrated hydrochloric acid or phosphoric acid (sp. gr. 1·8) were used in all cases. When bicarbonate treatment was employed the amount of acid was increased to 30 c.c.

A titration figure of 1 c.c. $\frac{N}{10}$ sodium hydroxide corresponds to 32 parts of sulphur dioxide per million on 100 grm. of food. With very small amounts of sulphur dioxide, titration with $\frac{N}{10}$ alkali is not sufficiently accurate, so when the titration figure was less than 0·5 c.c. the gravimetric results alone have been given.

It will be seen that the agreement between the volumetric and gravimetric figures is satisfactory, and that even in the case of mustard and onions, only the merest trace of barium sulphate, less than 1 mgm., was obtained.

Several of the samples examined were sent to me by well-known analysts, who had determined the sulphur dioxide by different methods. Their results are shown in the last column. My best thanks are due to them for their co-operation.

Sample No.	Food.	Amount taken, grm.	Sulphur dioxide found (parts per million).				Found by independent analysts, using different methods.
			By direct distillation with acid.		After treatment with alkali.		
			By titration.	Gravimetric.	By titration.	Gravimetric.	
1	Cornflour ..	100	29	29	35	35	27
	,, (repeated)	,,	22*	30*	32	33	27
2	Cornflour ..	,,	90*	90*	88*	88*	86–87
3	Cornflour ..	,,	22*	16*	24*	20*	9–10
4	Cornflour ..	,,	75*	78*	—	—	64
5	Cornflour ..	,,	24*	23*	—	—	18
6	Cornflour ..	,,	—	Nil*	—	—	—
7	Port wine ..	,,	24	22	24	21	—
8	Port wine .. (sample 7) + 67·2 mgm. SO_2	,,	677	690	—	—	—
9	Dried apricots	,,	768	768	851*	852*	—
10	Dried apricots	,,	752*	749*	762*	765*	774
	,, ,,	,,	696	701	698	704	774
11	Fresh nectarines + 1 grm. Na_2SO_4	200	—	1*	—	—	—
12	Sultanas ..	100	—	Nil	—	Nil	—
13	Gelatine ..	,,	413	414	—	—	—
14	Gelatine ..	25	2509*	2554*	2470*	2485*	2306
15	Gelatine ..	100	—	—	366	368	—
16	Sausages (beef)	,,	—	Nil	—	1	—
17	Sausages (pork)	,,	—	2*	—	—	—
18	Sausages (pork)	,,	190*	195*	—	—	—
19	Corn syrup .. (freshly made)	100	368	373	365	370	378
20	Corn syrup (4 months old)	,,	397*	398*	392*	391*	373 (410 when freshly made)
21	Corn syrup (2 months old)	40	340*	324*	—	—	350 (when freshly made)
22	Sugar (plantation (white)	100	35*	32*	38*	32*	—
23	Sugar (plantation white)	,,	42*	37*	42*	37*	35–36
	,, ,,	66	41	39	—	—	35–36
24	Jam (raspberry)	100	—	5*	—	9*	—
25	Mustard (yellow and brown mixed)	,,	—	2	—	—	—
26	Onions ..	,,	—	1	—	—	—

In the case of dried apricots it is probable that the results shewn are slightly too low, and that distillation for longer than one hour is necessary before the whole of the combined sulphurous acid is decomposed. On boiling the mixture in the flask (sample

No. 10) for three further periods each of half-an-hour, the following results were obtained :—

Time of boiling.	With hydrochloric acid.			With phosphoric acid.		
	c.c. $\frac{N}{10}$ NaOH required	SO_2 pts. per million.		c.c. $\frac{N}{10}$ NaOH required.	SO_2 pts. per million.	
		By titration.	Gravimetric.		By titration.	Gravimetric.
One hour ..	23·50	752	749	21·75	696	701
Next ½-hr.	0·75	24	44	0·65	21	40
Next ½-hr.	0·30	10		0·30	10	
Next ½-hr.	0·25	8		0·20	6	
Total 2½ hrs.	24·80	794	793	22·90	733	741

When dried apricots are boiled with hydrochloric acid (20 c.c. in 500 c.c. of water) the mixture in the flask becomes dark brown, probably owing to decomposition of sugars, etc. With phosphoric acid, on the other hand, the amount of decomposition is usually very slight. This is also the case with cornflour and some other foods. It is conceivable that if extensive decomposition occurs, slight reduction of sulphates might take place, which would account for the continued evolution of traces of sulphur dioxide. During the last half-hour's boiling, therefore, in the above experiments, one gramme of sodium sulphate was added to the flask contents, and the same addition was also made in the blank experiment on fresh nectarines (sample No. 11). Fresh apricots were not available. The results show that no appreciable reduction of sulphates takes place under these conditions.

It must be concluded, therefore, that with dried fruits prolonged boiling in strongly acid solution is necessary before all combined sulphurous acid is decomposed. Preliminary treatment with sodium bicarbonate cannot be depended on to effect this decomposition completely. Possibly some compound akin to lignin sulphonic acid, which is decomposed with extreme slowness on boiling with acid, is present in sulphured dried fruits. When any doubt is felt as to whether the separation of sulphur dioxide is complete, the flask contents may be boiled for a further 20–30 minutes, with the end of the delivery tube dipping into a test tube containing a small quantity of hydrogen peroxide coloured with brom-phenol blue and rendered faintly alkaline. If this solution does not change colour it shews that all the sulphur dioxide has been driven off. With the foods examined one hour's boiling was sufficient in every case, except for dried apricots.

Summary.

From a study of the literature on the determination of sulphur dioxide in foods, and from the experiments recorded in this report, the following main conclusions may be drawn :—

(1) Sulphurous acid combines with aldehyde and ketone groups in foods, and to a smaller extent, possibly, with other groups. It is separated from combination rapidly on addition of alkali and more or less slowly on distillation with acid.

(2) Direct titration of foods or food extracts with iodine, after addition of alkali followed by acidification, may give fairly good results with some foods, but this is probably due, in most cases, to a balancing of errors.

(3) Distillation, according to one or other of the various modifications proposed, and with the necessary precautions against oxidation, is the only reliable method for the majority of foods.

(4) Titration of the sulphur dioxide in the distillate, either as such or after oxidation to sulphuric acid, gives accurate results if precautions are taken to eliminate volatile organic compounds. Distillation in a current of carbon dioxide through a reflux condenser into pure hydrogen peroxide, and titration of the sulphuric acid formed, can be applied with satisfactory results to all foods.

(5) With dried fruits the last traces of sulphur dioxide are given off with extreme slowness on boiling, even in strongly acid solution. Preliminary treatment of the food with sodium bicarbonate solution does not make any appreciable difference to the results.

(6) Gravimetric determination as barium sulphate gives accurate results in nearly all cases. Bromine or iodine may be used as oxidizing agents, except when the distillate contains appreciable amounts of volatile sulphur compounds. In such cases oxidation with hydrogen peroxide, and precipitation at room temperature with barium chloride, permits of a sharp distinction between sulphur dioxide and other volatile sulphur compounds, including hydrogen sulphide.

(7) The amount of sulphur dioxide in foods decreases on keeping, the rate of decrease under the same conditions varying greatly with different foods.

Much of the analytical work for this Report has been carried out by my assistant, Mr. W. A. Godby.

G. W. MONIER-WILLIAMS.

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