more or less perfectly measures the attraction of the active group for the water molecule. Thus the presence of a very polar group such as COOH, CO, CN, OH, or $CONH_2$, is sufficient to make the molecule of an organic substance soluble in water if the polar group does not have to pull into the solution a slightly polar group which is too long or too large. While slightly polar groups such as CH_3 are attracted by water, the attraction is much smaller than that of the polar groups. The active groups given above (and ether also) contain either oxygen or nitrogen atoms. The sulfur atom is much less active than either of these, but is much more active than the methyl group. Double or triple bonds between carbon atoms act as active groups, and benzene shows a much larger value for this free energy decrease than the corresponding six carbon atom hydrocarbons which do not contain double bonds.

4. True (or molecularly disperse) *solubility is a molecular scale phenomenon,*[1] and is dependent upon the attractions of the different parts of the various molecules for each other, and upon the shapes and sizes of the molecules which must be fitted together to make a solution. The space occupied by a molecule depends upon the extent of its kinetic agitation so the solubility of substances is highly dependent upon the temperature.

In a later paper we will present a more extended series of data, and will discuss the solubility of slightly polar substances in each other.

CHICAGO, ILL.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE IODOMETRIC DETERMINATION OF SULFUR DIOXIDE AND THE SULFITES.

BY JOHN B. FERGUSON.

Received December 29, 1916.

Although the determination of sulfur dioxide is one of the most important in the whole realm of gas analysis, it is only recently that any serious attempts[2] have been made to determine the conditions under which accurate analyses are obtainable, and these attempts have been confined to the determination of small amounts of sulfur dioxide in air in relatively large samples (2500 cc.). Furthermore, the methods advocated by the various investigators are not of general application. The writer, during an extended investigation of volcanic gases, has been confronted with the somewhat different problem of analyzing very accurately small gas samples (30 cc.) containing amounts of sulfur dioxide ranging from 0.3 to

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[1] For an excellent discussion of the related large scale properties of liquids see a paper by Hildebrand, THIS JOURNAL, **38,** 1452–73 (1916).

[2] Report Selby Smelter Commission, *Bull. Bur. Mines,* **98,** 200 (1915); *Chem. Abs.,* **10,** 4, 436 (1917); Seidell and Meserve, *J. Ind. Eng. Chem.,* **6,** 298 (1914).

50.0% of the total mixture. The solution of this problem necessitated an investigation of the methods in use and in the following paper are indicated the limitations of the existing methods and procedures, the most important sources of error, and the most suitable method found for general application.

In 1854 Bunsen showed that the reaction

$$H_2SO_3 + 2I + 2H_2O = 2HI + H_2SO_4$$

takes place quantitatively only when the concentration of the sulfurous acid does not exceed 0.04%. Finkener[1] and Volhard[2] later found that this reaction can be utilized for the determination of large amounts of sulfurous acid if the acid is added to the iodine solution, thus avoiding any excess of the former. On these investigations the various iodometric methods for the determination of sulfur dioxide are based. These methods may be thus summarized:

1. **Seidell and Meserve**[3] (small amounts).—The sufur dioxide is dissolved in a starch solution and to this is added a known iodine solution until the blue starch-iodide color appears.

2. **Marston**[4] (small amounts).—The sulfur dioxide is dissolved in a starch solution containing a little iodine and an iodine solution is added to this until a blue color is obtained which exactly matches the color shown by the starch solution after a blank determination.

3. **Selby Smelter Commission**[5] (small amounts).—This is the Marston method modified in such a way as to eliminate certain sources of error and it enables one to obtain accurate analyses in the field where a reducing atmosphere would attack any unprotected iodine solutions. Aside from changes in apparatus such protection necessitates, the essential differences may be said to consist in the mode of obtaining gas samples and the care taken with the blank determinations. By means of partially evacuated bottles the use of water in sampling is eliminated and in the blank attention is paid to the errors that may arise from moisture, the reaction of iodine on rubber and the influence of light, temperature or time on the color of the starch iodine solutions.

4. **Reich**[6] (various methods).—The gas mixture is drawn through a starch iodide solution of known iodide content until the solution becomes decolorized.

5. **Sulfite Method** (various amounts).—The sulfur dioxide is absorbed in a solution of either potash or soda and the sulfite determined in either of the following ways:

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[1] Finkener and Rose, "Quantitative Analysis," 1871, p. 937.

[2] *Ann.*, **242,** 94 (1887).

[3] *J. Ind. Eng. Chem.*, **6,** 298 (1914).

[4] Report Selby Smelter Commission, p. 189.

[5] *Ibid.*, p. 200; *Chem. Abs.*, **10,** 4, 436 (1916).

[6] F. Reich, Berg und Hüttenmann, *Ztg.*, **1858.**

(*a*) The sulfite solution is added to a measured volume of an iodine solution containing hydrochloric acid until the color of the starch indicator is discharged.

(*b*) The sulfite solution is added to such a measured volume of an iodine solution containing hydrochloric acid as to insure excess of iodine and this excess is then determined by titrating with a solution of thiosulfate in the usual manner.

6. Excess Iodine Method (various amounts).—The sulfur dioxide is dissolved directly in an excess of the iodine solution and the excess is determined with thiosulfate and starch.

In all of these methods the sulfur dioxide is calculated from the amount of the iodine reduced.

Since the accuracy of the determination is dependent to a great extent on the ability of the analyst to hit off the starch iodide end point, it may not be out of place to quote from a paper by E. W. Washburn[1] concerning this point—a paper that does not seem to be as well known as would have been expected. He says:

> "Preparation of the starch solution. This solution prepared as directed in Treadwell's Analytical Chemistry[2] and preserved in small bottles is eminently satisfactory. A large supply should be prepared at one time, as solutions prepared at different times are liable to give somewhat different end points. When properly prepared the first color with iodine is *pink*. Starch solutions giving blue or greenish blue color as first shade should be rejected. The 'soluble' starch of commerce is not to be recommended for the finest work........The shade of pink which is close to what is called the sensitive pink in polarimetry is much more sensitive to small changes than are the blue tints obtained by the further addition of iodine."

Washburn used a solution having this pink color as a color standard for his titrations instead of titrating to the disappearance of the color, and also found it necessary to make blanks which were titrated to the color of the color standard. Under the best conditions the blanks corresponded to as much as 0.8 cc. 0.001 N iodine. A further point emphasized by this author and also by Treadwell is the necessity of the presence of sufficient iodide in the solution to develop the proper color with the starch indicator.

The first three methods given for the determination of sulfur dioxide may be considered together. They are essentially the same; the differences consist in the manner of the handling of the solution and gas and for this reason the third is without doubt the best. Too great care cannot be taken if correct analyses of mixtures containing small amounts of sulfur dioxide are desired.

The Reich method can be used only in special cases in which large volumes of gas are obtainable. For very accurate work it cannot be

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[1] E. W. Washburn, THIS JOURNAL, **30**, 42 (1908).

[2] Treadwell, "Analytical Chemistry," **2**, p. 513 (1904).

recommended, since there is no adequate method for determining the end point, no provision for making blanks, and the procedure is such that the starch is added to a fairly strong iodine solution (a procedure sure to render the indicator less sensitive and the end point more doubtful) unless such volumes of gas are taken as to render these sources of error negligible.

The sulfite method is very useful in those cases in which the analyst wishes to absorb both sulfur dioxide and carbon dioxide from the same gas sample, but is subject to several sources of error. Some of these were investigated by the writer in the following manner: Various amounts of carbon dioxide and sulfur dioxide which had been carefully dried over phosphorus pentoxide were measured out and transferred into dry glass containers over dry mercury to form mixtures of different compositions. The absolute necessity of the most careful drying of all the apparatus as well as the gas mixtures cannot be too strongly emphasized and will be discussed at greater length later in this paper. These mixtures after standing for a week were analyzed by the following procedure:

Procedure.—A sample is drawn into a dry Hempel buret overy dry mercury and measured. It is then forced into a pipet containing a 0.4% solution of potash and the pipet well shaken. This solution is then run into a beaker containing an excess of a 0.02 *N* solution of iodine containing little more than enough hydrochloric acid to neutralize the alkali. After the pipet has been carefully washed out with distilled water and the washings added to the solution in the beaker, the excess iodine is determined with a 0.02 *N* solution of thiosulfate using starch as an indicator. A blank experiment is made and the difference between the iodine used up in the blank and in the analysis gives the iodine reduced by the sulfur dioxide.

The apparatus consisted of a buret[1] equipped with a Pettersson correction tube and a simple Hempel pipet modified by the addition of a thistle tube and two stopcocks to render the filling, emptying and washing of the pipet as simple as possible.

TABLE I.—ANALYSES OF DRY CO_2-SO_2 MIXTURES USING THE SULFITE METHOD.

SO_2 in mixture. Per cent.	SO_2 taken. Cc.	SO_2 recovered. Cc.	SO_2 loss. Cc.
2.25	2.034	1.718	0.316
2.25	1.867	1.527	0.340
1.40	1.305	1.035	0.270
1.40	1.114	0.875	0.239
2.92	2.716	2.405	0.311
11.60	6.149	5.527	0.622
11.60	8.143	7.194	0.949

0.1 cc. 0.02 *N* iodine solution corresponds to 0.0228 cc. SO_2 at 0° and 760 mm.

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[1] A complete description of such a buret will be found in "Gas Analytische Methoden," W. Hempel, p. 44, or in "Gas Analysis," Dennis, p. 91.

The analyses of the more dilute mixtures show losses of sulfur dioxide of approximately the same magnitude, *viz.*, 0.3 cc. This would indicate but one chief source of error which would be the oxidation due to the oxygen dissolved in the alkaline solution. If the same volumes of solution and washings are always used, such a source of error can be corrected for and the method then used with a fair degree of accuracy. With the more concentrated mixture the loss may arise from two or three sources. The first and most important would be the oxidation by the oxygen dissolved in the alkali; the second, the oxidation by the oxygen that becomes dissolved in the alkaline sulfite solution prior to its addition to the iodine solution, and the third, the loss of the sulfur dioxide from the sample before the latter comes in contact with the alkali. In the case of such mixtures, therefore, this method, with a suitable correction factor, could be used only when no great accuracy is desired.

There seems to be no good reason why the correction factor should not come into more general use. The remarkable ease with which a careful worker can repeat almost any procedure and get the same result is well known. For this reason the writer believes that many analyses done hurriedly by easy methods might be made of real value if the analyst would obtain and apply a proper correction factor. This particularly applies to those cases where the analyses must be done in a very short time and are at present only of comparative value.

The procedure 5 (*a*) in which the sulfite solution necessarily would be in contact with air for a considerable length of time was not checked at all, since by it the oxidation losses would certainly exceed those occurring when procedure (*b*) was used.

The excess-iodine method is suitable for both large and small amounts of sulfur dioxide and is strictly accurate. For small amounts it gives results comparable to those obtained by the Selby Smelter Commission method. The following experiments will demonstrate what can be expected of it: Two mixtures of dry air and sulfur dioxide were made up in an all-glass apparatus[1] and analyzed. The apparatus was so designed that the gas comes in contact with dry glass, dry clean mercury, and two stopcocks lubricated with but a thin film of Travers' stopcock lubricant prior to reaching the iodine solution. Unfortunately samples of more than 35 cc. could not be measured, so that it was impossible to work with very dilute mixtures. This should not detract much from the value of the results, since the chief interest lies in the actual amounts of sulfur dioxide lost.

Procedure.—The sample, about 35 cc. measured at constant volume and temperature, is forced to bubble through an iodine solution contained

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[1] This apparatus will be described later in some papers dealing with various gaseous equilibria.

in a pipet. It is left in contact with the solution for five minutes[1] and then the solution is drawn off into a beaker to which the necessary washings are added. To this solution is added a thiosulfate solution until the iodine color almost disappears, then the starch indicator and more thiosulfate until the solution has the pink color of the color standard already made up. A blank is at once made by repeating the procedure, leaving out the gas mixture, and the solution so obtained is also brought to the color of the standard. From the different amounts of thiosulfate used, the excess iodine and hence the iodine reduced is calculated, the difference between the iodine reduced in the blank and in the analysis gives the amount reduced by the sulfur dioxide and thus the amount of this gas. The blank amounted to approximately 0.7 cc. in the case of the 0.001 *N* solutions.

TABLE II.—ANALYSES OF DRY AIR-SO_2 MIXTURES USING THE EXCESS-IODINE METHOD.

SO_2 in mixture. Per cent.	SO_2 taken. Cc.	SO_2 recovered.		I solution strength used.
		Cc.	Per cent.	
4.5	1.667	1.671	100.2	0.02 *N*
0.365	0.0943	0.0934	99.04	0.001 *N*
0.365	0.1460	0.1428	97.8	0.001 *N*
0.365	0.1354	0.1361	100.5	0.001 *N*
0.365	0.1255	0.1273	101.4	0.001 *N*

0.1 cc. 0.02 *N* solution of iodine corresponds to 0.0228 cc. SO_2 at 0° C. and 760 mm.

0.1 cc. 0.001 *N* solution of iodine corresponds to 0.00114 cc. SO_2 at 0° C. and 760 mm.

It is not possible for every analyst to have at his disposal an all-glass apparatus such as the writer used, and since correct analyses of sulfur dioxide mixtures require so much care in manipulation and sampling to avoid losses of this constituent, a few of the sources of error will be discussed in some detail.

Oxidation.

From the table of analyses just given it can be seen at once that in dry gas mixtures of air and sulfur dioxide no oxidation takes place. The two mixtures used were not analyzed until a week or ten days after they were made up.

Moisture.

Water may act in two ways: It may simply dissolve the sulfur dioxide and hold it in solution or it may catalyze the oxidation of this gas.

Both Seidell and Meserve and the Selby Smelter Commission were impressed with the magnitude of this source of error. The former found on moist days that their sulfur dioxide losses greatly exceeded those occurring on dry days and laid it to the catalysis by the water vapor of the

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[1] Since the pipet was part of an all-glass apparatus it could not be shaken and the time allowed for the gas absorption was far in excess of that needed when the pipet can be shaken.

oxidation of the sulfur dioxide. The latter may be quoted as follows: "Unless the aspirator was absolutely dry, requiring a treatment of alcohol and ether, there was a surprisingly large and variable absorption of the sulfur dioxide" and attributed this to solution in the water film on the glass, to a reaction between the glass and the gas or to both. The present writer has observed no evidence of any reaction between the glass and the sulfur dioxide. Indeed the fact that the retention of the gas appears to follow Henry's law would seem to eliminate this possibility. He has observed, however, in moist mixtures some slight deposits of sulfur on the walls of the containers if the mixtures are kept a long time, due probably to oxidation of the sulfur dioxide according to the following equation:

$$3SO_2 + 2H_2O \leftrightarrows 2H_2SO_4 + S$$

These observations, which fit in well with those of Bichowsky,[1] indicate that such oxidation is a source of error which can be neglected unless the mixtures are kept a long time. The loss of sulfur dioxide by solution in the film of moisture adhering to all glassware, is however, a different story. Even glass apparatus that had been dried out at room temperature by repeated washings, extending over several days, with air dried with phosphorus pentoxide, showed considerable adsorption. Owing to the design of the apparatus used for testing the iodine method this was the only feasible method of drying, so that for very accurate work the apparatus has first to be washed out with a gas mixture of similar composition to that which is to be analyzed.

Rubber Connectors.

Graham[2] long ago showed that rubber was permeable to various gases. The relative volumes of each gas passing through a rubber membrane in a given time as determined by him are given below:

Nitrogen	1.0
Carbon monoxide	1.11
Air	1.149
Ethylene	2.148
Oxygen	2.556
Hydrogen	5.5
Carbon dioxide	13.585

In 1893 Reychler[3] extended this investigation to sulfur dioxide. His conclusions may be summarized as follows:

1. Unvulcanized rubber saturated with sulfur dioxide at room temperature and atmospheric pressure contains about 24 times its volume of this gas.

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[1] F. R. Bichowsky, now of this laboratory, investigated this reaction while at the University of California and has kindly communicated his results, as yet unpublished, to the writer.

[2] *Phil. Mag.*, **1866**, 399.

[3] *Bull. Soc. Chim. de Paris*, **9**, 404–409 (1893).

2. Rubber behaves much like a thin layer of liquid. The rate of solution of this gas in, and the evolution from the rubber surface, greatly exceeds the rate of transfer of the gas through the rubber.

3. The rate of transfer through the rubber estimated on the same basis as Graham used in his table would exceed 150.

A simple experiment made by the writer illustrates the velocity with which this solution takes place. A piece of new black rubber tubing 20 cm. long, of 6 mm. bore and 2 mm. wall, was filled with sulfur dioxide and the ends closed with clamps. In two hours the tube was quite flat; the sulfur dioxide had been all absorbed. Much to the writer's surprise, in a similar experiment, using hydrogen sulfide instead of sulfur dioxide, the tube flattened in about four hours so that if this gas were added to Graham's list the value given for it would be about 75. A similar experiment with carbon dioxide resulted in a partially flattened tube the next morning.

These experiments indicate the necessity of distinguishing between the two kinds of permeability of rubber to the various gases and place sulfur dioxide and hydrogen sulfide in a different class from the rest of the gases investigated. In ordinary gas analysis, the solution of these two gases in the rubber connectors may be a considerable source of error, although in the case of the other gases such errors may be negligible. The following analyses made by the excess-iodine method, using the pipet and buret previously described, seem to confirm this for the mixtures containing the higher concentrations of sulfur dioxide.

TABLE III.—ANALYSES OF DRY CO_2-SO_2 MIXTURES USING THE EXCESS-IODINE METHOD WITH AN APPARATUS HAVING RUBBER CONNECTORS.

SO_2 in mixture. Per cent.	SO_2 taken. Cc.	SO_2 recovered. Cc.	SO_2 loss. Cc.
2.92	1.973	1.926	0.037
...	2.003	1.954	0.049
...	2.599	2.544	0.055
...	2.786	2.748	0.038
...	2.716	2.651	0.065
10.60	7.890	7.718	0.172
...	7.031	6.908	0.123
...	7.610	7.478	0.132
...	8.191	8.034	0.157
...	5.419	5.255	0.164

0.1 cc. 0.02 *N* iodine solution corresponds to 0.0228 cc. SO_2 at 0° and 760 mm.

The losses during analysis are probably not as large as stated, for it is likely there was some loss of the sulfur dioxide through the rubber connections in making up the gas mixtures. The large and variable losses found upon analyzing the mixture containing the higher concentration of sulfur dioxide would show that for such mixtures, *i. e.*, containing 10% or more of the gas, the rubber connections are a real source of error; with the more dilute, however, such errors may perhaps be neglected.

Sulfites.

Treadwell[1] suggests that soluble sulfites be determined as follows: "Dissolve the sulfite in distilled water, add this solution to an excess of an iodine solution made acid with hydrochloric acid and determine the excess by means of a thiosulfate solution." This procedure is subject to several errors as the following experiments by various procedures will show:

Procedure 1.—0.5 g. of anhydrous sodium sulfite analyzed as suggested by Treadwell.

Procedure 2.—0.5 g. of anhydrous sodium sulfite analyzed in the same manner as in Procedure 1, but air-free water was used and the sulfite solution protected from the air.

Procedure 3.—0.5 g. of the salt added in the solid state to the iodine solution, instead of first being dissolved in distilled water and then determined as in Procedure 1.

Procedure 4.—Procedure 1 repeated, using a dilute solution of potash instead of distilled water.

Procedure 5.—0.5 g. of the salt dissolved in acid bromine water and the total sulfur determined gravimetrically. The sulfur found was calculated to a sulfite basis.

The following table gives the percentage of sodium sulfite[2] recovered by the various procedures:

TABLE IV.—Na_2SO_3 RECOVERED.

Procedure	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.	5. Per cent.
	90.18	92.2	94.8	90.68	96.5
	...	92.2	94.5	...	..
	...	..	94.7	...	..

The oxidation losses may arise from the oxygen in the water or solution in which the sulfite is dissolved and from the oxygen carried into the solution by the solid salt. The results by Procedures 1 and 2 indicate that both these occur, and by Procedure 4 that the presence of alkali retards rather than catalyzes this reaction, an effect one might have predicted since it is hardly likely the oxidation takes place on the un-ionized part of the salt in the solution. There is no means of telling how close the values given under Procedure 3 approximate to the true sulfite content, but they are probably near the truth since it is doubtful if the air carried into the iodine solution by the solid salt would have time to react with the salt

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[1] "Analytical Chemistry," **1906,** II, 536.

[2] The description of the anhydrous sodium sulfite to be found in Merck's index places the Na_2SO_3 content between 85 and 90%.

before the iodine solution had completely oxidized the latter. For this reason Procedure 3 is recommended in preference to that given by Treadwell.

Conclusions.

For the very accurate determination of large or small amounts of sulfur dioxide the excess-iodine method is recommended.

For small amounts only, either the excess iodine or the Selby Smelter Commission method should be used, depending on which is the more convenient under the given working conditions.

The Reich method may be used for either small or large amounts, but will yield accurate analyses only when sufficiently large samples are taken to render the uncertain end point a negligible source of error.

When carbon dioxide and sulfur dioxide are to be determined on the same sample, the sulfite method can be used to advantage. With mixtures containing not over 3 or 4% a suitable correction factor will render the results fairly accurate, but with higher concentrations the uncertainty increases.

The scheme of employing a correction factor does not receive the consideration which it deserves and could be used to some advantage in many other analyses.

If the analyst intends his analyses to approximate to the truth he must observe the following conditions:

1. The gas sample must not come in contact with even a trace of moisture prior to its reaching the absorbent.

2. The analyzing apparatus must be free from all rubber connectors when exact analyses of mixtures containing 10% or more of sulfur dioxide are desired. For very accurate work it would be better to dispense with them entirely, although this source of error for mixtures containing less than 3% of sulfur dioxide may be neglected.

3. Mixtures of sulfur dioxide and air when dry do not react appreciably, but when moist a slow oxidation takes place. For this reason it is impossible to recover from a moist container, even by pumping, the initial amount of sulfur dioxide if the gas mixture has been in the container for any great length of time.

The following procedure for the analysis of such soluble sulfites as anhydrous sodium sulfite is recommended: The solid salt is dissolved directly in an excess of an iodine solution containing sufficient hydrochloric acid and the excess iodine is determined with thiosulfate. This eliminates several sources of error due to oxidation of the salt by agents other than the iodine solution.

WASHINGTON, D. C.