DETERMINATION OF SULPHUR TRIOXIDE IN THE PRESENCE OF SULPHUR DIOXIDE, TOGETHER WITH SOME ANALYSES OF COMMERCIAL LIQUID SULPHUR DIOXIDE

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ABSTRACT

A method for determining sulphur trioxide in sulphur dioxide has been developed for use in a study of the heat of formation of sulphur dioxide. It may find application also in control work in the manufacture of sulphur dioxide, sulphites, and sulphuric acid, and in the analysis of oxygen-free products of combustion of fuels. None of the methods given in the literature appeared suitable for the purpose. Therefore a method has been devised for the complete removal of sulphur trioxide by precipitation as barium sulphate in a slightly acid solution of barium sulphite, and filtration and washing of the precipitate with oxygen-free distilled water in an atmosphere of oxygen-free nitrogen. The method has been applied to the analysis of eight samples of commercial liquid sulphur dioxide.

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I. INTRODUCTION

The analytical method described in this paper was developed in connection with a study of the heat of formation of sulphur dioxide. It is published at this time on account of its possible application in control work in the manufacture of sulphur dioxide, sulphites, and sulphuric acid, and in the analysis of oxygen-free products of combustion of fuels. The literature contains a number of different methods which have been used for this determination. Berthelot [1] in his work on the heat of formation of sulphur dioxide burned a definite amount of sulphur and absorbed the gas in the amount of iodine solution that would be required if all of the sulphur were burned to sulphur

[1] M. Berthelot, "Sur la chaleur de formation des oxydes du soufre," Ann. chim. [5], 22, p. 422; 1881.

dioxide. Any unused iodine was regarded as a measure of the sulphur trioxide present in the gas. Thomsen [2] condensed the sulphur trioxide on the walls of the platinum combustion chamber, washed it out with water and titrated. Ljungh,[3] using the principle of the Reich-Lunge method,[4] determined dioxide plus trioxide by absorption in standard sodium hydroxide, and the dioxide by absorption in standard iodine solution. Pellet [5] absorbed the trioxide in concentrated hydrochloric acid and determined it gravimetrically by precipitation with barium chloride. Hawley [6] used a sheet of filter paper moistened with water to collect the trioxide and then titrated the resulting sulphuric acid. Richter [7] collected the trioxide in condenser tubes and determined it in the usual gravimetric way. Dunn [8] investigated the Reich-Lunge method [4] of estimating sulphur trioxide by difference and found it inaccurate. In his own method he absorbed trioxide plus dioxide in barium chloride solution containing 10 to 15 per cent of hydrochloric acid, removed the dioxide by boiling and determined the trioxide in the usual gravimetric way. Saillard and Bregmann [9] used an electrical conductivity method. Dieckmann [10] absorbed the gases in sodium hydroxide and determined the relative amounts of trioxide and dioxide by acid titration using double indicators. Sander [11] used standard sodium hydroxide as an absorbent for trioxide plus dioxide, added mercuric chloride to liberate a quantity of hydrochloric acid equivalent to the dioxide, and then titrated with standard sodium hydroxide. Gille [12] collected the trioxide in a plug of cotton. Schmidt [13] used as absorbents iodine solutions and varied the concentration for the purpose of getting selective absorption of the trioxide and dioxide.

None of these methods appeared suitable for the present purpose and a method comprising the following essential features was accordingly devised. The sulphur trioxide is removed from the gas

[2] Julius Thomsen, "Thermochemische Untersuchungen," Johann A. Barth, Leipzig, **2**, p. 245; 1882.

[3] H. Ljungh, "Zur Bestimmung des SO_3-Verlustes in den Abgasen einer Kontaktschwefelsäurefabrik," Chem.-Zeitg., **33**, p. 143; 1909.

[4] G. Lunge, "Technical Methods of Chemical Analysis," English Translation of 2d. German ed., Gurney & Jackson, London, **1**, pp. 299-303; 1908.

[5] H. Pellet, "Sur le dosage de l'acide sulfureux et de l'acide sulfurique dans les gaz du four à soufre," Bull. assoc. chim. sucr. dist., **27**, p. 468; 1909.

[6] H. G. Hawley, "Determining sulphur trioxide in flue gas," Eng. Min. J., **94**, p. 987; 1913.

[7] Erich Richter, "Über die Bestimmungen von SO_3 in Schwefelofengasen," Z. angew. Chem., **26**, p. 132; 1913. Also Wochbl. Papierfabr., **54**, p. 1521; 1923.

[8] E. M. Dunn, "Determination of gases in smelter flues," Bull. Am. Inst. Min. Eng., **80**, p. 2051; 1913.

[9] E. Saillard et Dr. Bregmann, "Détermination de l'acide sulfureux et de l'acide sulfurique des gaz des fours à soufre par conductibilité électrique," Rev. gén. chim., **20**, p. 69; 1917.

[10] R. Dieckmann, "Über eine vereinfachte Methode zur Bestimmung von Schwefeldioxyd und Schwefeltrioxyd in den Röstgasen," Papierfabr., **19**, p. 285; 1921. Also Chem.-Zeitg., **45**, p. 885; 1921.

[11] A. Sander, "Über die titrimetrische Bestimmung freier schwefliger Säure." Chem.-Zeitg., **38**, p. 1057; 1914. "Eine neue Methode zur Untersuchung der Röstgase und der Sulfitlauge," Papier-Zeitg., **45**, p. 1842; 1920. "Über die Bestimmung von Schwefeldioxyd neben Schwefeltrioxyd in Röstgasen und Oleum," Chem.-Zeitg., **45**, p. 261; 1921.

[12] H. Gille, "Über Absorption chemischer Nebel," Z. angew. Chem., **39**, p. 401; 1926.

[13] E. Schmidt, "Über Röstgasanalyse," Papierfabr., **23**, p. 229; 1925. "Die Bestimmung von Schwefeltrioxyd in Röstgasen," Z. angew. Chem., **39**, p. 732; 1926.

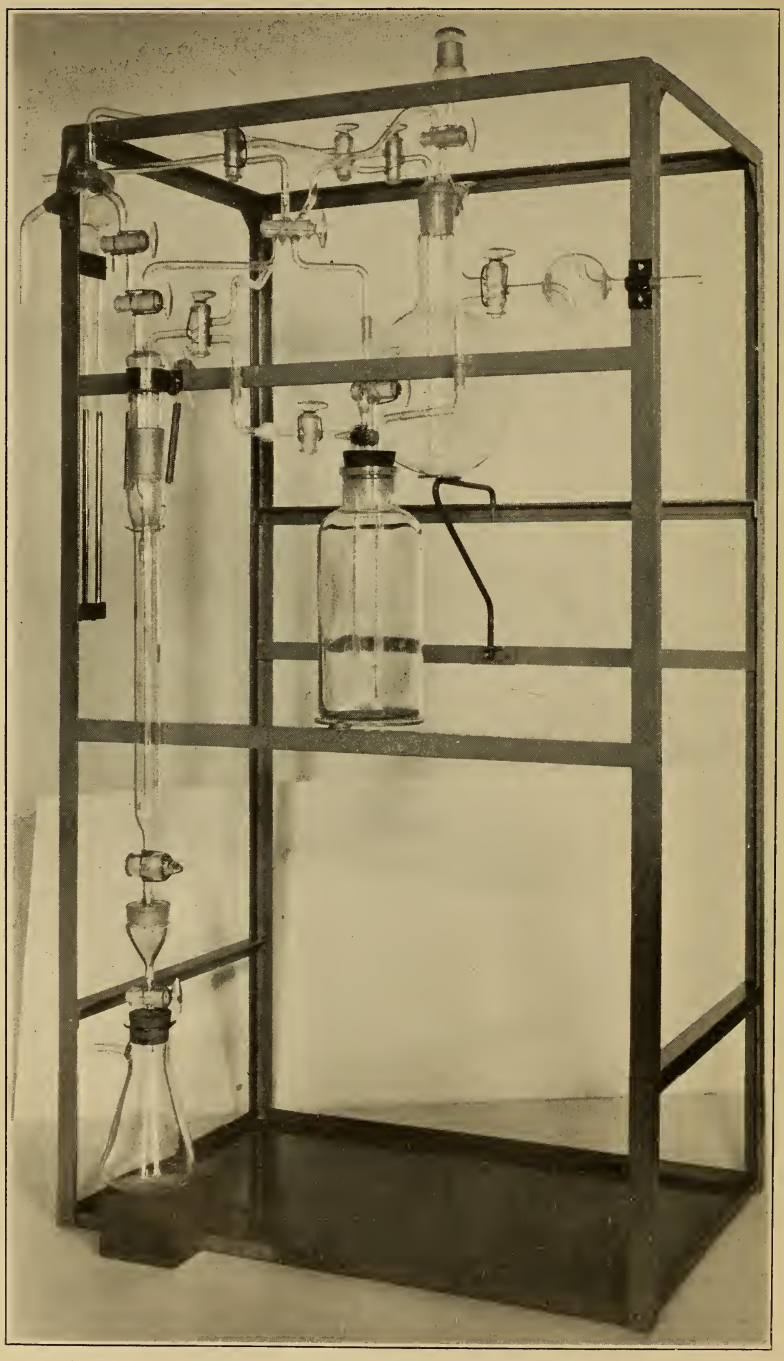


FIG. 1.—*Apparatus used, with modified form of analytical tube*

stream by means of a special filtering device; the sulphur trioxide is precipitated by a nearly saturated and slightly acid solution of barium sulphite which must be free from oxygen; and the barium sulphate is filtered and washed in an atmosphere of nitrogen free from oxygen. Various difficulties and sources of error involved in the earlier methods are thus eliminated.

II. SULPHUR TRIOXIDE IN GASEOUS SULPHUR DIOXIDE

1. APPARATUS

A photograph of the actual apparatus used with the modified form of analytical tube is shown in Figure 1. A diagrammatic sketch of the apparatus is shown in Figure 2. *A* is a small metal cylinder containing sulphur dioxide. *B* and *D* are glass safety traps. *C* is a glass flow meter containing water. *E* is a bottle used for the preparation of the barium-sulphite reagent. This bottle is fitted with a paraffined four-hole rubber stopper through which pass the sulphur dioxide inlet tube *2–F*, inlet or outlet tube *o–G*, inlet tube *4–*G_1, and the barium-sulphite outlet tube *H–5–g*, which is equipped with either an alundum filtering tip at *H*, or a plug of cotton at *I*, to hold back any loose particles of precipitate which might otherwise be carried over with the barium-sulphite reagent.

J is the analytical tube into which clear barium-sulphite reagent from bottle *E* is forced for the purpose of absorbing the sulphur trioxide. In the lower part of tube *J* is sealed a sintered-glass filter plate, *N*, the porosity of which is suitable for filtering barium sulphate by means of suction without danger of loss. Below this plate is a two-way stopcock, *8*, the stem, *R*, of which extends through a rubber stopper, *j*, into suction flask *S*. Tube *J* is fitted at the top with a ground-glass stopper, *h*, in which are sealed three tubes, one closed by two-way stopcocks *6* and *7*, the second by three-way stopcock *12*, and the third by two-way stopcock *10*. The inlet tube *12–M*, through which the gas sample is admitted, ends in either an alundum filtering tip, or a sintered-glass plate, *M*, for the purpose of collecting any sulphur trioxide present as mist or fog.[14] *U* is an inlet with ground-glass stopper for the introduction of hot hydrochloric acid. *W* is a mercury gauge used to regulate the pressure of the nitrogen admitted to the apparatus at *e*. The gas to be analyzed is admitted through inlet *f*.

Y is a flask for the preparation of oxygen-free distilled water. It is fitted with a ground-glass stopper, *k*, containing three tubes *17–z*, *18–*Z_1, and *19–*Z_2. *X* is a funnel tube with a ground-glass stopper through which distilled water may be introduced into flask *Y*.

[14] See footnote 13, p. 278.

Ground-glass joints *b*, *d*, and *g* permit the removal of bottle *E* for cleaning and refilling. The connection to cylinder *A* is made by threaded brass joint *a*.

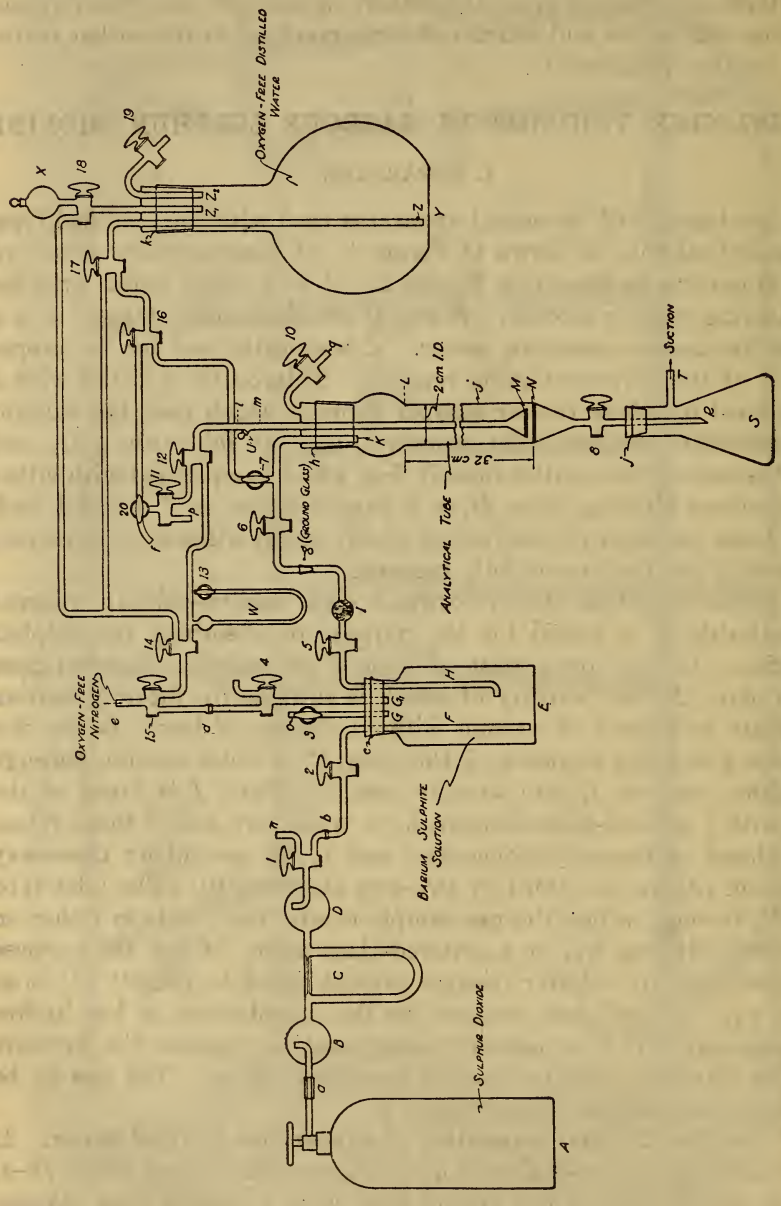


FIG. 2.—*Apparatus for the determination of sulphur trioxide in the presence of sulphur dioxide*

2. PROCEDURE

Through inlet *o* about 500 ml of 0.02 normal hydrochloric acid, containing 5 g of barium chloride ($BaCl_2.2H_2O$), is introduced into bottle *E*. With stopcocks *4* and *5* closed and stopcock *3* open sulphur

dioxide from cylinder *A* is run into bottle *E* through stopcocks *1* and *2* and inlet *F* until the solution is saturated. Stopcocks *1* and *2* are then closed. Nitrogen[15] is passed in through stopcocks *15* and *4* and inlet G_1 and out through stopcock *3* in order to remove all the oxygen from that line. Stopcock *4* is then closed and stopcock *3* left open.

Nitrogen is then passed through stopcocks *15*, *14*, and *12* into tube *J* and thence through stopcocks *6* and *5*, opening *H* and stopcock *3*. Stopcock *3* is then closed. In a similar manner oxygen is driven out of line *N–8–R*. In the initial determination lines *K–7–16–17–Z*, *14–17–Z*, and *14–18–*Z_1 are thus freed from oxygen. Oxygen is removed from line *11–12* by suction at *f*, and from line *20–16* in the initial determination by suction at *p*.

Oxygen-free distilled water is prepared in flask *Y* by boiling distilled water with nitrogen bubbling through it by way of line *14–17–Z–19*.

Stopcocks *8* and *6* are closed and stopcocks *7* and *10* are opened and, by means of nitrogen pressure exerted at inlet Z_1 through stopcock *18*, about 20 ml of the oxygen-free distilled water is forced through line *Z–17–16–7–K* into tube *J*. With stopcocks *7* and *8* closed and stopcocks *10*, *6*, and *5* open, and with nitrogen entering bottle *E* through stopcock *4* and inlet G_1, about 80 ml of the clear barium-sulphite reagent is forced through line *H–g–K* into tube *J*, which is thus filled to height *L*. Stopcocks *6* and *5* are then closed. The sample of gas to be analyzed is then admitted at *f* and drawn or forced through stopcocks *20*, *11*, and *12* and tip *M* into the barium-sulphite reagent. The amount of gas used can be determined by an appropriate measuring device at outlet *q*. Any sulphur trioxide which may have condensed in line *20–11–12–M* is washed into tube *J* with oxygen-free distilled water admitted through stopcock *20*. After the precipitate has settled the solution is filtered by means of suction applied at *T* through filter plate *N* into flask *S* containing one or two drops of sulphuric acid for the purpose of showing whether the filtrate contains excess barium. A stream of nitrogen admitted through line *15–14–12–M* is allowed to follow the effluent solution at approximately atmospheric pressure as indicated on gauge *W*. Oxidation of any sulphurous acid or barium sulphite is thus prevented. The precipitate is now washed several times, or until free from barium, with oxygen-free distilled water forced, by nitrogen pressure at inlet Z_1, from flask *Y* through line *Z–17–16–7–K* into tube *J*. The wash-

[15] Nitrogen from a cylinder was freed from oxygen by passing it through copper-ammonia-ammonium chloride reagent (W. L. Badger, J. Ind. Eng. Chem., 12, 161; 1920). Ammonia thus introduced into the nitrogen was then absorbed in sulphuric acid (1:1). Any carbon dioxide present was removed by soda-lime, and water vapor by "Dehydrite."

ings are sucked through filter plate *N* and stopcock *8* into flask *S* and discarded.

Tube *J* may now be disconnected from suction flask *S* and from its ground-glass stopper *h*. With the aid of a so-called "policeman" and ordinary distilled water from a wash bottle most of the barium sulphate is transferred from tube *J* to a weighed platinum dish. Any film of precipitate still adhering to the inner wall of tube *J* is dissolved in boiling 2-normal hydrochloric acid. Any precipitate formed in the tube above tip *M* from sulphur trioxide mist is likewise treated with the boiling 2-normal hydrochloric acid introduced through inlet *U*. The combined hot acid washings, amounting to about 200 ml, are then drawn by suction through filter plate *N* into a clean suction flask and transferred to the weighed platinum dish containing the main portion of the barium sulphate, and the whole evaporated to dryness. The residue is treated with two or three drops of dilute sulphuric acid, heated until free from fumes, ignited over a Tirrill burner, cooled in a desiccator, and weighed as barium sulphate. A small blank, due mainly to nonvolatile residue from the hydrochloric acid and determined as explained below, is substracted. (Table 2.)

3. EFFICIENCY OF METHOD

Tests on analytical tube *J* were made to determine its efficiency in removing sulphur trioxide. For this purpose a tube similar to analytical tube *J* was inserted between outlet *n* and inlet *f*. This intermediate tube contained the same kind and depth of barium-sulphite reagent as tube *J*. Sulphur dioxide from cylinder *A* was then bubbled, at the rate of 40 ml a minute for 90 minutes, by way of stopcock *1* through this reagent and then by way of stopcocks *20*, *11*, and *12* and tip *M* through the reagent in tube *J*. An appreciable quantity of barium sulphate was precipitated in the intermediate tube but none in tube *J*, indicating that the procedure is satisfactory for the complete removal of small amounts of sulphur trioxide.

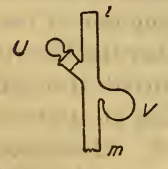


FIG. 3.—*Means of introducing sulphur trioxide*

A still more conclusive test of the method was then made as follows: Tube *J* was filled to height *L* with the barium-sulphite reagent. A slow stream of nitrogen was admitted to the apparatus at *e* and run through stopcocks *15*, *14*, and *12* and tip *M* into the barium-sulphite reagent. A known amount of sulphur trioxide was then introduced into the nitrogen stream by heating 1 ml of standard sulphuric acid in bulb *V* (fig. 3), which had been sealed into line *12–M* and filled through inlet *U* by means of a 1 ml pipette graduated in hundredths of a milliliter. The remainder of the procedure was the same as explained above under II, 2.

The results obtained are given in Table 1.

TABLE 1

No.	Standard H_2SO_4 used	SO_3 equivalent	SO_3 found
	ml±0.003	*g*	*g*
1	1.000	0.0412	0.0409
2	1.000	.0412	.0411
Average			.0410

Blanks on this test were run in a similar manner, except that no sulphur trioxide was introduced into the nitrogen stream. The results of these blanks are given in Table 2.

TABLE 2

No.	Residue weighed as $BaSO_4$	SO_3 equivalent
	g	*g*
1	0.0003	0.0001
2	.0003	.0001

4. POSSIBLE SIMPLIFICATION OF METHOD AND APPARATUS

Some attempts were made to simplify the method so as to avoid the necessity of carrying out the operations in an atmosphere of nitrogen. All such attempts failed, however, because of the rapidity with which the barium-sulphite reagent undergoes oxidation on contact with the atmosphere. The use of an oxygen-free atmosphere is therefore necessary if reliable results are to be obtained.

The analytical tube *J* may, however, be modified if desired so as to avoid the necessity of using the sintered-glass filter plate *M*. Such a modified form is shown in Figures 1 and 4. Below stopcock *8* (fig. 4) is a tubular extension, *P*, with a small inner-sealed tube ending at tip *O*. Extension *P* is joined by a heavy rubber band or a ground-glass joint, *i*, to a funnel-shaped tube, *Q*. The funnel is fitted with a platinum filtering cone and an ashless filter paper. On the lower end of funnel *Q* is a two-way stopcock, *9*, connected to suction flask *S* in the same way as in the apparatus shown in Figure 2. Precipitation of sulphur trioxide is accomplished in tube *J*, but filtration is carried out in funnel *Q*. This modified analytical tube does not, however, reduce the time required for a determination, since hot hydrochloric acid must be used to wash the analytical tube and must be evaporated just as in a determination carried out with analytical tube *J* shown in Figure 2.

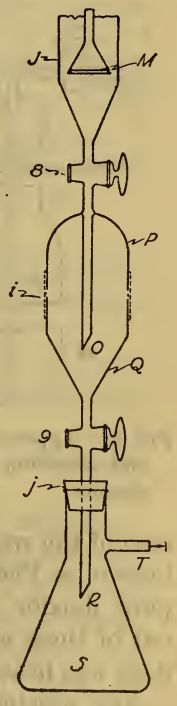


FIG. 4.—*Modified form of analytical tube*

III. SULPHUR TRIOXIDE IN LIQUID SULPHUR DIOXIDE

1. APPARATUS

The apparatus used for sampling and distilling the liquid sulphur dioxide is shown in Figure 5. *A* is a Pyrex flask with a narrow calibrated neck and ground-glass stopper fitted with inlet and outlet tubes, each containing a three-way stopcock; *s* is a threaded brass connector and *w* a ground-glass joint.

2. PROCEDURE

Flask *A* is filled with nitrogen and placed in a Dewar flask. The cylinder of sulphur dioxide is shaken and then inverted. Flask *A* is then connected to the needle valve on the cylinder by means of joint *s* and filled with liquid sulphur dioxide to a point just above mark *x*. The flask is disconnected and, with stopcock *21* closed and stopcock *22* open through by-pass *v*, it is connected to analytical tube *J* (fig. 2) at inlet *f* by means of ground-glass joint *w*. Inlet *r* is sealed to an extension from *d* with de Khotinsky cement. As soon as enough of the sample has been distilled through by-pass *v* to bring the meniscus to mark *x*, stopcock *22* is turned so as to allow the gas to pass through line *f–20–11–12–M* into the barium-sulphite reagent. The pressure in flask *A*, as noted on a mercury gauge sealed in the line between outlet *u* and stopcock *22*, and the rate of distillation may be regulated by raising or lowering the Dewar flask. When distillation is complete the residual sulphur dioxide gas in flask *A* is flushed out into the reagent with nitrogen. In the case of the wet sample, *3*, the residue contained some white crystals, known as Pictet's crystals and supposed to be a compound of sulphur dioxide and water. The sulphur dioxide was readily driven out of these crystals by very gentle heating. The water left in the flask was heated in a nitrogen stream until free from sulphur dioxide.

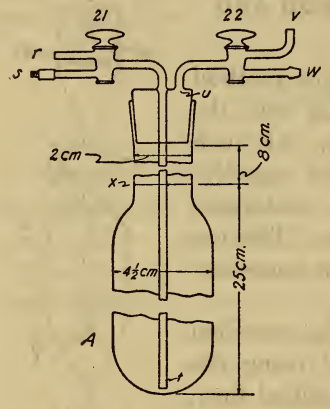


FIG. 5.—*Apparatus for sampling and distilling liquid sulphur dioxide*

Any precipitate formed in the analytical tube is treated as explained above in the analysis of sulphur dioxide gas. In some of the determinations the modified form of analytical tube shown in Figures 1 and 4 was used and found very satisfactory.

Sulphuric acid in the residue is determined by precipitation with barium chloride in the usual gravimetric way.

3. RESULTS

The following eight samples of liquid sulphur dioxide from commercial sources were analyzed:

1. Specially purified and dried by fractionation.
2. Commercial product; partially purified and dried by fractionation.
3. Factory product; not fractionated to remove water.
4. Commercial product; dried with sulphuric acid.
5. Commercial product; dried with sulphuric acid.
6. Commercial product; dried with sulphuric acid.
7. Dried twice with sulphuric acid; slightly contaminated with oil from compressor during second drying.
8. Same as 7.

All samples were taken from 35-pound lots except sample 6 which came from a 5-pound cylinder. About 200 g was used for each determination and complete distillation required from 2¾ to 4 hours. In no case was any precipitate found in the analytical tube, showing the gas to be free from sulphur trioxide. Only in samples 3, 7, and 8 was any sulphur trioxide found in the residue. Results for the residue from sample 3 could not be checked and varied from a trace to 0.0032 per cent of sulphur trioxide, indicating nonuniformity of sample. In each of samples 7 and 8, 0.0011 per cent of sulphur trioxide was found.

IV. SUMMARY

1. A nearly saturated and slightly acid solution of barium sulphite free from oxygen is used as the reagent for precipitating sulphur trioxide.

2. A means is provided for filtering and washing the precipitated barium sulphate with oxygen-free distilled water in an atmosphere of oxygen-free nitrogen.

3. Results are given for eight different samples of commercial liquid sulphur dioxide.

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