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Determination of the Sulfur Content of Gases from Boiler Furnaces[1,2]

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The form and the quantity in which sulfur exists in the products of combustion are important in connection with their action on the refractories of the furnace, the metal of preheaters, economizers, and steel stacks, and with the acids and gases emitted from the stack. The equilibrium equation shows that at furnace temperatures the sulfur will be present as SO_2 and that SO_3 will be formed as the gases cool.

Apparatus and methods are described for sampling the gases after they have passed the boiler tubes and from the furnace; these are designed to reduce the possibility of catalytic action between the points of sampling and analyses. At the lower temperatures an iron pipe with glass lining is used, and at furnace temperatures a copper glass-lined water-cooled sampler. A suction pump draws the gases at a constant rate of 0.1 cubic foot per minute through the apparatus which absorbs the sulfur gases, after which they pass through a flowmeter. The absorption apparatus for the SO_3 and SO_2 determination consists of one bottle with a fine-grained dry alundum thimble which retains the droplets of H_2SO_4 and a second bottle with a coarser alundum thimble immersed in a NaOH solution containing some H_2O_2 which absorbs the SO_2. Water is run through the glass tubing into the first thimble and bottle and the SO_3 determined by titrating with NaOH.

The second bottle is titrated with standard acid to determine the SO_2.

Results of tests to determine the accuracy of this method are given. When only the total sulfur is required, the first bottle is omitted; if the gases contain soot and tar which would clog the alundum thimble, the impinger principle is utilized, there being two impinger bottles in series. The composition of the gases by Orsat is also determined and from these data and the coal analysis the ratio of the sulfur in the gases to that in the coal can be computed.

. . . .

THE importance of the effect of the small concentrations of sulfur dioxide and sulfur trioxide in boiler-furnace gases on the life of the refractories, on the external corrosion of economizers and preheaters, and on the pollution of the outside air has made it desirable to have a small portable apparatus that can be used for the rapid determination of these gases in the range of concentration in which they exist in a boiler furnace. The apparatus here described is the result of work carried out by the Pittsburgh Experiment Station of the United States Bureau of Mines in an investigation of the service conditions of refractories, conducted jointly with the Special Research Committee on Boiler-Furnace Refractories of the American Society of Mechanical Engineers. The apparatus was checked for accuracy and made up into a test kit at the Engineering Experiment Station of the University of Illinois for use in an investigation of the prevention of corrosion by flue gases, being conducted in coöperation with the Utilities Research Commission.

The methods for the determination of SO_2 and SO_3 that have been described in the literature have not proved suitable for analysis of boiler-furnace gases. Their deficiencies have existed in one or more of the following features: (1) Iodometric or other reductimetric methods are excluded because of the existence of reducing agents in the gases besides SO_2; (2) the condensation of H_2SO_4 even at temperatures as high

as 200° C. prevents the collection of the gas for subsequent analysis; and (3) the rapid oxidation of SO_2 by the oxygen present in the gas prevents scrubbing the gas by water or any solution before the separation of SO_2 and SO_3 has been made. A simple portable apparatus that can be assembled in the average power-plant laboratory is essential.

Hawley (*2*) has shown that, although SO_3 combines with water vapor to form a fog which will pass through water or a solution of alkali without being completely absorbed, it may be separated from the gases by a filter. Nestell and Anderson (*3*) used Hawley's method for the separation of SO_3 and SO_2 by employing a paper filter. The SO_2 was then absorbed and oxidized by an excess of a standard solution of Na_2CO_3 containing H_2O_2. The SO_3 collected was determined by titration with standard alkali and the SO_2 was determined from the excess Na_2CO_3 by titration with standard acid. The application of these principles has led to the development of a simple and rugged portable apparatus suitable for power-plant work.

Reactions of Sulfur in Combustion of Coal

Sulfur occurs in coal in amounts ranging from 0.5 to 7 per cent. When coal is burned on a grate or in powdered form, a certain percentage of sulfur, usually low, remains in the ash and the remainder unites with the oxygen and passes out of the furnace with the gases. Sulfur dioxide may be assumed to be the primary product of the combustion, and the presence of SO_3 is due to oxidation of SO_2 at temperatures lower than those of combustion.

The reaction of SO_2 with oxygen is very slow except in the presence of catalysts. In boiler furnaces the ash particles carried by the gases, as well as surfaces with which the gases

come in contact, should act as catalysts. The ratio of the partial pressures of SO_3 and SO_2 is expressed by

$$\frac{p_{SO_3}}{p_{SO_2}} = K \sqrt{p_{O_2}}$$

when K is a constant that depends on the temperature. Bodenstein and Pohl (1) have shown that K has a value of 31.3 at 982° F. and 0.013 at 2732° F. If the oxygen content of the combustion gases is 5 per cent by volume, the maximum SO_3:SO_2 ratios in the presence of an efficient catalyst would be 7 at 982° F. and 0.003 at 2732° F.
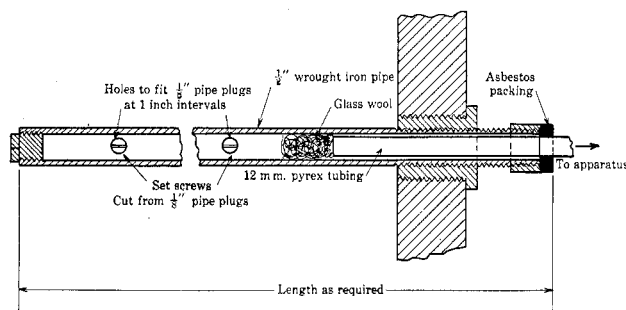
Figure 1—Gas-Sampling Tube

When the gases are sampled in the furnace it is sufficient, therefore, to determine the total sulfur and compute it as equivalent SO_2; beyond the boiler tubes, where a knowledge of the SO_3 and SO_2 is necessary, the gases should be cooled quickly and possibility of catalytic action avoided.

Description of Apparatus and Method

The apparatus required is (1) a sampling tube, (2) an absorption system, (3) a gas meter, (4) a source of reduced pressure, (5) an Orsat apparatus, and (6) connecting glass tubing.

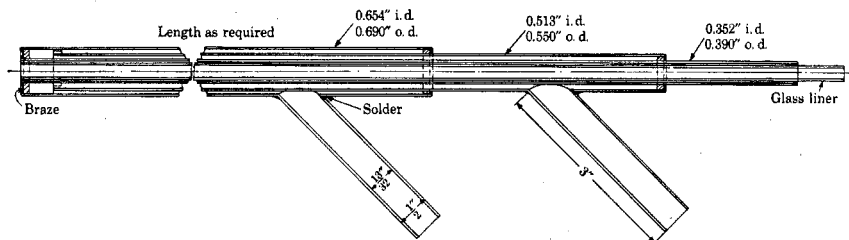SAMPLING TUBE—Figure 1 shows the sampling tube used

Figure 2—Water-Cooled Sampler with Glass Liner for Sampling SO₂ from Furnace Gases

to collect the gases in the economizer and preheater where the temperature of the gases does not exceed 900° F. (482° C.). A $1/2$-inch (1.3-cm.) iron pipe long enough to reach half-way across the setting at the point of sampling is closed at one end by a plug or cap and has holes fitted with $1/8$-inch (3-mm.) pipe plugs at 12-inch intervals along its length. A sample may be drawn from any one point by removing a pipe plug, and the average composition of the stream is computed from the average of the several samples. A 12-mm. Pyrex tube inserted through a cap at the outer end extends several inches inside the setting. Moistened asbestos paper is packed around the glass to prevent air from passing into the pipe. A tuft of glass wool placed before the end of the glass tube in the iron pipe filters out any dust carried by the gas.

Figure 2 shows a water-cooled sampler which may be used where the temperature is as high as 3000° F. (1649° C.). It is made of thin copper tubing in lengths to suit. The cooling water passes to the end of the sampler and then back to the outlet. A water pressure of at least 75 pounds per square

inch (5.3 kg. per sq. cm.) is necessary to insure sufficient flow when the tube extends 6 feet into the gases and where the temperature exceeds 2600° F. (1427° C.). A glass tube extends through the center of the sampler to the end so that the gases do not come in contact with the metal. An average value of the gas stream can be obtained by inserting the sampler to definite positions, or the gas-absorption apparatus may be mounted on a movable support so that it can be moved across the stream of gas during the period of sampling. The sampler should be slightly inclined so that any condensation will flow toward the absorption bottles.

ABSORPTION APPARATUS FOR SO₂ AND SO₃—Figure 3 shows diagrammatically the apparatus for the determination of SO_2 and SO_3 and its relation to the other apparatus. Figure 4 is a photograph of the apparatus assembled in a portable cabinet; an Orsat apparatus is mounted on the back of the cabinet. A and B are 500-cc. wide-neck bottles. The alundum thimbles are carried by inverted Gooch funnels; that of bottle A is cemented to the funnel by a high-melting de Khotinsky cement; the thimble and funnel of bottle B are held together by a short length of rubber tubing.

The gases from the sampler which have been cooled below the dew point of H_2SO_4 pass through the dry, fine-grain alundum thimble, which retains the droplets of acid. The second bottle, B, contains a standard NaOH solution and some H_2O_2; 50 cc. of 0.2 normal base with 10 cc. of 3 per cent H_2O_2 are usually sufficient. The coarse alundum thimble serves as an efficient bubbler and the SO_2 is absorbed. After the sample has been collected about $1/4$ cubic foot (7 liters) of air is drawn through to remove any SO_2 from the first bottle.

The volume of SO_3 in the sample is found by washing out the glass sampling tube and the first alundum thimble and titrating the resultant solution with standard alkali. The washing is accomplished by passing water through the alundum tube while the suction pump is running. A 3-way cock in the glass tubing just beyond the sampler permits this to be done without dismantling the set-up. The volume of SO_2 collected in bottle B is found by titrating the excess NaOH with standard acid, using methyl orange or the new methyl red–methylene blue indicator.

A rate of flow of 0.1 cubic foot (2.8 liters) per minute has been found satisfactory; the rate is measured by the capillary orifice meter, and is kept con-
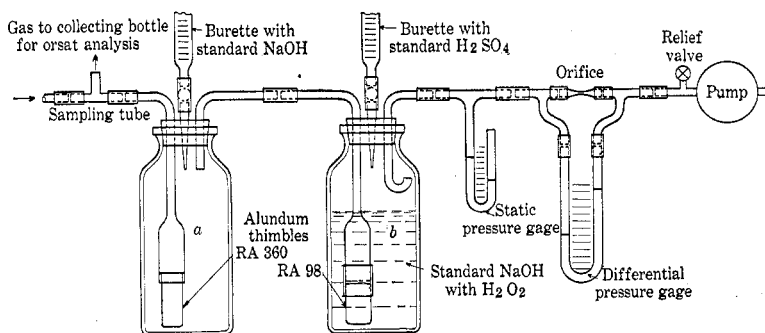
Figure 3—Apparatus for Determination of SO₂ and SO₃ in Flue Gases

stant by adjusting the relief valve ahead of the suction pump. The volume of gases drawn is computed from the average rate of flow and the time of sampling. A wet meter may be added as a check or for greater accuracy if desired, but the inherent inaccuracies in sampling the gases because of stratification and variations in rates of flow of the gas stream make the orifice flowmeter accurate enough.

A continuous sample of the gases is collected during the period of each sampling and is analyzed by the Orsat.

ACCURACY OF METHOD—The accuracy of the apparatus and method as described was determined by the analysis of gas-air mixtures which contained known amounts of SO_2 and SO_3. The former was generated from $NaHSO_3$ and H_2SO_4 and was stored and measured in a mercury-sealed gas buret. A measured volume of SO_2 was mixed with air and passed through a tube which contained a weighed amount of analyzed H_2SO_4 and which was heated electrically to about 450° F. (232° C.) This SO_2-SO_3-air mixture was drawn through the apparatus. The titrations were then carried out just as in the ordinary procedure. Table I gives the results of the tests.

Table I—Analysis of Synthetic Mixtures

VOLUME OF SO_2 TAKEN Cc.	VOLUME OF SO_2 FOUND Cc.	RECOVERY Per cent	WEIGHT OF SO_3 TAKEN Gram	WEIGHT OF SO_3 FOUND Gram	RECOVERY Per cent
86.3	84.5	98.0	0.1092	0.1072	98.4
88.0	84.0	95.4	0.1046	0.1055	100.8
88.8	89.1	100.2	0.1184	0.1196	101.0
88.3	89.9	101.7	0.1110	0.1063	96.0
88.0	86.9	98.8	0.1180	0.1092	99.8
Average		98.9			99.2

Table II—Theoretical Maximum Amounts of SO_2 in Flue Gases

| CONSTITUENT	COAL A			COAL B		
Moisture	2.90			11.35		
Ultimate analysis, dry coal:						
Carbon	79.86			57.36		
Hydrogen	5.02			5.41		
Oxygen	4.27			18.02		
Nitrogen	1.86			1.05		
Sulfur	1.18			4.76		
Ash	7.81			13.40		
	100.00			100.00		
Excess air, per cent	20	60	100	20	60	100
Dry flue-gas analysis, per cent by volume:						
CO_2	15.1	11.2	9.0	14.8	11.0	8.8
SO_2	0.08	0.06	0.05	0.45	0.34	0.27
Weight of SO_2 per cubic foot of dry gas, at standard conditions, grams	0.0681	0.0507	0.0404	0.3750	0.2795	0.2280
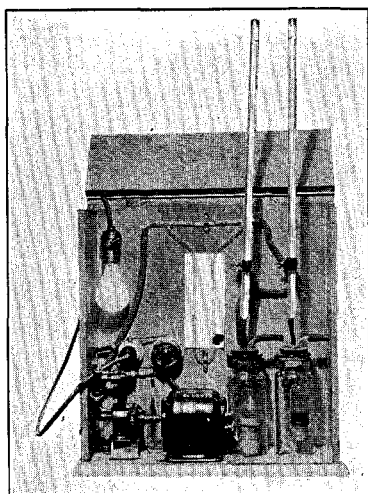
Figure 4—Assembly of Apparatus for Determination of SO_2 and SO_3

DETERMINATION OF TOTAL SULFUR IN GASES AS SO_2—A simpler apparatus and procedure can be employed if it is not desired to determine SO_2 and SO_3 separately, and a determination of the total sulfur is sufficient. One method is to use the assembly in Figure 3 but omit bottle *A*. The thimble immersed in the NaOH solution in bottle *B* is depended upon to break up the gas bubbles so that the fine SO_3 mist will be absorbed. The procedure is similar to that previously described.

Trouble caused by clogging of the thimble has been experienced with this method when the gases contain soot and tar. Figure 5 shows an alternative method which utilizes the impinger principle and has the advantage of having a lower pressure drop. Two impinger bottles are used in series so that the second bottle will absorb the sulfur gases when the first becomes sufficiently saturated to pass them. The efficiency of absorption by this method has been checked by putting a third bottle in series and also by using iodine as an indicator.
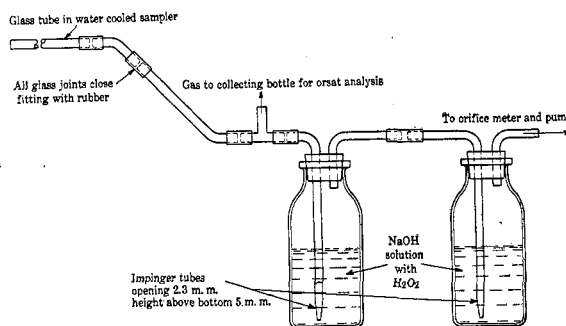

Figure 5—Arrangement of Apparatus for Determination of SO_2 Content of Furnace Gases

Comparison of Sulfur in Gas with That in Coal Burner

The volume of sulfur gases per unit volume of flue gas will vary with the excess air. Sherman and Rice (4) have suggested a comparison of the ratio of sulfur to carbon in the gas; if the weight of sulfur is computed in grams per cubic foot of flue gas at 32° F. and standard pressure, the weight of carbon per cubic foot is given by

$$\text{Wt. } C = 15.2 (CO_2 + CO)$$

where CO_2 and CO are the volumes of these gases per cubic foot of the sample from the Orsat analysis. The fraction of the total sulfur in the coal which appears in the flue gas may then be computed as follows:

$$\text{Fraction of S in gas} = \frac{\text{Ratio S:C in gas}}{\text{Ratio S:C in coal}}$$

Table II gives the theoretical amounts of SO_2 when burning two coals with different percentages of excess air.

Acknowledgment

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Spain Looks to Promotion of Chemical Industry

The Spanish Government is giving special attention to the promotion of its chemical industry. The Minister of Public Works recently stated that 400,000 kilowatts of electric energy would be necessary to produce Spain's annual requirements of 80,000 tons of nitrates. The Council of Energy is in charge of this project, which will cover a period of years. Eventually Spain hopes to produce nitrates as cheaply as Germany.