

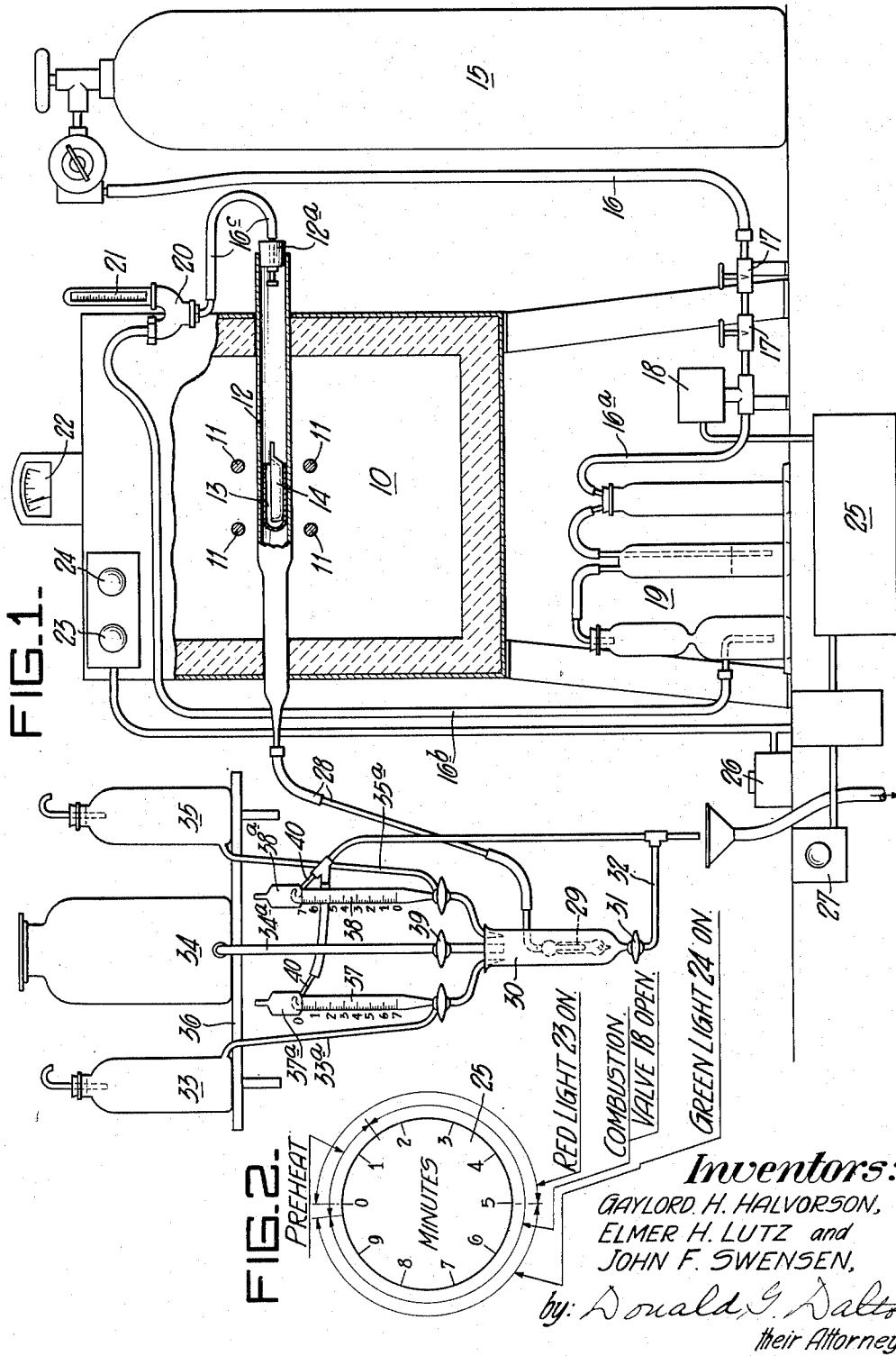
Feb. 16, 1954

G. H. HALVORSON ET AL

2,669,504

METHOD FOR DETERMINING SULFUR CONTENTS BY COMBUSTION

Filed Aug. 10, 1951



UNITED STATES PATENT OFFICE

2,669,504

METHOD FOR DETERMINING SULFUR
CONTENTS BY COMBUSTIONGaylord Herbert Halvorson, Elmer Herman Lutz,
and John Fosmark Swensen, Duluth, Minn.

Application August 10, 1951, Serial No. 241,366

1 Claim. (Cl. 23—230)

1

This invention relates to the determination of the amount of sulphur contained in metals such as iron and steel and also other materials such as the slag from open-hearth steel furnaces.

The sulphur content of such materials has been determined heretofore by the combustion of a powdered sample in oxygen, and simultaneously titrating iodometrically the SO_2 evolved. The conventional practice, however, requires from 20 to 30 minutes for each determination and the constant attention of an analyst throughout that time. In addition, it involves considerable possibility of error because the titration is performed by comparison with a standard blue. Powdered iron cannot be used, furthermore, to cover a slag sample as is desirable to accelerate the combustion of the sulphur, because the evolution of SO_2 in the presence of iron is so rapid that it is practically impossible to maintain by successive additions the excess of iodate solution needed to absorb the SO_2 completely. It is accordingly the object of our invention to provide a method and apparatus requiring a minimum of time and attention, permitting the use of powdered iron on the sample and capable of producing more accurate determinations than have been possible heretofore.

In a preferred embodiment and practice, we provide titration apparatus and a combustion furnace having an oxygen supply controlled by automatic timing means whereby the combustion stage of the process, when once initiated, continues to completion without further attention. The SO_2 evolved is caused to bubble through a titration cup containing an acidified starch solution and an excess of a compound which releases iodine in the presence of acid, e. g., an iodine salt such as KIO_3 . After completion of the combustion and the combination of all the evolved SO_2 with the iodine in the solution, the excess iodine is back-titrated by the addition of a matched standard solution of a compound which combines with iodine, such as $\text{Na}_2\text{S}_2\text{O}_3$, until the normal blue color of the starch-iodate solution is just completely discharged. The sulphur content may then be read from the volume of the thiosulphate solution required for the back-titration. The entire process can be completed in about six minutes and the accuracy of the results is materially greater than that of previous methods. Only the titration requires special attention but this may be accomplished in a short time.

A complete understanding of the invention may be obtained from the following detailed descrip-

2

tion and explanation which refer to the accompanying drawings illustrating the present preferred embodiment. In the drawings:

Figure 1 is a diagrammatic elevation, with parts in section, showing the apparatus; and

Figure 2 is a chart showing the operating cycle of the automatic timer.

Referring now in detail to the drawings and, in particular, to Figure 1, the apparatus there shown includes a combustion furnace 10 of any suitable type having, for example, electric-resistance radiant heating elements 11 and a tubular muffle 12 extending therethrough. A foraminous shield 13 about midway of the muffle is adapted to receive a combustion boat 14 containing a sample of the material the sulphur content of which is to be determined. Oxygen is supplied to the muffle 12 from a cylinder 15 through hose sections 16, 16^a, 16^b and 16^c. Manual regulating valves 17 and an electromagnetic spring-closed shut-off valve 18 are connected in series between sections 16 and 16^a. A drier 19 composed of a plurality of bottles containing suitable moisture absorbents is connected between sections 16^a and 16^b. A fitting 20 having a pressure gauge 21 is connected between sections 16^b and 16^c. Section 16^c is connected to a plug 12^a removably disposed in the right-hand end of muffle 12.

Furnace 10 is provided with an indicating pyrometer 22 and red and green signal lights 23 and 24. These lights and valve 18 are controlled by an automatic timer 25 in a manner to be explained later. The timer is of a known type available commercially so it is unnecessary to describe it in detail. It comprises essentially a motor-driven contact drum adapted to close and open circuits in a predetermined sequence when once started by operation of a push-button 26 and, after going through its cycle, to stop itself in starting position. A push-button 27 permits the timer to be stopped at any point if desired, in case of emergency.

The left-hand end of muffle 12 is reduced and is connected by hose and tube links 28 to a nozzle 29 suspended in a titration cup 30 and discharging downwardly therein. Cup 30 has a drain cock 31 and a waste connection 32. Reagent bottles 33, 34 and 35 mounted on any convenient support such as a shelf 36 contain, respectively, a solution of a compound which releases iodine in the presence of acid, such as an iodate, an acidified starch solution and a matched solution of a compound which combines with iodine such as a thiosulphate. The precise composition and

concentration of these solutions will be given in detail later. Bottles 33 and 35 are connected by hose and tube links 33^a and 35^b, to the lower ends of self-filling burettes 37 and 38, respectively, adapted to supply measured quantities of solution to cup 30. Bottle 34 has a delivery pipe 34^a leading to the cup with a stop cock 39 therein. The cup and burettes are mounted on any suitable supports, not shown. Waste connections 40 extend from the overflow chambers 37^a and 38^a on the upper ends of the burettes.

The method of our invention utilizes the known effect of SO₂ in discharging the normal blue color of a starch-iodine mixture by combining with the iodine. Instead of the conventional practice of titrating the mixture continuously as SO₂ is evolved and absorbed therein, by adding an iodate in solution to maintain a given standard blue, however, we start with an excess of iodate in solution and, after combination of all the evolved SO₂ with the iodine in the mixture, we back-titrate by adding a compound which combines with iodine to cause the blue color of the mixture to be fully discharged. Our invention thus has an end point which may be detected much more accurately than a given shade of blue may be maintained in the starch-iodine mixture by the conventional practice.

Before proceeding with a detailed explanation of the method of our invention, it is necessary to give the composition and concentration of the several solutions employed. The reagent in bottle 34 is a solution containing sufficient starch to exhibit the typical blue color in the presence of iodine and sufficient acid to cause a reaction with an iodate and an iodide to produce iodine for combination with the SO₂ evolved on combustion of the sample in boat 14. In order to prepare the acidified starch solution, we first make up a stock solution of starch by dissolving 6 g. of soluble starch in 1000 ml. of boiled distilled water. We then take 180 ml. of the stock solution and add it to 1000 ml. of water. The resulting solution is acidified by the addition of a concentrated acid, e. g. 15 ml. of HCl, and used to fill bottle 34.

The standard iodate solution is made up by dissolving .72 g. of an iodate such as KIO₃, 350 g. of an iodide such as KI, and .8 g. of an alkali such as KOH, in 4000 ml. of boiled distilled water. The resulting solution is used to fill bottle 33. The KI serves to stabilize and the KOH maintains the solution slightly alkaline.

The standard thiosulphate solution matched to equal the concentration of the iodate solution is made up by adding 4.95 g. of Na₂S₂O₃ and .4 g. of Na₂CO₃ to 4000 ml. of boiled distilled water.

The preferred practice of our invention in determining the sulphur content of a material such as open-hearth furnace slag is carried out by placing in boat 14, exactly 1 g. of the slag in finely powdered form. The sample is then covered with 1 g. of powdered iron of known sulphur content. Stop cock 39 is then opened to admit about 50 ml. of the acidified starch solution from bottle 34 to cup 30. A predetermined quantity, i. e., 7 ml. of the standard iodate solution is then added to cup 30 from burette 37. This causes the starch solution to turn blue because of the free iodine released by the reaction of the iodate, iodide and acid. With the furnace at a temperature between 2300 and 2400° F., preferably about 2350° F., plug 12^a is removed and boat 14 is inserted in muffle 12. Plug 12^a is then replaced and push-button 26 is operated. This starts the

timer 25 which is set to open valve 18 after a short period allowed for preheating the sample. Preheating is not essential but is usually desirable to insure complete combustion of the sulphur. Valves 17 are adjusted to cause oxygen to flow from tank 15 through muffle 12 at the desired rate, e. g., about 2 liters per minute when valve 18 is opened.

As shown graphically in Figure 2, timer 25 energizes red light 23 as soon as it starts in response to operation of push-button 26. A short time later, say in about 1.5 minutes, the timer energizes the magnet of valve 18 causing the latter to open. The resulting flow of oxygen over the preheated sample and the powdered iron covering it causes oxidation of the sulphur in both the sample and the covering. The SO₂ thus formed flows through nozzle 29 and bubbles upwardly through the starch-iodate solution, partly discharging the blue color thereof by combining with the iodine. When the flow of oxygen has continued for a time sufficient to oxidize the sulphur present in the sample and its powdered iron covering, say about 3.5 minutes, timer 25 operates to de-energize red light 23 and energize green light 24. This signifies to the analyst that the oxidation or combustion stage of the process is completed and that the titration may be effected whenever convenient. Valve 18 remains open, however, for several minutes longer, say 5 minutes, whereupon the timer de-energizes the magnet of the valve, permitting it to be closed by its restoring spring, and also light 24, then stops itself in starting position. The continued flow of oxygen thus effected insures that all the SO₂ formed will be carried over to cup 30 and released in the starch-iodate solution. It will be apparent from the foregoing that the apparatus requires no attention from the analyst after the operation of push-button 26 until it is convenient for him to perform the titration.

The bubbling of SO₂ through the solutions in cup 30 results in a reaction with the iodine therein, partially discharging the blue color thereof. After completion of the combustion as explained above, it is only necessary to add to cup 30 sufficient Na₂S₂O₃ from burette 38 to cause the last trace of blue to disappear, leaving the solutions colorless. The amount of standard thiosulphate solution required to do this indicates the sulphur content of the sample and the powdered iron covering. The actual sulphur content of the sample, of course, is the total indicated sulphur less the known sulphur content of the powdered iron covering. The total sulphur content may be read directly from burette 38 if it be calibrated from bottom to top as shown. Thus a burette reading of 3.6 ml. indicates .036% sulphur.

The foregoing procedure requires slight modification if the sample has a sulphur content exceeding .07% since, in that event, the 7 ml. of iodate solution initially added to the starch acid solution will not afford an excess leaving some remainder to be titrated by the addition of thiosulphate. This condition will be indicated, of course, by the discharge of the blue color of the mixed solutions before all the SO₂ has been evolved. In that case, it is necessary to make a second run using, say 14 ml. of iodate solution. If the blue color persists after completion of combustion and is then discharged by the addition of 3.6 ml. of thiosulphate, for example, the total sulphur content of the sample and covering is .036+.07 or .106%. If the blue color is still discharged before completion of combustion, an

5

additional 7 ml. of iodate should be added to a fresh quantity of starch solution and a further run made and so on until the blue color persists after all the SO_2 has been evolved. If after adding, say 14 ml. of iodate solution, the sulphur content turns out to be lower than .07 and more than 7 ml. of thiosulphate is required to reach the end point, an adjustment must be made figuring that each 7 ml. of thiosulphate offsets 7 ml. of iodate, to secure a direct reading. Alternatively the sulphur content in any case is given by the difference between the total amounts of iodate and thiosulphate solutions used.

After completion of the titration, cup 30 is drained by opening cock 31. The boat 14 is removed from the furnace and the apparatus is then ready for the next run.

When a sulphur determination is to be made on a high-sulphur slag, it is preferable to use only .5 g. thereof as a sample. The procedure is otherwise the same as that explained above. The indicated sulphur content (after deducting that of the powdered iron covering) must be doubled, however, because of the smaller sample used. Usually 14 ml. of iodate solution will be required to maintain an excess thereof after completion of combustion of a slag sample.

When a sample of iron or steel is to be analyzed for sulphur content, it is subjected to the process described above, after being finely pulverized as by an air hammer, but no covering of powdered iron is necessary, of course, since the finely divided condition of the sample will cause rapid combustion thereof in oxygen.

Our invention is characterized by numerous advantages some of which have already been mentioned, i. e., the greater accuracy and the reduction in the amount of time and attention required. The use of a powdered iron covering over the sample which is desirable to accelerate the evolution of SO_2 and reduce the required furnace temperature, is permitted without requiring the close attention heretofore necessary, amounting almost to a practical impossibility, to keep the titration up with the SO_2 evolution. That is to say, our invention permits advantage to be taken of the iron covering without impairing the accuracy or requiring the exercise of extreme care in titration. This results from the fact that in our invention, the titration is not performed simultaneously with the combustion but only after combustion is complete and all the SO_2 evolved has combined with the iodine. The concentrations of the iodate and starch solutions are such as to maintain the dissociated iodine stable under varying conditions of SO_2 evolution.

6

Although we have disclosed herein the preferred practice of our invention, we intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

We claim:

In a method of determining the sulphur content of a sample of material, the steps including adding to an acidic starch solution a predetermined amount of a solution containing iodine in excess of that needed for combination with all the sulphur in the sample covering the sample with powdered iron, heating the sample to a temperature above 2300°F. in the presence of oxygen thereby effecting combustion of the sulphur contained in the sample, conducting the gas from said combustion through said solution thereby causing combination of the sulphur dioxide in said gas and some of the iodine, then adding to the solution, a solution of a sulphur compound until the color of the starch solution is wholly discharged, and noting the quantity of the solution of sulphur compound so used.

GAYLORD HERBERT HALVORSON.
ELMER HERMAN LUTZ.
JOHN FOSMARK SWENSEN.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,224,044	Francis et al. -----	Dec. 3, 1940
2,332,943	Sobers -----	Oct. 26, 1943
2,336,075	Derge -----	Dec. 7, 1943
2,382,301	Dreher -----	Aug. 14, 1945

OTHER REFERENCES

- Griffin et al., "Ind. and Eng. Chem.," pp. 862-867, August 1932.
Muller, "Ind. and Eng. Chem., Anal. Ed.," page 226, vol. 7, No. 4, July 15, 1935.
Kar, "Ind. and Eng. Chem., Anal. Ed.," pages 244-246, vol. 7, No. 4, July 15, 1935.
Tschernikhov, "Ind. and Eng. Chem., Anal. Ed.," pages 309-311, vol. 7, No. 5, Sept. 15, 1935.
Katz, "Analytical Chemistry," pages 1040-1047, vol. 22, August 1950.
Jacobs, "Anal. Chem. of Industrial Poisons, Hazards, and Solvents" 2nd ed. (1949), pages 314-316, published by Interscience Publishers, N. Y. C.
A. S. T. M. Methods of Chemical Analysis of Metals, 1946 ed., pages 91-92. Published by American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa.