

ART. VIII.—*On a new Process for the determination of Sulphur in Organic Compounds, by combustion with Oxygen Gas and Peroxyd of Lead; by C. M. WARREN.*<sup>1</sup>

IN my former communication "On a Process of Organic Elementary Analysis by Combustion in a Stream of Oxygen Gas,"<sup>2</sup> I treated exclusively of the determination of carbon and hydrogen in volatile liquid hydrocarbons,—my experiments up to that time having been confined to the analysis of substances of this class. It was my intention, however, to have applied the process before this to other classes of bodies, and especially to have tested its applicability, with suitable modifications, for the analysis of organic substances containing other elements.

Other work with which I was then occupied, and to which this process was only incident, as already stated in the paper referred to, has prevented me from extending the research beyond the requirements of my other investigations.

Having recently had occasion to determine sulphur in some volatile liquid compounds, for which neither of the processes now in use seemed satisfactorily adapted, I was naturally led to make an effort to utilize my safety-tube and the stream of oxygen in this species of analysis also. But the fact that sulphur is usually, at least, but partially converted into sulphuric acid by combustion in oxygen gas seemed at first to present a difficulty not to be easily overcome. It soon occurred to me, however, that the well-known reaction between sulphurous acid and peroxyd of lead, by which the former is completely converted into sulphuric acid, might probably serve to remove this objection. Furthermore, that, by placing the peroxyd of lead within the combustion-tube in the manner which I shall presently describe, and by maintaining the peroxyd of lead at a temperature sufficient to prevent condensation of water within the combustion-tube, the carbon, hydrogen, and sulphur might all be determined from the same portion of substance. This result has been accomplished.<sup>3</sup>

<sup>1</sup> From the Proceedings of the American Academy, March, 1865.

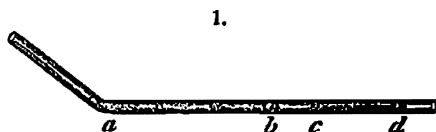
<sup>2</sup> Proceedings of the American Academy, 1864, p. 251.

<sup>3</sup> Carius (*Annalen der Chemie und Pharmacie*, 1860, cxvi, 28) has observed that when substances rich in sulphur are burnt with oxyd of copper—a tube containing peroxyd of lead being placed between the chlorid of calcium tube and the potash bulbs in the usual manner—the determination of carbon is too high. And on the other hand he found that, with substances rich in carbon, the determination of the carbon was too low. In the latter case, the peroxyd of lead was supposed to absorb and retain carbonic acid; and in the former, sulphurous acid was found to pass unabsorbed through the peroxyd of lead.

<sup>4</sup> The incomplete absorption of the sulphurous acid may be reasonably accounted for on the supposition that a channel was formed, by handling or jarring, along the top of the peroxyd of lead, which indeed would be very likely to occur in using, by

Referring to my former paper above mentioned for details regarding the construction and use of the apparatus employed, I need here describe only such modifications as have been found expedient to adapt the process to this special purpose.

The combustion-tube being packed with pure asbestos between the points *a* and *b*, fig. 1, and the space—about two inches in length—between *b* and *c* left vacant, a plug of pure asbestos is placed at *c*, and the space between *c* and *d*, about three or four inches in length, then filled with a mixture of pure asbestos and peroxyd of lead, and finally a plug of asbestos is placed at *d*. As the sulphuric acid formed is to be absorbed by, and finally determined from, the peroxyd of lead,—in order to obviate the necessity of treating the whole of the asbestos in the tube to obtain the sulphuric acid, which would be troublesome, and at the same time preserve the asbestos packing in the posterior part of the tube in a fit condition for future use,—it is important that the asbestos plug at *c* should be packed closely enough to prevent any particles of the peroxyd of lead from passing back of this plug.



As already stated, the object of mixing asbestos with the peroxyd of lead is to prevent the formation of a channel along the top. In this manner but a short column of the mixture of asbestos and peroxyd of lead will suffice to secure complete conversion of the sulphurous acid. The combustion is conducted precisely as for the determination of carbon and hydrogen alone, except that the portion of the tube which contains the peroxyd of lead is maintained at a gentle heat, sufficient to prevent condensation of water in that part of the tube and at the cork, but avoiding a temperature which would decompose the peroxyd of lead. As usual, the water formed is absorbed in a chlorid of

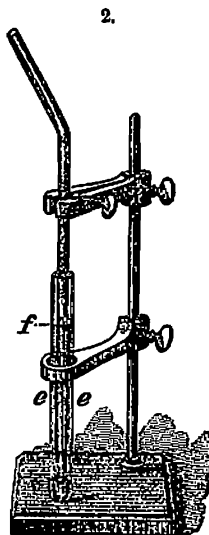
itself, so heavy a powder. Through such a channel sulphurous acid might pass, in so small proportion, without coming in contact with the peroxyd of lead. It will be seen that the liability to the formation of a channel is obviated in my process by mixing the peroxyd of lead with a large proportion of asbestos. The asbestos serves also to increase the porosity of the mass, and in this manner also to lessen the chances of escape of sulphurous acid without coming in contact with the peroxyd. I may here add that, in making the combustion with oxygen in presence of asbestos, the quantity of sulphurous acid which reaches the peroxyd of lead is by no means very large. In a preliminary experiment, in which carbonate of soda was employed instead of peroxyd of lead, (the substance burnt being bisulphid of carbon), the carbonate of soda was found to contain within about 9 per cent of the equivalent of sulphur; and a portion of the deficiency it is not unlikely may have been taken up by the impure asbestos that was employed in this instance.

Concerning the other source of error in the determination of carbon which Carius mentions, it will suffice to remark that, in my process, the peroxyd of lead is kept at so high a temperature that the absorption of carbonic acid appears to be prevented.

calcium tube, and the carbonic acid in Liebig's potash bulbs with a mulder tube attached.

After the close of the combustion, when the tube shall have sufficiently cooled it is carefully removed from the furnace, the mixture of peroxyd of lead and asbestos cautiously drawn out into a beaker glass, by means of a bent iron wire, and the tube then inverted within another tube, *ee*, closed at one end, as shown in fig. 2. The mixture of peroxyd of lead and asbestos contained in the beaker glass is now treated with a strong solution of bi-carbonate of soda, and left to stand for about twenty-four hours, with frequent shaking.

Solution of bi-carbonate of soda is also poured into the tube *ee* until the level of the liquid shall have reached a point, *f*, on the combustion-tube, a little above that which was occupied by the plug *c*, and this is also left to stand as the other. After the lapse of sufficient time for the reaction to be completed, the solution is filtered from the asbestos mixture, including also the solution in the tube *ee*, and not omitting to carefully rinse out the anterior portion of the combustion-tube. The asbestos mixture upon the filter is then thoroughly washed, the filtrate concentrated by evaporation, and the sulphuric acid precipitated with chlorid of barium.



The following results of analyses of bi-sulphid of carbon indicate the degree of accuracy afforded by this process.

The preparation employed was commercial bi-sulphid of carbon, which was first subjected to re-distillation.

*Analysis 1.* 0.1414 gram of bi-sulphid of carbon gave 0.0806 of carbonic acid, and 0.8592 of sulphate of baryta.

			Calculated.	Found.
Carbon,	C	6	15.79	15.61
Sulphur,	S <sub>2</sub>	32	84.21	83.70
			<hr/> 100.00	<hr/> 99.31

*Analysis 2.* 0.274 gram of the same substance gave 0.158 of carbonic acid, and 1.6768 of sulphate of baryta.

			Calculated.	Found.
Carbon,	C	6	15.79	15.73
Sulphur,	S <sub>2</sub>	32	84.21	84.05
			<hr/> 100.00	<hr/> 99.78

*Analysis 3.* In this analysis, in which I was prevented from determining the carbon, 0.1537 of bi-sulphid of carbon gave 0.9461 of sulphate of baryta, corresponding to 84.5 per cent of sulphur.

The mixture of asbestos and peroxyd of lead employed was of that which had already been used in the preceding analyses, and may possibly have contained a trace of undecomposed sulphate of lead, as the per-cent of sulphur found in this case is 0.8 per-cent above, while in the preceding analyses it was a fraction below the theoretical quantity. Trusting, however, that the results already obtained will be deemed sufficient to show the method to be a good one, I have not thought it advisable at this time to further repeat the analysis of this substance. I may here state that I have already applied the process in the analysis of bodies containing hydrogen, and have obtained satisfactory results which will soon be published.

The important advantage thus gained of being able to determine the different elements from the same portion of substance, considering also the simplicity of the process, can hardly fail, I think, to secure for this preference over the older methods.