

ART. XXIV.—*On a New Process of Organic Elementary Analysis for Substances containing Chlorine*; by C. M. WARREN.

ORGANIC bodies containing chlorine—and probably those also, that contain bromine and iodine—may be analyzed by a process analogous to that which I have already described for substances containing sulphur.¹

As in that process, so also in this, the substance is burnt in a stream of oxygen gas, in the manner described in my first paper, on organic Elementary Analysis.²

Similarly, also, as in the analysis of sulphur compounds, the chlorine is absorbed and retained during the combustion, by a suitable substance placed in the anterior end of the combustion tube; this substance being subsequently removed, and the chlorine determined therefrom in the usual manner. The carbon and hydrogen, in either process, are determined from the same por-

¹ Proceedings of the American Academy, March, 1865; this Journal, Jan., 1866, xli, 40.

² Proceedings of the American Acad., 1864, p. 251; this Journal, xxxviii, 387.

tion of the substance as the sulphur or chlorine, in a manner similar in other respects to that described for simple hydrocarbons.^a

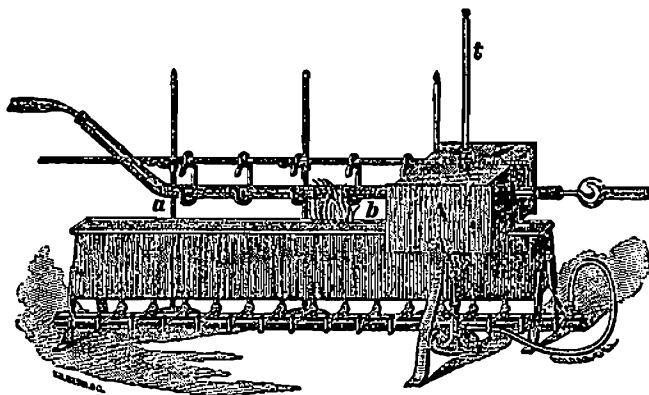
In pursuing this research some difficulty was experienced, as was anticipated, in finding a substance which would absorb and retain the whole of the chlorine, under conditions that would at the same time insure that every trace of the carbonic acid and water should pass through unabsorbed.

The search for this substance was confined to the oxyds of the heavy metals, as these alone, from their strong affinity for chlorine, and weak affinity for carbonic acid, seemed to give encouragement of success.

The difficulty, however, in finding such a substance was chiefly due to the circumstance that most of the chlorids of these metals are either too volatile, or begin to suffer decomposition at too low a temperature; it being requisite that the absorbing substance, and the newly formed chlorid of the same, should bear to be heated sufficiently to prevent both condensation of water and absorption of carbonic acid; and at the same time avoid a temperature high enough to occasion any appreciable decomposition of the chlorid.

This question of temperature became, therefore, a prominent one in the investigation, as evidently the success of the process must depend, in a great degree, on the proper management of the temperature of the absorbing substance, within such limits as might be found to give satisfactory results. Hence, my first step was to devise means to secure the necessary control of the temperature of that part of the combustion tube which should contain this substance.

1.



For this purpose was constructed a sheet-iron air-bath or chamber, A, fig. 1, provided with two holes—one on each side—to

^a *Loc. cit.*

receive the combustion tube, and a tubulure in the top for a thermometer. One end of the air-bath is made to rest on the combustion furnace, and the other, which projects a few inches from the front of the furnace to make room for a lamp, is supported by a leg resting upon the table. The bulb of the thermometer is placed in a central position, in the interior of the bath, close by the side of the combustion tube.

The temperature of the air-bath, and consequently of the substance contained in the combustion tube within, is easily regulated by means of a Bunsen's burner placed under the front end of the bath, as shown in fig. 1. With the exception of the air-bath, the apparatus employed is the same as that used in the analysis of substances containing sulphur, a full description of which is given in the papers above referred to.

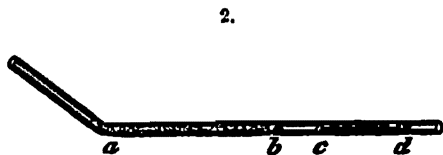
The substance that I have found best adapted to absorb the chlorine, for substances easily combustible, is brown oxyd of copper, prepared by precipitation with potassa and ignition over a gas flame.

Difficultly combustible substances, like chloroform, are not completely burnt in oxygen in contact with asbestos alone, but require the presence of a body having affinity for chlorine; otherwise there is formed a liquid body, difficultly volatile,—probably a chlorid of carbon,—which condenses in the vacant part of the tube, from *b* to *c*, fig. 2, and which cannot be entirely burnt off and save the analysis. In such cases the absorbing substance is mixed with the asbestos occupying the back part of the tube, where the combustion takes place. It is evident that oxyd of copper would not answer for this purpose, as at so high a temperature dichlorid of copper would be formed, which, being insoluble in dilute acids, would interfere with the determination of the chlorine. Oxyd of zinc has been found to give good results with such substances.

The preparation of the combustion tube, and the arrangement of the mixture of asbestos and the absorbing substance, is the same—except in the case last mentioned—as in the analysis of substances containing sulphur, as shown in fig. 2, viz., the space between *a* and *b*, about

10 inches in length, is packed with pure asbestos; between *b* and *c*,—a space of about two inches,—being left vacant, a plug of asbestos

is placed at *c*; the space between *c* and *d*, 4 to 5 inches in length, is filled with an intimate mixture of asbestos and brown oxyd of copper; and, finally, a plug of asbestos is placed at *d*.



After the combustion, the chlorid, together with the excess of oxyd, is extracted from the asbestos by means of dilute nitric acid.

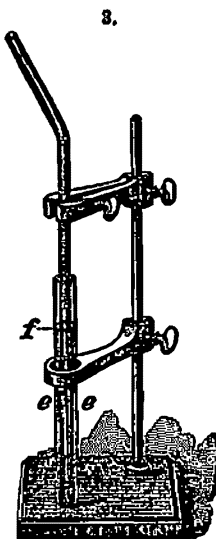
To facilitate the removal of what may adhere to the sides of the tube, the apparatus shown in fig. 8 will be found serviceable as in the analysis of sulphur compounds.

I. Experiments with Oxyd of Lead and with Oxyd of Copper, placed in the anterior end of the combustion tube, as absorbents of Chlorine in the analysis of substances difficultly combustible.

The substance selected for analysis, as a test of the process for that class of bodies which are difficultly combustible, containing but a small percentage of hydrogen, was commercial chloroform. The preparation employed was first subjected to redistillation.

Its boiling point was found to agree essentially with that assigned to pure chloroform in Gerhardt's *Traité de Chimie*. When the usual tests were applied, no impurity could be detected.

Experiment 1.—A mixture of oxyd of lead and asbestos was placed in the anterior end of the combustion tube, between *c* and *d*, fig. 2, as previously described. As chlorid of lead was supposed to bear a pretty high temperature, without volatilization or decomposition, the use of the air-bath was omitted in this experiment, and the oxyd gently heated with a small flame from the combustion furnace. The combustion had not proceeded far when it became apparent, from deposition of minute drops of liquid on the sides of the vacant part of the tube,—from *b* to *c*, fig. 2,—that the combustion of the chloroform was incomplete, although no doubt could exist as to the presence of an excess of oxygen. This deposit of liquid, which, as already stated, was supposed to be a chlorid of carbon, was found to be difficultly volatile, suffering partial decomposition, and leaving on the tube a brown deposit, which was not entirely removed by ignition in a stream of oxygen. The high temperature employed to burn off this deposit occasioned excessive heating of the posterior end of the mixture of lead oxyd and asbestos; and this may have been the cause, to some extent, of the excess in the determinations of carbon and hydrogen, although subsequent analyses indicate that the sample of chloroform under examination contained a larger percentage of these elements—particularly of the latter—than belongs to pure chloroform. This experiment gave 11.47 per cent of carbon, and 1.87 per cent of hydrogen. Theory



gives 10.07 per cent of carbon, and 0.85 per cent of hydrogen. The mixture of asbestos and oxyd and chlorid of lead was removed from the tube, and treated in the usual manner with a solution of bicarbonate of soda to obtain a soluble chlorid. This operation was found extremely tedious. Even after treatment for more than two weeks, with occasional fresh portions of the bicarbonate and frequent agitation, the decomposition of the lead chlorid was still found to be incomplete, and the operation was abandoned. As this is given in the text books as a good process for the separation of chlorine from chlorid of lead,⁴ I am led to presume that in this case the excess of heat employed gave rise to the formation of an oxychlorid, which is, doubtless, more slowly acted upon by the bicarbonate. This single experiment does not, therefore, prove that oxyd of lead may not be employed in this process with good results, when used for easily combustible substances, and excessive heat is avoided. But it will, unquestionably, be found preferable to use a substance which will give *directly* a soluble chlorid.

Experiment 2.—This experiment was conducted as the last, with only this difference, viz. that oxyd of copper was substituted for the oxyd of lead. No better results, however, were obtained. The reappearance of the difficultly volatile liquid in the vacant part of the tube, while there was assurance of there being no deficiency in the supply of oxygen, served to confirm the impression gained by the preceding experiment,—that chloroform could not be completely burnt in oxygen alone, but that a substance having affinity for chlorine would have to be mixed with the asbestos, at the point where the combustion takes place.

II. *Experiments with Oxyd of Zinc, mixed with the asbestos in the posterior part of the combustion tube, as absorbent of Chlorine in the analysis of substances difficultly combustible.*

As already indicated, the chief object of this set of experiments was to determine whether the presence, at the point where combustion takes place, of an oxyd capable of combining with the chlorine would have the effect to prevent the formation of the difficultly volatile liquid above mentioned, and thus remedy that defect in the process.

Experiment 1.—In this experiment, three grams of oxyd of zinc were intimately mixed in a mortar with the quantity of asbestos necessary to fill the space between *a* and *b*, fig. 2, and that part of the tube then packed with this mixture in the usual manner. A similar mixture composed of asbestos and only one gram of oxyd of zinc was placed between *c* and *d*. The space between *b* and *c* was left still vacant, in order to be able to observe the effect. On account of the volatility of the chlo-

⁴ H. Rose, *Chimie Analytique*, new French edition, p. 801.

rid of zinc, it was deemed advisable to retain the use of the air-bath to control the temperature of the anterior portion of the combustion tube, which, in this experiment, was not allowed to exceed 160°C . The result was, as anticipated, that no such condensation of liquid between *b* and *c* occurred. In order to gain from this experiment some idea of the degree of volatility of chlorid of zinc under such circumstances, the two columns of asbestos were treated for chlorine, separately. The solution obtained from the anterior column was found to contain but a trace of chlorine, giving only a milkiness with nitrate of silver; showing that the chlorid of zinc does not travel far through a column of asbestos from the point where the flame plays directly on the tube.

Results of the Analysis.—0.2067 gram of chloroform gave 0.0798 of carbonic acid, 0.0276 of water, and 0.7372 of chlorid of silver.

		Calculated.		Found.
Carbon	C_2	12	10.0671	10.5273
Hydrogen	H	1	0.8473	1.4514
Chlorine	Cl_3	106.2	89.0856	88.0455
		100		100.0242

Experiment 2.—In this experiment, the whole length of the combustion tube from *a* to *d* was packed with a mixture of asbestos and four grams of oxyd of zinc. The temperature of the anterior end of the combustion tube was regulated, as in the previous experiment, by means of the air-bath.

Results of the Analysis.—0.1339 gram of chloroform gave 0.0506 of carbonic acid, 0.0156 of water, and 0.4768 of chlorid of silver.

		Calculated.		Found.
Carbon	C_2	12	10.0671	10.3062
Hydrogen	H	1	0.8473	1.2733
Chlorine	Cl_3	106.2	89.0865	87.9014
		100		99.4809

These two analyses, agreeing as they do so closely, indicate that the chloroform analyzed contained larger percentages of carbon and hydrogen,—especially of the latter,—and a correspondingly smaller percentage of chlorine than the theoretical quantities; occasioned, probably, by the presence of some impurity. This view is supported by calculations made on the assumption that the excess might have arisen from volatilization of chlorid of zinc, or from incomplete absorption of the chlorine; which would make the chloroform contain from two to six per cent more than the theoretical quantity of chlorine. These results are regarded, therefore, as satisfactorily establishing the utility of this process in the analysis of chloroform. But the

analysis of this body, containing as it does eighty-nine per cent of chlorine, and only eighty-five hundredths of one per cent of hydrogen, must be considered as an extreme case, and does not prove the process a good one for other classes of substances.

The next step, therefore, was to determine whether the process would be equally efficient in the analysis of substances rich in hydrogen, the combustion of which would give rise to the formation of a large quantity of hydrochloric acid. The substance selected for analysis, to settle this question, was chlorid of amyl.

III. *Experiments with Oxyd of Zinc, as an absorbent of Chlorine in the analysis of substances rich in Hydrogen.*

In these experiments the oxyd of zinc was employed in the same manner as above described for the analysis of chloroform. The chlorid of amyl, which was the subject of analysis, was prepared in the usual manner. Its boiling-point was 102° , 8 corrected.

The following results of two analyses with oxyd of zinc indicate that this oxyd combined with and retained some of the carbonic acid. This result was not anticipated, as in the analysis of chloroform the determination of carbon was uniformly slightly in excess.*

The results of these two analyses are as follows:—

1.—0.1922 gram of chlorid of amyl gave 0.8513 of carbonic acid, 0.1854 of water, and 0.2528 of chlorid of silver.

		Calculated.		Found.
Carbon	C ₁₀	60	56.3910	40.85
Hydrogen	H ₁₁	11	10.3383	10.72
Chlorine	Cl	35.4	33.2707	32.47
		100.		93.04

* Since the above was written, I have observed upon reviewing my notes,—not only of experiments with oxyd of zinc, but also with oxyd of copper, that in every analysis in which I made note of carbonization, or blackening of the asbestos in the combustion tube,—which may sometimes occur from too rapid distillation of the substance, or, what amounts to the same thing, a deficiency in the supply of oxygen,—there was a loss in the determination of the carbon, and generally, also, in that of the chlorine; while the hydrogen would agree pretty nearly with the theoretical quantity. I am, therefore, at the present writing, inclined to suspect that the carbonization may have had some connection with the deficiency in the carbon determinations in these instances, although the blackening would readily and completely disappear as soon as a sufficiency of oxygen was supplied. The momentary blackening of the asbestos occurred in both of the analyses of chlorid of amyl with oxyd of zinc, but, as already intimated, was not regarded at the time of serious consequence, as similar phenomena in the analysis of hydrocarbons by my process were generally attended with good results. It may, therefore, remain an open question, whether the oxyd of zinc may not serve a good purpose in the analysis of substances of the class now under consideration.

2.—0.1657 gram of chlorid of amyl gave 0.8314 of carbonic acid and 0.1608 of water.

		Calculated.		Found.
Carbon	C ₁₀	60	56.3910	54.56
Hydrogen	H ₁₁	11	10.3383	10.74
Chlorine	Cl	35.4	33.2707	

IV. *Experiments with Oxyd of Copper, as absorbent of Chlorine in the analysis of substances rich in Hydrogen.*

In these experiments, for the reason previously stated, the oxyd of copper could only be placed in the anterior end of the combustion tube, where it might be maintained at a tolerably low temperature. After two or three experiments,—which were but partially successful,—it became apparent that the range of temperature within which oxyd of copper could be made serviceable to absorb the chlorine was probably rather limited.

It was observed, for example, that at 150° to 160° even brown oxyd of copper, which had been but gently ignited, would fail to absorb nearly all the chlorine, and consequently the determination of the carbon, and sometimes that of the hydrogen, would be in excess. In one experiment, in which the oxyd of copper was kept at about 153° C., its appearance had suffered no change, and it was found to contain only 8.29 per cent of chlorine, or only about one quarter of the theoretical quantity. When a sufficiently high temperature is employed, on the contrary, the posterior end of the column of oxyd of copper and asbestos has the appearance of being entirely changed into yellow chlorid of copper, the rest of the column remaining, for the most part, of its original dark color.

In another experiment, with the oxyd of copper kept at a temperature of about 160°, only about fourteen per cent of chlorine was obtained.

In both of these experiments the carbon determination was considerably in excess, and in one of them the hydrogen also. The oxyd of copper employed had been strongly ignited.

Before proceeding further with these somewhat random experiments, it was deemed advisable to *determine* the temperature at which chlorid of copper begins to give off chlorine, in order to know how far it would be safe to raise the temperature of the air-bath in conducting an analysis. By making use of the air-bath to regulate the temperature of the chlorid of copper, this determination was easily made. During the heating of the chlorid, a current of air from the air-gasometer was admitted through the tube in which it was contained.

Observations.—At 243° not a perceptible trace of chlorine was given off. After the lapse of fifteen minutes, at 250°, the nitrate of silver into which the gas was conducted, was observed to be

slightly milky; this may, therefore, be taken as about the temperature at which chlorid of copper begins to suffer decomposition. At 267° , a solution of nitrate of silver was instantly precipitated.

Thinking that perhaps the small quantity of chlorine evolved under these circumstances might be taken up again and retained if oxyd of copper were present, and possibly, also, that in that case a higher temperature might be safely employed—to make the conditions of the experiment conform in this particular to those which exist in an analysis, all but one inch of the chlorid of copper was removed from the tube, and in its place was put a mixture of asbestos and oxyd of copper, occupying a space of four inches in length, forward of the chlorid. The experiment was then repeated. Prolonged heating in a current of air, and afterwards in oxygen, during which the thermometer rose to 350° , produced no reaction with nitrate of silver. From this it appears that the chlorine, which was given off below this temperature from chlorid of copper, when this is mixed with oxyd of copper, is absorbed and retained by the latter; hence, that so high a temperature as 350° may be safely employed for the air-bath in conducting an analysis by this process.

Analysis 1.—In this analysis the oxyd of copper employed was prepared in the ordinary way and strongly ignited. The space in the tube occupied by the mixture of asbestos and oxyd of copper was five inches in length, and contained just five grams of the oxyd. During the experiment, the temperature of the air-bath was maintained at about 350° . At the close of the combustion there was no appearance of chlorid of copper, except in the first half-inch at the back end of the column of the mixture of oxyd of copper and asbestos; showing that the temperature employed was favorable for rapid and complete absorption of the chlorine.

Results of the Analysis.—0.1682 gram of chlorid of amyl gave 0.3486 of carbonic acid, 0.1633 of water, and 0.2233 of chlorid of silver.

		Calculated.		Found.
Carbon	C ₁₀	60	56.8010	56.522
Hydrogen	H ₁₁	11	10.3383	10.761
Chlorine	Cl	35.4	33.2707	32.773
		100		109.056

Analysis 2.—The oxyd of copper employed was of the same preparation as that used in Analysis 1. The space occupied by the mixture of asbestos and oxyd of copper was only $3\frac{1}{2}$ inches in length, but contained the same quantity, viz. 5 grams of the oxyd of copper, as used in the previous analysis. The temperature of the air-bath ranged from 250° to 253° . At the close

of the combustion, it was found that all but $\frac{1}{2}$ inch at the forward end of the column of mixed asbestos and oxyd of copper had the appearance of containing chlorid of copper. By comparison with the corresponding observation in Analysis 1, it will be seen that the appearance of the chlorid extends over more than five times the space in this analysis that it did in the former, showing that with strongly ignited oxyd of copper a temperature higher than 250° , even as high as 350° , is more favorable for the absorption of the chlorine. The following results of the analysis, however, are equally accurate with those of the preceding analysis.

0.1669 gram of chlorid of amyl gave 0.3457 of carbonic acid, 0.1612 of water, 0.2213 of chlorid of silver.

		Calculated.		Found.
Carbon	C ₁₀	60	56.3910	56.489
Hydrogen	H ₁₁	11	10.3383	10.785
Chlorine	Cl	35.4	33.2707	32.732
		100		100.008

Analysis 3.—Under the impression that an oxyd of copper which had been less strongly ignited might be effectual to absorb the chlorine at a lower temperature, I employed in this and the two following analyses a preparation of brown oxyd of copper, obtained by precipitation with potash and ignition over an ordinary gas flame. In this analysis the temperature of the air-bath ranged from 150° to 158° . The space occupied by the asbestos mixture was four inches in length, and contained three grams of the oxyd. Although the results of the analysis indicate that the temperature of the air-bath was too low, they also show, by comparison with the results obtained in operating with strongly ignited oxyd at about the same temperature of the air-bath (see p. 163), that the brown oxyd is decidedly preferable in respect to the temperature required. This was also shown by the appearance of the oxyd after combustion,—the newly formed chlorid being confined, in the case of the brown oxyd, to a much shorter space.

Results of the Analysis.—0.1640 gram of chlorid of amyl gave 0.3504 of carbonic acid, 0.1562 of water, and 0.1884 of chlorid of silver.

		Calculated.		Found.
Carbon	C ₁₀	60	56.3910	58.268
Hydrogen	H ₁₁	11	10.3383	10.582
Chlorine	Cl	35.4	33.2707	28.360
		100.		97.210

Analysis 4.—Used the same preparation of oxyd of copper as in analysis 3, viz., the brown oxyd. Temperature of the air-

bath reached 170°. Slight carbonization occurred just at the close of the combustion, from extending the heat backward too soon, under a wrong impression that the substance was all burnt. Were it not for this circumstance, it is believed that this would have been a good analysis, although the temperature of the air-bath was kept so low. That a higher temperature of the bath is desirable, however, is shown by the fact that the chlorid of copper appeared diffused over a space of 2½ inches. The length of the column of mixed asbestos and oxyd of copper was only four inches in this experiment, containing *but one gram* of the oxyd.

Results of the Analysis.—0·1568 gram of chlorid of amyl gave 0·3195 of carbonic acid, and 0·1522 of water.

		Calculated.		Found.
Carbon	C ₁₀	60	56·3910	55·574
Hydrogen	H ₁₁	11	10·3383	10·784
Chlorine	Cl	35·4	33·2707	

Analysis 5.—The oxyd of copper employed was of the same preparation as that of analyses 3 and 4. The temperature of the air-bath, however, was considerably higher, ranging from 240° to 247°. The mixture of asbestos and oxyd of copper occupied a space of five inches in length, but contained only two grams of the oxyd. At the close of the combustion there was no appearance of chlorid of copper, except at the back end of the column, a space ¼ of an inch in length.

Results of the Analysis.—0·1631 gram of chlorid of amyl gave 0·3388 of carbonic acid, 0·1557 of water, and 0·2157 of chlorid of silver.

		Calculated.		Found.
Carbon	C ₁₀	60	56·3910	56·542
Hydrogen	H ₁₁	11	10·3383	10·607
Chlorine	Cl	35·4	33·2707	32·649
		100·		99·798

It can hardly have escaped observation, that the quantity of oxyd of copper or oxyd of zinc required to absorb the chlorine by this process is extremely small, in consequence of its being uniformly diffused through a large mass of asbestos; hence it is obvious that but little of a solvent is needed to extract the chlorid. In this respect the new process bears a striking contrast to the old one, which involves the use of a large quantity of lime, necessitating a corresponding quantity of acid, and introducing disagreeable manipulation, which tend to increase the liability to error.

I have not yet tried the process recently described by Carius,*

* *Annalen der Chemie und Pharmacie.*

as the difficulty which I had found in obtaining tubes that would bear the pressure incident to his process for the determination of sulphur gave no encouragement of better success in the use of his process for the determination of chlorine, which is performed in a similar manner, although more complicated.

The advantage which my process affords, of being able to determine the three elements, carbon, hydrogen, and chlorine at a single combustion, without the introduction of any difficult or hazardous manipulation, induces the belief that it will be found preferable to any other that has been devised.