

Determination of Oxygen
in

Organic Bodies

Thesis

by
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Determination of Oxygen in Organic Bodies

The determination of oxygen in organic was at first made by difference, by subtracting the sum of the percents of the other elements from 100, the difference being called oxygen; but of course it varied from the true percent by the errors made in the determination of the other elements.

Several methods have been proposed for the direct determination of oxygen, a short account of which is given below.

M. Maumené (Vgl. Compt. rend 2V 432
Ann. f. prat. chem. LXXXVIII 185. Chem. Central 1863 49
Jahrb. f. Ha. d. Chem 1862 552. Ann. de Chim. et de Phys. Nov. 1855.)
recommends heating the organic body with

litharge which contains a quarter of its weight of phosphate of calcium; he determines the carbonic oxide and water in the ordinary way and from the weight of lead reduced determines the amount of oxygen obtained from the litharge which subtracted from the total amount contained in the water and Carbonic oxide absorbed should give the amount of oxygen contained in the organic body analysed.

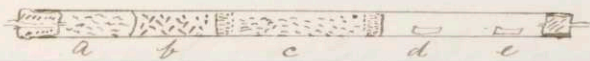
The method which is really a method of difference would be a difficult one to perform and the use of litharge would be objectional in as much as it is likely to contain peroxide of lead as well as the oxides of other metals and even metallic lead

E.H. Baumhauer (Liebig's Ann. xc. 228)
Ann. Chem. Phys. 1854 740
Chem. Gaz. 1854 313) suggests igniting the substance with oxide of copper and after the completion of the combustion, a known quantity of oxygen gas is passed over the hot

reduced copper changing it to the oxide; he connects the ends of his combustion tube with graduated tubes so that if an excess of oxygen is passed over it is collected and can be measured.

W. Baumhauer (Archives Néerlandaises 1.179. *Jes Zeit.* V 141 *Ann Chem Phys* [3] XIV 327 *Zeit of Chem* 1866, 428. *Jahr. For Chem* 1866 3 812 *Jour prakt. Chem* C1 257. *Bull. Soc. Chim* VI. (131)) describes an improvement on his former process.

A combustion tube is filled in the following manner beginning at the anterior end:



(a) a layer of copper turnings, (b) a layer of porcelain previously washed with chlorhydric acid and ignited, (c) a layer of strongly ignited coarse grained oxide of copper (between plugs of asbestos) (d) the substance in a porcelain boat or in a glass bulb, (e) a porcelain boat containing a weighed portion of AgIO_3 (iodate of silver).

He first passes over hydrogen gas, heating the copper turnings to reduce any oxide that may exist on their surface.

The hydrogen is then displaced by nitrogen the oxide of copper is then heated and the substance is burned in an atmosphere of nitrogen.

As soon as the organic substance is completely burned or at least completely carbonized, the sodate of silver is gradually heated whereby the still remaining carbon is burned and the copper reduced from the oxide of copper is re-oxidized, the excess of oxygen being retained by the copper turnings; the gaseous products are displaced by nitrogen and the absorption apparatus weighed.

He then attaches a weighed chloride of Calcium tube and heats the copper turnings to redness, allowing the rest of the tube to cool, and then passes over hydrogen gas; the oxidized portion of the copper turnings being reduced; the water is absorbed by the chloride of calcium tube and weighed; the weight of this water gives the quantity of oxygen contained in the sodate of silver beyond that

which was required for the complete combustion of the organic body.

These are both methods of difference and are liable to considerable error.

Mr Stromeyer's process (Rept d Chim III 1869 391 Vgl. Ann d Chem u Pharm CXXVII 247. Jahrbuch Chem. 1862) consists in determining the quantity of oxide of copper reduced by dissolving the contents of the tube in a mixture of chlorhydric acid and ferric sulphate, determining by oxide of manganese the quantity of ferrous salt produced by the reducing influence of the reduced copper and of the oxide of copper.

It is a long and troublesome operation liable to a great many errors and only gives the result by difference.

A. Ladenburg (Ann Chem u Pharm CXXXV. 1. Zeit f Chem 1865 497 - Zeit f Anal Chem IV 192 - Jour f Prakt Chem XCVI 346 - Chem Central 1865 911 - Ann Chim Phys. V. 486

Bull. Soc. Chim. IV 261 - Jahr in For d Chem 1865. 129) has described a method of organic analysis in which he heats with sulphuric acid and a weighed quantity of iodate of silver in a sealed tube at 170° - 200° ; he weighs the tube then opens it, exhausts, seals it up and weighs it again; he then opens it and determines the quantity of (IAg) iodide of silver formed.

C. G. Wheeler (Bull. Soc. Chim. VI 1866 130 - Jour of Pract Chem t xxvi 239. 1865 no. 20.) describes a method, differing a little from Baumstam's in which he uses chlorate of potash to supply the oxygen, but he calculates the oxygen of the organic body by difference.

A. Mitscherlich (Pogg. Ann. cxxx. 536. Fres Zeit vi. 13) has devised a new method of organic analysis which serves among other things for the direct estimation of oxygen.

The combustion is performed in a tube filled with charcoal in a current of chlorine gas in which the hydrogen is wholly changed to chlorhydric acid while the oxygen forms

carbonous and carbonic oxides.

The chlorhydric acid formed is absorbed by a concentrated solution of nitrate of lead, which according to the author does not absorb free chlorine.

The free chlorine is absorbed by an alcoholic solution of stannous chloride or ferrous sulphate; the (CO_2) carbonic oxide by hydrate of potassium and the (CO) carbonous oxide by passing it through a series of bulbs filled with a solution of cuprous chloride in chlorhydric acid.

In a subsequent communication (Deut. Chem. Gesell. 1-45 - Bull. Soc. Chim. (2) X 378) Mitscherlich describes a simplified method by which the carbon, hydrogen and oxygen may be determined in a single operation; the chlorine is supplied by potassium platonic chloride, a substance which gives up its chlorine when heated with organic bodies.

The substance to be analysed is placed

in a porcelain tube filled with a mixture of pumice stone and potassium platonic chloride (containing about 8 grams. of platinum).

The air in the apparatus is displaced by nitrogen and the tube heated to redness; water is absorbed by phosphoric oxide, chlorhydric acid by nitrate of lead, free chlorine by stannous chloride and carbonic oxide by hydrate of potassium.

The gases remaining in the tube are displaced by nitrogen and the absorption apparatus weighed.

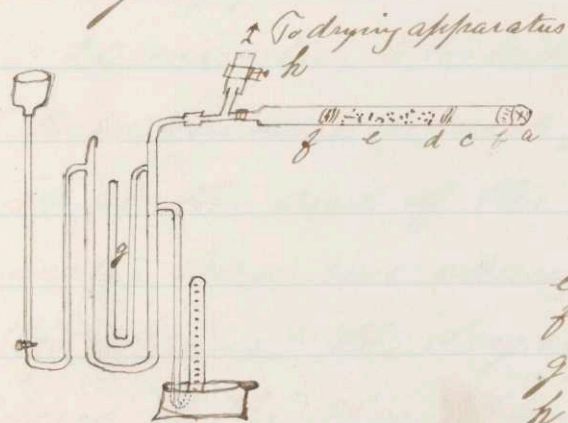
The porcelain tube is again heated to redness and a stream of oxygen passed through turning the carbon that remains to carbonic oxide which is absorbed and weighed.

Mitscherlich's methods are troublesome, require considerable apparatus and are liable to error from the use of charcoal in the first method and neglecting the carbonous oxide that probably is formed in the second.

The following are a few experiments that were tried with a view to ascertain whether it would be possible to burn the substance in a tube filled with charcoal, changing the oxygen to carbonous oxide and carbonic oxide, the resulting gases being pumped into a graduated tube, measured and afterwards analysed.

The first point considered was whether all of the gases could be pumped out of the charcoal with out the aid of heat.

The form of pump that was used in this experiment, as well as in subsequent ones, was a Sprengel's syphon mercury pump of the following construction



- a = substance
- b = plug asbestos
- c = Air space
- d = plug of asbestos
- e = charcoal
- f = plug of asbestos
- g = manometer
- h = screw clip

In the first experiment the combustion tube which was closed at one end and drawn down at the other was connected by one arm of a T with the pump; the T was also connected with a set of drying tubes so that it was possible to admit dry air after the tube was exhausted without breaking any of the joints.

The experiment was performed in the following manner: After the joints were well wired they were covered with a gutta percha cement, the connection with the drying apparatus was closed with a screw clip, a graduated tube filled with mercury inverted in the mercury trough and the delivery tube of the pump placed under it; the pump was then started and when the manometer showed that a vacuum had been obtained the pump was stopped and the apparatus allowed to stand 20 minutes, to test the joints and also to see if the charcoal would give up any more gas; if at the end of the 20 minutes the manometer had not changed the air was admitted through the drying apparatus, the tube exposed to the atmosphere for 15 minutes

and the screw clip then closed.

Meanwhile the gas collected had been measured the tube refilled with mercury and inverted in the trough; when the apparatus had been partially exhausted, the tube was heated up to a red heat, the gas was then turned out, the pump started and the tube completely exhausted; in order to make sure that the exhaustion was complete the tube was heated up a second time.

The following figures show that all the gas could not be obtained by the pump alone and that the results varied so that it was found necessary afterwards to work in Vacuum.

With pump alone	Heating & then pumping
75.600 $\overset{2}{\text{c.c}}$	87.366 $\overset{3}{\text{c.c}}$
75.388 "	81.135 "
75.635 "	83.934 "

As before stated the subsequent experiments were performed in Vacuum.

The first substance used for analysis was anhydrous oxalic acid as it was thought that the decomposition would be simpler and also as it could easily be obtained pure.

A weighed quantity of the oxalic acid was placed in the closed end of the tube (see sketch p 9) and kept in place by a plug of asbestos, an air space of 2-3 inches was then left and the charcoal placed on a second plug of asbestos so that it was possible to heat the part of the tube containing the charcoal red hot without danger of volatilizing the oxalic acid.

The tube was alternately pumped out and heated until it was possible to heat the part of the tube containing the charcoal to a low red heat without having the manometer change appreciably; The delivery tube of the pump was then placed under the inverted graduated tube, the part of the tube containing the charcoal was heated to a low red heat and then the oxalic acid was heated so as to partially relieve the vacuum, the heat was then increased under the charcoal

When the tube was red hot the oxalic acid was completely volatilized, the tube was then allowed to partially cool and then was pumped out.

After the gases had been measured over mercury hydrate of potassium was introduced to absorb the carbonic oxide and the remaining gases (CO)(H) carbonous oxide and hydrogen measured over water.

The reaction was expected to be the following

$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} + 2\text{C} = \text{CO}_2 + 2\text{CO} + \text{H}_2$$

but as it was found that part of the water passed over the hot charcoal unchanged a chloride of calcium tube was placed between the tube & the pump to absorb the aqueous vapor.

The following are the results that were

obtained	without CaCl_2 tube	with CaCl_2 tube
Theory	65.798 %	72.151 %
71.11 %	65.092 %	78.42 %

As the results obtained with oxalic acid were far from satisfactory, pure cane ^{sugar} was next employed but the only result obtained was that the resulting decomposition was not as simple as had been supposed, as in addition to the carbonous and carbonic oxides, hydrogen and water, a hydrocarbon was also formed which the hot charcoal failed to break up.

In the sugar analysis the gases were pumped into the graduated tube, measured and then submitted to gas analysis.

The following are the figures obtained:

<u>Theory</u>	<u>Expt</u>
51.46	19.27

The facts to be learned from these experiments are:

1st That all the gases cannot be pumped out of charcoal without the application of heat.

2nd That the decomposition of organic substances in vacuo differs from what would have been theoretically presupposed.

In concluding I would heartily
thank Professors King and Ordway for
their kind advice and assistance and
I am sorry that I have not a more sat-
isfactory result to offer them.

Remain

Your obt. servant

Chas. C. D. Fish