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Combustion Analysis; Estimation of Carbon & Hydrogen

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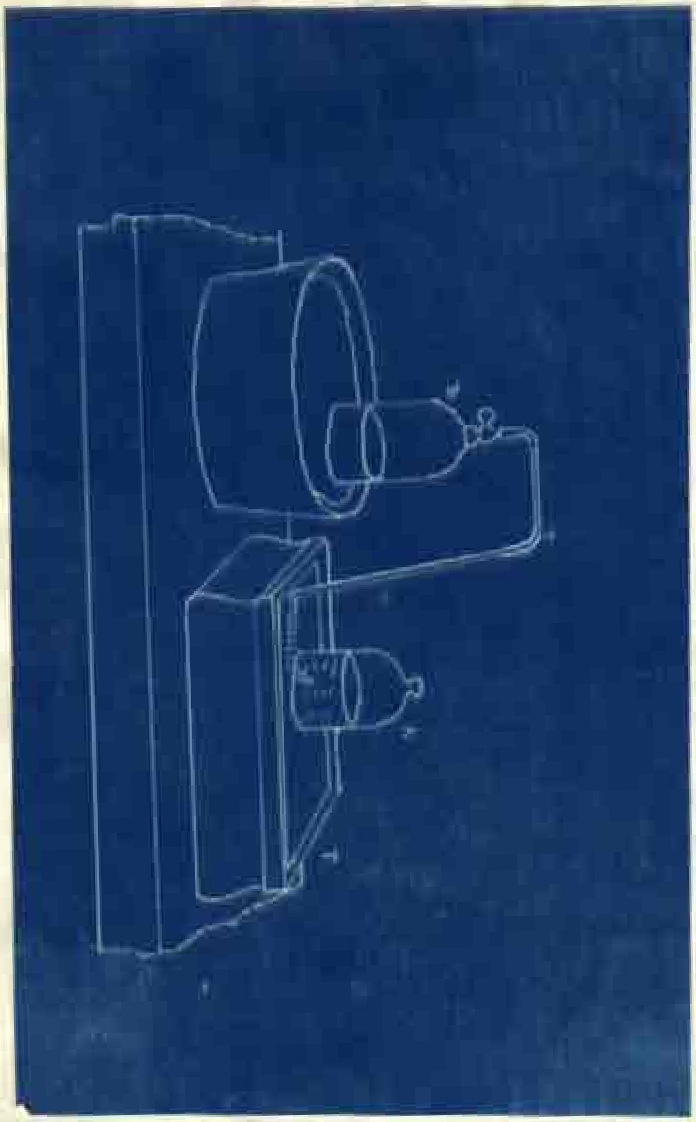
The first successful attempt to determine quantitatively the composition of an organic substance was made by the great French chemist, Antoine Laurent Lavoisier. His original communication was presented to the French Academy of Sciences in 1781. The work may be found recorded in the reports of that body published in the years 1781-1787.

Lavoisier's method in theory is essentially like the present, though the original apparatus has been much improved. The substance to be analysed is carefully oxidised, the carbon to carbon dioxid and the hydrogen to water. From the weights of these products the percentage of carbon and hydrogen is calculated. He employed in his researches the apparatus represented in Plate I.

A graduated bell-jar A, filled with air standing over mercury in the trough T; into the bell-jar A, was introduced a lamp, the wick carrying a small piece of phosphorus. A second jar B, contained oxygen over water and was connected with the bell-jar A, by a glass tube t. The oil or alcohol for analysis was poured into the lamp and the phosphorus ignited with a hot wire. Combustion immediately took place, which was completed by passing in oxygen from

PLATE I.



the jar B. The carbon dioxid formed was absorbed by an aqueous solution of potassium hydrate, and from the volume of the gas with that of the oxygen remaining, the results calculated.

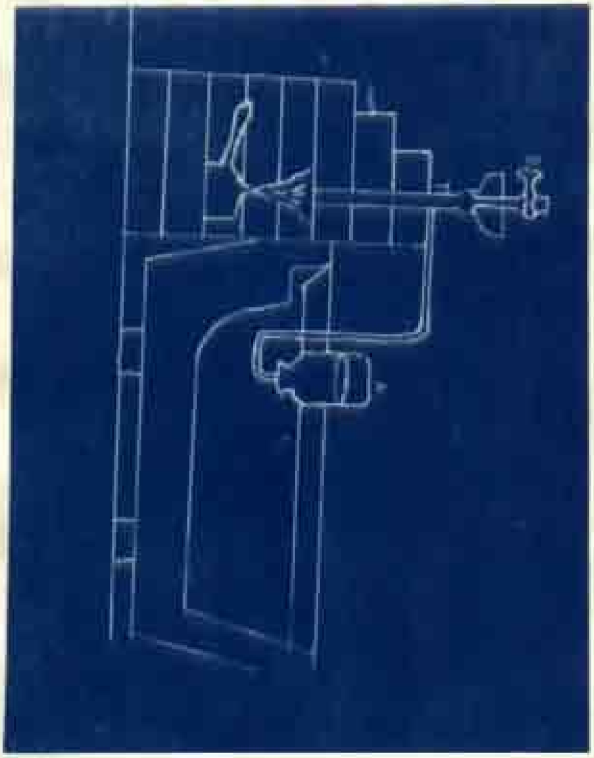
At the time when this work was done, means for the accurate determination of scientific constants had not been developed, and Lavoisier's results are obviously incorrect. Neither the exact formulae of carbon dioxid and water, nor the specific gravity of the two gases had yet been ascertained. Still we may consider the results obtained by him of value: for if the original data be recalculated with modern constants, his analysis will compare very favorably with subsequent and more famous work on this subject.

Later the method was modified by the use of lime water for absorbing the carbon dioxid, the water by a "deliquescent" salt.

In 1804 Theodor V. Saussure, Thénard and Berthelot worked on the subject of combustion analysis. They mixed the organic substance with oxygen in a state of vapor, and exploded the gaseous mixture. The products of explosion were analysed, and the formula thus ascertained. Thénard decomposed the substance at red heat, collecting the resulting gases for analysis. While these investigations followed in an era of higher chemical development, the results of these experiments were not so accurate as the work of Lavoisier.

The investigations of Gay Lussac and Thénard proved far more satisfactory. Following in the wake of Lavoisier's later work, they tried oxidising the substance with potassium chlorate, collecting the carbon dioxid in a bell-jar and absorbing with potassium hydrate, making an indirect determination of the water. Their apparatus is original and interesting. (Plate II) The finely divided organic substance is mixed with potassium chlorate in powder. The resulting mixture is pressed into small pills and dried. A hard glass tube T, closed at one end is placed on a charcoal furnace or an alcohol lamp. The tube is fitted with a glass stopcock S, having a pit bored into its side. A weighed quantity of pills is taken, one is placed in the pit of the stopcock S, which is turned and the pill falls to the bottom of the red-hot tube T, where it is immediately vaporized. The gases formed are collected over mercury in the graduated bell-jar A. As soon as all are added, hydrogen is mixed with the contents of the receiver and the mixture exploded. The carbon dioxid is absorbed by caustic potash, and from the volume of the two gases with the weight of the substance the quantity of water is found. Nineteen organic substances were analysed by this method, four containing nitrogen.

PLATE II.



The work of Berzelius in 1814 with his improved method was very important in establishing that "all organic compounds although in most cases possessing a somewhat complicated composition, obey the laws of constant and multiple proportion applicable to inorganic compounds." Here the apparatus is somewhat similar to the present form. The combustion tube T, is drawn out to a fine point, not unlike a bayonet, and contains a mixture of the substance with potassium chlorate in layers. (Plate III) The heat is supplied from a charcoal furnace and the products of combustion are driven into absorption apparatus. The combustion was completed with oxygen. The results of Berzelius paved the way for the classical researches of Justus von Liebig at the laboratory in Giessen, and the present system of combustion analysis.

The investigations of Liebig extended from 1823-1831. The potash bulb was nos described until the latter date. His method is as follows; The oxidising agent is cupric oxid, previously dried to insure accurate results. The combustion takes place in a hard glass tube T, drawn out to a fine point at one end P. Cupric oxid is poured into the tube to the point O, then if the organic substance is a solid, non-volatile or difficultly volatile, 0.2 gm.- 0.3 gm. are taken and placed

PLATE III.

in a small mortar. Cupric acid is added and a thorough mixture made. This is then poured into the tube to a certain point D, the space depending on the combustibility and volatility of the substance. Next, the tube is fitted with a cork C, bearing a calcium chlorid tube Ca, and a potash bulb K. (Plate IV) Heat is applied carefully so that the gas passes regularly through the potash bulb. The potash bulb carries a small tube h, filled with small lumps of potassium hydrate, to insure complete absorption and prevent the exit air from carrying away any aqueous vapor in the potash bulb. Oftentimes a few pieces of solid potassium chlorate are placed in the bayonet tube. On heating, oxygen is generated which completes the combustion. When no more bubbles pass through the potash apparatus, the tip of the tube is broken off with the pliers and then attached to a caustic potash and calcium chlorid absorption apparatus. The weighed potash tube is attached to an aspirator and air sucked through the apparatus to allow the aqueous vapor and carbon dioxid to pass into the absorption tubes. Then after this has been satisfactorily completed, the tubes are disconnected and weighed. The differences in weights give the carbon dioxid and water found. Volatile liquids are weighed in small glass tubes, having a long point, fig. 1. The point is broken off and the

PLATE IV.

tube dropped into the combustion apparatus and cupric oxid is added as before.

Difficultly volatile liquids are weighed in short glass tubes, into which the liquid is added by a capillary tube. They are placed in the combustion tube with cupric oxid as usual. Lead chromate has been used as an oxidising agent with good results. Many chemists use a similar apparatus, but making the combustion in a stream of oxygen. Another form of tube has been devised about 12-15 mm wide, (fig. 2) the length varying with the furnace used. This is fitted tightly with bored corks. About five centimeters from the cork is left free, then follows a copper oxid spiral a, and forty-five centimeters of coarse cupric oxid, and lastly a short copper oxid spiral. The combustion is made in a manner similar to Liebig's, the organic substance being burnt in a platinum or porcelain boat. W. Kopfer has used a tube fitted with platinum black and asbestos, which is especially accurate in the determination of hydrogen. The combustion is carried on in a stream of oxygen or air.

With these modern methods which are the result of over a hundred years of patient investigation, organic chemistry has been placed on a firm basis and the old line between organic and inorganic chemistry has disappeared.