

# THE MICRO-ANALYTICAL DETERMINATION OF CARBON AND HYDROGEN

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**Abstract**—The determination of carbon and hydrogen is the most important method of analysis carried out as a means of establishing the structure and purity of organic compounds. Since Pregl<sup>1</sup> developed the micro-method of determination nearly 50 years ago, this scale of working has been adopted in most analytical laboratories throughout the world.

In the last few decades many important modifications and also completely new methods have been described in the literature, which cover modifications in the conditions for the combustion; the way in which nitrogen oxides are removed; and new methods for the determination of the combustion products of carbon dioxide and water. These trends of development are the result of the progress towards greater accuracy, simplicity and a more rapid method of analysis not often achieved with the earlier Pregl method. The trends are discussed.

THE most important method in the organic analytical laboratory is the determination of carbon and hydrogen. With this method it is possible to obtain with one analysis two values which are very important and significant for every organic compound. Pregl, the founder of organic micro-analysis, developed, nearly 50 years ago, a micro-method for carbon and hydrogen determination. This method has been used since in hundreds of analytical laboratories and there are many analysts still today working with the original Pregl method<sup>1</sup>.

In the last few decades many important modifications and also completely new methods have been described, and one can classify them for discussion into three main groups:

- (1) Modifications in the conditions for combustion.
- (2) Modifications in the way in which nitrogen oxides are removed.
- (3) New methods for the determination of the combustion products, i.e. carbon dioxide and water.

## (1) *Modifications of the Conditions for Combustion*

The so-called "universal filling" of Pregl (CuO/PbCrO<sub>4</sub>, Ag and PbO<sub>2</sub>) is very useful, but it is important to work exactly according to the directions given by him to obtain accurate and reliable results, particularly with "difficultly burning" compounds. About 20 years ago combustion catalysts were introduced such as the vinosites developed by Reihlen<sup>2</sup>, which consist of mixtures of different metal oxides that facilitate combustion of organic matter at low temperatures (500 to 700°C). Mainly they catalyse the oxidation of carbon monoxide and methane.

An important development has been the introduction of high temperature furnaces, working above 800°C, as used by Belcher and Ingram<sup>3</sup> in their "empty tube" combustion method, which permits combustion without any oxidizing filling or catalyst. In this kind of method the sample is burned in a fast stream of oxygen. Korshun<sup>4</sup> also

developed a method on the same principle, while a modification of it has been described by Kirsten<sup>6</sup>. This author fitted a nickel tube into the combustion tube which becomes oxidized and burns the sample at a high temperature of 1000°C in a fast stream of oxygen. The introduction of such methods made it possible to develop apparatus for automatic combustion, of some advantage, because all compounds can be burned in the same way. Working with the original Pregl method this is impossible and every compound has to be burned individually. It is interesting that in the last few years methods have been developed which permit the condition of low combustion temperatures by the use of catalysts of a different kind to those introduced two decades ago. There are, for example, two such methods which we tested in our laboratories over a period of several months. In one of them, due to Körbl<sup>6</sup>, use is made of the thermal decomposition product of silver permanganate, which is packed into the combustion tube in a short layer in place of the usual type of filling. In the other method recommended by Večera<sup>7</sup>,  $\text{Co}_3\text{O}_4$  on asbestos is used in a similar manner. With both methods it is possible to use combustion temperatures below 700°C. The analyses done by the authors and also our own proved that every type of organic compound can be analysed.

Finally, it is pertinent to mention tube fillings which permit the determination not only of carbon and hydrogen, but also other elements simultaneously. Several authors have described methods for the determination of carbon and hydrogen with silicon, phosphorus, sulphur or fluorine<sup>8-11</sup>.

### (2) *Modifications in the Way in which Nitrogen Oxides are Removed*

The most important source of error in the classical carbon and hydrogen determination is the lead dioxide which is used for the absorption of the nitrogen oxides. The reagent, at 180°C, absorbs the nitrogen oxides, but it retains also some water and carbon dioxide. Changes in the temperature of the lead dioxide furnace have therefore some influence on the result of the estimation. These conditions have been studied by Lindner<sup>12</sup> and by Boetius<sup>13</sup>. In view of these anomalies many attempts have been made to find an acceptable substitute. Principally there are two possible means, namely the absorption and chemical reaction of the oxides of nitrogen or the reduction to  $\text{N}_2$  or  $\text{N}_2\text{O}$ . Many external absorbents have been suggested, such as concentrated sulphuric acid<sup>14</sup>, concentrated sulphuric acid and potassium dichromate<sup>15</sup> or diphenylamine<sup>16</sup>, and different preparations of manganese dioxide<sup>17-19</sup>. Lindner<sup>12</sup> was the first to recommend the use of copper for the reduction of the nitrogen oxides. Copper is also used in methods published by Kainz<sup>20</sup> and Unterzaucher<sup>21</sup>. It has also been shown that nickel serves to reduce the nitrogen oxides<sup>22</sup>. In using these reagents it is necessary to burn the substance either in a stream of nitrogen, using metal oxides to provide the source of oxygen, or in a stream of air. External absorbents have also been recommended which effect reduction of the oxides of nitrogen to  $\text{N}_2$  and  $\text{N}_2\text{O}$  that are not retained in the water and carbon dioxide absorption tubes. Hussey and co-workers<sup>23</sup>, for example, recommended ammonium sulphamate and Cross and Wright<sup>24</sup> suggested the use of trihydroxyl ammonium phosphate, both reagents being used under normal combustion conditions with the sample burned in a stream of oxygen.

### (3) *New methods for the Determination of the Combustion Products*

Up to 10 years ago only the gravimetric method of finish had been employed for determination of the carbon dioxide and water produced, and only recently have some

modifications of the absorption tubes been suggested<sup>25-27</sup>. Nevertheless it seems that the Pregl absorption tube is still preferred. Moreover, rubber or silicone connexions are still regarded as being sufficiently reliable, although some authors recommend ground-joint connexions for the tubes<sup>28-31</sup>.

The first attempt to determine the combustion products titrimetrically was carried out by Lindner<sup>12</sup> in 1935, and Johansson<sup>32</sup> published a few years ago a method using the Karl Fischer titration for the water determination and an iodometric procedure for carbon dioxide. The most successful approach seems to be the iodometric determination developed by Unterzaucher<sup>33</sup>, in which the carbon contact principle of the oxygen determination is employed to convert the oxygen of the carbon and hydrogen combustion products into carbon monoxide. Both elements are determined by titration of the iodine liberated upon reaction of the carbon monoxide with iodine pentoxide, oxidizing the iodine to iodate in the usual manner.

During the past year or so some methods have been described wherein the combustion products are determined by a gas volumetric or manometric procedure<sup>34-38</sup>. Most of these methods work on the principle that water and carbon dioxide are fractionated by freezing out, and after the combustion is finished, the partial pressures or the gas volumes are measured. The entire system is evacuated to  $10^{-3}$  mm Hg. Such methods are important for the analysis of compounds containing carbon-14. It is very easy to determine the <sup>14</sup>C activity in a proportional counting tube after the carbon determination has been finished<sup>39, 40</sup>. Moreover, it should also be possible to fractionate the combustion products by gas chromatography.

Finally the following points are raised for deliberation: It would be very useful, not only for testing a published new method but also for developing new procedures, to have an internationally accepted set of test compounds. It would also be highly desirable that the results of routine analyses are reported only to one decimal place because until now no method is known where the limits of error are smaller than  $\pm 0.1$  per cent of the theoretical values.

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## The micro-analytical determination of carbon and hydrogen

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## DISCUSSION

Mr. G. INGRAM (U.K.) (Chairman) said that some discussion on the merits of both the "empty tube" and catalytic methods of combustion would be of great value in view of the interest shown recently in the use of catalysts such as  $\text{AgMnO}_4$ . It was worthwhile noting that the catalytic technique required a lower temperature condition than did the "empty tube" method of combustion. There was, however, little doubt that the latter technique possessed a number of advantages not inherent in the catalytic method.

He had introduced in 1943 the silver oxidation type of catalyst (silver orthovanadate, thermally decomposed before use), which had properties similar to the silver permanganate introduced about 10 years later by Dr. Körbl. In spite of prior knowledge of the capabilities of the silver catalysts, work was started in about 1948 on the investigation of the "empty tube" procedure, because of the advantages it seemed to offer at the time. That the rapid method of combustion was now used in a large number of laboratories in the U.K. surely proved that it had merits not offered by the other methods. He hoped that others taking part in the discussion would give some account of their experiences with the two kinds of methods.

Dr. W. J. KIRSTEN (Sweden) commenting on the relative merits of the catalyst and the empty tube methods, considered that the catalysts always had a tendency to be specific, and that in his experience the use of a high temperature was a more reliable means of securing quantitative combustion. Catalysts at high temperature appeared to be liable to interferences caused by metal halides and/or volatile metallo-organic compounds. After many years of experience of other methods they had always returned to the use of the "empty tube".

Mr. P. GOUVERNEUR (Holland) said that he had pleasure in confirming the attractive properties of silver orthovanadate. He had used this reagent to remove halogen and sulphur in a macro carbon-hydrogen technique. This had been employed for a number of years in those cases where the accuracy required was greater than could be obtained by the use of a micro-method. The reagent, used on a pumice carrier, had an outstanding capacity and when exhausted the colour change from yellow to deep brown was remarkably sharp.

He also mentioned that a small layer of silver metavanadate (10–20 mesh) on top of the manganese dioxide in the nitrogen oxide absorption apparatus was useful to indicate the exhaustion of the dioxide. The metavanadate changed its colour from yellowish-brown to orange, as had earlier been observed by Mr. Ingram.

Dr. J. R. HUDSON (U.K.) asked whether the silver vanadate catalyst was effective in the combustion of compounds which contained fluorine.

Mr. INGRAM replied that in his experience silver vanadate catalyst also retained fluorine combustion products.

Dr. KIRSTEN then referred to automatic combustion methods. He was using the same combustion arrangement as described in his paper (p. 132) on sulphur determination. In this procedure, on heating the sample, the gaseous products were burned first, while the volatilized products distilled to the end of the capsule. The carbonaceous residue was then burned and finally the distillation products got the most efficient treatment. They were volatilized, passed back inside the capsule through the hot movable furnace, were mixed with excess oxygen and passed once more through the movable furnace into the long furnace. This allowed them to obtain a complete automatic combustion and sweeping out in 7–8 min.

Mr. L. BLOM (Netherlands) drew attention to the possibility of titrating the carbon dioxide liberated in the determination of carbon and hydrogen, using the method he had published in 1955 in *Anal. Chim. Acta*. With this method (combined with the combustion of de Vriess and van Dalen, *Anal. Chim. Acta*, 1952, which was very rapid) it was possible to perform C—H analysis in 12–15 min, with accurate results even on a very small scale (0.1–0.2 mg). The same method was used for oxygen in organic compounds and for low amounts of carbon in steel, with an accuracy at least as good as with the usual methods. Since he was intending to try the determination of water via reaction with calcium carbide, combustion of the acetylene and titration of the CO<sub>2</sub>, he asked Dr. Malissa if he had had any experience of this method especially regarding the rapidity of acetylene production.

Dr. H. MALISSA (Germany) replied that he intended to investigate the method mentioned very soon.

Mr. BLOM considered that the advantages of the "empty tube" combustion method were to be found in the fact that there was a rapid gas stream. The "emptiness" itself of the tube was not essential. The silver wool was placed at the end of the tube where the temperature was not too high.

Dr. MALISSA added that there was not only the advantage of rapid gas flow. Unknown side reactions, which occurred especially at high temperatures when packed tubes were used, were avoided.

Dr. F. EHRENBERGER (Germany) asked Dr. Schöniger why he preferred to use silicone tubing instead of ground glass joint connexions.

Dr. SCHÖNIGER replied that he had found the silicone tubing easier to manipulate — a point of value where untrained staff were concerned.

Dr. EHRENBERGER then said that in his opinion the "empty tube" combustion method had two disadvantages: it was necessary to use very long furnaces at a very high temperature, and it was not possible to burn a substance "individually" — and this was especially necessary in the combustion of aromatic compounds.

Dr. KIRSTEN pointed out that one of the great advantages of the "empty tube" method was undoubtedly the long life of the combustion tube, which could be used for several thousand analyses.

Mr. INGRAM suggested that another advantage of the "empty tube" method was the lower rate of conversion of the nitrogen in organic compounds to nitrogen oxides. This was due to the absence of any catalysts or oxidizing agents in the combustion tube. The absorption of the nitrogen oxides was therefore more effective because of the low concentration (high dilution with oxygen), and the life of the absorbent (manganese dioxide) was considerably lengthened.

Dr. S. GORBACH (Germany) said that a furnace must be constructed in such a way that the insulation was sufficient. One should get the desired temperature with the smallest amount of electrical energy. Only with such furnaces was it possible to avoid additional heating of the laboratory.

Dr. MALISSA replied that the room temperature in relation to working capacity was not so serious. In the iron and steel industries people were working day after day near ovens running at 1200°–1350°C.

Dr. EHRENBERGER pointed out the difference between analyses carried out in a University laboratory and those in industry. In a University one was usually concerned with very pure substances containing only a few elements. In industry, particularly in the production control laboratory, one could have many more "foreign" metallic and non-metallic elements.

## The micro-analytical determination of carbon and hydrogen

Mr. T. R. F. W. FENNEL (U.K.) remarked that with regard to the gravimetric finish, he would like to have opinions on the merits of Flaschenträger and Pregl-type absorption tubes (possibly with a widened bore).

Dr. W. T. CHAMBERS (U.K.) replied that the simplified type of absorption tube in borosilicate glass described in BS.1428, Part A1, had precision bore capillaries. Diffusion through the capillaries was approximately equal to that of the Pregl-type tube.

Mr. INGRAM in replying to Mr. Fennell's question said that in his opinion [the Flaschenträger tubes were far superior to the Pregl type. Micro-analysts in the U.K. in particular favoured the Pregl type because manufacturers until recently did not supply Flaschenträger tubes of the required standard. In particular, the stoppers were badly ground and the average weight and the dimensions were often outside the limits for micro-analytical usage. Manufacturers now were able to provide suitable tubes and since more people were using them, particularly in conjunction with the "empty tube" method of combustion, their manufacture should be guided by a British Standard Specification.

Another reason for their unpopularity was the belief that these tubes were more difficult to wipe, and that in carrying out the operation there was the danger that stoppers might be eased out, so vitiating the analysis through faulty weighing, by removal of lubricant from the ground surfaces. Some 15 years' experience with the Flaschenträger tubes had shown that these beliefs were unfounded. Furthermore the weighing period was lessened, and more important still the diffusion phenomena, a potential source of weighing error associated with the Pregl type of tube, did not arise.

Mr. B. T. SAUNDERSON (U.K.) agreed with Mr. Ingram's comments on Flaschenträger tubes. He suggested that with the very efficient combustion techniques which could now be given to untrained personnel, the next advance in this determination must be some modification to the finish. He asked if anybody had tried, for example, a gas-solid chromatographic technique.

Mr. C. WHALLEY (U.K.) said that following the Discussion Meeting of the S.A.C. Microchemistry Group at Exeter, he had been carrying out experiments with catharometers for the determination of the  $\text{CO}_2$  produced in the combustion. He had not so far, however, considered the effect of water or of the other elements present. His results had been encouraging, but difficulties had been experienced in getting satisfactory integration of the catharometer response. He hoped to get some information on this before long. At the moment it did appear as if the maximum accuracy attainable might be of the order of 1 per cent, but it was possible that integration might improve this.

He had also experimented with the use of a conductivity cell using barium hydroxide as absorbent, and felt that this might well prove to be the most accurate physical method for the determination of carbon dioxide.

Dr. GORBACH remarked that in his laboratory a special cell recommended by Beckman Inc. was used for measuring humidity in gases. The results that were obtained with such a modified cell led them to believe that it should be possible to use this method for the determination of water. In principle, the method was based on the electrolysis of the water after its absorption onto a thin layer of phosphorus pentoxide.

Mr. F. P. JOHNSON (U.K.) said he could confirm the use of the phosphorus pentoxide electrolytic cell mentioned by Dr. Gorbach as very useful for the determination of small amounts of water. They had used this type of cell successfully for the determination of as little as 1 p.p.m. water in a gas stream.

Mr. BLOM reported that the Beckman method was used in their laboratory for determination of humidity in gases, but he would like to know how long a C—H determination took when using this method, for he was afraid that it would prove to be inconveniently long.

Mr. WHALLEY objected strongly to any idea that progress towards instrumentation was a bad thing. He was convinced that such progress must come to the field of organic micro-analysis, as it had come to other branches of analysis. It was a disgrace that no really new ideas for the determination of carbon and hydrogen should have been advanced for the last 60 years or so. In no other branch of analytical chemistry had progress been so slow.

Admittedly, instrumentation was expensive, but he believed that industry would provide the money if it were shown to be necessary. It was unrealistic to condemn new methods and apparatus because they were expensive — the ultimate return might far repay the initial outlay.

Mr. SAUNDERSON said that from the industrial point of view it was necessary to eliminate the need for technique as far as possible. The ideal was to place an instrument in front of untrained personnel knowing that they could handle it with only the briefest training.

Professor F. L. WARREN (South Africa) suggested that it was important for the meeting to encourage the newer methods which would make C—H determinations more automatic or rapid quite regardless of the cost or difficulties which might have to be overcome.

Dr. HUDSON mentioned a method in the literature for the determination of water by measuring the difference in conductivity which it produced in a solution of oxalic acid in acetone. He asked if this could be used to determine the amount of water produced in a micro-combustion.

Dr. SCHÖNIGER replied that he had no experience of this method. He then went on to point out the difficulties of comparing results obtained by different workers, particularly in different countries. He advocated the use of an international set of standard samples; this was at the moment under consideration.

Dr. MALISSA explained that the IUPAC Commission on Microtechniques had, 2 years ago, started on recommendations for test substances, and he hoped that these would appear within a short time.

Mr. S. BANCE (U.K.) asked whether it was proposed to hold a large sample of each test substance from which analysts would be issued with a small portion, or whether it was merely proposed to issue the names of the various substances agreed upon. He also enquired whether anyone could report upon any results of the collaborative study of the carbon and hydrogen determination instigated by Večeřa.

Dr. SCHÖNIGER replied that the Commission could not buy or sell material or recommend companies, so that the provision of a large sample was not possible.

Dr. GORBACH suggested that in comparing results it would be desirable to give in publications not only the standard deviation of twenty analyses on one compound but also the standard deviation of 200–300 routine production analyses. Furthermore, analyses which were much too high or too low should be included. Tests in this manner on the Pregl method as modified by K. Bürger had given a standard deviation of ca.  $\pm 0.5$  per cent.

Mr. P. R. W. BAKER (U.K.) said that any relaxation of the generally accepted error of  $\pm 0.3$  per cent was in the analyst's hands. If the analyst could do no better than  $\pm 0.4$  per cent then the organic chemist would have to accept this. He agreed with Dr. Schöniger's view that results should be quoted to one decimal place only.