DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS[1]

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I. INTRODUCTION

Although oxygen is one of the most commonly occurring constituents of organic compounds, and although methods for its direct determination have been the subject of extensive investigation, this element is still most frequently determined by difference. It is apparent that the methods available for its direct determination are not wholly satisfactory, else they would be more widely applied in preference to a determination by difference. The determination by difference places the sum of all the errors upon oxygen, and eliminates the possibility of checking the analysis by totaling the determined constituents. A reliable direct determination would permit such a check, and would be particularly valuable for the purpose of differentiating between compounds which have similar carbon and hydrogen content, but which differ in their oxygen content.

The determination of oxygen by difference becomes more unsatisfactory with increasing complexity of the substances being analyzed. The greater the number of constituents to be determined, the more desirable is a direct method for oxygen which will serve as a check on the analysis. In recent years, therefore, attention has been directed to the problem of determining oxygen directly in

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organic compounds. There often are cases where a determination of the oxygen content would be a more positive index to the purity or nature of the substance under consideration than the usual elemental determinations. The need for a direct determination of oxygen in coal, for example, has been pointed out frequently (11, 19, 33, 60, 97).

The fuel technologist is vitally interested in the direct determination of oxygen in coal; the knowledge of the exact oxygen content would aid him in the study of coal formation and utilization, and would permit the calculation of more precise heat balances. The indirect determination of oxygen in coal is complicated by the presence of inorganic oxides and water of composition, as well as by the number of elements which must be determined before the amount of oxygen can be calculated by difference. The result is usually regarded as a poor approximation. It is significant that many of the papers dealing with the direct determination of oxygen in organic compounds have come from laboratories devoted to coal research. A method for the direct determination of small amounts of oxygen would be of value in studying the nature and oxidation of such materials as lubricating oils, asphalts, and rubber.

To present the other side of the picture, Dennstedt, forty-five years ago, in his account of the development of organic analysis (15), had the following to say of a method for the determination of oxygen in organic compounds: "That one, however, can manage very well without such a method is seen in the history of the development of organic chemistry. One sees no place where the progressive development could have been checked by the lack of such a method."

However, the almost one hundred papers published on the determination of oxygen during the past two decades have indicated the need for such a method. Despite this amount of work, no entirely satisfactory method has yet been developed. This fact is succinctly stated by Hans Meyer (59) in the latest (1938) edition of his well-known book on organic analysis: "The methods developed to the present for the determination of oxygen are extremely bothersome and not of general applicability, so that they are scarcely ever used by anyone besides their discoverers."

It is the purpose of this paper to present a critical examination of the available methods for the direct determination of oxygen on the basis of (*1*) the experience of those who have used them and (*2*) the inherent simplicity or complexity of the technic and the precision and accuracy possible. The methods which are described in the literature may be conveniently classified under three main headings on the basis of the method of decomposition, and they are so discussed in this paper. The most important of the technics suggested have been those based upon complete oxidation of the compound with a measurement of the oxygen consumed, catalytic hydrogenation to form water, and thermal decomposition over carbon to form carbon monoxide. It is the hope of the authors that this review may aid in the further development of successful methods for solving the problem.

Previous reviews (1, 7, 14, 15, 59, 95) of the work on the determination of oxygen in organic compounds have been fragmentary and uncritical; the most helpful has been the short introduction to a paper on the topic by Kirner (30). The review by Skanovi-Grigor'eva (86) was, unfortunately, not available to the authors; the length of the review suggests that it might be valuable, although the abstract describes it as chiefly a review of German literature. The present review is based in part on a previous paper by the authors, only an abstract of which was published (20).

In the discussion which follows, deviations of analytical results from the calculated values are expressed in terms of absolute percentage, unless otherwise stated.

II. Methods Based on Complete Oxidation of the Compound

These methods depend upon completely oxidizing the sample by means of an inorganic oxidizing agent or gaseous oxygen. The amounts of water and carbon dioxide formed in the oxidation are determined, giving, by calculation, the total amount of oxygen in the products of combustion. From this value is subtracted the quantity of oxygen supplied by the oxidizing agent, the difference being the amount of oxygen which was present in the substance being analyzed.

A. OXIDATION WITH AN INORGANIC OXIDIZING AGENT

1. Dry oxidation

The earlier methods for the determination of oxygen in organic compounds were based upon oxidizing the organic substance with materials such as potassium chlorate, cupric oxide, silver iodate, potassium dichromate, or other agents which readily yield oxygen. One such method was proposed as early as 1811 by Gay-Lussac and Thenard (23), who oxidized organic compounds containing carbon, hydrogen, oxygen, and nitrogen with a known amount of potassium chlorate. From a determination of the products of combustion and the amount of potassium chlorate unconsumed, the amount of oxygen in the compounds could be calculated. Carbon and hydrogen were determined at the same time.

Persoz (69) oxidized the sample in a sealed tube with mercuric sulfate and collected the resulting gases in a bell jar. The carbon dioxide, sulfur dioxide, nitrogen, water, and mercury formed in the reaction were determined. From these data the carbon, oxygen, nitrogen, and sulfur present in the sample were calculated.

Baumhauer (3) developed a method for determining oxygen in compounds containing carbon, hydrogen, oxygen, and nitrogen, using cupric oxide to oxidize the compound. The amount of oxygen supplied by the cupric oxide was determined by heating the residual oxidizing agent in oxygen and measuring the contraction in the gas volume. From the determination of the water and carbon dioxide formed and the oxygen removed from the cupric oxide during combustion, the amount of oxygen in the compound was calculated. In a modification of the method (4), the reduced copper was reoxidized with a known weight of silver iodate. The excess oxygen from the silver iodate was absorbed upon a mat of copper and determined by reducing the resulting copper oxide in a stream of hydrogen and weighing the water formed. With the addition of an azotometer, carbon, hydrogen, oxygen, and nitrogen could be determined on the same sample.

Boswell (9) also utilized combustion with cupric oxide in a stream of nitrogen, but greatly simplified the determination of the oxygen removed from the cupric oxide. The sample was vaporized in a stream of nitrogen and passed over a known amount of cupric oxide suspended on asbestos. The oxidizing power of the cupric oxide was previously determined by reduction with hydrogen. The products of combustion were absorbed and weighed, and the loss in oxidizing power of the cupric oxide was determined by reduction with hydrogen as before. Simple calculations gave the amount of oxygen in the substance analyzed. Hydrogen was determined simultaneously. The results were accurate to within about 0.3 per cent for hydrogen, and to within 0.3 to 1.0 per cent for oxygen.

Stromeyer (91) determined oxygen in compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, and chlorine, using a mixture of cupric oxide and sodium carbonate as oxidizing agent. After oxidation, the contents of the tube were dissolved in hydrochloric acid and ferric sulfate solution was added. The ferrous ion formed, as determined by titration with potassium permanganate solution, was a measure of the amount of oxygen given up by the cupric oxide. The results were always low and the method failed entirely with nitrates and nitro compounds.

Still another method for determining the amount of oxygen given up by cupric oxide was suggested by Prout (72). The used cupric oxide was agitated with dilute sulfuric acid and an amount of copper equivalent to the oxygen given up remained undissolved, because cuprous oxide when treated with dilute sulfuric acid yields cupric sulfate and metallic copper, the latter being insoluble in cold dilute sulfuric acid. A similar technic was employed by Porret (71).

A recent paper by Trautmann (92) describes the complete analysis of urea in a single operation, the oxidation being carried out with cupric oxide powder in a measured volume of nitrogen. Air is passed over heated copper in a glass tube; the resulting nitrogen is dried by passage over phosphorus pentoxide and is then collected in a gas buret. This nitrogen is used to sweep the combustion tube and train during oxidation of the sample with cupric oxide, and is collected in a second gas buret together with nitrogen from the urea. The increase in volume represents the urea nitrogen. The weights of water and of carbon dioxide formed in the combustion are determined by absorption with phosphorus pentoxide and soda lime. From these data, together with a knowledge of the oxygen supplied by the cupric oxide, the complete elementary analysis of the urea is obtained.

A mixture of litharge and calcium phosphate was employed by Maumene (45) as the agent for completely oxidizing organic compounds. The sample was fused with litharge and a small amount of calcium phosphate. The litharge furnished the oxygen necessary to complete the oxidation of the compound to water and carbon dioxide, which were determined by the usual absorption methods. A determination of the amount of metallic lead formed gave the amount of oxygen necessary to complete the oxidation. The amount of oxygen in the compound being analyzed could then be calculated. No data were given concerning the types of compounds analyzed, nor were results reported to indicate the precision and accuracy possible.

Mitscherlich (63, 64, 65) developed an ingenious although exceedingly complicated technic, comprising combustion with mercuric oxide. The water, carbon dioxide, and, in the case of nitrogen-containing compounds, nitric oxide were absorbed and weighed. The resulting metallic mercury was sublimed into a small tube and weighed, thus supplying information as to the amount of oxygen required to complete the combustion. It was claimed that sulfur, phosphorus, chlorine, bromine, and iodine, as well as carbon, hydrogen, oxygen, and nitrogen, could all be determined by a single combustion. The former elements were retained by the mercury and were determined in the residue.

2. *Wet oxidation*

A number of wet oxidation methods have been proposed. Ladenburg (40) used concentrated sulfuric acid and silver iodate in a sealed tube at elevated temperatures, determining the excess silver iodate by an iodide–thiosulfate procedure. Good results were obtained with compounds of carbon, hydrogen, and oxygen. Phelps (70) employed a digestion mixture of chromic acid and sulfuric acid for the oxidation, using a known weight of potassium dichromate. After the oxidation was complete, the excess dichromate was determined by adding hydrochloric acid, absorbing the liberated chlorine in an arsenite solution, and determining the excess arsenite with a standard iodine solution. Compounds of carbon, hydrogen, oxygen, and nitrogen were studied, the poorest results being obtained with the nitrogen-containing compounds. The method was not applicable to volatile or difficultly oxidizable compounds.

Strebinger (90) determined oxygen by finding the amount of potassium iodate required to complete the oxidation of the substance. An independent determination of the other constituents was necessary. The sample was heated with concentrated sulfuric acid and a weighed amount of potassium iodate until no further evolution of iodine vapor occurred. The excess potassium iodate was then determined by titration with sodium thiosulfate solution. Good results were reported for compounds containing not only carbon, hydrogen, and oxygen, but also halogens and sulfur. Certain nitrogen-containing compounds gave poor results: namely, compounds which gave poor results in the Kjeldahl determination, such as nitro, azo, and heterocyclic compounds, hydrazones, and osazones. Stanek and Nemes (87, 88), who adapted Strebinger's technic to a micro method, experienced the same difficulty.

Although a great deal of research has been done upon both wet and dry oxidation methods with a variety of oxidizing agents, none of these methods has been found to be very satisfactory. In addition to disadvantages peculiar to each of the methods described, there are certain general objections to this technic. A number of weighings are required, usually accompanied by excessive calculation, and the determination of the oxygen consumed is frequently very indirect. The assumption is made that all of the oxygen is converted to carbon dioxide, whereas it is possible that a portion is converted to carbon monoxide, unless provision is made to insure oxidation of the latter. The method is usually inapplicable to nitrogen-containing compounds, owing to the formation of various nitrogen oxides and other compounds. It is necessary that the oxidizing agent used be free from moisture and impurities. This condition is often difficult to fulfill, resulting in inaccuracy in determining the oxidizing power of the reagent.

The advantages of the method are simplicity of apparatus and manipulation, especially with the wet methods, and the possibility of determining carbon, hydrogen, and oxygen simultaneously. The latter, however, might be considered a disadvantage in some cases, since it is not only a possibility but a necessity that carbon and hydrogen also be determined. That is, the method does not permit a determination of oxygen only, although the analyst might frequently be interested in no constituent other than oxygen.

In view of the many disadvantages of the method compared to the few advantages, and particularly the many probable sources of error under all except ideal conditions, it is not surprising that little attention is now given to this technic.

B. COMBUSTION WITH A KNOWN VOLUME OF OXYGEN

Glockler and Roberts (24) first proposed the determination of oxygen in organic compounds by burning the substance in oxygen, followed by a measurement of the products of combustion and the volume of oxygen consumed. Carbon, hydrogen, and oxygen were thus determined simultaneously. They arranged the combustion train as a closed circulating system to insure complete combustion with the minimum amount of oxygen. Only platinized asbestos was used as filling for the combustion tube. The commonly used cupric oxide was omitted in order to avoid the possibility that the copper resulting from reduction during combustion might be reoxidized to a different extent than formerly. The ordinary carbon–hydrogen assembly was used with the introduction into the closed system of a Ramsay buret, for measurement of the oxygen before and after combustion, and of a Sprengel pump, previously calibrated to produce the usual flow of oxygen through the combustion tube. The oxygen was produced from solid potassium permanganate. The necessary temperature and pressure corrections were made to convert the volume to the weight of oxygen consumed. The oxygen content of the sample was readily calculated from the weight of the products of combustion and the weight of oxygen consumed. A period of 45 min. was allowed for complete combustion and 15 min. in addition to sweep the combustion tube thoroughly, 2 hr. being required for a complete analysis. Samples of approximately 30 to 35 mg. were employed.

Data are given for four determinations on benzoic acid, the average of the four being 0.69 per cent low for oxygen. Perhaps the best evaluation of the method as applied by the authors is their statement that "one would naturally take the per cent of oxygen as obtained by difference as the more accurate figure after having demonstrated by this method that oxygen actually is contained in a given compound."

In the same year, Dolch (16) proposed a variation of the method which depends upon combustion of the sample in an oxygen–nitrogen mixture of known or determinable composition, e.g., air, and determination of the carbon dioxide content of the effluent gases. Dolch and Will (17) gave further details in a later publication. The composition of the oxygen–nitrogen mixture serves as a reference and a direct measurement of the oxygen consumed is not made; it is not necessary to know the volume of the combustion gases, but only the percentage of carbon dioxide in the gas mixture after combustion, plus the carbon and hydrogen content of the sample. This procedure offers no advantages over that presented by Glockler and Roberts and is subject to greater errors; consequently, the attention of subsequent investigators, except for criticism by Beek and Waard (5) and by Schuster (82), has been confined to applying and improving the technic of Glockler and Roberts.

In the following six years, 1928–1934, a number of papers on the method appeared. Dumke (19) extended the method to the analysis of cane sugar, urea, trinitrobenzene, and coal. It was assumed that the nitrogen in the urea, trinitrobenzene, and coal samples was liberated during combustion as elemental nitrogen, and that the sulfur in the coal other than that remaining in the ash was converted to sulfur trioxide, and was retained as sulfuric acid in the phosphorus pentoxide tube. The average of two determinations on urea was 1.1 per cent high for oxygen. A single determination on trinitrobenzene was 1.3 per cent high. The averages on three samples of coal varied from 0.7 per cent low to 1.5 per cent high for oxygen, compared to a calculation by difference. The percentage of hydrogen was high in almost every determination.

Stock, Lux, and Rayner (89) adapted the method to the determination of small quantities of hydrogen and oxygen in active charcoal. Hellman (26) described a volumetric determination of the combustible constituents of solid and liquid fuels, based upon burning the fuel in a closed system with oxygen, and measuring the contraction in volume and the carbon dioxide produced. Dolch and Will (18) have also reported on the method as applied to the determination of oxygen in coal products.

Kirner (30) has made a critical study of the method, and adapted it to the microdetermination of oxygen. He pointed out that previous investigators neglected to make accurate corrections for the effect of temperature and pressure on the gas volume, and concluded that "the apparent concordance of their results was largely due to fortuitous compensation of errors of considerable magnitude." In analyzing the data presented by Glockler and Roberts (24), Kirner notes that the mean error of their carbon determination was −0.12 per cent, and of their hydrogen determination +0.41 per cent, which should result in a high value for oxygen; however, the mean error reported for oxygen was −0.69 per cent. The discrepancy is accounted for by an inaccurate measurement of the oxygen consumed, this error more than compensating for the errors in the carbon–hydrogen determination. The results reported by Dumke (19) and Dolch and Will (18) are subject to the same criticism. Kirner emphasizes the necessity for a very precise carbon–hydrogen determination, since errors in the carbon determination are multiplied by 2.7, and those in the hydrogen determination by 8.0 in calculation of the percentage of oxygen.

Kirner's apparatus (figure 1) is a closed system similar to that used by previous investigators, but is adapted to the analysis of 10-mg. quantities. Commercial tank oxygen is passed through the customary purifying train before being admitted to the system. The Pregl universal filling is used for the combustion tube, except that a 40 per cent palladium–asbestos catalyst is substituted for the copper oxide–lead chromate filling, because blank experiments showed that the latter caused a loss in oxygen. Circulation of the oxygen is maintained by a Sprengel pump. Ascarite is used to absorb the carbon dioxide, and phosphorus pentoxide to absorb the water.

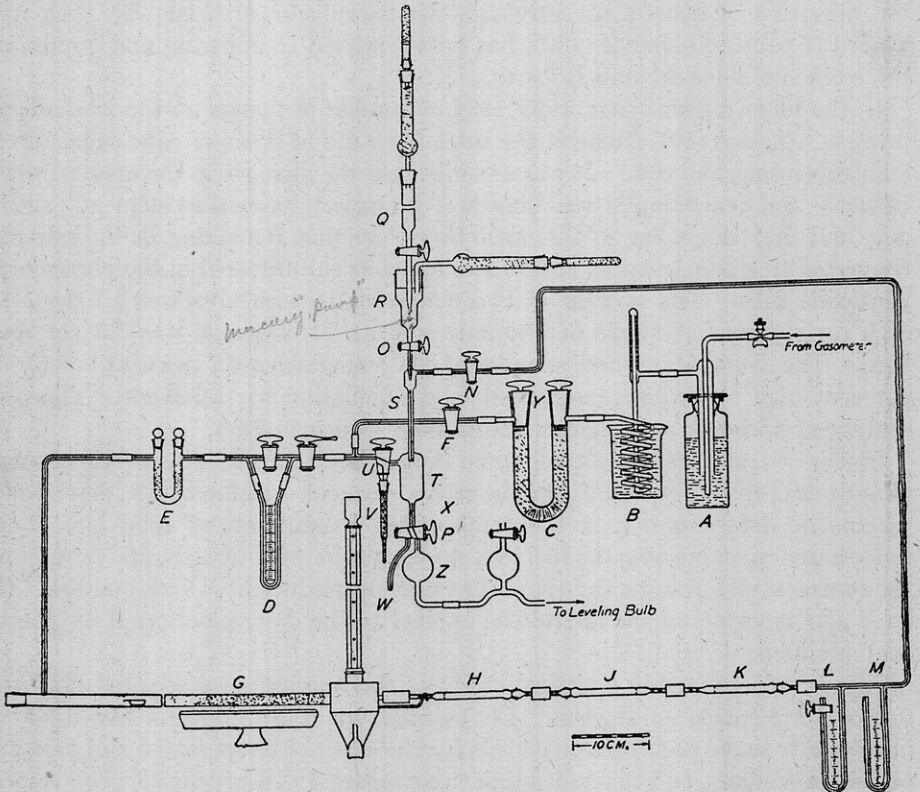

FIG. 1. Apparatus for the determination of oxygen by complete combustion with gaseous oxygen (from Kirner (30)).

The apparatus and technic employed by Kirner are designed to minimize errors in the determination of the oxygen consumed. The volume of the apparatus is measured, and the temperature and pressure are determined at the beginning and the end of each experiment. These precautions were neglected by previous workers. Provision is made for accurate control of the temperature by housing the entire apparatus in a constant-temperature box, with heating elements and fans actuated by a thermoregulator. A temperature constant to within ±0.02°C. may be maintained by this means. Other precautions to give greater precision and accuracy include a flowmeter and manometer in the combustion train to insure the maintenance of the optimum rate of gas flow and pressure, and the running of blanks to determine the volume of oxygen lost by diffusion through the numerous rubber connections (nineteen in all).

Results are given for ten compounds, three of which contained chlorine or bromine. The results for the seven compounds containing only carbon, hydrogen, and oxygen average 0.29 per cent high, and the three halogen compounds average 0.58 per cent high for oxygen. Kirner concludes that a precision of about 0.4 per cent may be obtained in the determination of oxygen, provided that precautions are taken to obtain a determination of hydrogen accurate to within 0.05 per cent and a very accurate carbon determination.

In subsequent publications, Kirner has shown that the method is applicable to the determination of oxygen in compounds containing sulfur (31), in compounds containing nitrogen (32), and in coal (33). Obviously, this method for the determination of oxygen cannot be applied to compounds containing sulfur and nitrogen unless it is known to what extent the sulfur and nitrogen are oxidized. In the case of sulfur compounds, Dolch and Will (18) assumed that sulfur dioxide is the sole product, whereas others (19, 87, 88) have assumed that the sole product is the trioxide. On the basis of available data on the sulfur dioxide–sulfur trioxide equilibrium, it is to be expected that 99 to 100 per cent of the equilibrium mixture would be the trioxide under the conditions existing in the combustion tube. To confirm this, Kirner (31) analyzed samples of diphenyl sulfone and phenyl *p*-toluenesulfonate. The former would be expected to yield sulfur dioxide upon thermal decomposition, provided no further oxidation occurred, and the latter would be expected to give sulfur trioxide. With both compounds, the amount of oxygen consumed was about 99.8 per cent of that calculated, assuming the sulfur to be oxidized to the trioxide, followed by retention of the sulfur trioxide by the silver wire in the combustion tube and by subsequent conversion from sulfite to sulfate by the excess oxygen. Thus it appears reasonably certain that in the analysis of a sulfur-containing compound by this method, sufficient oxygen is consumed by the sulfur to convert substantially all of the latter to sulfate, which is retained by the silver as silver sulfate. Kirner obtained good results employing 0.9978 as a correction factor.

Investigators (19, 22) previous to Kirner who have used the volumetric combustion method to determine the oxygen in nitrogen-containing compounds have assumed that the nitrogen was converted solely to elemental nitrogen. Dumke (19), for example, assumed that the nitro groups in trinitrobenzene were reduced to elemental nitrogen during combustion of the compound by gaseous oxygen. Kirner recognized that this was highly improbable and attempted to determine the fate of the nitrogen under the conditions of the analysis so that the method might be applied to nitrogen-containing compounds. He postulated that the thermal decomposition products of nitrogen-containing compounds might include ammonia, cyanogen, hydrogen cyanide, nitrogen peroxide, nitric oxide, and elemental nitrogen, and that these initial products would yield only nitrogen peroxide and nitrogen in proportions which, under given conditions, would be dependent upon the nature of the nitrogen linkage in the substance being analyzed.

To obtain the desired information, five compounds, chosen to give an example of amido, amino, heterocyclic, nitrile, and nitro linkages, were analyzed. It was found that amines and amides gave 26 per cent of the nitrogen as nitrogen peroxide (NO_2) and 74 per cent as elemental nitrogen (N_2), whereas nitriles, nitro, and heterocyclic nitrogen compounds gave 59 per cent as nitrogen peroxide and 41 per cent as nitrogen. The results indicate that, using these empirical ratios, oxygen may be determined in nitrogen-containing compounds with a mean accuracy of about 0.2 to 0.3 per cent.

Kirner applied the information acquired in the analysis of pure compounds to the analysis of coal and coal products (33). Good results were obtained for oxygen in coal when it was assumed that 59 per cent of the nitrogen was converted to nitrogen peroxide, and 41 per cent to elemental nitrogen, suggesting strongly that the greatest part of the nitrogen in coal is in heterocyclic linkage.

The volumetric combustion method for the direct determination of oxygen has many disadvantages. To obtain an accuracy of 0.5 per cent or better, very accurate determinations of hydrogen, carbon, and the oxygen consumed are required. Any error in the determination of carbon or hydrogen is increased several fold. The oxygen consumed must be obtained as the difference between two comparatively large volumes. Such accurate determinations are possible only with complicated and expensive apparatus. If sulfur or nitrogen is present, a separate determination of these constituents must be made. In the case of nitrogen, certain empirical assumptions, which necessitate a knowledge of types of nitrogen linkage in the compound, must be made with regard to the ultimate fate of the nitrogen in the substance analyzed.

The chief advantage of the method lies in the fact that in the hands of a careful and experienced worker, carbon, hydrogen, and oxygen may be determined simultaneously with reasonable accuracy, using apparatus and technic similar to that employed in the Pregl carbon–hydrogen determination. Halogens, sulfur, and nitrogen offer no complications, such as poisoning of the catalyst, except that separate determinations of the latter two elements must be made.

III. DESTRUCTIVE CHLORINATION

Mitscherlich (61) presented a method for the direct determination of carbon, hydrogen, and oxygen by destructive chlorination at red heat, the products being carbon dioxide, carbon monoxide, and hydrogen chloride. The oxygen-containing compounds, carbon dioxide and carbon monoxide, were absorbed in potassium hydroxide solution and cuprous chloride solution. Determination of the hydrogen chloride gave the hydrogen content. Mitscherlich claimed to have made 319 determinations by this method. A modification (62) involved decomposition over potassium hexachloroplatinate in an atmosphere of nitrogen, the products being water, carbon dioxide, hydrogen chloride, and chlorine. A determination of the first three of the products gave the amounts of carbon, hydrogen, and oxygen present. The procedure was time-consuming and not very accurate. Apparently, no one other than Mitscherlich has ever used the method.

IV. Reduction Methods

A variety of methods has been applied for determining oxygen in organic compounds by reduction; these are best described under several subdivisions which follow. In general, it may be said that reduction is a more direct attack upon the problem than oxidation, because in the reduction methods the products of the reaction contain only the oxygen which was in the compound, rather than the oxygen of the compound plus the amount added to complete the oxidation.

A. REDUCTION BY MEANS OF A METAL

Cretier (13) proposed a method for the simultaneous determination of carbon, hydrogen, and oxygen which involved heating the sample with a known quantity of magnesium to red heat. Oxygen in the sample is retained as magnesium oxide. The excess magnesium is determined by measurement of the volume of hydrogen evolved when the residue is treated with acid, from which data the amount of oxygen in the residue may be calculated. The evolved gases contain hydrogen, methane, and carbon oxides which have escaped reduction, and therefore an analysis of this gas mixture is necessary.

Determinations were reported for only sucrose and acetic acid. The results obtained were very inaccurate, because of the uncertainty of the composition of the resulting residue, and because of the usual errors encountered in gas analysis. The method is not applicable to compounds containing elements other than carbon, hydrogen, and oxygen.

B. HYDROGENATION

1. The ter Meulen method

The first mention of the determination of oxygen in organic compounds by hydrogenation appears in a paragraph announcement by Wanklyn and Frank (96) in 1863. However, no details or data were given and the hydrogenation method is commonly known as the ter Meulen method, since ter Meulen was the first to give experimental details and the results of the analysis of compounds (46). The method consists of (*1*) vaporizing the sample in a stream of hydrogen; (*2*) cracking or pyrolyzing the compound at a high temperature, yielding products which depend upon the composition of the compound; and (*3*) hydrogenating these products in the presence of a nickel catalyst between 300 and 400°C. to convert all of the oxygen to water, which may be absorbed and weighed.

The essential parts of the experimental arrangement are the cracking surface and the hydrogenation catalyst; the latter is also referred to as the methanation catalyst or as the reduction catalyst. Figure 2, which will be discussed later, illustrates a typical apparatus used in the catalytic hydrogenation method for the determination of oxygen in organic compounds. The presence of elements other than carbon, hydrogen, and oxygen in the sample necessitates means for removing the hydrogenation products of these elements or for correcting for their effect on the oxygen determination. Consideration of this can be deferred until later.

Since the publication of ter Meulen's original paper in 1922, the hydrogenation method has been studied extensively by ter Meulen and others. Many improvements have been made, including the extension of the method to compounds containing nitrogen, sulfur, and halogens. Of the almost fifty papers which have been published on this method, some are polemical, deriding or praising the method; one interesting series consisting of three such communications (5, 51, 98) is the result of an article by Dolch and Will (17) in 1931 criticizing the original ter Meulen method adversely. Many authors have discussed the method in connection with the analysis of coal and its products (2, 5, 6, 10, 11, 17, 29, 51, 68, 81, 82, 83, 95). The majority of the papers, however, have dealt with the best cracking and hydrogenation or methanation catalysts for the process and the optimum conditions for carrying out the cracking and hydrogenation reactions.

The reactions involved in the method are essentially very simple. The sample is pyrolyzed in the vapor phase or on the cracking surface to carbon monoxide, carbon dioxide, water, methane and other hydrocarbons, free carbon, and solid organic residues. The presence in the sample of elements other than carbon, hydrogen, and oxygen results in the formation of other products. The oxygen is supposedly present in the pyrolysis products only as water and carbon oxides. On passage of these products over the hydrogenation catalyst, the oxygen in the carbon oxides is converted to water according to the reactions:

$$CO + 3H_2 = H_2O + CH_4$$

$$CO_2 + 4H_2 = 2H_2O + CH_4$$

Table 1 lists some of the more important modifications of the ter Meulen method that have been proposed, but this list is not exhaustive. The nature and temperature of the cracking surface and of the hydrogenation catalyst proposed, used, or discussed are given, together with elements which may be present when using the technic described.

In his earliest descriptions (46, 47) of the method, ter Meulen employed nickel suspended on asbestos, maintained at 350°C., as the only catalyst. Samples of 100 mg. were used. The oxygen of the compound was converted to water and carbon dioxide, which were absorbed and weighed; the results on four compounds were accurate to ±0.5 per cent. In subsequent publications ter Meulen introduced the cracking catalyst, using platinized asbestos (48) or plain asbestos (49). The use of more active forms of reduced nickel improved the final conversion to water; the inconvenience of freeing the asbestos used as support for the nickel from its moisture was avoided by the use of a nickel boat filled with reduced nickel (58). The publication of a monograph by ter Meulen and Heslinga (54) on catalytic methods for the combustion analysis of organic compounds and its immediate translation from the original Dutch into French and German (55, 56)

TABLE 1

Determination of oxygen by catalytic hydrogenation

DATE	REFERENCE	SAMPLE* SIZE	CRACKING SURFACE AND TEMPERATURE	HYDROGENATION CATALYST AND TEMPERATURE	ELEMENTS PRESENT
1863	Wanklyn, Frank (96)				
1922	ter Meulen (46, 47)	b		Nickel–asbestos, 350°C.	C, H, O
1924	ter Meulen (48)	b, c	Platinum–asbestos, 1000°C.	Nickel–asbestos, 350°C.	C, H, O, N, S, X
1926–7	ter Meulen (54, 55, 56, 57)	c	Asbestos, *ca.* 1000°C.	Nickel and asbestos, 350°C.	C, H, O, N, S
1930	ter Meulen *et al.* (58)	c	Platinum–asbestos, 1000°C.	Powdered nickel in nickel boat, 350°C.	C, H, O, N, S, X
1930	Schuster (81)		Platinum–asbestos, 1000°C.	Nickel, 350°C.	Applied to coal
1931	ter Meulen (50)		Asbestos, red heat	Powdered nickel in nickel boat, 350°C.	C, H, O, N, S, X
1933	Russell, Fulton (73)	c	Platinum–quartz, 750°C.	Thoria–nickel, 350°C.	C, H, O
1934	ter Meulen (52)	c		Thoria–nickel, 350°C.	C, H, O, S, Cl
1934	Lacourt (36)	c		Thoria–nickel, 400°C.	C, H, O, N, S
1934	Russell, Marks (74)	c	Platinum–quartz, 750°C.	Thoria–nickel, 350°C.	C, H, O, N
1935	Gauthier (22)		Pumice, nickel spiral, 650°C.	Nickel–pumice	C, H, O
1935	Marks (44)	b, c	Platinum–quartz, 750°C.	Thoria–nickel, 450°C.	Oils
1936	Hennig (27)	a		Nickel–pumice	C, H, O
1936	Inaba, Abe (29)	a	Platinum–silica gel, 900–950°C.	Thoria–nickel, 300–350°C.	Applied to coal
1936	Lacourt (37)	a	Nickel spiral, red heat	Thoria–nickel, 350–400°C.	C, H, O, S
1936	Russell, Marks (75)	c	Platinum–quartz, 750°C.	Thoria–nickel, 350°C.	C, H, O, N, S
1937	Afanas'ev (2)	c	Platinum–quartz, red heat	Thoria–nickel, 350°C.	Coal; C, H, O, etc.
1937	Goodloe, Frazer (25)	b, c	Nickel chromite, 750°C.	Nickel chromite, 400°C.	C, H, O, N, S, X
1937	Kirner (34)	a	Nickel gauze roll, 1000°C.	Thoria–nickel, 350°C.	C, H, O
1937	Lacourt (38)	a		Thoria–nickel	C, H, O
1937	Lacourt (39)	a	Nickel–chromite, red heat	Nickel chromite, 450°C.	C, H, O, N, S, X
1937	Lindner, Wirt (42)	a	Nickel spiral, 950°C.	Nickel, 350°C.	C, H, O, N, S, X
1937	Unterzaucher, Bürger (94)	a	Platinum–quartz, 1000°C.	Thoria–nickel, 300°C.	C, H, O
1938	Unterzaucher, Bürger (95)	a	Platinum–quartz, 1050°C., and nickel spiral, 650°C.	Thoria–nickel, 300°C.	C, H, O, N, S, coal
1940	Bürger (12)	a	Quartz wool, 1100°C.	Thoria–nickel, 300°C.	C, H, O, N, S, X
1941	Morikawa *et al.* (66, 67, 68)	c	Platinum–silica gel, 950°C.	Thoria–nickel, 350°C.	C, H, O, N, S, coal
1941	Shriner (84)	b, c	Nickel chromite, 750°C.	Nickel chromite, 400°C.	

* Sample size: a = 10 mg. or less; b = 10 mg. to 0.10 g.; c = 0.10 g. or over.

served to bring the method for the determination of oxygen to the attention of chemists. A second edition in French (57) soon followed.

Dolch and Will (17) attempted to apply the ter Meulen method to the determination of oxygen in oxalic acid, with very unfavorable results. In four analyses, the experimentally determined values varied from 72.5 to 75.2 per cent compared to a theoretical value of 76.2 per cent oxygen. On the basis of their experimental work and theoretical considerations, Dolch and Will made the following indictment of the method:

(*1*) The method fails to give accurate results in the analysis of a simple substance even when the directions of ter Meulen are carefully followed.

(*2*) A large proportion of the oxygen of the substance being analyzed occurs in the hydrogenation products as carbon dioxide rather than as water, whereas ter Meulen claims that the reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

goes very nearly to completion under the conditions of the analysis.

(*3*) The hydrogenation products of a coal sample contain an appreciable amount of carbon monoxide, as determined by reaction with iodine pentoxide, for which no provision is made in the ter Meulen method.

(*4*) ter Meulen fails to give clearly the optimum reduction temperatures for preparation of the catalyst, and the optimum temperature for hydrogenation.

(*5*) Their conclusions are supported by Schuster (82), who states that the method is unsatisfactory for the determination of oxygen in coal.

To these charges the following reply was made (51):

(*1*) Literature cited shows the results of forty-nine analyses of thirty-three compounds with a maximum error of 0.1 per cent.

(*2*) ter Meulen gives the results of a determination of oxygen in oxalic acid as 76.0 per cent compared to the theoretical value of 76.2 per cent. No carbon dioxide was obtained in this experiment. The possibility of error due to too rapid volatilization of the sample, use of too little hydrogen, or an inactive catalyst is mentioned.

(*3*) It is known that unsaturated hydrocarbons result from the dry distillation of coal and that these products will react with iodine pentoxide, thus accounting for the "carbon monoxide" found by Dolch and Will.

(*4*) ter Meulen cites the pages of his book on which he gives the proper temperatures for reduction of the catalyst and for carrying out the hydrogenation reaction.

(*5*) Schuster's objections to the ter Meulen method are solely on the grounds of its inapplicability to coal analysis because of ash reactions, and the reference cited by Dolch and Will actually refutes their claims, since Schuster obtained excellent results for the determination of oxygen in benzoic acid.

Beek and Waard (5) also came to ter Meulen's defense, stating that they obtained results within 0.25 per cent of theory when using the method with samples of 100–200 mg. They hydrogenated a 50-mg. sample of oxalic acid over a period of 1 hr., and obtained no carbon dioxide. Beek and Waard maintain that ter Meulen has given the experimental details clearly, and attribute the failure of Dolch and Will to too rapid heating of the sample, against which ter Meulen expressly warned. It was not intended that a large proportion of the oxygen should be weighed as carbon dioxide, as in the work of Dolch and Will. When the amount of carbon dioxide formed is small, no carbon monoxide is obtained.

Beek and Waard also took this opportunity to criticize the method proposed by Dolch and Will for the determination of oxygen (see II B), stating that it could be shown by calculation that the method would not give accurate results.

In a later publication, Will (98) attempted to explain the reason for his and Dolch's failure with the method. He stated that the only respect in which they failed to follow ter Meulen's directions was with regard to the temperature of reduction of the catalyst, since they did not consider ter Meulen's "approximately 350°C." as a precise statement and consequently employed a lower temperature. Will also believed that part of their difficulty was due to too large a sample size. He insisted that the presence of carbon monoxide in the exit gases in their experiments was proven beyond question, and pointed out that the presence of unsaturated hydrocarbons as products of a catalytic hydrogenation, as suggested by ter Meulen, is very unlikely. Will questioned the utility of a method wherein so many factors, and particularly the catalyst, must be subjected to such careful control.

Regardless of whether the criticism leveled by Dolch and Will was justified, it is fortunate that subsequent investigation of the method has resulted in improvements which have largely obviated the difficulties experienced by these investigators.

The technic of determining oxygen in organic compounds by catalytic hydrogenation received a major advancement in the suggestion made by Russell and coworkers (44, 73, 74, 75) that the nickel methanation catalyst prepared by the reduction of nickel oxide be replaced by a promoted nickel catalyst obtained by the reduction of a mixture of nickel and thorium oxides prepared in a special manner. The basis for use of this catalyst is found in a discussion of the promoter action of thoria on nickel catalysts by Russell and Taylor (76), in which the reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

was studied on promoted and unpromoted, supported and unsupported, nickel catalysts. This application of a study of the nature of catalytic surfaces to the determination of oxygen in organic compounds is an outstanding example of how fundamental theoretical or physical chemical knowledge can be used to improve and develop an analytical procedure.

The adoption of thoria-promoted nickel methanation catalysts was instantaneous, being immediately acknowledged as superior by ter Meulen (52) and being used by practically all of the experimenters working with the method with only one or two notable exceptions. Using thoria-promoted nickel, Lacourt (36) reported the results on the determination of oxygen in eighteen compounds, some of which contained nitrogen and sulfur, to be accurate to 0.2 absolute per cent, on the average. With this catalyst, all of the oxygen in the sample finally appears as water (34, 73). Newer methods of preparing and regenerating the catalyst have improved its life and efficiency, largely eliminating the earlier disadvantages of tedious preparation and ready susceptibility to poisoning. Russell and Fulton (73), in their publication describing the use of thoria-promoted nickel as methanation catalyst, also suggested the use of platinized quartz as the cracking surface to replace the platinized or plain asbestos heretofore used.

In 1935 Gauthier (22) used pumice as the cracking surface and nickelized pumice as the hydrogenation catalyst.

An interesting development in the hydrogenation technic is due to Goodloe and Frazer (25), who proposed the use of nickel chromite for both cracking agent and hydrogenation catalyst. They found that this substance is capable of absorbing a large amount of sulfur without a serious impairment of efficiency. A further advantage claimed for it was that it yields only elemental nitrogen from compounds containing nitrogen, eliminating the necessity for the absorption of ammonia from the gases issuing from the hydrogenation tube. Analyses of 45- to 135-mg. samples were successfully carried out in 1 hr. In a laboratory manual for quantitative organic analysis, Shriner (84) gives Goodloe and Frazer's procedure for the use of students. Shriner (85) states that lengthy conditioning of the nickel chromite catalyst is required, and that experience is necessary in order to obtain consistently good checks. Beginning students frequently get very erratic results, but with practice results accurate to 1 relative per cent may be expected.

In 1937 Kirner (34) published a thorough study of the micro ter Meulen method, using 200-mesh nickel gauze heated to 1000°C. for pyrolyzing the sample and thoria-promoted nickel and nickel wire as hydrogenation catalyst. The experimental set-up is illustrated in figure 2. The conventional Pregl purification train, A to E, is employed, except that platinized asbestos heated to 400°C. is used in the preheater D. Beginning at the exit end, the combustion tube contains an asbestos resistance plug (2 mm. long), 3 cm. of compressed nickel wire, 14 cm. of 2 per cent thoria–nickel catalyst, and a 17-cm. roll of 200-mesh nickel gauze. The mean accuracy of the results on six compounds containing only carbon, hydrogen, and oxygen was ±0.10 per cent. Kirner found it necessary to deduct an empirical blank which is less than the blank actually determined; this was interpreted as indicating a hidden compensating error in the method. Low results and a voluminous deposit of carbon were obtained in the analysis of sucrose; this difficulty with polyhydroxy compounds has been reported by others. The topics of the blank value, sucrose analysis, and regeneration of the catalyst are discussed in some detail.

Unterzaucher and Bürger (94, 95) also described a microanalytical method for the determination of oxygen in organic compounds which is applicable to compounds containing nitrogen and sulfur, yielding good results on 3- to 5-mg. samples. Their later work (95) is worthy of mention, since they critically studied many of the factors involved.

In the most recent micro procedure published, Bürger (12) used a quartz tube, 60 cm. long and 0.8 cm. in diameter, connected at the inlet end to an electrically heated copper spiral and a tube of phosphorus pentoxide for purification of the hydrogen, and at the exit end to a water absorber and a Mariotte bottle for regulating the gas flow. The tube filling, beginning at the exit end, consists of (*1*) a small wad of silver wool, (*2*) 18 cm. of powdered nickel formate containing 10 per cent thoria (reduced *in situ*), (*3*) 3 cm. of silver wool, (*4*) 4 cm. of nickel spiral, (*5*) a thin layer of silver wool, (*6*) 2 cm. of very pure granulated calcium oxide, and (*7*) 16 cm. of quartz glass wool.

The cracking surface is heated to 1100°C. and the contact material to 300°C. The procedure is essentially as follows: (*1*) a 3- to 5-mg. sample in a platinum boat is inserted in the combustion tube, (*2*) the tube is swept from the exit end with hydrogen for 5 min. to displace air, (*3*) the absorber and Mariotte bottle are connected to the combustion tube, (*4*) the hydrogen flow is regulated to 8 ml. per minute, (*5*) the sample is volatilized with a hot flame, and (*6*), after the passage of 100–200 ml. of hydrogen, the water absorber is weighed.

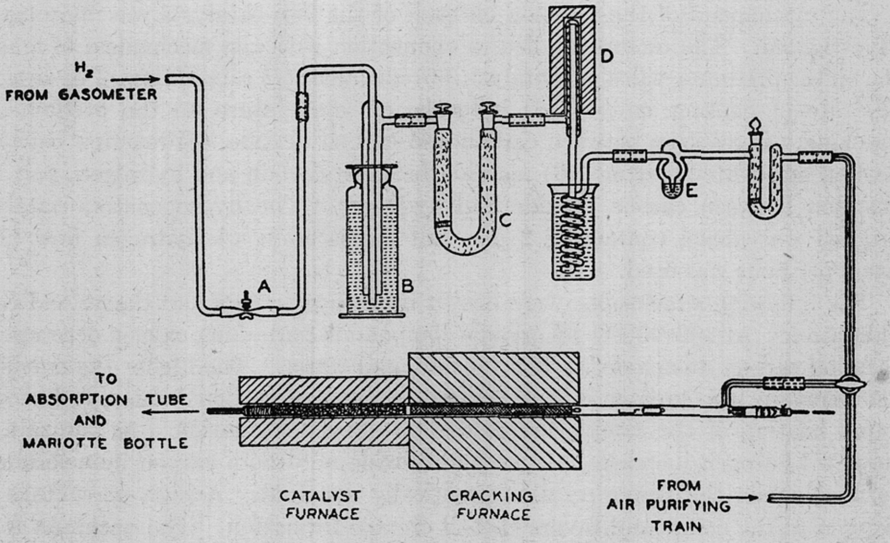

FIG. 2. Apparatus for the determination of oxygen by hydrogenation (from Kirner (34))

Compounds containing nitrogen, sulfur, or halogens can be analyzed, although a separate determination of the halogen content is necessary. The use of calcium oxide, nickel, and silver in removal of interfering elements will be discussed in a subsequent section.

Lacourt (37, 38, 39) has done some interesting work on the micro hydrogenation method for determining oxygen in organic compounds. In an early publication she found an accuracy of ±0.2 per cent on analyzing twenty-one compounds (37), but claimed an accuracy of better than ±0.1 per cent in a later paper using an improved form of the method (38). The analysis of twenty samples of succinic acid for oxygen gave results varying from 54.20 to 54.40 per cent, with an average value of 54.24 per cent, as compared to a calculated oxygen content of 54.31 per cent.

In 1941 the results of a critical study of the hydrogenation method were published in three articles by Morikawa, Kimoto, and Abe (66, 67, 68). The study was originally undertaken to ascertain the reason for the success of Abe's technic (29) with sucrose, which Kirner (34) and others had been unable to analyze successfully by the ter Meulen hydrogenation method. Using a platinum–silica catalyst (66), excellent results were obtained if certain critical factors were controlled. A cracking temperature of 950°C. is necessary, 200°C. higher than originally used for platinized quartz (73); the reducing temperature must be about 350°C., poor results being obtained if the temperature is below 300°C. or above 400°C.

The mechanism of the reaction on each of the two catalysts was thoroughly investigated. The factors studied in connection with the mechanism of cracking on the platinum–silica gel catalyst (66) included: (*1*) rate of flow of hydrogen, (*2*) rate of heating sample, (*3*) influence of temperature on the products of cracking, (*4*) reaction between carbon and carbon dioxide, (*5*) reaction between carbon and water (steam), (*6*) reaction between carbon and hydrogen, and (*7*) reaction between carbon dioxide and hydrogen. The hydrogenation catalyst studied was nickel containing 2 per cent thoria (67). A hydrogen flow of 5 liters per hour was used.

The following conclusions were drawn from experiments and theoretical considerations: At 800–900°C. all organic compounds containing oxygen decompose, forming carbon monoxide, carbon dioxide, and water. The higher the cracking temperature, the greater is the relative amount of carbon monoxide formed; rapid heating of the sample favors carbon dioxide formation. As the rate of flow of hydrogen increases, less carbon dioxide and more carbon monoxide are formed, while the water remains practically constant. A high percentage of oxygen in the compound favors carbon dioxide formation. The optimum temperature for reduction of carbon monoxide and dioxide on the nickel–thoria catalyst is 350°C. Above 400°C. the reduction of carbon dioxide may be incomplete. Too rapid cracking of the sample or a decrease in the concentration of hydrogen relative to that of the carbon oxides increases the amount of unreduced carbon oxides. Ethane and ethylene formed during cracking are converted to methane on the nickel–thoria catalyst. Hydrogen sulfide poisons the catalyst and should be removed between cracking and reduction. Morikawa, Kimoto, and Abe (68) applied the knowledge collected in regard to the hydrogenation method to a study of the decomposition of sucrose, cellulose, lignin, and coal by hydrogenation at various temperatures, which enabled them to indicate the relative stability of different types of oxygen bonds.

In a significant study (44), Marks applied the method to the determination of oxygen in oxidized oils, obtaining a precision of ±0.1 per cent or better and an expected accuracy compared to calibration determinations of ±0.2 per cent or better.

In general, aliphatic compounds are readily cracked to gaseous products between 600 and 800°C. with little carbon deposition, thereby maintaining the efficacy of the cracking surface (74). The deposition of considerable amounts of carbon by aromatic compounds which may require cracking temperatures up to 1100°C. results in rapidly diminishing effectiveness of the cracking surface.

The need for efficient and complete decomposition has also been pointed out by Gauthier (22), who warned of the danger of solid or liquid samples or their decomposition products distilling into the water absorber.

Successful use of the method depends to a considerable extent upon vaporizing the sample very slowly and uniformly over a period of time, e.g., 30 min., when using samples of 0.1 to 0.2 g. (55, 73).

A relatively high rate of hydrogen flow has been advocated because this tends to prevent deposition of carbon on the catalyst and decreases the sweeping time involved. For the macro method, flows of 90 ml. per minute (73) have been used, although 5 ml. of hydrogen per minute has been found satisfactory for the micro technic (34). The purification of the hydrogen used in the ter Meulen method has been critically discussed by Lindner and Eickhoff (43).

(a) Presence of elements in addition to carbon, hydrogen, and oxygen

As was previously mentioned, the presence in the sample of elements other than carbon, hydrogen, and oxygen complicates the determination, owing to the formation of hydrogen derivatives of these additional elements, e.g., ammonia, hydrogen sulfide, and hydrogen halides. In the analysis of samples containing these elements, the interfering hydrides can be removed prior to the water absorption or the amount of interfering hydride absorbed by the desiccant can be determined and the oxygen value suitably corrected. If the hydride of the nitrogen, sulfur, or halogen is formed quantitatively, the independent determination of the hydride in the desiccant permits the simultaneous determination of the oxygen and the additional element. Other possibilities are the use of catalysts or agents which prevent the formation of the undesired hydrides, or of desiccants which do not absorb the hydrides other than water.

Compounds containing nitrogen yield both elemental nitrogen and ammonia in the cracking and hydrogenation processes. Since the ammonia formed would be absorbed in the simple calcium chloride tube used in the method as first proposed, leading to erroneous results for oxygen, ter Meulen (48) recommended that a special absorption tube be used, one part containing dilute sulfuric acid and the other part containing calcium chloride. The ammonia is absorbed in the sulfuric acid and determined by back titration, the amount found being subtracted from the increase in weight of the absorption tube to give the increase due to the water alone. A similar procedure was suggested for halogen compounds, with a silver nitrate solution in the absorption tube to retain halogen acids. Russell and Marks (74) proposed the use of pellets of sodium hydroxide as absorbent for the water in the analysis of nitrogen-containing compounds, because this reagent absorbs no ammonia. Similarly, freshly ignited calcium oxide has been recommended (94).

Russell and Marks (74) report that 33 to 85 per cent of the nitrogen in representative organic compounds is converted to ammonia when platinized quartz the thoria–nickel catalysts are used, whereas no ammonia is formed when the nickel chromite catalyst is used (25).

Linder and Wirth (42) and others have used calcium oxide in the hydrogenation tube to absorb the hydrogen halides formed in the analysis of halogen-containing compounds. The reaction of the hydrogen halides with the calcium oxide produces an equivalent amount of water, which is absorbed by the desiccant.

$$2HX + CaO = H_2O + CaX_2$$

This method, accordingly, necessitates a separate determination of the halogen present in order to correct the oxygen value, which is calculated from the weight of water absorbed.

A method claimed to be better than the calcium oxide technic consists in combining the hydrogen halides with ammonia and condensing the product in a cool section of the combustion tube (12). Another method suggested (48) consists in inserting a known quantity of silver nitrate at 120°C. between the two catalysts and determining the excess silver nitrate titrimetrically, from which a suitable correction can be applied to the weight of water found. Goodloe and Frazer (25) used a short layer of silver sulfate at 111°C., preceding the water absorber, to remove halogens.

A solution containing silver sulfate and sulfuric acid, located in the fore part of the water absorber, has been utilized (48) in the analysis of compounds containing halogen with or without nitrogen. The excess silver ion was determined by thiocyanate titration, and the ammonia was distilled from the solution after alkalization and was titrated. Good results for oxygen were obtained even in the analysis of chloranil, which contains 57.4 per cent chlorine.

Unterzaucher and Bürger (95) employed a 3-cm. roll of nickel gauze and a layer of calcium oxide, heated at 600–700°C., between the cracking catalyst and the hydrogenation catalyst. The nickel gauze retains sulfur, and the calcium oxide reacts with the halogen acids as previously described.

The removal of sulfur is highly desirable, since it is retained by the cracking surface and poisons the nickel hydrogenation catalyst in a single run (29). In the analysis of coal and other organic materials, sulfur has been removed by a layer of nickel oxide, NiO, located between the cracking surface and the hydrogenation catalyst (29). A layer of finely divided nickel at 150°C., inserted after the cracking agent, effectively removes sulfur (48); this material maintained at 125°C. will remove sulfur, halogen, or both, but removal of the halogen may not be complete. The thoria-promoted nickel catalyst seems to be more resistant than unpromoted nickel to poisoning by the hydrogen sulfide formed in the pyrolysis and reduction of sulfur-containing compounds in the presence of hydrogen. Bürger (12) used silver wool to remove sulfur from the exit gases.

(b) Preparation of catalysts

The cracking surface can be prepared by ignition of asbestos treated with 10 per cent platinic chloride solution (2), or by ignition of 20-mesh granulated quartz with 5 per cent ammonium chloride and enough 10 per cent platinum chloride to wet the mass (73). Kirner (34) used merely a roll of 200-mesh nickel gauze, while the Japanese workers have used platinized silica gel (29, 67).

The nickel chromite catalyst proposed by Goodloe and Fraser (25) is prepared by reduction of nickel ammonium chromate on heating at 200°C.

$$NiCrO_4 \cdot (NH_4)_2CrO_4 \cdot 6H_2O = Ni(CrO_2)_2 + N_2 + 10H_2O$$

Directions for the ready preparation of the double salt are given by Goodloe and Fraser.

Nickel alone is not adequate to accomplish efficiently the quantitative reduction of the carbon oxides to methane and water. When used a long time, even a highly active nickel catalyst gives progressively decreasing values for oxygen (95). ter Meulen's nickelized asbestos catalyst had to be removed after every determination, the carbon deposits burned out in a stream of air, and the mixture of nickel oxide and asbestos replaced in the tube and reduced (55). The efficiency of the catalyst can be maintained by the addition of promoters such as the so-called water-forming catalysts, e.g., the difficultly reducible aluminum, titanium, and thorium oxides. The most satisfactory methanation, hydrogenation, or reduction catalyst is active nickel containing 2 to 10 per cent of thoria. To make such a catalyst (73, 95), a mixture of the nickel and thorium oxides is prepared by heating the nitrates or formates either in or out of the combustion tube. The mixture is reduced *in situ* with hydrogen. The initial reduction at 300–400°C. usually requires a period of 48–72 hr., while regenerative reductions can usually be done overnight at 400°C. (73). Russell and coworkers (73, 75) recommended regenerating the catalyst by first oxidizing it to remove deposited carbon and then reducing it. It has been claimed that the catalyst is rendered more resistant to poisoning by sulfur if it is reduced at 450°C. instead of at 400°C. (75).

For the analysis of compounds containing sulfur, it has been recommended that a thoria-promoted nickel catalyst supported on granular quartz be used (75). The thin layers of nickel present are readily activated by reduction in hydrogen overnight at 500°C.

ter Meulen (55) advised the use of iron-free nickel oxide in preparing the catalyst, since iron slows up the rate of reduction.

(c) Determination of water formed

Various substances have been proposed and used as absorption agents for the water produced in the reaction, including calcium chloride (29, 48, 50, 73), calcium oxide (95), calcium sulfate (2, 25, 34, 37, 44), lithium hydroxide (95), magnesium perchlorate (37), and sodium hydroxide (29, 74). These, of course, involve the gravimetric determination of the water formed.

When an unpromoted or unactivated nickel catalyst is used for the hydrogenation process, as was true of all or most of the work prior to that of Russell and Fulton (73), not all of the oxygen present is converted to water. This necessitates the use of an absorbent for carbon dioxide, following the water absorbent, for the determination of any carbon dioxide present in the exit gases.

Lindner and Wirth (42) used the hydrogenation procedure with a titrimetric determination of the water formed. The exit gases are brought into contact with naphthyldichlorophosphine oxide ($C_{10}H_7POCl_2$, "phosphin"), which reacts with any water present to give hydrogen chloride. The latter is then absorbed and determined by titration with standard base. Lacourt (38, 39), apparently independently, suggested a similar titrimetric method. The hydrogenation products are bubbled through cinnamoyl chloride, the water reacting with the acid chloride to give cinnamic and hydrochloric acids, which are absorbed in alkaline solution.

To conclude and summarize the discussion of the catalytic hydrogenation or ter Meulen method for determining oxygen in organic compounds, the main advantage of this method is that it gives a direct and independent determination of the oxygen present in the compound, without the necessity of a knowledge of the carbon and hydrogen present. If, however, halogen is present, its determination is usually also necessary.

The disadvantages of the method are the complications introduced by the presence of elements other than carbon, hydrogen, and oxygen; the poisoning of the catalyst by sulfur and halogen, resulting in decreased activity and the need for frequent renewal; the voluminous deposition of carbon in the tube by many or most compounds; and the fact that the factor for oxygen ($O/H_2O = 0.88$) is unfavorable. Some workers report that a more or less empirical blank is necessary, and almost all workers have difficulties with certain polyhydroxy compounds, particularly sucrose.

2. Miscellaneous hydrogenation methods

Sadtler (77) reported the determination of oxygen in asphalt by reducing the material with hydrogen in the presence of iron wool at a high temperature, converting the oxygen to water. Sulfur is retained by the iron. Any hydrocarbons are condensed out of the resulting gases before the water vapor is absorbed in a calcium chloride tube. The assumption is made that there is complete reaction to give water as the only oxygen-containing product, which is probably not what actually occurs. The method was applied only to asphalt samples and no pure compounds were analyzed to check the method.

Reduction with hydrogen over finely divided carbon at white heat was suggested by Boswell (8). The products of the reaction are water, carbon dioxide, and carbon monoxide. The water is absorbed in sulfuric acid, the carbon dioxide is absorbed in soda lime, and the carbon monoxide is oxidized to carbon dioxide with iodine pentoxide at 170°C. and is then absorbed in soda lime. The results of single analyses of five compounds are presented, the average error being 0.3 absolute per cent. The chief faults of this method lie in the facts that three oxygen-containing products must be determined, thus increasing the chances for error, and that no provision is made for compounds containing elements other than carbon, hydrogen, and oxygen. Ten weighings of absorption tubes are required for each analysis.

C. THERMAL DECOMPOSITION OVER CARBON

A new attack on the problem of determining oxygen in organic compounds was recently proposed by Schütze (78, 79, 80), who described a semimicro method which he stated had been in use for several years (since 1936) with very successful results. In this procedure the sample is thermally decomposed in a stream of nitrogen and the cracked products are led over carbon at 1000°C., resulting in the formation of carbon monoxide. The carbon monoxide is then oxidized at room temperature with iodine pentoxide, yielding carbon dioxide and iodine.

$$5CO + I_2O_5 = 5CO_2 + I_2$$

Either the carbon dioxide or the iodine may be determined: the former by absorption in Ascarite, or the latter by titration with standard thiosulfate solution.

The time required for an analysis is given as 1 hr. The results of the analysis of five compounds, including compounds containing sulfur, halogen, and nitrogen, were accurate to ±0.2 per cent or better for oxygen contents of 13 to 34 per cent.

At the same time, an adaptation of Schütze's method to microchemical apparatus was made by Zimmermann (99). Using 5-mg. samples, Zimmermann obtained results accurate to 1 relative per cent of the oxygen content, e.g., 26.40 per cent instead of 26.21 per cent, with compounds containing nitrogen, sulfur, and halogen in addition to carbon, hydrogen, and oxygen. However, it was necessary to use rather large blank values, e.g., 100 γ of carbon dioxide. Apparently the large blank values were caused by air trapped in the apparatus, including the sample boat, during the process of adding the sample and removing the combustion boat after the analysis. This effect, which is of great importance in the determination of oxygen, has also been discussed by Kirner (34). Zimmermann claimed that the apparatus was suitable for automatic combustion and he indicated how several sets of apparatus could be handled simultaneously.

Unterzaucher (93) in 1940 made certain improvements in Zimmermann's apparatus and procedure which resulted in the elimination of the large blanks mentioned. In addition to the determination of oxygen in pure compounds, he was interested in the determination of small amounts of oxygen such as might be present in impurities like oxidation products. Unterzaucher's apparatus is shown in figure 3.

The apparatus from Nos. 1 to 10 inclusive is designed to supply nitrogen at constant pressure and to purify it by the removal of any oxygen that might be present. A quartz combustion tube is used with a 12-cm. layer (18) of small carbon particles electrically heated to 1120°C. No. 16 is a small electric furnace moved by a synchronous motor and used to burn the sample in the platinum boat (17). Coarse-grained potassium hydroxide (21) is employed to remove sulfur, halogen, and nitrogen compounds. The iodine pentoxide in No. 22 is heated by

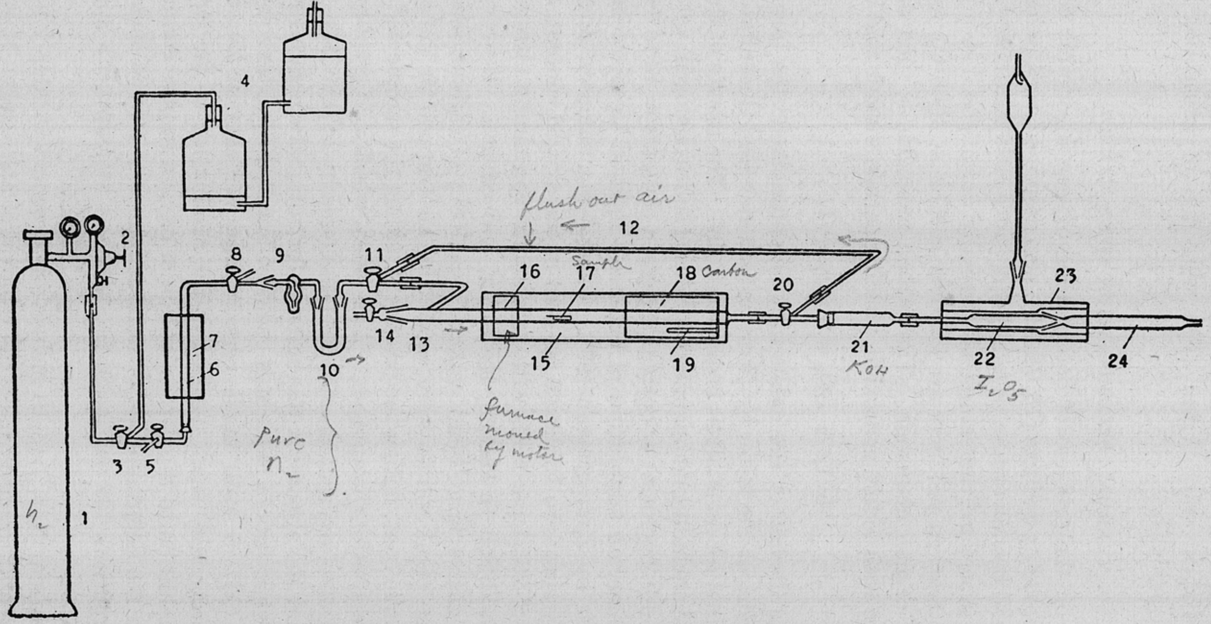

FIG. 3. Apparatus for the determination of oxygen by thermal decomposition over carbon (from Unterzaucher (93))

refluxing glacial acetic acid in the mortar (23). The sides of the absorption tube (24), which are indented to increase their surface, are moistened with 20 per cent sodium hydroxide solution. The principal innovation in the apparatus is the flushing tube (12) by use of which, in conjunction with the proper stopcocks (11, 14, 20), the air can be very effectively and simply removed from the combustion tube after the sample has been inserted.

In Unterzaucher's procedure, the gas mixture resulting from thermal decomposition of the sample in oxygen-free nitrogen is passed over carbon heated to 1120°C., resulting in quantitative conversion of the oxygen to carbon monoxide. After the removal of interfering gases by solid potassium hydroxide, the carbon monoxide is oxidized to the dioxide by iodine pentoxide heated to 118°C. The iodine produced is volatilized out of the iodine pentoxide tube, absorbed in dilute sodium hydroxide, and oxidized to iodate with bromine. After the addition of potassium iodide solution and acidification, the iodine formed is titrated with 0.02 *N* sodium thiosulfate solution. Since 1.000 ml. of 0.02000 *N* thiosulfate solution is equivalent to only 0.1333 mg. of oxygen, the procedure is suitable for the accurate measurement of small amounts of oxygen.

The most effective carbon found by Unterzaucher was lampblack-type carbon obtained from I. G. Farbenindustrie A.-G. which was moistened, dried, cut into small cubes, and ignited in nitrogen. Another effective manner of preparing the reduction medium is to press the wet paste of carbon through a glass nozzle of 1-mm. diameter and to crush the resulting threads after they have been dried and ignited in nitrogen. Experiments show that it is possible to prepare a satisfactory carbon by the cracking of a suitable organic substance in nitrogen. In general, a single carbon filling suffices for the life of the combustion tube.

The sample weight commonly is 3 to 4 mg., although in compounds of very low oxygen content a 20- to 30-mg. sample may be used; samples as large as 100 mg. have been employed when determining oxygen due to an impurity. The flow of nitrogen is regulated to 8–12 ml. per minute, 300 ml. being used in each determination. An analysis requires 30 min.

The samples analyzed included solids and liquids containing nitrogen, halogen, and sulfur in addition to carbon, hydrogen, and oxygen. The amount of oxygen in the sample and the type of linkage have no effect. The determination of oxygen in amounts of 0.1 to 0.7 per cent in oxygen-free compounds to which minute amounts of oxygenated compounds were added was satisfactory.

The necessity of using a high temperature was indicated by a series of determinations on pure substances at various temperatures.

Unterzaucher claimed that in many cases this method, as used during 1939 in the I. G. laboratories, was superior to the usual methods of elementary analysis. The analysis of twenty-six compounds gave results for oxygen differing from the theoretical values by an average of only 0.1 per cent.

Korshun (35) tested Schütze's procedure with pure organic compounds, checking the final step by determining both the carbon dioxide and the iodine formed. The liberated iodine was absorbed by activated copper and the carbon dioxide by Ascarite. A single determination required 30 to 40 min.

The principal disadvantage of the method involving reduction over carbon to carbon monoxide is the high temperature needed. A high temperature is required because fundamentally this method involves the water gas reactions of reducing water and carbon dioxide by contact with carbon at high temperatures.

$$H_2O + C = H_2 + CO$$

$$CO_2 + C = 2CO$$

These reactions necessitate the use of high temperatures. The work cited (93), unpublished experiments (21), and available thermodynamic data indicate that a temperature exceeding 1000°C. and probably near 1100°C. is necessary for substantially complete conversion to carbon monoxide under the necessarily dynamic conditions of the method.

The advantages of the method are very real when compared to the other two technics,—complete combustion and catalytic hydrogenation,—which have been extensively investigated for the determination of oxygen in organic compounds. The apparatus is simpler than that required for complete combustion in oxygen and no complicated calculations are necessary. There is no catalyst to be poisoned as in the ter Meulen method, and any carbon formed by pyrolysis of the compound usually serves to increase the contact mass for the conversion of oxygen to carbon monoxide. The presence of elements other than carbon, hydrogen, and oxygen apparently has no effect on the applicability of the method. Furthermore, the factor used to calculate the oxygen ($O/CO_2 = 0.3636$) is very favorable. Inherently the method is simple, accurate, and dependable.

This method is probably the most promising attack on the problem of determining oxygen in organic compounds. Work which was in progress at Purdue University (21), and which was interrupted by the necessity of using the available manpower and apparatus on war problems, indicates the possibility of using a simpler experimental set-up than Unterzaucher employed (93), and a more active reducing medium in producing carbon monoxide than carbon alone.

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