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# Advances in Analytical Chemistry and Instrumentation

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**VOLUME I**

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## New Ideas In Organic Microanalysis

Part I. C—H, O, N, Halogens, S, and  
Other ElementsWOLFGANG SCHÖNIGER, *Sandoz Ltd., Basel, Switzerland*

I. Introduction.....	200
II. Balances.....	200
III. Determination of Carbon and Hydrogen.....	202
1. Modification of Conditions for Combustion.....	203
2. Modifications in the Way in Which Nitrogen Oxides Are Removed.....	206
3. New Methods for the Determination of the Combustion Products... ..	207
IV. Determination of Oxygen.....	209
1. Variations of the Carbon Filling.....	209
2. Procedures to Eliminate the Interference of Disturbing Elements Present in the Substance.....	210
A. Fluorine Containing Compounds.....	211
B. Sulfur Containing Compounds.....	212
C. Phosphorus Containing Compounds.....	212
D. Compounds Containing Little or No Oxygen... ..	213
3. Determination of the Carbon Monoxide Formed on the Carbon Contact.....	213
A. Iodometric Determination.....	213
B. Determination of Carbon Dioxide.....	214
C. Other Procedures.....	215
4. Simultaneous Determination of Other Elements.....	215
5. Other Methods.....	216
V. Determination of Nitrogen.....	217
1. Determination by Dry Combustion.....	217
A. Modifications of the Dumas-Pregl Method.....	217
B. New Methods.....	219
2. Determination by Wet Combustion.....	220
A. Procedures for the Kjeldahlization... ..	220
B. Methods for the Determination of Ammonia.....	222
C. Other Methods.....	223
VI. Determination of Halogens (Cl, Br, I) and Sulfur.....	224
1. Oxidation Methods.....	224

A. Combustion with Oxygen.....	224
B. Decomposition with Oxidizing Reagents.....	225
2. Reduction Methods.....	226
A. Catalytic Procedures with Hydrogen.....	226
B. Procedures with Reducing Reagents.....	226
3. Determination of the Elements.....	227
A. Halogens.....	227
B. Sulfur.....	228
VII. Other Elements.....	230
1. Phosphorus.....	230
2. Arsenic, Antimony, Boron.....	231
3. Selenium, Silicon, Metals.....	231
References.....	232

## I. INTRODUCTION

Since Pregl developed quantitative organic microanalysis about 50 years ago, these methods have become well known all over the world. In the first decades microanalytical procedures were used only in a few laboratories, mainly at universities, and done by most qualified people—often by the director of the institute, himself, because he had been the one who had been trained by Pregl at Graz. Since these early times the Pregl methods have become very important tools of the organic chemist and today nearly every chemistry department and every large company have their own microanalytical laboratories doing all the analyses required for efficient research work. The original methods have been modified and simplified, and new procedures have been developed. The purpose of the following pages is to provide information on modifications and new methods in the field of elementary organic microanalysis and to review them critically. Also new procedures shall be recommended which have been tested either in the author's laboratory or elsewhere.

## II. BALANCES

Today practically no one employs the original free swinging microbalance, the so-called "assay balance," which was recommended by Pregl. It should be mentioned, however, that in cases where the most exact and reliable weighings are necessary, the undamped microbalance is still the best one available (1). More commonly damped

balances are used, since they offer sufficient accuracy and reproducibility of results (e.g., Ainthworth, Ch. Baker, Oertling, Stanton, Bunge, Sartorius). A new type of microbalance, which was introduced by the Mettler Instrument Corp., is based on the principle of weighing by substitution. The maximum load (20 g.) is placed on both sides of the asymmetric beam. When a load is put on the pan the analyst must remove an equivalent weight from the load side to bring the balance to equilibrium. To determine a weight with a Mettler balance, one follows this procedure:

Determine zero as usual and correct where necessary. After arresting the balance, place the substance to be weighed on the pan and close the sliding window. Partially release the pans (move the arrest lever as far to the right as it will go) and set the approximate weight by adjusting the weight control knobs. Now release completely, (turn the lever to the left) and wait until the projected scale comes to rest, or in the case of time weighing, until the exact point of time has been reached. At this point, adjust to the second and third decimal places by quickly turning the micrometer knob, and then read the weight. Do not keep your hand on the micrometer knob or attempt to turn it with the movement of the optical scale in order to locate the point of rest, for the heat radiated by the hand is sufficient to influence the balance.

Absorption tubes used for the C—H determination are weighed in a similar manner. After removing the tubes from the combustion apparatus (if gloves are used for this purpose only the tips need be cleaned and it is not necessary to wipe the whole absorption tube) deposit them beside the balance. Check and, where necessary, correct the zero, and after 3 min. from the time the tubes were set down beside the instrument, place the water absorption tube on the balance. The mechanical weights are properly set, and after an additional 2 min. release the balance and determine the exact weight. Now the carbon dioxide tube is placed on the balance and is finally weighed after the elapse of another 2 min. period. It is not extremely important to observe the times noted here, since these are dependent on the skill of the analyst, but rather to weigh always at exactly the same times as is necessary when operating other balances. Balances of this type, as well as other damped balances, are used in the author's laboratories, and no difference in accuracy and reproducibility has been noted.

The balance room should be air conditioned at all times. The optimum conditions are 21 to 25°C. and 45 to 55% R.H. The outlets of the system should be situated so that there is no apparent movement of air. The type of table upon which the balance is mounted is most important. In order to eliminate shocks and vibrations and to preserve the precision and sensitivity of the balance, different systems for vibration-free mounting have been described. Steyermark (2,3) recommends two systems. The newer one consists of a heavy, reinforced concrete inertia block (c.a. 800 lb.) which rests upon compressed springs. The table of Gysel and Strebel (4) can also be used if there is sufficient space in the weighing room and if no heavy machines are running in the neighborhood. Another setup, (5) which is based on the research work of Howard (6) and a report by Kirner (7), where the balances are mounted on stone plates, has been very useful in the author's laboratories. These plates rest on three tetrahedrons consisting of golf balls and which are held in position by iron rings. Instead of the golf ball tetrahedrons, three supports which consist of one wooden hemisphere resting on three golf balls can also be recommended. The rings are attached to an iron plate which is put on a support fixed in the wall. These units are protected from disturbances by the operator by means of wood-work which is completely separated from the support.

### III. DETERMINATION OF CARBON AND HYDROGEN

The most important determination in the organic analytical laboratory is that of carbon and hydrogen. With this method it is possible to obtain, with one analysis, the two values which are important and significant to every compound. Realizing this, Pregl at first developed the micro method for the determination of carbon and hydrogen, a procedure which in its original form is still successfully used by many analysts.

In the past few years many important modifications and also completely new methods have been described, which may be classified into three main groups: (1) modifications in the conditions for the combustion; (2) modifications in the way in which nitrogen oxides are removed; and (3) new methods for the determination of the combustion products—carbon dioxide and water.

#### 1. Modifications of Conditions for Combustion

The so-called "universal filling" of Pregl ( $\text{CuO/PbCrO}_3$ , Ag, and  $\text{PbO}_2$ ) is very useful, but it is important to work exactly according to the directions given by him in order to obtain accurate and reliable results, particularly with "difficultly burning" compounds. A big step forward was made by Reihlen (8) who introduced combustion catalysts, such as the Vinosites. They consist of mixtures of different metal oxides (Cu, Pb, Cr, Mn, Ag) that facilitate combustion of organic matter at relatively low temperatures (500 to 700°C.). Mainly, they catalyze the oxidation of carbon monoxide and methane. In the last few years methods have been developed which permit still lower combustion temperatures by the use of catalysts other than those of the type just mentioned. There are two such methods which have been tested in the author's laboratories over a long period and are now in constant use for routine analysis.

Körbl (9) introduced the use of the thermal decomposition product of silver permanganate as a catalyst. Silver permanganate, itself, is easily prepared in a pure state and the decomposition proceeds with deflagration at 150°C. A voluminous black product is obtained which can be used directly for filling the combustion tube. Further heating at 500°C. leads to a material corresponding to the formula  $\text{AgMnO}_3$ ; at temperatures of 790°C. and higher this product loses more oxygen (10,11). An improvement in the mechanical properties of this catalyst may be achieved when the decomposition of silver permanganate is carried out at 90 to 95°C. for 24 hr. In this case no deflagration occurs and the catalyst particles retain the shape and size of the original crystals (12), even when heated to 500°C. in the combustion tube. This catalyst is used only in a layer, 3 to 4 cm. long, in the combustion tube. Since it contains very finely dispersed metallic silver, no additional absorbent for the halogens (with the exception of fluorine) and sulfur is necessary (13). For the analysis of fluorinated compounds (14) a layer of  $\text{Pb}_3\text{O}_4$  on pumice, 3.5 cm. long, (15) must be introduced in the combustion tube behind the catalyst, and the whole filling heated to 550°C. by a single furnace.

Večefa and Synek (16,17) introduced cobalto-cobaltic oxide on asbestos as a catalyst, and they claim some advantage over the above mentioned thermal decomposition product of silver permanganate.

Horáček and Körbl (18) have prepared a series of similar catalysts by the reaction of ferrous, manganous, cerous, or cobaltous salts

with silver nitrate in ammoniacal or strongly alkaline solutions. The precipitates formed consist of the higher oxides of the appropriate metals containing finely dispersed metallic silver. Very short layers of all these catalysts proved to be highly effective for the complete combustion of organic compounds at 550°C. The absorption capacity for halogens and sulfur is also very high. It seems that in the field of catalysis of the combustion of organic matter new substances still can be found.

Another approach to secure complete combustion was made by the introduction of high temperature furnaces working above 800°C., as used by Beleher and Ingram (19-22) in their "empty tube" combustion method, which permits combustion without an oxidizing filling or catalyst. In this method the sample is burned in a fast stream of oxygen. A modification of it has been described by Kirsten (23), in which he has fitted a nickel tube into the combustion tube, which becomes oxidized and burns the sample at 1000°C. in a fast stream of oxygen. The introduction of such methods made it possible to develop apparatus for automatic combustion with the advantage that all compounds can be burned in the same way. Using the original Pregl method, this is impossible since every compound must be burned individually. Also these methods can be further developed because today it is possible to attain much higher temperatures.

Finally it is pertinent to mention methods which permit the determination not only of carbon and hydrogen, but also the simultaneous determination of other elements. These procedures are based on the so-called pyrolysis principle, first used by Marek (24).

The compound to be analyzed is weighed out into a quartz test tube, not into a platinum boat. This tube is placed in a quartz combustion tube with its open end directed toward the high temperature section of the combustion tube, which is heated by a furnace to a temperature of 850 to 950°C. The full flame of a gas burner is applied at the open end of the test tube and slowly moved back toward the sample, and a current of oxygen, 35 to 50 ml./min., is passed through the combustion tube. Korshun (25) has shown that under these conditions oxidation of the hydrogen in the organic compound is practically 100% complete, and that of the carbon 95 to 100% complete within the test tube or at its opening in a 2 to 3 cm. long zone which is heated by the gas flame. The section of the combus-

tion tube heated by the long stationary furnace (8 to 10 cm. long) is sufficient to ensure complete oxidation of the remaining unoxidized pyrolytic products.

This procedure may be used for solids and liquids. Liquids of sufficiently high boiling point are weighed directly into the test tube with the aid of a capillary pipet, care being taken to avoid contact with the walls of the test tube. Hygroscopic solid compounds are weighed into a test tube with a ground-in stopper, dried, and reweighed. The stopper is removed just before insertion into the combustion tube. Volatile liquids are weighed into capillaries in the usual manner and the sealed end broken off immediately before placing the capillary into the test tube. Highly volatile liquids (e.g., pentane) are placed into the test tube in sealed capillaries, which are opened within the combustion tube by heating the tube at the site of the sealed tip of the capillary. A sudden rush of the vapors through the heated zone into the combustion tube has to be avoided, otherwise the results will, as a rule, be low due to incomplete combustion. According to Korshun and Klimova (26,27) less nitrogen oxides are produced than when the combustion is carried out in a boat. For the absorption of these nitrogen oxides, different reagents can be used (see p. 206). The real advantage of this pyrolysis procedure has already been mentioned, namely, that it is possible to determine certain other elements in addition to carbon and hydrogen.

For the simultaneous determination of carbon, hydrogen, and sulfur (28) an absorption tube filled with silver wool or silver on a pumice carrier (29) is attached to the combustion tube and kept at 650 to 700°C. Some halogen-containing compounds may give low results for carbon and hydrogen due to the formation of halogen-containing pyrolysis products which inhibit the quantitative oxidation of carbon monoxide among the combustion products (30). To overcome this difficulty a wad of silver wool, heated to 600°C., is placed between the test tube and the furnace. A platinum contact can also be used. In this case carbon, hydrogen, and halogen or sulfur can be determined simultaneously.

Compounds containing silicon are subjected to slow combustion (31), or an asbestos pad carrying chromium sesquioxide or vanadium pentoxide may be inserted into the test tube and tared with it (32). The asbestos quantitatively holds back all the silica formed and the



metal oxides prevent the formation of silicon carbide. Additionally also halogen (33) or sulfur (34) can be determined.

For the analysis of phosphorus-containing compounds a similar arrangement has been recommended. The test tube is partially filled with granulated pumice which reacts well with phosphorus pentoxide. Taking the weight before and after the combustion gives the amount of phosphorus. If the sample also contains sulfur it is recommended to use powdered quartz etched with concentrated alkali to retain the phosphorus pentoxide (35). The sulfur is determined by using an absorption tube filled with silver wool.

For the simultaneous determination of carbon, hydrogen, and fluorine the following procedure is recommended (36). The test tube with the sample is placed inside a quartz sheath with a perforated bottom containing a layer of magnesium oxide 15 to 18 cm. in length and the whole assembly is then placed in the combustion tube. After the analysis the absorption tubes for carbon dioxide and water are taken off and the magnesium fluoride that is formed is subjected to pyrohydrolysis with water vapor at 1000°C. The resulting hydrogen fluoride is determined alkalimetrically or by titration with thorium nitrate. According to Mázor (15) the pyrolysis products are brought into contact with  $Pb_2O_4$ . After the analysis the resulting lead fluoride is extracted and the fluorine is determined gravimetrically as lead chlorofluoride.

## 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 were studied by Lindner (37) and Boetius (38). In view of these early difficulties many attempts were made to find an acceptable substitute.

Principally there are two possible means for the removal of the nitrogen oxides, namely, the absorption and chemical reaction of the oxides of nitrogen, or the reduction to  $N_2$  and/or  $N_2O$ . Both gases are neither absorbed in the water absorption tube nor in the

carbon dioxide tube. Many external absorbents have been suggested, such as concentrated sulfuric acid (39), concentrated sulfuric acid and potassium dichromate (40) or diphenylamine (41), and different preparations of manganese dioxide (42,43). Only the last is of importance and is used. Lindner (37) was the first to recommend the use of copper for the reduction of the nitrogen oxides to  $N_2$ . Copper is also used in the methods published by Kainz (44) and Unterzaucher (45). It has also been shown that nickel serves to reduce these oxides (46). When use is made of these reagents it is necessary to burn the substance either in a stream of nitrogen, using metal oxides to provide the source of oxygen for the combustion of the organic matter, or in a stream of air. Reagents which affect reduction of the oxides of nitrogen to  $N_2$  and  $N_2O$  that are not retained in the carbon dioxide absorption tube have been recommended by Hussey and co-workers (47), (ammonium sulfamate) and Cross and Wright (48) (trihydroxyl ammonium phosphate). Both reagents can be used under normal combustion conditions, with the sample being burned in a stream of oxygen. The absorber with the reagent has to be placed between the water and carbon dioxide absorption tube. Care must be taken that no water vapor condenses in the capillaries of the water absorption tube.

## 3. New Methods for the Determination of the Combustion Products

Until 10 years ago only the gravimetric method of finish was employed for the determination of the carbon dioxide and water produced and only recently some more important modifications of the absorption tubes have been suggested (49-51). Nevertheless it seems that the Pregl absorption tube is still preferred by a plurality of microanalysts. Moreover, rubber (or better still, silicone) tubing connections are still regarded as being sufficiently reliable, although some authors recommend ground-joint connections for the tubes (52-54).

The first attempt to determine the combustion products titrimetrically was carried out by Lindner (37) in 1935. This method never gained any importance until recently when Belcher published a new procedure for the carbon dioxide absorption (55) and a new reagent for the determination of water (56). He recommends succinyl chloride as a hydrolytic reagent instead of the  $\alpha$ -naphth-

oxydichloro-phosphine suggested by Lindner. The water reacts according to the equation



and the resulting hydrochloric acid can be titrated. Carbon dioxide is absorbed in excess barium hydroxide solution containing barium chloride and the excess is back-titrated after the absorption has taken place with hydrochloric acid in the presence of *o*-cresolphthalein indicator. One disadvantage of this method, especially in the determination of the water, is the blank value. This is due to the slight volatility of the reagent. Johansson (57) published, a few years ago, a method using the Karl Fischer titration for the water determination and a complicated iodometric procedure for carbon dioxide. A conductometric method for the carbon dioxide determination is given by Malissa (58). In combination with a rapid, high temperature combustion one carbon determination is completed within 3 min.

The most successful approach seems to be the iodometric determination developed by Unterzaucher (59), 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 as follows:

The sample is burned in a stream of air, and pure nitrogen is used, after the combustion has taken place, as a carrier gas. The water is separated from the carbon dioxide by freezing it out at  $-70^\circ\text{C}$ . in a special cooling device. Halogens are removed by metallic silver, sulfur with lead chromate. The absorption of the excess oxygen from the air used for the combustion and the decomposition of nitrogen oxides is by means of heated copper. After the carbon dioxide has been converted into carbon monoxide and titrated, the cooling trap containing the water is warmed and the water brought into reaction with the carbon to again get carbon monoxide. An analysis requires about 75 min. The author claims that using a 3 to 4 mg. sample the accuracy of the carbon determination is  $\pm 0.1\%$  absolute, of the water determination  $\pm 0.04\%$  absolute. Due to the very favorable calculating factors (1 ml.  $0.02N \text{Na}_2\text{S}_2\text{O}_3 = 50.04 \mu\text{g. C}$  and  $16.8 \mu\text{g. H}$ ) this method can be highly recommended for ultramicro work.

During the past few years some methods have been described wherein the combustion products are determined by a gas volumetric

or manometric procedure (60-64). Most of these methods work on the principle that water and carbon dioxide are fractionated by freezing out with dry ice/acetone and liquid air, respectively, 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. One disadvantage of these manometric methods is that the manometers have to be prepared by the analyst himself (two liquid manometers) and then empirically calibrated. It can be expected, however, that in the near future manometers admitting an electric measurement will be developed. Such methods are very important for the analysis of compounds containing  $\text{C}^{14}$ . It is very easy to determine the  $\text{C}^{14}$  activity in a proportional counting tube after the carbon determination has been completed (65). A method for the wet combustion of organic compounds has been developed in our laboratories and has been in daily use for more than 3 years in our isotope department (66). Moreover, it is also possible to fractionate the combustion products by gas chromatography, and recently two such methods have been developed (273,274).

#### IV. DETERMINATION OF OXYGEN

Although the determination of the oxygen content in organic compounds is very important, a reliable method for a direct determination was developed only about 20 years ago. Since this micro method was published by Unterzaucher (67-70) a host of modifications has been reported.

In the past years, improvements, such as modifications of the following sections of the original Schütze-Unterzaucher procedure, have been published: (1) variations of the carbon filling; (2) procedures to eliminate the interference of disturbing elements present in the substance; (3) determination of the carbon monoxide formed on the carbon contact; (4) simultaneous determination of other elements; and (5) other methods.

##### 1. Variations of the Carbon Filling

In the original Unterzaucher procedure a carbon contact (gas black of special grade) heated at  $1120 \pm 5^\circ\text{C}$ . is used. Aluise and co-workers (71), Kirsten (72), Colson (73), Lacourt (74), Moelants and Wesenbeck (75) investigated the sources of blank values which were

obtained when working according to the procedure described by Unterzaucher (e.g., 70).

It seems that the ash content of the carbon used, as well as the nature of the elements present in the ash are very important. It is also of some influence if the carbon is in an amorphous state or crystallized (graphitized) to some extent (76). Furthermore the temperature recommended by the author has to be controlled very carefully. For this purpose, a special furnace with a precise temperature controlling system has been developed by Schöniger (77). Because of the difficulties arising when working with this high temperature, the publications of Oliver (78), Oita and Conway (79) and Korshun and Bondarewskaya (80) seem to be important. They all report that a tube filling of platinized carbon successfully converts all oxygen-containing cracking products of the compound to be analyzed, to carbon monoxide at 900°C.

According to Oliver (78) this platinized carbon is prepared as follows: Dissolve 3 g. of platinum pieces in aqua regia and evaporate to a small volume. Add water and again evaporate. Dilute to about 50 ml. with water and add 3 g. of carbon. Evaporate to a paste and finally dry at 150°C. Break the mass into small pieces and heat it in a tube in an atmosphere of nitrogen at 900°C. for about 2 hr. Complete the reduction of the platinum chloride by passing hydrogen through the tube at the same temperature until the issuing gas is neutral to moist litmus paper.

The results reported by the authors and those given in a comparative study by Steyermark (81) are good.

## 2. Procedures to Eliminate the Interference of Disturbing Elements Present in the Substance

According to Unterzaucher (70), the method can be used without difficulty for organic substances that contain carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, and iodine. Accurate oxygen values may be obtained if sulfur is present, but difficulties will sometimes be encountered. Fluorine and phosphorus cause considerable interference, the results are not satisfactory, and the apparatus can be damaged. On the other hand substances containing arsenic or mercury can be analyzed without any difficulty.

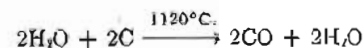
In the analysis of the heavy metal salts of organic acids (e.g., Fe, Cu, or Co containing compounds), the entire oxygen will be obtained

in the results without any difficulty, because the metal oxides on which the salts are based are reduced to metals. The situation is different with respect to aluminium and magnesium salts which leave their metals behind in the sample boat in the form of the oxides. After weighing these oxides their oxygen content can be calculated and added to that found in the analysis. The situation seems to be similar with calcium salts. It is remarkable that, on the other hand, potassium and sodium salts behave in the same manner as the heavy metal salts. They yield the entire oxygen content directly if sufficient carbon is present. It is recommended, therefore, to add to the weighed sample an organic substance that does not contain oxygen and that will give sufficient carbon in the boat on being cracked. According to Unterzaucher (69) the induline base is suitable for this purpose.

Other authors also report that erroneous results can be obtained when the substances to be analyzed contain oxygen in amounts below 1% and yield considerably large amounts of hydrogen during the cracking process (petroleum products). To overcome the difficulties just mentioned, some suggestions recently have been made (85,86).

### A. FLUORINE CONTAINING COMPOUNDS

Mázor (82) reported that any  $H_2F_2$  formed when the substance is decomposed reacts with the silica of the combustion tube to give water. This reacts with the heated carbon contact to give carbon monoxide:



To overcome this unwanted reaction a layer of magnesium nitride approximately 1 cm. long is introduced into the combustion tube in front of the carbon contact. It is heated, by the radiation of the carbon contact furnace, to 200 to 300°C. Any  $H_2F_2$  formed during the combustion then reacts with the magnesium nitride:



The magnesium nitride is stable at the temperatures that are attained.



## B. SULFUR CONTAINING COMPOUNDS

The sulfur error arises in that although most of the sulfur in a sample is converted to hydrogen sulfide, which can be scrubbed out by ascarite, some carbon disulfide and carbonyl sulfide are also formed, which cannot thus be removed. Reaction of carbon disulfide with iodine pentoxide forms carbon dioxide and gives, when the final determination is gravimetric, too high results. On the other hand, if carbonyl sulfide is formed the results will be low because the carbonyl sulfide contains part of the oxygen present in the sample. In order to avoid these sources of error different methods have been suggested.

The most promising method (79) seems to be that of passing the gas stream that emerges from the carbon contact over heated copper (500 to 900°C.). Probably the following reactions occur:



Another modification for sulfur containing substances is suggested by Bürger (83). When hydrogen, as a carrier gas, is used instead of nitrogen all the sulfur present will be converted to hydrogen sulfide, which can easily be removed by passing the gases over ascarite. He claims that by this method all errors, due to sulfur present in the substance, can be avoided. Also the oxygen content in metallo-organics and metal salts, provided the metal components can be released from their oxides by hydrogen, can be determined.

Maylott and Lewis (84), and Dundy and Stehr (85) also carried out investigations on the interference of sulfur compounds. They recommend using a liquid nitrogen trap which is placed between the reaction tube and the oxidation tube. Any carbon disulfide and carbonyl sulfide is by this means prevented from entering the oxidation tube. Dixon (86) finds that by this procedure oxygen will be lost as carbonyl sulfide.

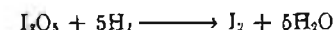
It seems that the use of copper at 900°C. is the best method of analyzing sulfur containing compounds.

## C. PHOSPHORUS CONTAINING COMPOUNDS

Until now no procedure has been developed to make it possible to determine the oxygen content in substances containing phosphorus.

## D. COMPOUNDS CONTAINING LITTLE OR NO OXYGEN

Dundy and Stehr (85) reported results for the oxygen content of hydrocarbon samples, which were reported to no oxygen, as high as 2.5% when working with the original Unterzaucher method. Dixon also (86) found similar errors and gave the explanation that the large quantity of hydrogen present in the pyrolysis gases, from hydrocarbons, reacts with iodine pentoxide to a small extent, according to the equation



It is, therefore, recommendable to use a modified procedure when applying the oxygen determination to petroleum products. The sample is pyrolyzed as usual in a stream of pure nitrogen and the oxygen converted to carbon monoxide. Then the carbon monoxide is oxidized to dioxide and determined by one of the procedures given in the section under Sulfur Containing Compounds.

Another possibility for eliminating large quantities of hydrogen from the pyrolysis products is the procedure given by several authors (87,88), in which the interfering hydrogen is removed by diffusion through a heated palladium thimble.

## 3. Determination of the Carbon Monoxide Formed on the Carbon Contact

## A. IODOMETRIC DETERMINATION

In his first publications Unterzaucher recommended the iodometric titration (e.g., 67) instead of the gravimetric determination described by Zimmermann (89) for semimicro analysis. In the beginning a special grade iodine pentoxide was used.

In the past few years it was found (90) that due to the different manufacturing temperatures of the iodine pentoxide preparations some authors used anhydroiodic acid ( $\text{HI}_2\text{O}_8$ ) and others iodine pentoxide.  $\text{HI}_2\text{O}_8$  allows the carbon monoxide to be determined iodometrically even in the presence of hydrogen, since this oxidant, in contrast to iodine pentoxide, does not react with hydrogen.

In view of the importance of these findings for the iodometric oxygen determination, the procedure for the preparation of  $\text{HI}_2\text{O}_8$  shall be described: Add an excess of iodic acid or dehydrated iodic

acid to boiling nitric acid, 60% by volume. Boil the solution with the undissolved excess for approximately 1 hr., after which time a saturated solution is obtained. Filter the solution through a glass filter and set it aside at room temperature for about 24 hr. Separate the brilliant crystals formed from the solution, wash them with 68% nitric acid and dry them at room temperature by first sucking pure air over them for about an hour. In this manner the adherent nitric acid is almost completely removed. Subject the product, for some time, to further drying, either at room temperature in a desiccator containing solid alkali and phosphorus pentoxide, or in an oven at 120°C.

The preparative work described should be carried out away from bright daylight, otherwise decomposition will occur, as can be seen from the crystals assuming a pink or reddish color. It should be pointed out that, after the decomposing influence of bright daylight was discovered and then avoided during the preparation of the reagent, the crystals were for the first time obtained without the slightest pinkish color. If the substance prepared according to this procedure is completely dry, it proves to be neither hygroscopic nor sensitive to light.

#### B. DETERMINATION OF CARBON DIOXIDE

Some authors (85,86,91-96) prefer the oxidation of carbon monoxide to dioxide and the determination of the latter either gravimetrically or volumetrically. The use of this method has the advantage that the temperature of the carbon contact can be lowered to 1000°C. because any carbon dioxide not being reduced to monoxide would be determined anyway.

It seems that the best way to oxidize the carbon monoxide is the reaction with copper oxide at temperatures over 600°C. (86). The carbon dioxide so formed, has to be dried by passing the gases over a desiccant. After the quantitative absorption in a Pregl absorption tube the carbon dioxide is determined gravimetrically. Oxidizing with either iodine pentoxide or  $\text{H}_2\text{O}_5$ , as described earlier in the section under Iodometric Determination, has the disadvantage that the iodine formed is not so easily absorbed.

For the volumetric determination of the carbon dioxide obtained by one of the two reactions given above, a procedure described by

Ehrenberger and co-workers (97) seems to be recommendable. The carbon dioxide is absorbed in a special filtration vessel in an alkaline solution of barium chloride and titrated potentiometrically, continuously during the combustion. According to the authors correct oxygen values were also obtained in samples containing considerable amounts of halogen and sulfur.

#### C. OTHER PROCEDURES

A colorimetric determination of the carbon monoxide has been described by Walton and co-workers (98). Harris (99) recommended the combustion with helium as carrier gas and the determination of the carbon monoxide by measuring the thermal conductivity of the effluent gas. Other gases formed by the pyrolysis of the sample, e.g., nitrogen and hydrogen, cause interferences.

A manometric method for measuring carbon dioxide has been reported by Holowchak and Wear (100). The carbon dioxide is collected in a liquid nitrogen trap and, after the residual gases have been pumped out by means of a vacuum pump, is determined manometrically with a two liquid manometer in a standard volume.

Kono and co-workers (101) developed a gravimetric method. They describe a procedure where the iodine formed by the reaction of carbon monoxide with iodine pentoxide is absorbed on a roll of silver net. By taking the weight before and after the analysis the amount of oxygen can be calculated. This method seems to have no advantage over the other procedures.

#### 4. Simultaneous Determination of Other Elements

Studying the conditions under which the oxygen is converted to carbon monoxide, Korshun and Bondarewskaja (80) found that it is also possible to determine the halogen content in the same sample. The method is based on the probability of evolution of halogens as hydrogen halides during the pyrolysis of the sample, in contact with hydrogen. Since the formation of hydrogen halides occurs at the expense of hydrogen generated in the decomposition, difficulties are encountered if the sample contains little or no hydrogen. In this case a considerable quantity of hydrogen halides are also retained by the catalyst and are only slowly removed by the carrier gas. It is, therefore, recommended by the authors to mix the samples with

standard hydrocarbons, e.g., paraffin wax, to supply the needed hydrogen. It seems that by combination with the procedure of Bürger (83) a potentially much more elegant solution of the simultaneous determination of oxygen and halogen might be achieved.

### 5. Other Methods

It should be mentioned that before the pyrolysis procedure, with subsequent conversion of all oxygen into carbon monoxide, was developed by Schütze (102), Zimmermann (89) and Unterzaucher (67-70), Ter Meulen (103) described the following macro method:

The substance is evaporated in a steam of hydrogen as the carrier gas and pyrolyzed at 1000°C. The resulting products are hydrated over a special nickel catalyst at 400°C. and the resulting water is determined gravimetrically. In the past years Smith and co-workers (104) described a modification of this method. They recommend a special nickel-thorium catalyst for the hydration, prepared as described by Russel and Fulton (105), and platinized quartz for the pyrolysis. They claim that in a series of consecutive determinations the time required for one determination is only 15 min. and that with small modification the method is also applicable to compounds containing nitrogen. Nitrogen can be hydrated to ammonia on the catalyst which is absorbed on the anhydrous in the water absorption tube. By filling this tube with sodium hydroxide pellets, according to Russel and Fulton it is possible to quantitatively retain all water produced, without error due to ammonia. If the catalyst is poisoned by sulfur—Russel and Marks have shown that 200 to 400 mg. of sulfur will be held back by the catalyst before it fails to give quantitative conversion of oxygen to water—it is recommendable to use a new charge of catalyst.

Instead of the gravimetric determination of the water Lindner (106) suggested the volumetric determination using naphthyl dichlorophosphine oxide as a reagent to react with the water vapor. The succinyl chloride introduced by Belcher and co-workers (107) should be a more reliable reagent for the same purpose.

Sheft and Katz (108) use  $\text{BrF}_3\text{SbF}_6$  for the oxygen determination in inorganic compounds. They heat the sample in a special nickel reaction tube with the reagent up to a temperature of 500°C. Under these conditions oxygen is liberated as  $\text{O}_2$  and determined man-

metrically. Preliminary experiments indicated that oxygen could also be quantitatively recovered from certain oxygen containing organic compounds. This procedure should be of importance for the analysis of compounds containing  $\text{O}^{18}$ .

Another completely new method which can be used also for the carbon and nitrogen determination in organic compounds has been described by Grosse and co-workers (109-111). The substance to be analyzed, is pyrolyzed in vacuum in a platinum reaction vessel; it is not necessary to accomplish quantitative combustion. A known amount of a heavy oxygen mixture of  $\text{O}_2^{16}$ ,  $\text{O}^{16}\text{O}^{18}$ , and  $\text{O}_2^{18}$  is added. After the reaction is completed the isotope ratio in the gas sample is determined by means of the mass spectrometer. The amounts of oxygen, carbon, and nitrogen, follows from the simple mixture rule. For details of this procedure which, until now, was limited to liquid samples and to the semimicro scale, the original paper must be consulted.

## DETERMINATION OF NITROGEN

Principally there are only two, generally used methods for the determination of nitrogen in organic substances. According to Dumas the compound to be analyzed is combusted in an atmosphere of carbon dioxide and the volume of nitrogen liberated is measured. According to Kjeldahl the organic material is destroyed with sulfuric acid, various catalysts have to be added, and the nitrogen is converted to ammonium acid sulfate. The ammonia is liberated and either titrated or determined colorimetrically.

### 1. Determination by Dry Combustion

The so-called micro Dumas method seems to be very simple when the original Pregl procedure is used and was believed to handle successfully all types of compounds. Nevertheless experience has taught that many substances require some modifications. From the large number of publications dealing with this method only the most important shall be mentioned.

#### A. MODIFICATIONS OF THE DUMAS-PREGL METHOD

One main disadvantage of this method is the fact that the substance has to be decomposed in an atmosphere of carbon dioxide.

The oxygen needed for complete combustion is supplied from cupric oxide. In the original Pregl method the substance had to be mixed with finely powdered cupric oxide in the combustion tube. For this reason the tube had to be taken out of the apparatus after each analysis. The method was, therefore, very time consuming.

The first real progress was achieved when Gysel (112,113) introduced the so-called by-pass. The combustion tube remains in the furnace and during the introduction of the sample the carbon dioxide flows in the reverse direction. The substance to be analyzed is mixed in the boat with a mixture of lead chromate and cupric oxide.

Zimmermann (114) described an automatic combustion train which gives excellent results. The sample still has to be mixed with powdered cupric oxide in the combustion tube before each analysis. The substance is burned in a closed system and a special mercury filled vessel has to be used for pressure regulation. The gaseous combustion products are collected in this vessel. After the decomposition, which takes place in a closed system, is completed, these gases are swept into the nitrometer by means of a rapid stream of carbon dioxide over the hot combustion tube filling. One determination can be completed in 25 min.

Two very rapid micro procedures, also based on the Dumas principle, have been described by Shelberg (115) and Schöniger (116). The sample mixed with powdered cupric oxide is precombusted in a separate exchangeable combustion tube which is connected with the apparatus by a ground glass joint. As many as four analyses can be made in 1 hr. Belcher and Bhatti (117) used this method for the nitrogen determination in coke on a semimicroscale with good results. Gustin (275) developed a completely automatic method based on the procedures just mentioned.

Hozumi and co-workers (118-120) tested different metal oxides ( $MnO_2$ ,  $Co_2O_3$ ,  $NiO$ , and  $CuO$ ) which can be used to promote the oxidation of refractory organic nitrogen compounds. They found that the following arrangement is the best:

The sample is placed on a shallow platinum boat and inserted into the tube. A nickel boat containing approximately 150 mg. of  $Co_2O_3$  is placed next to the platinum boat and the combustion is carried out at temperatures over  $850^\circ C$ . Since  $Co_2O_3$  starts decomposing at  $750^\circ C$ . and liberates oxygen at a constant rate between  $800$  and  $850^\circ C$ ., complete combustion is achieved.

This method is used with the following slight modifications in the author's laboratories and gives excellent results. The platinum boat with the sample is placed in a nickel boat (width 8 mm., height 5 mm., length 20 mm.). Approximately 200 mg. of a mixture of  $Co_2O_3$  and lead chromate (4:1) is added to the substance. This boat is placed before the side arm of the combustion tube with the stop cock of the nitrometer closed. After 5 min. all air will be swept out by the carbon dioxide and the open end of the tube is closed. The nickel boat is pushed in place (4 cm. in front of the filling) with a magnet and the movable burner ( $900^\circ C$ .) is started. Between the carbon dioxide supply and the combustion tube is the pressure equilibration vessel recommended by Zimmermann (114).

#### B. NEW METHODS

Unterzaucher (121,122) published a method where the substance is introduced in a platinum boat into the combustion tube and burned in a gas stream of carbon dioxide and oxygen. The combustion tube is filled with copper oxide and copper, which is at the end of the tube filling. Any excess of oxygen is removed by the copper. In the original method the mixture of oxygen and carbon dioxide is obtained by passing the latter through a 30% solution of hydrogen peroxide. Because it was impossible to obtain a controlled amount of oxygen by this procedure, Cropper and co-workers (123) and Manser and Egli (124) suggested to generate the oxygen electrolytically.

Ingram (125) combined this method with the "empty tube" principle already used by Belcher and Ingram (126) for the C-H determination.

Kirsten (127-129) pointed out that the reaction



can be very useful for the combustion of compounds which are difficult to burn. The combustion tube is filled with granulated nickel oxide. This part of the tube is kept at  $1000$  to  $1050^\circ C$ . At the end of the tube a short layer of hopcalite, heated to  $100^\circ C$ ., is placed to remove any carbon monoxide before the gases enter the nitrometer. Before the substance placed in a platinum boat is introduced, a capsule of platinum gauze filled with nickel oxide is inserted into the tube. Prior to the analysis the combustion tube is swept air-free



by means of a by-pass. The movable burner has a temperature over 1050°C. A modified nitrometer is also recommended. A simplified procedure based on this method is described by Clark and Dando (130).

## 2. Determination by Wet Combustion

Since Kjeldahl first published his method for the nitrogen determination about 75 years ago, a large number of publications have appeared in the literature. This method is applicable to many types of organic compounds although it is sometimes referred to as being that for the determination of aminoid nitrogen.

### A. PROCEDURES FOR THE KJELDAHLIZATION

Principally, the main problem lies in the fact that it is very hard to transform every kind of organic bound nitrogen into ammonia. According to its behavior, when digested, there are four main groups of organic compounds (131): (1) compounds with N—H linkages, (2) compounds with heterocycles, (3) compounds with N—N linkages, and (4) compounds with NO and NO<sub>2</sub> groups.

Because it is impossible to review all the papers that deal with the Kjeldahl procedure which appeared in the past years only the most important ones shall be mentioned.

Compounds which belong to groups (1) and (2) are relatively easy to digest by adding a catalyst to the sulfuric acid. A great deal of research work has been done to find the best catalysts. Reviews on this subject have been published from time to time (132–135).

As it seems today, the important factors are the time needed for digestion, the temperature, and the concentration of potassium sulfate. Mercury appears to be superior to other catalysts (e.g., copper, selenium). Therefore, the procedure recommended by Steyermark (136), based on the collaborative studies under the direction of Willits and Ogg (137–139) is in the author's opinion the best for compounds of groups (1) and (2).

Compounds with N—N, NO, and NO<sub>2</sub> linkages (groups (3) and (4)) must be reduced prior to digestion. This fact was first recognized by Friedrich (140) who recommended the reduction of the substance before the kjeldahlization with hydroiodic acid and red phosphorus. According to Ogg and Willits (141), this method is satisfactory only

for the nitrogen-oxygen linkages and completely unsatisfactory when nitrogen is connected to another nitrogen atom.

Ma and co-workers (142) recently described a micro method applicable to aromatic nitro compounds. The sample is placed in a Kjeldahl flask and is dissolved in a mixture of acetic acid and methanol containing a little hydrochloric acid. Subsequently, it is reduced with zinc metal. Sulfuric acid is added, the organic solvents are distilled off, and the residue mineralized in the usual manner.

While this method is only useful for substances of group (4), the procedure given by Steyermark and co-workers (143) gives excellent values with a variety of substances including those containing N—N, N=N, NO and NO<sub>2</sub> groupings, where the nitrogen to nitrogen linkage is not part of the ring (nitrogen may be linked to oxygen as part of a ring). The method is not yet reliable for compounds where the nitrogen is connected to nitrogen as part of a ring. The authors hope that some modifications might be effective. For nitrates they recommend treatment with salicylic acid as has been suggested by Dickinson (144).

Because of its importance the accurate procedure for the determination of nitrogen in azo and nitro compounds, oximes, isoxazoles, hydrazines, and hydrazones, as described by the authors, shall be given (144a):

"From 5 to 8 mg. of sample, 0.2 ml. of 98 to 100% formic acid, and 0.1 ml. of concentrated hydrochloric acid, specific gravity 1.18, in a 30-ml. micro-Kjeldahl flask (preferably, Soltys type) . . ., are heated in a water bath (80° to 85°C.) until the sample is dissolved. To this are added 80 mg. of zinc dust (nitrogen-free), and the contents mixed by swirling for about 2 minutes, and heated in the water bath for 5 additional minutes. Then 40 mg. of iron powder (prepared by hydrogenation) are added and the flask is swirled for 2 minutes to effect mixing. To this are added 0.1 ml. of concentrated hydrochloric acid, specific gravity 1.18, and 0.15 ml. of ethanol, and the mixture is again heated for 5 minutes (water bath). Every 5 minutes a 0.1-ml. portion of concentrated hydrochloric acid is added, with swirling and heating in the water bath, until the iron is dissolved. While the flask is swirled under a hood, 1.0 ml. of concentrated sulfuric acid, specific gravity 1.84, is added (cautiously), and the contents are warmed until the evolution of gas (hydrogen chloride) has subsided. Then 0.65 gram of potassium sulfate, 0.016 gram of mercuric oxide,



and, finally, 0.5 ml. of concentrated sulfuric acid, specific gravity 1.84, are added. (It is preferable to add the sulfuric acid in this manner rather than all at once, because the final 0.5 ml. can be used to wash down any materials adhering to the walls.)

The mixture is boiled on a micro-Kjeldahl digestion rack for 4 hours, making certain that boiling is vigorous enough so that refluxing takes place almost half-way up in the neck of the flask. The digest is transferred to the micro-Kjeldahl distillation apparatus (preferably the one-piece model) . . . , 7.5 ml. of sodium hydroxide-sodium thio-sulfate mixture . . . are added, and the ammonia is distilled out into boric acid solution (8 minutes with the delivery tube below the boric acid solution, 2 minutes with it above). The distillate is then titrated with 0.01*N* hydrochloric acid, using bromocresol green-methyl red mixture . . . as the indicator. A blank determination should be run using all of the materials, minus the sample, and going through the entire procedure. Any blank value so obtained should be subtracted."

#### R. METHODS FOR THE DETERMINATION OF AMMONIA

**Distillation Apparatus.** The apparatus as designed by Pregl is still widely used. An all-glass, one-piece model can also be recommended. Both types have been recommended by the Committee for the Standardization of Microchemical Apparatus, Division of Analytical Chemistry, ACS (145). A simplified one-piece model is used in Europe (146).

**Volumetric Procedures.** The normal method is the absorption of the ammonia, liberated from the alkalinized digestion liquid in an excess of standard acid and back-titration from the hot solution with standard alkali. Either methyl red or a mixture of methyl red with methylene blue can be used as an indicator for the titration.

Another method which is quite often used is the absorption of the ammonia in an aqueous solution of boric acid. After the distillation is finished, the boric acid solution of ammonia is titrated with standard hydrochloric acid using bromocresol green-methyl red or methyl red-methylene blue as an indicator.

According to Belcher and Bhaty (147) it is possible to determine the ammonia directly after the digestion without distillation, if the substance to be analyzed does not have to be reduced as in section

under Procedures for the Kjeldahlization. The sample is destroyed with sulfuric acid using a mixture of sodium sulfate and mercuric sulfate as a catalyst. After the digestion the solution is neutralized, the ammonia oxidized with hypochlorite, and a known volume of standard arsenite acid added. The excess of the latter is back-titrated with standard hypochlorite.

**Colorimetric Procedures.** Since these methods are normally used for the determination of very small amounts of nitrogen, it should only be mentioned that the ammonia can be determined either by Nessler's reagent (e.g., 148) or according to Van Slyke (e.g., 149) with hypochlorite and phenolate.

#### C. OTHER METHODS

A completely new way for the determination of nitrogen was found first by Ter Meulen (150,151) who hydrogenated the nitrogen by using nickel and thorium dioxide as a catalyst. Lacourt (152) transferred this method to the micro scale. Holowchak and co-workers (153) suggested a nickel-magnesium catalyst, which is recommended also by King and Faulconer (154). Gelman and Korshun (155) also published a method based on this principle. The sample is pyrolyzed in a quartz test tube and the resulting products are passed with a rapid stream of hydrogen through the combustion tube, with metallic iron at 400°C. serving as a catalyst.

Zinneke (156) modified the Kjeldahl procedure by combination of a special digestion apparatus with a combustion tube. The sample is digested with sulfuric acid and a mixture of selenium, cupric sulfate, mercuric oxide and sodium sulfate is used as a catalyst. He obtains ammonia and nitrogen, both of which are determined titrimetrically or volumetrically. If platinum black is added to the digestion mixture, nitrogen is gained from the ammonium sulfate formed and the total nitrogen content is determined only by volumetric methods.

Finally the procedures of Fedoseev and Ivashova (157) and Schöniger (158) shall be mentioned. The organic material is heated with magnesium powder in the absence of air. All nitrogen is converted to magnesium nitride. The reaction product is decomposed with acid and then subjected to the normal Kjeldahl distillation procedure. This method seems to be important with reference to the possibility of determining the sulfur as well as the chlorine (bromine) and the

nitrogen content in an organic compound, if these elements are present together, using a single sample.

## VI. DETERMINATION OF HALOGENS (Cl, Br, I) AND SULFUR

Despite the fact that the elements mentioned are in different groups of the periodic system, it is possible to discuss the methods for the quantitative analysis of these elements in organic compounds. The organic bound element that is to be determined has to be "mineralized," i.e., conversion into an inorganic form which can be easily determined by conventional methods. There are two possible procedures by which this may be accomplished, namely, (1) oxidation methods, and (2) reduction methods.

### 1. Oxidation Methods

#### A. COMBUSTION WITH OXYGEN

The Pregl method and a host of variations are generally applicable. The sample is burned in a stream of oxygen over a platinum contact. It is useless to describe all the papers which have appeared on this subject since they are already reviewed by several authors (159-163).

About 25 years ago Grote and Krekeler (164) reported a special combustion setup with a tube having two built-in quartz frits and which used temperatures above 1000°C. Belcher and Ingram (165) also applied their "empty tube technique" to the determination of these elements.

The method of Voight (166) has been further developed by Wickbold (167,168), to be an excellent procedure of general applicability. The sample is vaporized in a stream of oxygen and burned in a special hydrogen-oxygen burner which is placed in the combustion tube (see also Ehrenberger (169)).

In the past years a very simple method for the decomposition of organic compounds has gained widespread approval. This is the technique of burning samples in a closed flask filled with oxygen. Based on a macro method published by Hempel (276) and Mikl and Pech (170,171), for plant control purposes only (172), Schöniger (173,174) used this principle for micro determinations. The author

showed that this procedure could be used in routine microanalysis for halogens and sulfur with an accuracy as good as, or better than, that of the slower, more complicated classical methods which have been mentioned above.

The principle of the procedure is that an absorption liquid, the kind depending on the element to be determined, is placed in a conical flask which is then filled with oxygen. The sample is wrapped in a piece of ashless filter paper (2.5 × 2.5 cm.) from which hangs a "fuse" consisting of a small strip of the same paper. This paper is inserted in a piece of platinum gauze attached to a platinum wire which in turn is sealed into the ground glass stopper of the flask. The fuse is then ignited and the stopper quickly inserted into the flask. The combustion is complete within a few seconds and the flask is then shaken for 5 to 10 min. to ensure complete absorption of the combustion products. The required ion may then be determined by any suitable procedure. With this method it is possible to determine not only halogens and sulfur, but also, as was shown by several authors, phosphorus (175-179), arsenic (177), boron (177,180), mercury (181), zinc, calcium, cadmium (180), and carbon-14 (182). A historical review of this method has been published by MacDonald (183).

#### B. DECOMPOSITION WITH OXIDIZING REAGENTS

The oldest and still most widely used method is the micro version of the Carius technique. The substance to be analyzed is destroyed by heating with nitric acid in a sealed, heavy-walled combustion tube at a temperature of 250 to 300°C. for several hours.

The oxidation of an organic compound with sodium peroxide in a crucible was first suggested by Pringsheim (184). Parr (185) used a closed system for the decomposition, the so-called Parr-bomb thus modifying the procedure so as to make it generally applicable. This principle was applied by several authors to the microanalysis of organic compounds. A few years ago Wurzschnitt (186) published a modification which represents significant progress in this field of analytical work. Ethylene glycol is added to the sample, before the sodium peroxide is introduced into the metal bomb. This reagent is oxidized at 50 to 60°C. by the sodium peroxide. By this means it is possible to ignite the decomposition at a low temperature.

## 2. Reduction Methods

### A. CATALYTIC PROCEDURES WITH HYDROGEN

Ter Meulen was one of the first to introduce hydrogenation methods for the determination of these elements. For the sulfur determination he recommended the use of a platinum catalyst; for the halogens, according to his first publications, it is only necessary to decompose the substance in a stream of hydrogen mixed with ammonia at temperatures over 600°C. (187), or to use a special nickel catalyst at 300 to 400°C. (188). Lacourt (189,190) and Wiesenberger (191) found that when these hydrogenation methods are used, low results will sometimes result—especially in the determination of sulfur—because of the carbon residue in the sample boat. Irimescu (192) tried to improve the method. Kirsten (193), in the determination of sulfur, used a hydrogenation procedure. He suggested that the substance to be analyzed be first burned in a stream of oxygen and then the sulfur oxides that are formed, be reduced to hydrogen sulfide with a hydrogen-oxygen flame.

Summarizing the literature it can be stated that the hydrogenation methods based on the principles mentioned above cannot be applied to every kind of organic compound. For this reason they are not recommended.

### B. PROCEDURES WITH REDUCING REAGENTS

Considerable progress in the method of analysis was achieved when Bürger (194,195) found that it is possible to use the well-known method of Vohl (196) for the detection of halogens and sulfur also for the quantitative determinations of these elements.

According to this procedure, modified later by Kainz and co-workers (197-199) for the halogens and by Zimmermann (200-203) for the sulfur, the substance to be analyzed is fused with potassium in a sealed tube. Schöniger (204) and Radmacher and Mohrbauer (205) used magnesium and lithium, respectively, for the same purpose.

This widely spread method is used especially for the sulfur determination in the modification as described by Zimmermann (200-203). After the reduction with potassium is finished, the sealed tube is broken off and the contents are dissolved in acid using a special distillation apparatus. The hydrogen sulfide generated is determined

iodometrically as in the section under the determination of sulfur as sulfide.

It shall be mentioned that by using magnesium for this technique it is possible to determine two or three elements in one sample. Schöniger (204,206) and Fedoseev, and Ivashova (207,208) have shown that by proper means nitrogen, halogens, and sulfur can thus be determined. By heating a compound containing these elements in a nitrogen-free atmosphere with magnesium, the magnesium halides, nitride, and sulfide will be obtained. Digestion of these reaction products with acid gives hydrogen sulfide, which can be distilled off. The halides remain in the solution, the nitride gives ammonium sulfate if sulfuric acid has been used. The halide can then be determined by titration, and finally the ammonia is estimated according to Kjeldahl. It can be expected that procedure of this kind will gain importance in the near future.

Another reduction method which is of some value for the halogen determination is the reaction of the substance in solution with sodium. At first organic solvents were used (209,210), and later liquid ammonia was recommended (211). Also, sodium biphenyl was suggested for the reductive removal of halogen (212).

## 3. Determination of the Elements

### A. HALOGENS

**Chlorine and Bromine.** All oxidation and reduction methods finally give the halides. These have been determined gravimetrically in the beginning, according to Pregl, by precipitation as silver halide, a method which is still used today in many laboratories.

Another gravimetric procedure is the direct absorption of the halide formed on metallic silver. By taking the weight of a silver gauze roll before and after the analysis the amount of halogen present can be determined. The best known method on this principle is described by Safford and Stragand (213). Different modifications of these procedures have been described, some authors recommend the use of specially prepared silver (214). Kirsten (215) examined the use of zinc for the absorption of the halogens.

Most frequently the absorption is made in alkaline solutions (e.g., sodium hydroxide with some hydrogen peroxide added) and the halide is determined titrimetrically. It seems to be of no use to list

the host of methods and modifications which have been described, because excellent reviews have already appeared in journals and handbooks (e.g., 160,216,217). In the author's opinion the best method is the potentiometric titration using an automatic apparatus, if a large number of determinations are made every day. When only a few analyses per day are requested, one of the titrimetric procedures that uses an indicator should be applied. If the sample to be analyzed does not contain nitrogen, the acidimetric procedure according to Vieböck (218,219) can be used. Hydroxyl ions are titrated, resulting from the reaction of the halide with mercuric hydroxy cyanide. Excellent results have been obtained with the following simple methods:

For the chlorine determination an argentometric titration with an absorption indicator (220) is used. If bromine is to be determined the iodometric procedure as recommended first by Kolthoff (221,222) is applied. In cases where chlorine and bromine are present in the compound, the iodometric titration gives only the bromine content. A second combustion where the halogen is determined argentometrically gives the sum of chlorine and bromine. By calculation it is possible to find the chlorine content.

**Iodine.** For the determination of iodine there is only one method which can be highly recommended, namely, the multiplication procedure first introduced by Leipter (223) and Vieböck and Brecher (224). All iodine, regardless if it is present in the absorption liquid as free iodine, iodide, or hypoiodite, is oxidized to iodic acid with bromine. The excess of bromine is then destroyed with formic acid, a certain amount of iodide is added, and the liberated iodine titrated with thiosulfate.

Kainz (197) suggested for the oxidation a solution of chlorine in sodium acetate-acetic acid if only small amounts of iodine are present.

#### B. SULFUR

**Present as Sulfate.** All oxidation procedures, as previously mentioned, (see p. 224) will finally give by some means, sulfate. When the first micro methods for the sulfur determination were published (the Carius method and the catalytic combustion procedure), only gravimetric means of finish were recommended. Later different titrimetric methods were suggested without being generally recognized.

The method of Hallet and Kuipers (225), also recommended by Steyermark (226,217), is one of the most used. The sodium or potassium sulfate obtained after the Carius combustion is titrated in 50% alcoholic solution with standard barium chloride, using tetrahydroxyquinone as an indicator. Another titrimetric procedure has been suggested by Belcher and co-workers (227). After precipitation of the sulfate with 4-amino-4-chloro diphenyl an alkalimetric method is applied.

Today, the best method seems to be the titration of sulfate with barium perchlorate as introduced by Fritz and co-workers (228,229). This method quickly found wide approval and is recommended by many laboratories (230-232). The principle of this titration is the following: The sulfate formed by one of the combustion methods, as listed in the section under Combustion with Oxygen, is neutralized. Isopropanol is added to get on 80% solution. The sulfate is finally titrated with standard barium perchlorate (in 80% isopropanol) in the presence of thorin (or thorin-methylene blue, recommended by Wagner (232)). Sharp end points can be obtained if the amounts of phosphate, nitrate, chloride, and fluoride present in the titration liquid are not too large. This will not occur when micro analytical determinations are carried out. Inglis (233) pointed out that this method can also be used when the combustion has been carried out with sodium peroxide. Fritz and co-workers (229), too, arrive at the same conclusions. The solution has to be treated with a cation exchange resin before the titration.

Finally the complexometrical determination using *o*-cresolphthalein Complexon as indicator (234), and the titration with barium chloride and a conductometric end point indication (235) shall be mentioned.

When the sulfur oxides formed during the combustion are absorbed by silver (the mechanism of this reaction has been studied very accurately by Večeřa (236)), the silver sulfate can be determined either gravimetrically or after elution, titrimetrically. Such methods were published lately by Zinneke (237), Bladh and co-workers (238) and Večeřa and Šnobl (239).

For the determination of very small amounts of sulfate (e.g., in petroleum products after oxidation) a conductometric procedure is suggested by Hurdy and Mair (240). Bertolacini and Barney (241) have chosen a colorimetric way of finish, by using the reaction of the



sulfate formed with barium chloranilate, leading to the liberation of the intensively colored chloranilic acid.

**Present as Sulfide.** For the reduction method as described by Zimmermann, as in the section under Procedures with Reducing Reagents, the following method has been chosen by the author. The hydrogen sulfide generated is absorbed in a buffered solution of cadmium acetate. The precipitated cadmium sulfide is transferred into a solution of standard iodate and iodide. Acid is added and the liberated hydrogen sulfide reduces an equivalent amount of iodine. The excess of the latter is then titrated with thiosulfate. Dirscherl (242) described minor modifications, designed to remove certain sources of error.

Večeřa and Spěvák (243) use a colorimetric method, based on the formation of Lauth's violet with *p*-phenylenediamine and ferric chloride, whereas Martin and Floret (244) determined the hydrogen sulfide as methylene blue. This way of finish has already been suggested by Roth (245) for the determination of traces of sulfur in organic compounds. According to Trifonov and co-workers (246), the hydrogen sulfide can also be estimated polarographically.

## VII. OTHER ELEMENTS

### 1. Phosphorus

For the decomposition of organic compounds containing phosphorus the wet combustion with a mixture of sulfuric and nitric acids in a Kjeldahl digestion flask is still the most frequently used method. The oxidation with sodium peroxide in a bomb has been recommended by several authors (247,248). Jureček and Jeník (249) use fusion with magnesium in a sealed tube. The magnesium phosphide thus formed is decomposed with acid, the phosphine absorbed in bromine water, and the resulting phosphoric acid determined by one of the normal procedures.

Most recently the combustion in the closed flask as introduced by Schöniger for the halogen and sulfur determination (250,251) has been applied by several authors. The substance to be analyzed is decomposed in the usual way, as in section under Combustion with Oxygen, and the resulting phosphoric acid can be estimated, according to Fleischer and co-workers (252-254) either titrimetrically or colorimetrically. Belcher and MacDonald (255) recommend a

modification of the well-known quinoline phosphomolybdate method and Merz (256) uses the colorimetric way of finish. He also points out that with this procedure the simultaneous determination of phosphorus and the halogens (chlorine, bromine, or iodine) is possible, if these elements are present in a compound.

The phosphoric acid formed by one of the above mentioned combustion procedures can be determined either gravimetrically as ammonium phosphomolybdate (the formula of this precipitate has been found empirically by Pregl (257)), or colorimetrically. The latter method is based on the work of Taylor and Miller (258), and Roth (259) who found that in a mixture of molybdic and phosphomolybdic acids, only the latter is reduced to heteropoly blue if treated with reducing reagents. Since both methods are well known standard procedures they shall only be mentioned in passing.

### 2. Arsenic, Antimony, Boron

Jureček and Jeník (260-262) also used the reduction with magnesium for the determination of arsenic and antimony. After the mineralization the arsenic acid can be estimated iodometrically or alternatively, colorimetrically after arsine is absorbed in a pyridine solution of silver diethyldithiocarbamate. For the estimation of antimony a colorimetric procedure is recommended.

Corner (253) has shown that the closed flask method can also be used for the determination of organically bound arsenic. In a modified apparatus the sample is at first burned as usual. Arsenite, as well as arsenate, is formed. The author recommends the distillation of all the arsenic as trichloride, after reduction to the lower valency state with hydrazine dihydrochloride. It should also be possible to apply the potentiometric titration as described by Lévy (263) to this procedure.

Boron may be estimated after a closed flask combustion, as has been reported by Corner (253) and found to be true in the author's laboratories. The neutralized absorption liquid is treated with mannitol, thus obtaining a di-diol complex of the boric acid, which can be titrated with standard alkali (264).

### 3. Selenium, Silicon, Metals

Kainz and Resch (265) recommend for the determination of selenium, the decomposition with sodium peroxide and an iodometric



finish, whereas Kondo (266) suggested the gravimetric determination of the black selenium, after the selenic acid has been reduced with hydrazine. The silicon content of organosilicon compounds can be determined as previously described (see p. 205) together with the carbon and hydrogen. Alternatively the sample can be evaporated with 25% oleum and fuming nitric acid containing 20% of oxides of nitrogen: the residual silica is weighed (267). Fusion with sodium and potassium carbonates has also been suggested for the decomposition. The melt is dissolved and the solution, after neutralization, is treated with ammonium fluoride and is titrated acidimetrically (263).

According to Southworth and co-workers (269) the closed flask method can be applied to the determination of mercury. After the combustion the mercury is absorbed in concentrated nitric acid, the pH of the solution is adjusted to 7.5, and the mercury is titrated amperometrically with ethylenedinitrilotetraacetic acid.

Recently, Belcher and co-workers (270) have shown, as has already been mentioned, that the flask combustion method can also be used for the micro determination of other elements in organic compounds.

The determination of metals in organic compounds has been reviewed by Belcher and co-workers (271) and more recently by Sykes (272).

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