AUTOMATION IN ORGANIC MICRO-ELEMENTAL ANALYSIS

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INTRODUCTION

Since the time, about six years ago, when I gave a detailed report\(^1\) on automation in organic micro-elemental analysis many problems have been clarified both with respect to fundamentals and to experimental technique. At present we have at our disposal many \textit{“automatic”} devices which have passed the stage of trials and are now being tested in some research and industrial laboratories for their possible continuous use and scope of application with respect to the rapidly changing analysis programmes.

As far as we know these are all automatic devices which at the utmost carry out automatically the analytical operations up to the typing out of the results, but are not coupled with a feed back into the production programme, and thus are unable to contribute to the control of production. Consequently we are dealing here with the typical case of automation \textit{in} analytical chemistry and not with the automation \textit{with} analytical chemistry. I have given a lecture on this difference recently\(^2\), Automatic organic elementary analysis is an excellent example with which the whole problem can be demonstrated together with its solution. Up to about ten years ago mostly modifications of the classical methods were in use which erroneously became known as automatic. Though these modifications did involve a certain mechanization, they could by no means be classed as representing a true change in the sense of automation. While it cannot be denied that the attempts to modify the classical Pregl method with a view to obtaining speed with at least the same accuracy and certainty of the analytical procedures, were indeed expedient, essential progress will only come from radical change in methods and objectives. I wish to mention in this connection that in the organic chemical industry—as compared to metallurgy, and especially to the iron and steel industry—automatic analysis is very seldom used.

The concept \textit{automation} is at present very widely applied and often understood to mean a partial or total replacement of manual operations or of a series of operations during analysis up to the evaluation of the results. The extensive use of the concept deprives it of all accuracy and often reduces it to a synonym for mechanization and instrumentation. To achieve a distinction between these conceptions I wish to give a closer definition of all three, which have one thing in common, namely that they involve a reduction of operations and activities performed by man in the course of analytical processes.

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Thus mechanization refers to movements (adjustment of the burner, filling of the burettes, etc.), and instrumentation to the transfer of information, i.e. to the production and evaluation of measured data. Automation on the other hand refers to the use of systems which replace at least partly human decisions, through a combination of mechanization and instrumentation.

This trend of thought may be logically followed up and we arrive through the evaluation and the pre- and post-signalling of measurements and analytical data to the control of (chemical) processes or to the automatic end-point of an analytical method. If the evaluated measuring data are fed into a process, we have reached the field of kybernetics. Rationalization may be introduced at any of the stages mentioned in order to achieve a change in the present state of an analytical laboratory. Thus we may draw the following scheme:
Mechanization—artifact movements; Instrumentation—production of information; Automation—mechanization + instrumentation + signalling of results; Kybernetics—automation + input of information.

An analytical process may be considered as consisting of the following steps:
Analysis = Sampling + Preparation of the sample + Measurement + Evaluation of the measured data = Result.

Translated into the simplified language of the representatives of automation this means that sampling and the preparation of the sample are the input to the system, the chemical reaction forms the basis of the measurement when measurement itself is carried out by machines which immediately or with the help of a second machine perform the evaluation of the data, all this being given the simplified concept of the “black box” which of course contains a series of individual instruments, and finally this whole instrumentation and mechanization leads to the output of the analytical results. It is quite obvious that this process includes a series of applications of mechanics, chemistry, physics, and mathematics. Chemistry plays the dominating part in the selection of the reaction to be used, as well as in the preparation of the sample and the measurement. Physics is decisive in the true measuring process, as we are always dealing with signals of different origins. Functional statistical mathematics comes into the picture in establishing correlations between the measured data and leads through physics and the use of measuring and control techniques into the field of kybernetics, which, as the last link, includes the transfer of the predetermined, and their input—often called feed back—into the process.

Now, if we wish to automatize an analytical process, we have to compile first of all a list of the available methods which may lead to the desired analytical goal. From this list we may then choose a selection of processes which are suitable for automation, i.e. processes for which the available instrumentation may be coupled into a satisfactory system. However, it is a matter of opinion where such attempts start to become ridiculous. In order to clarify this a little more we shall discuss one of the most recent examples of attempts at automation in analytical chemistry, namely the so-called automatized carbon, hydrogen analysis.

The five main steps which are common to nearly all standard procedures
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are: (1) weighing of the sample; (2) combustion; (3) absorption; (4) conditioning; and (5) weighing of the end product.

The time consumed by each step may be expressed by the relative proportions: 1:5:2:10:2. This shows that, if we have to pay attention to the speed of the determination, conditioning prior to weighing is the time determining factor; followed next in time consumption by the combustion process. There is further an extraordinary discrepancy between the weight of the absorption tube and the weight of the component to be absorbed, which today, with constantly decreasing amounts of the substance, calls for higher analytical precision and this must not be overlooked if we aim at true development.

Thus if we wish to automatize organic elementary microanalysis it will be expedient to formulate our reasoning along the lines indicated in Figure 1.

*Figure 1. Principles of the scheme for automatic organic elementary microanalysis*

This diagram shows the enormous number of possibilities and indeed there are more than 30 suggestions (*Table 1*) for the combustion of organic compounds alone, although these can be reduced to a few basic types. Though non-destructive methods seem to be at first sight more favourable, if considered more closely they appear to be greatly limited by the problem of the matrix effect, at least when the analysis has to be carried out on samples with varying compositions. If, however, we wish to introduce a continuous analytical check of some product to ascertain its constant composition, and if the initial product is essentially always of the same type, then the advantages lie with the non-destructive, mainly x-ray and absorption analytical methods.

However, for most of the laboratories engaged in elementary microanalysis it will be simpler for some time to come to construct automatic methods of analysis based on the collection and evaluation of the decomposition
products of the combustion process. These products must of course be reproducible and unequivocal. Hence I must enter into some argument with the generally accepted form of combustion, viz. pyrolysis.

<table>
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<tr>
<th>S. No.</th>
<th>Method</th>
<th>Combustion temperature (°C)</th>
<th>Gas velocity (ml/min)</th>
<th>End point determining method</th>
<th>Time taken (min)</th>
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**PYROLYSIS**

**The role of thermal decomposition**

In order to discuss this problem in detail we will have to consider many equilibria, and also the tremendous developments in the field of gas
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chromatography. Depending on the compound, on pressure, temperature and the carrier gas, there are such innumerable pyrolytic decomposition products formed that it would indeed be difficult to write a general treatise on them. In addition, the initially formed gaseous components are often transformed in order to be accessible to the measuring principle applied.

The first task therefore is to find the simplest possible combustion conditions, and these can of course be realized by the use of very high temperatures at which nearly all organic compounds undergo thermal decomposition. The use of oxygen of high purity guarantees simple and uniform decomposition products. These products are again subject to thermal decomposition, depending on the nature of the product, the pressure, temperature and on the catalyst present. By catalysts we understand here not the oxygen donors, such as CuO and WO₃, but true catalysts, such as Pt, and further, the catalytic action of the walls of the vessel and of the sample holder.

If however we consider but briefly the combustion of organic substances in the empty tube with pure oxygen then we have the simple reaction equations:

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 + 94.3 \text{ kcal/mole} \\
2H_2 + O_2 & \rightarrow 2H_2O + 57.1 \text{ kcal/mole} \\
S + O_2 & \rightarrow SO_2 + 69.3 \text{ kcal/mole} \\
N_2 + O_2 & \rightarrow 2NO - 42.2 \text{ kcal/mole} \\
2P + O_2 & \rightarrow P_2O_5 + 360.0 \text{ kcal/mole} \\
Si + O_2 & \rightarrow SiO_2 + 202.0 \text{ kcal/mole} \\
Se + O_2 & \rightarrow SeO_2 + 56.0 \text{ kcal/mole} \\
Te + O_2 & \rightarrow TeO_2 + 77.0 \text{ kcal/mole}
\end{align*}
\]

We know that these seemingly simple equations in fact represent the results of a number of consecutive intermediary reactions and depend on the pressure and temperature. Even in the case of the simplest carbon–hydrogen compounds the following products can be identified: H, CH₃⁺, CO, CO₂, C₂H₂ and C₂. It is therefore an obvious proposition to try to control the combustion process in such a way that the equilibria should be shifted as far as possible in favour of the stable end products which can be treated relatively easily by analytical methods. It will therefore be expedient to be able to analyse the highest number of organic compounds with different compositions without having to account for the equilibrium conditions, and to choose the highest temperature at which the thermal decomposition of the end product is still insignificant. Starting from the theoretical works of Schwarz–Bergkamp⁴ we found also by our own experiments⁵ that at a temperature of about 1200°C with a hot surface of about 50 cm²/mg carbon, and a retention time of at least 1 sec, the oxygen excess being 10–20 per cent, the quantitative pyrolytic oxidation of the overwhelming majority of organic compounds takes place at flow rates of 200 cm³/min. This seems to be the solution of a further important point towards automation, because the use of heat-stable combustion tubes closed only on one side, without a combustion catalyst (which anyhow are mostly only oxygen donors) represents a considerable step forward towards
a simplified introduction of the sample. This had already been reported elsewhere. Pyrolysis in an inert gas atmosphere on the other hand demands the use of so-called combustion catalysts.

**Some remarks on oxidation catalysts**

As a great number of automatized C, H methods are still based on the use of "catalysts" I shall deal here briefly with these methods too, but should like to add straight away that in the majority of these methods no catalysts, but simply oxygen donors are applied which decompose at various temperatures with the splitting off of oxygen. This is not altered by the fact that some of these agents serve also as adsorbents in the determination of carbon dioxide and water in the combustion of the by-products formed. The most important development in this field is due to Körbl who used the decomposition products of silver permanganate and to Večerák who introduced the use of mixed cobalt oxides. The first "catalyst" is essentially a microporous manganese dioxide matrix covered with finely divided metallic silver and can be used at relatively low temperatures and rapid oxygen streams. The action of silver consists mainly in the removal of halogens and sulphur from the combustion gases, but this effect based on chemisorption leads to a more or less rapid "exhaustion", i.e. poisoning of the "catalyst". The second product permits also the use of low working temperatures, and is less sensitive towards the halogens and sulphur. Consequently these elements must be removed prior to the determination of carbon dioxide and water with the help of external absorbers, that is to say absorbers which lie outside the true combustion process.

Kainz and coworkers have tested a large number of catalysts and have arrived at the following sequence, by using methane as a test substance, which shows quite clearly the efficiency of the various catalysts. Thus cobalt dioxide is indeed one of the most efficient combustion promoters.

**Oxidation in the empty tube**

More than 20 years have passed since Belcher and Spooner first suggested the use of empty tubes in elementary analysis, a method which is being more and more frequently adopted in combustion technique. We too have been investigating the possibilities of this method for more than ten years.

Kainz and Horwatisch used paraffin as test material and achieved with slow combustion at 800°C a 100 per cent oxidation. We used anthracene as test substance, and found that at 1000°C with a 20 to 30 times higher flow rate of pure oxygen about 10 sec are sufficient to bring about complete oxidation.

If we compare the oxidation of paraffin under different conditions, as carried out by Kainz and Horwatisch, with our own experiments, we find a confirmation of the aforesaid.

These experiments, together with our earlier reasonings and the communication by G. Ingram prove the general applicability of such methods. Moreover Pregl's method, though very accurate, is in fact fairly complicated. For this reason it is highly liable to disturbances and should be modified further. During the work on the oxidation of organic compounds in an empty tube it was found that with a tube diameter of 20 mm, a linear
flow rate of 60 cm per min (about 190 ml per min) and at a temperature above 700°C, the time is sufficiently long for the quantitative oxidation of methane which is known to be resistant to oxidation. Kainz and Scheidl have also provided evidence for the effective use of the empty tube.

If we now take another step forward and use for combustion not only an empty tube but one which is closed only at one end, then we have again taken an important step towards automation as this will have the following advantages. As far as thermal dissociation of carbon dioxide and water is concerned there is no limit on the use of higher temperatures up to 1200–1400°C, provided appropriate tube material is used, and there are only very few organic substances which will not burn in a pure oxygen stream at such temperatures. If now the flow rate of oxygen, which serves both as a combustion promoting agent and a carrier gas, is over 200 cm³ per min, then the combustion of micro-quantities will take place in much less time than one minute, and in most cases by explosion. It is quite clear that this involves a considerable saving in time. Further, the introduction of the sample into a tube which is open at one end only is the simplest possible procedure, and thus a further advantage of the method which may serve for the automation of C, H, and S determinations. There is no doubt that combustion in the empty tube provides in most cases a simpler working technique than the usual Pregl method. Combustion of organic substances in an empty tube open at one end only may be carried out in two different ways: (1) by the rapid introduction of a micro platinum crucible or boat into the combustion tube which had been heated up to 1200–1400°C; (2) by the slow introduction of the crucible or boat with the help of a special device so that the test tube substance reaches the hottest zone of the tube in 1, 2, 10 or 20 min.

We have used three different devices for the introduction of the sample into the combustion tube. Essentially they consist of a 500 mm long quartz tube which has an external diameter of 7 mm and a bore of 5 mm. Depending on whether a crucible or boat is used, the quartz tube, which is provided with a thermocouple, carries at one end a fixture or cartouche which is open either in or against the direction of the oxygen stream. If a crucible is used, the oxygen passes directly over it. In the case of a boat the vapours of the substance (i.e. of its decomposition products) come into direct contact with the oxygen only outside the cartouche.

The suction of the pump draws the reacting gases together with their decomposition and reaction products through the hot zone where the reaction is completed. Each reaction occurs more or less violently and noisily. Even when the reaction is more rapid than the actual pump performance there is no danger (with samples of about 3 mg) that the combustion products may be blown out through the open end of the tube, as the buffer volume of the tube used by us was about 100 cm³ and this, together with a suction performance of about 270 cm³ per min, provides sufficient security.

A second possibility for the reaction is afforded by two counter-current gas streams when the cartouche is opened against the direction of the oxygen stream. This brings about an intensive mixing and a longer dwelling time of the reaction mixture in the hot zone, but the effect of the reaction is
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higher and there is a greater danger of material loss through the open end of
the tube at lower suction performances (40 ml per min).

If a catouche open in the direction of the oxygen stream is used there
is at first a temporary oxygen deficiency. Immediately after the substance,
i.e. its pyrolysis products, have left the catouche they will be mixed with
ample quantities of oxygen. The vapours of the substance are gradually fed
into the oxygen; consequently the reaction can proceed only slowly. There
are losses of the material even with samples of the size of about 5 mg. If
we consider thermal dissociation we find that with an oxygen excess of about
10 per cent, under atmospheric pressure and at temperatures up to 1500°C,
neither carbon dioxide nor water decomposes to any marked degree.

Summing up the problems of pyrolysis we may state that for quantitative
oxidation of organic substances in an open tube the following conditions
must be met: (i) a surface with a temperature of at least 1000°C, and a
size of 30–50 cm² per mg of carbon; (ii) a dwelling time of at least one
second; (iii) an oxygen excess of 10 to 20 per cent; (iv) end determination
by means of electric conductometry.

MICROANALYSIS USING ELECTRICAL CONDUCTOMETRY

Measurement of combustion products by electrical conductivity

In conductometry it is always very convenient, from the standpoint
of sensitivity, to measure H⁺ or OH⁻ because they have the highest equiva-
 lent conductivity (above 400 for H⁺ and about 170 for OH⁻). Furthermore
the dissociation of an electrolyte, the mobility of ions, and the temperature
of the electrolyte play an important role. To be as accurate as possible for
the whole measurement, we also have to take into account the velocity of the
chemical absorption reaction and the reaction products formed. As far as
dissociation is concerned, the degree of dissociation should be as near as
possible to 1. This means that we can only use alkali hydroxides and barium
hydroxide, but not ammonium hydroxide. To avoid the formation of
insoluble reaction products during the absorption of carbon dioxide,
barium hydroxide should not be used as an electrolyte. After the combustion
the second part of the procedure starts—the absorption. In practical work
the absorption of the gaseous products will take place very often before the
combustion is finished. Also the measurement and registration of the change
in conductivity can take place before the absorption is finished. This means
that during the whole analytical procedure, two or more processes are
running at the same time. We therefore have a registration device that also
signals the end of the analyses. This eliminates the need to wait for a fixed
time before making the final weighings or other measurements.

If the measurement of carbon dioxide is accurate then the whole problem
is solved. Without going into the chemical and physical reaction between
a more or less dilute solution of alkali hydroxides and carbon dioxide, we are
perfectly convinced that the electrical conductivity is the best means of
indicating and measuring the reaction. The principles of conductometry
are simple and the absorption of carbon dioxide leads in every case to a
decrease in conductivity due to the removal of the hydroxyl ions. Even if the
absorption is not exactly 100 per cent, this disadvantage is less serious than

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it might appear and can be overcome by keeping the conditions completely constant during the entire analysis. A pump system, developed by Schmidts and Baasch, works so accurately that constant gas-flow conditions are guaranteed. Because the conductivity depends on the temperature the conductivity cells are totally immersed in an oil bath. To obtain a good difference signal, two indicator points are necessary, one in the pure solution and the other in solution where the absorption takes place.

**The apparatus**

Since the product measured in the determination of carbon, hydrogen, and oxygen is always carbon dioxide, the design of the apparatus can be similar or identical for each of these components; only the transport gas need be changed. We can therefore say that in principle the whole apparatus consists of four main parts: (i) the gas purification system (oxygen or nitrogen); (ii) the combustion trains; (iii) the measuring cells and pump system; and (iv) the recording system.

In principle, any combustion train which attains the required temperatures can be used. It is important that the combustion tube is made of porcelain or platinum or, for lower temperatures, from quartz, and that it is not stoppered during the combustion process; otherwise the pumping system will not function. At the same time an essential simplification of the combustion tube is possible, since no special chemical filling is required. At very high temperatures an explosive type of combustion may occur. Our experiments with organic and inorganic materials have shown, however, that this has no influence on the carbon and sulphur determinations. A sudden increase in the concentration of carbon or sulphur dioxide is not dangerous, as the pumping system is capable of extracting all the gas produced by samples containing up to 5 mg of carbon.

For every measuring cell, i.e. for each gas component, a separate pump is required that extracts gas from the gas stream and immediately passes it under constant pressure into the reaction chamber of the measuring cell. According to the requirements the capacity of the pumps can either be 70, 100, or 270 cm³/min.

After purification, oxygen is passed into the combustion tube at a flow rate of 3 l/min. A high percentage escapes from the open end of the tube and prevents carbon dioxide or other gases being drawn in from the atmosphere.

The gas of the carbon determination is purified from sulphur dioxide by means of an absorber.

The recording system consists of two specially compensated recorders which immediately and permanently register any change in conductivity in the cell.

**Determination of carbon**

Statistical studies with standard samples as recommended by the Commission on Microchemical Techniques of the IUPAC were made in order to compare the empty tube method with other techniques; Table 2 summarizes the results of these studies and shows that this new method is very satisfactory as far as CO₂ absorption is concerned.

Other than ease of automation, two further considerations relative to
Table 2. Statistical studies with standard analytical samples

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<th>Substance:</th>
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<td>Sulphamic acid</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>Thioarsenol</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>General</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>Compound</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>Compound II</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>Compound III</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
<tr>
<td>Compound IV</td>
<td>47.40</td>
<td>47.61</td>
<td>47.38</td>
<td>47.74</td>
</tr>
</tbody>
</table>

| Time taken for analysis (min) | 25 | 10 | 15.75 | 35.88 | 16.10 |

H. MALISSA
this method deserve mention, as pointed out earlier: (a) The method is
equently suitable for ultramicroanalysis. In the present method, 0·005 N
sodium hydroxide was used to determine 30 µg of carbon that was present as
tungsten carbide, with sufficient accuracy. A number of organic samples
were satisfactorily run with sample weights considerably less than 1 mg.
Since one obtains a needle deflection of 10 mm for 1 µg of carbon, one
may determine 1 µg or less carbon with certainty, if the weighing is suffi-
ciently accurate. Amounts of carbon lower than 1 µg were determined with
other absorbing solutions or concentrations of sodium hydroxide. (b) This
method, like gas chromatography, may be used for studying the combustion
characteristics of organic and inorganic compounds. Such investigations
could in a simple way help to determine various types of bonding in molecules
and could yield characteristic data for identification purposes.

Determination of hydrogen

As previously pointed out at Birmingham in 1958\textsuperscript{13}, the reaction of
water with calcium carbide, and the subsequent combustion of acetylene
to carbon dioxide and water, could be used for micro carbon–hydrogen
analysis. The first results were published soon after this. The work of Duswalt
and Brandt, as well as that of Sundberg and Maresh, concerning the
gas chromatographic micro carbon–hydrogen determination, show that
this was the right approach. The experiments of Lindner and later Belcher
and co-workers to obtain water-absorbable gaseous products which would
finally be determined conductometrically were not too successful and will
not be discussed now. For these reasons, and having investigated many
other products, we returned to the use of calcium carbide.

In 1961, the sensitivity of our arrangement was about 1 µg of hydrogen. Now,
with a new preparation technique and by using a glove box\textsuperscript{16}, it is
in the region of about 0·7 µg hydrogen. Having tested this reaction with
water of crystallization from CuSO\textsubscript{4} · 5 H\textsubscript{2}O, it was necessary for the
purpose of micro-elemental analysis to avoid any disturbance due to the CO\textsubscript{2}
coming from the carbon content of the sample. There were three possi-
bilities: (i) to remove the water from the gas stream by absorption on water-
free BaCl\textsubscript{2} or CuSO\textsubscript{4} and to release it by heating the water after all CO\textsubscript{2}
has been absorbed and recorded; (ii) to freeze out the water and to release
the water as above; or (iii) to find an absorption medium for CO\textsubscript{2} which
did not react with acetylene.

All three possibilities have been tried successfully. Numbers 1 and 2 need,
on the one hand, longer time and a change in transport gas; on the other
hand they have the great advantage that only one measuring and pumping
system, and only two gas purification trains, are necessary.

Determination of oxygen

Drekopf and Braukmann\textsuperscript{18} were the first who tried to use electrical con-
ductivity in oxygen determinations based on the work of Unterzaucher. In
1962 Salzer\textsuperscript{17} established a procedure which has since been used continuously
in Hüls (Germany). Recently, Drekopf et al. modified the old Drekopf
arrangement.
H. MALISSA

Determination of sulphur

The combustion products of a sulphur-containing compound consist mainly of carbon dioxide, sulphur dioxide, and water. Thus an absorption solution for sulphur dioxide must be found with which carbon dioxide and water do not interfere. It is simplest to avoid the absorption of carbon dioxide by using a sufficiently acid solution.

The sensitivity of this method depends on the initial acid concentrations; the weaker the acid, the greater the sensitivity. It should be borne in mind, however, that the acidity must be high enough to ensure the expulsion of carbon dioxide; pH measurements of individual absorption solutions before and after the introduction of the gas containing sulphur dioxide, water, and carbon dioxide do not show a noticeable difference. The most suitable pH range lies between 2.5 and 3.

As far as is known at present, nitrogen and nitrogen-containing products formed during the combustion do not interfere. Chlorine and bromine ions interfere more than iodine but can be removed by placing silver wool at the end of the combustion tube. A comparison of the last method due to Schöniger with our method is shown in Table 3.

Table 3. A comparison of the values obtained by Schöniger’s method and with by the method reported by the present author

<table>
<thead>
<tr>
<th>Compound</th>
<th>% S (calc.)</th>
<th>Flask method</th>
<th>Relative conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{x}%$</td>
<td>$\pm S%$</td>
</tr>
<tr>
<td>2-Nitroso-1-naphthal-4-sulphonic acid</td>
<td>10.15</td>
<td>9.87</td>
<td>0.064</td>
</tr>
<tr>
<td>Diphenylthiocarbazide</td>
<td>12.45</td>
<td>12.45</td>
<td>0.086</td>
</tr>
<tr>
<td>Diphenylthiocarbazone</td>
<td>12.50</td>
<td>13.49</td>
<td>0.056</td>
</tr>
<tr>
<td>1-Amino-2-naphthol-4-sulphonic acid</td>
<td>12.90</td>
<td>12.93</td>
<td>0.099</td>
</tr>
<tr>
<td>$\rho$-Tolyphenylsulphone</td>
<td>13.80</td>
<td>13.85</td>
<td>0.070</td>
</tr>
<tr>
<td>1-Aminonaphthaline-4-sulphonic acid</td>
<td>14.34</td>
<td>14.22</td>
<td>0.041</td>
</tr>
<tr>
<td>2,4-Dinitroterodanzenene</td>
<td>14.25</td>
<td>13.71</td>
<td>0.085</td>
</tr>
<tr>
<td>S-Benzylthiuronium chloride</td>
<td>15.82</td>
<td>15.93</td>
<td>0.066</td>
</tr>
<tr>
<td>Sulphanilic acid</td>
<td>18.51</td>
<td>18.57</td>
<td>0.069</td>
</tr>
<tr>
<td>Benzolsulphhydroxamic acid</td>
<td>18.51</td>
<td>17.97</td>
<td>0.092</td>
</tr>
<tr>
<td>Thiobarbituric acid</td>
<td>22.25</td>
<td>19.23</td>
<td>0.079</td>
</tr>
<tr>
<td>L(-)Cystine</td>
<td>26.75</td>
<td>26.37</td>
<td>0.042</td>
</tr>
<tr>
<td>Sulphonol</td>
<td>28.09</td>
<td>28.45</td>
<td>0.080</td>
</tr>
<tr>
<td>Thiosemicarbazide</td>
<td>35.13</td>
<td>35.25</td>
<td>0.074</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>38.28</td>
<td>38.08</td>
<td>0.079</td>
</tr>
<tr>
<td>Thioureac</td>
<td>42.12</td>
<td>42.27</td>
<td>0.057</td>
</tr>
<tr>
<td>Rhodanine</td>
<td>48.15</td>
<td>47.87</td>
<td>0.088</td>
</tr>
<tr>
<td>Rubenamic acid</td>
<td>53.25</td>
<td>53.04</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$\pm S\% = 0.077$  $\pm S\% = 0.10$

The total time of the simultaneous determination of carbon and sulphur is 3 to 4 min and the accuracy is shown in Table 3. From this result one can see that the overall standard deviation for C is $\pm 0.22$ and for S $\pm 0.15$ even through organic compounds containing N, NO, NH, Cl, etc. have been burned. The determination of sulphur by measuring the conductivity of a solution containing dilute sulphuric acid and hydrogen peroxide in
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comparison with a reference resistor could be extended into the ultramicro range. Sensitivity was increased from 0·5 to 0·05 µg S per millimeter recorder deflection by reducing the concentration of the absorption solution to 0·0002 n and adjusting the reference resistor.

Simultaneous determination of C and H

The determination of carbon was the first to be subjected to the relative conductometric method; since this method has been discussed in a considerable number of papers, it is only mentioned here for completeness.

For the determination of hydrogen, there were three different possibilities:

(a) Direct absorption of water in conc. sulphuric acid, resulting in a linear change of conductivity in the narrow limit of 99·83–99·78 per cent. This method was successfully applied by S. Greenfield and R. A. D. Smith\(^1\).

(b) Reaction with calcium carbide and combustion of the acetylene to CO\(_2\) which is absorbed in sodium hydroxide.

(c) Conversion of water to carbon monoxide by reaction with carbon, oxidation to carbon dioxide, and absorption in sodium hydroxide.

For several reasons we decided to use the second method: the reaction of calcium carbide with water vapour is rapid and, if a suitable branded reagent is selected, free of side reactions. The reaction itself is very sensitive, as will be demonstrated later on. Furthermore, we appreciated the fact that a mixture of acetylene and carbon dioxide is easily separated by means of soda asbestos, which absorbs the carbon dioxide formed by the sample combustion. Water and calcium carbide react according to the following reactions\(^2\):

\[
\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{CaO} \quad \Delta G_{25} = -25·32 \text{ kcal/mole}
\]

\[
\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2 \quad \Delta G_{25} = -42·36 \text{ kcal/mole}
\]

If the reaction products are included in the system, we find also:

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \Delta G_{25} = -17·04 \text{ kcal/mole}
\]

\[
\text{CaC}_2 + \text{Ca(OH)}_2 \rightarrow \text{C}_2\text{H}_2 + 2 \text{ CaO} \quad \Delta G_{25} = -8·23 \text{ kcal/mole}
\]

Based on the calculated \(G\)-values cited above, it would be expected that reaction (2) is preferred thermodynamically. This is not the case because reaction (2) is a combination of reactions (1) and (3). Reaction (1) has to occur first, forming \text{C}_2\text{H}_2 and \text{CaO}, and reaction (3) and therefore also (2) start only when the carbide surface approaches exhaustion by increasing the load. If in practice a sufficient excess of carbide is provided then it seems certain, at least for a considerable time, that reaction (1) occurs exclusively.

Experimental

The apparatus consists of the following parts:

(1) The gas purification unit for delivery of absolutely pure and dry oxygen, consisting of a quartz precombustion tube, kept at 1300°C; soda asbestos tubes for the absorption of carbon dioxide; two freezing traps, for the removal of water, cooled with an acetone-dry ice cooling mixture; and a Sicapent tube for final drying; and (2) the sample combustion train, with two tubes of
refractory porcelain of 18 mm inner diameter, in a furnace allowing a maximum temperature of 1400°C. Immediately after the oxygen stream has left the furnace a system of synchronized constant volume pumps simultaneously divides the combustion products into three parts. Each part is passed into its measuring unit, which contains the reference and the measuring conductivity cell. The first part of the combustion products is used for the determination of carbon converted to carbon dioxide. After being dried over calcium chloride, the gas is bubbled through 0.02 N sodium hydroxide. The formation of sodium carbonate results in a reduction of conductivity. The conductivity signals of fresh sodium hydroxide and carbonate-loaded hydroxide solution are amplified and fed into a modified Wheatstone bridge, which finally controls the phase-sensitive recorder motor. The response of the recorder is linear to the content of carbon dioxide. As it can be assumed that the determination of carbon by relative conductometry is generally known already, it will not be discussed further here.

The second part of the combustion gas is used for the determination of hydrogen. The gas will contain in any case water and carbon dioxide; by passing it over high purity calcium carbide, water is converted into acetylene, the latter is oxidized over copper oxide at 550°C to carbon dioxide, which is now passed into a measuring cell of the type used in part 1.

The problem and main difficulty in the determination of hydrogen using
the carbide method consists almost exclusively in the selection and pretreatment of the calcium carbide. The product used for the first experiment was of technical grade with an assay of only 68 per cent. It consisted of the usual big lumps which were crushed into smaller ones, and only the central parts of each one were meshed and sieved, using a set of sieves of 2, 1, 0·5, and 0·2 mm grain size. The different mesh fractions were stored and tried in the reaction tubes.

The results of the first trial series were not at all encouraging. The activity of the calcium carbide decreased rapidly when it was used for a long period, and the recorded response to carbon was not proportional to the sample content. Similar unsatisfactory results were obtained with a number of different grades of calcium carbide from different sources until we happened to obtain a sample produced by Cyanamid of Canada with an assay of 92·8 per cent, which yielded immediately far better and more promising results so that it was decided to carry on with the experiments. The use of high purity calcium carbide finally led to a positive result of our work. It seems that carbide of low grade does not react in accordance with reaction 1, but reactions 1 and 3 occur side by side in variable proportions.

Furthermore, it was found that the preparation of the calcium carbide reaction tube needs special care. The necessary operations like crushing, sieving, and filling were carried out in a glove box, which was rinsed several times with pure dry nitrogen and kept under slight pressure during work to prevent contamination by atmospheric moisture.

After the first promising results with the new brand of carbide, we started detailed research work to establish the optimum conditions. The purification and combustion train, as well as combustion temperature, were left unchanged, but the test series was performed with variations of oxygen flow rate by replacing the pump pistons; and with variations in the particle size and filling height in the calcium carbide reaction tubes, and of the shape of the reaction tubes and the concentration of the absorption solution. The acetylene combustion train was left unchanged.

### Table 4. Sensitivity of determination of hydrogen in connection with pumping speed and concentration of absorption solution

<table>
<thead>
<tr>
<th>Pumping speed (cm³/min)</th>
<th>Using 0·02 N soln Average H conc (µg/mm)</th>
<th>S (%)</th>
<th>Using 0·005N Soln Average H conc (µg/mm)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>0·836</td>
<td>± 0·011</td>
<td>0·223</td>
<td>± 0·0015</td>
</tr>
<tr>
<td>74</td>
<td>0·801</td>
<td>± 0·009</td>
<td>0·225</td>
<td>± 0·0012</td>
</tr>
<tr>
<td>273</td>
<td>4·012</td>
<td>± 0·320</td>
<td>1·021</td>
<td>± 0·170</td>
</tr>
</tbody>
</table>

After trying about 300 different variations, the optimum combinations were established. Optimum performance was reached by a combustion which results in the rather remarkable sensitivity of 0·2 µg H for a 1-mm recorder deflection with a coefficient of variation of about 1 per cent. Sensitivity is increased with decreasing flow rate of combustion products and decreasing concentration of absorption solution; however, total time for one determination will increase in this case (cf. Table 4).
<table>
<thead>
<tr>
<th>Compound</th>
<th>HE</th>
<th>C</th>
<th></th>
<th>%C calc.</th>
<th>%C found</th>
<th>±S(%)</th>
<th>H</th>
<th></th>
<th>%H calc.</th>
<th>%H found</th>
<th>±S(%)</th>
<th>Coefficient Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td></td>
<td></td>
<td></td>
<td>94.34</td>
<td>94.20</td>
<td>0.22</td>
<td></td>
<td></td>
<td>5.66</td>
<td>5.60</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
<td>93.80</td>
<td>93.40</td>
<td>0.22</td>
<td></td>
<td></td>
<td>6.20</td>
<td>6.46</td>
<td>0.11</td>
<td>0.24</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>O</td>
<td></td>
<td></td>
<td>68.85</td>
<td>68.83</td>
<td>0.15</td>
<td></td>
<td></td>
<td>4.96</td>
<td>4.93</td>
<td>0.12</td>
<td>0.22</td>
</tr>
<tr>
<td>Glucose</td>
<td>O</td>
<td></td>
<td></td>
<td>40.00</td>
<td>39.98</td>
<td>0.19</td>
<td></td>
<td></td>
<td>6.71</td>
<td>6.71</td>
<td>0.05</td>
<td>0.48</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>O</td>
<td></td>
<td></td>
<td>83.86</td>
<td>83.69</td>
<td>0.22</td>
<td></td>
<td></td>
<td>11.99</td>
<td>11.88</td>
<td>0.22</td>
<td>0.26</td>
</tr>
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<td>Melamine</td>
<td>N</td>
<td>28.57</td>
<td>28.47</td>
<td>0.10</td>
<td>4.80</td>
<td>4.74</td>
<td>0.09</td>
<td>0.35</td>
<td>1.90</td>
<td>0.35</td>
<td>1.90</td>
<td>0.35</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>ON</td>
<td></td>
<td></td>
<td>71.09</td>
<td>70.99</td>
<td>0.19</td>
<td></td>
<td></td>
<td>6.71</td>
<td>6.53</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>m-Dinitrobenzene</td>
<td>ON</td>
<td>42.87</td>
<td>42.59</td>
<td>0.05</td>
<td>2.40</td>
<td>2.19</td>
<td>0.19</td>
<td>0.12</td>
<td>8.68</td>
<td>0.12</td>
<td>8.68</td>
<td>0.12</td>
</tr>
<tr>
<td>Hippuric acid</td>
<td>ON</td>
<td>60.30</td>
<td>60.07</td>
<td>0.19</td>
<td>5.06</td>
<td>4.82</td>
<td>0.08</td>
<td>0.32</td>
<td>1.24</td>
<td>0.32</td>
<td>1.24</td>
<td>0.32</td>
</tr>
<tr>
<td>p-Fluorobenzoic acid</td>
<td>FO</td>
<td>60.01</td>
<td>60.25</td>
<td>0.18</td>
<td>3.60</td>
<td>3.57</td>
<td>0.13</td>
<td>0.30</td>
<td>3.64</td>
<td>0.30</td>
<td>3.64</td>
<td>0.30</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Cl</td>
<td></td>
<td></td>
<td>25.31</td>
<td>25.59</td>
<td>0.09</td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.35</td>
</tr>
<tr>
<td>5,7-Dibromo-8-hydroxyquinoline</td>
<td>NBrO</td>
<td>35.68</td>
<td>36.23</td>
<td>0.13</td>
<td>1.66</td>
<td>1.83</td>
<td>0.10</td>
<td>0.36</td>
<td>5.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Iodobenzoic acid</td>
<td>JO</td>
<td>33.90</td>
<td>33.72</td>
<td>0.26</td>
<td>2.03</td>
<td>1.99</td>
<td>0.07</td>
<td>0.77</td>
<td>3.52</td>
<td>0.77</td>
<td>3.52</td>
<td>0.77</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>P</td>
<td>82.45</td>
<td>82.62</td>
<td>0.11</td>
<td>5.72</td>
<td>5.40</td>
<td>0.12</td>
<td>0.13</td>
<td>2.22</td>
<td>0.13</td>
<td>2.22</td>
<td>0.13</td>
</tr>
<tr>
<td>Sulphonilic acid</td>
<td>SO</td>
<td>36.78</td>
<td>36.49</td>
<td>0.14</td>
<td>7.01</td>
<td>6.77</td>
<td>0.18</td>
<td>0.38</td>
<td>2.66</td>
<td>0.38</td>
<td>2.66</td>
<td>0.38</td>
</tr>
<tr>
<td>Sulphanilic acid</td>
<td>SON</td>
<td>41.60</td>
<td>41.50</td>
<td>0.22</td>
<td>4.08</td>
<td>4.07</td>
<td>0.15</td>
<td>0.53</td>
<td>3.68</td>
<td>0.53</td>
<td>3.68</td>
<td>0.53</td>
</tr>
<tr>
<td>Thiourea</td>
<td>SN</td>
<td>15.75</td>
<td>14.98</td>
<td>0.07</td>
<td>5.26</td>
<td>4.77</td>
<td>0.11</td>
<td>0.47</td>
<td>2.31</td>
<td>0.47</td>
<td>2.31</td>
<td>0.47</td>
</tr>
<tr>
<td>Phenylthiourea</td>
<td>SN</td>
<td>55.23</td>
<td>55.31</td>
<td>0.18</td>
<td>5.30</td>
<td>5.20</td>
<td>0.17</td>
<td>0.33</td>
<td>3.27</td>
<td>0.33</td>
<td>3.27</td>
<td>0.33</td>
</tr>
</tbody>
</table>
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The conditions finally adopted for further work were fixed as follows:
(a) Pumping rate from sample combustion train, 100–150 ml/min, flow rate for passing the carbide reaction vessels, 50–55 ml/min.
(b) Particle size of calcium carbide, 0.5–1.0 mm; filling height, 30 mm.
(c) Concentration of absorption solution, 0.02 N sodium hydroxide.

A large number of organic compounds were analysed under these conditions for carbon and hydrogen. As can be seen from Table 5, for this purpose we selected compounds recommended by IUPAC, and furthermore we tried to include all the common hetero elements. The interference of hetero elements or their volatile combustion products was eliminated by adding a scavenging tube with a silver wool filling working at 550°C followed by an absorption tube charged with Perhydrit (hydrogen peroxide–urea compound).

It is necessary to calibrate the system by treating a series of test samples. Some typical results are shown in Table 5 together with the respective statistical treatment of the results.

The overall standard deviation for results obtained by the empty tube method and the relative conductometric finish of combustion products was found to be ±0.19 per cent for carbon and ±0.16 per cent for hydrogen, with a working time of 10 min for each determination.

The simplicity of operation and maintenance is demonstrated by a description of the method: (i) Weigh sample in platinum boat; (ii) Rinse measuring cells once with absorption solution or double distilled water; (iii) Fill cells with a certain semiautomatically adjusted volume of fresh solution; (iv) Switch on connection to recorders; (v) Insert sample into furnace; (vi) Read recorder deflections; (vii) Compute results from recorder deflections; (viii) Break connection to recorders; (ix) Remove platinum boat from furnace; (x) Drain solution from cells.

For maintenance it is necessary to: (a) Replace the carbide tube after 10–20 determinations. (b) Refill the absorption solution after 100–200 determinations. (c) Replace fillings of various absorption tubes after about 1000 determinations.

![Diagram](image)

*Figure 3. A schematic diagram of the method used for the determination of carbon using high frequency titration*

**Determination of carbon using high frequency titration**

Recent investigations on the use of the "Oscillotitration" by Pungor showed that this apparatus is very well suited to a high frequency titrimetric finish of the carbon dioxide obtained in C, H analysis after thermal oxidizing decomposition of organic samples. A schematic diagram of the apparatus
is shown in Figure 3. The experiments included absorptions in sodium or barium hydroxide solution of the carbon dioxide resulting from the combustion of the sample. Graphic evaluation of the readings showed curves with two well defined breaks corresponding to the relative amounts of NaOH/Na₂CO₃ or Ba(OH)₂/BaCO₃, respectively. The degree of absorption was controlled by using a relative-conductometric device for determination of CO₂ in series with the high frequency absorption cell

![Graph](image)

Figure 4. Dependence of the signal from the absorbed carbon dioxide on the amount involved

which recorded the non-absorbed fraction of CO₂. Under the conditions of the test series absorption of CO₂ was rather incomplete with sodium hydroxide solutions of various concentrations. Barium hydroxide solutions, however, yielded satisfactory results. Figure 4 shows the dependence of the signal from the absorbed carbon dioxide on the amount evolved.

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