ELEMENTAL ANALYSIS BY GAS CHROMATOGRAPHY

VLASTIMIL REZL and JAROSLAV JANÁK

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

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I. INTRODUCTION

The development of organic chemistry and biochemistry and of the industrial processes related to them has been the result of intensive research into basic chemical reactions. Organic elemental analysis is part of this research. In the past, the structures of thousands of compounds were successfully deduced by combining the evidence obtained by means of chemical reactions with elemental analysis.

The classical approach to elemental analysis involved the development from macro- to micro- and thence to submicro-analysis. Information on this subject can be found in a series of publications[6,76,80,154,165]. In spite of the ingenuity and systematic approach of many workers, there is a series of problems connected with elemental analysis and particularly with its termination. Any attempt to make the

transition in analysis down to the submicro-scale is restricted by gravimetry. Remarkable progress[140] has been made in this field of analytical chemistry, following the rapid development of physical analytical methods.

The first papers on the applications of gas chromatography (GC) in elemental analysis[23,153,167] were published in 1960. Although GC was applied successfully to investigations of elemental analytical processes[82–84,149] on several occasions, the precision of the evaluation of gas chromatograms by mechanical or graphical means[4,77] was only *ca.* 0.5–1%. Hence the precision lagged relatively far behind the precision required in elemental analysis, above all in the determination of carbon. Only improved instrumentation, based on electronic processing of the detector signal, brought GC nearer to the demands of elemental analysis.

The development of chromatographic methods of separation introduced some attractive features. The gravimetric part of elemental analysis was shown to be replaceable, *e.g.*, by the measurement of the thermal conductivity of reaction products with a katharometer[79] whose sensitivity satisfied the demands of micro-scale analysis.

Soon after the first papers were published, several firms put on to the market instruments based on the chromatographic principle for the elemental analysis of carbon, hydrogen, nitrogen and sometimes also oxygen. However, they were soon shown to be unsatisfactory. It appeared to be necessary to carry out a great deal of research on combining and adapting GC and elemental analysis. After a decrease in interest, the renaissance started. At the same time, we cannot disregard the resignation of several firms that saw the commercial possibilities connected with the known success of GC rather than the problems of its combination with elemental analysis. The finding of appropriate methods, the achievement of the required precision and the automation of the operational functions were developed to such a level that the technique of elemental organic analysis by GC means was established definitely.

Some of the new analyzers do not use the instrumental elements of a gas chromatograph only (katharometer, electronic processing of the signal), but use directly a chromatographic principle of separation. The advantages that follow from this should therefore be explained in more detail, and also some restrictions must be pointed out, as their neglect often causes a failure during application.

II. ANALYSIS OF PROBLEM AND SURVEY OF KNOWLEDGE

The development of elemental analysis was aimed first of all at the elimination of the gravimetric part of the analysis and at the automation of the whole procedure. The determination of carbon, hydrogen, nitrogen, oxygen and sulphur was involved first of all. The following methods of detection were suggested: direct gravimetric detection (*e.g.*, refs. 11, 31 and 161), manometry, volumetry (*e.g.*, refs. 36, 41–43, 55, 74, 92, 94, 100, 112, 116, 130, 146, 150 and 163); titrimetry (*e.g.*, refs. 3, 28 and 56); IR absorption (*e.g.*, refs. 96 and 160); electrical conductivity (*e.g.*, refs. 45–47, 49, 50, 63, 87, 99, 105–107, 127, 142, 143 and 155); coulometry (*e.g.*, refs. 57, 58, 90, 111, 122 and 125); colorimetry (*e.g.*, refs. 51 and 113); mass spectrometry (*e.g.*, refs. 53 and 91); and thermal conductivity (*e.g.*, refs. 12–14, 18, 20, 21, 23, 24, 35, 39, 48, 70, 71, 86, 114, 115, 119, 132, 133, 135, 140, 151, 153, 156, 167–169, 171 and 172).

The measurement of thermal conductivity was used in the largest number of

applications. It is a universal method, as far as the response to reaction products in elemental analysis is concerned. The thermal conductivity cell is simple, sensitive and reliable. It has been sufficiently developed for use in modern GC. Also, the electrical accessories are simple and commercially available.

Newer methods of elemental analysis are all based on the mineralization of an organic compound in a stream of gas (often the carrier gas) or in a suitable gas under static conditions and, as a rule, in the presence of oxidative catalysts. We shall discuss the procedures in general from the viewpoint of the principal operations.

A. Weighing

Modern weighing techniques on micro-balances are rapid, and reliable ultra-micro-balances have been introduced.

For example, Oertling manufactures the Q 01 instrument with a maximum loading of 250 mg (precision ± 0.05 μg), having a quartz pendulum suspended on a quartz fibre. Mettler has introduced two types of balance, the UM-7 and UM-6, which weigh with a precision of ± 0.2 or ± 1 μg. Bunge manufactures an equal-armed damped ultramicro-balance for a loading of 0.75 g (precision ± 1 μg). Recently, the electromagnetic microbalance manufactured by Cahn (Cahn Gram Balance Model) has been especially successful. The pendulum is firmly connected to a coil which is placed in a magnetic field. The rotation moment induced by the sample weight is compensated by an electromagnetic moment. The necessary compensation current, which is proportional to the weight of the object on the balance pan, is measured. The precision is about ± 1 μg for the finest range. It is important that no specially designed surfaces or air-conditioned rooms are required with these balances and that they are almost insensitive to temperature changes and/or shocks. Sartorius manufactures a similar type of ultramicro-balance, the Model 4125 and Mettler the Model ME-22. These instruments have an electrical output so that the weight can be registered as an electrical signal.

These micro-balances are not suitable for classical gravimetric elemental analysis as they have a maximum load of only 1.0 or 1.5 g. However, they are excellent for the purposes of modern elemental analyzers.

B. Sample preparation and introduction into reaction space

The preparation of the sample plays a very important role in micro- and especially in submicro-analysis. Maximum purity of the sample and care during all manipulations are essential. The sample is, as a rule, weighed into boats from aluminium or platinum foil and, in most instances, is covered with a small amount of catalyst. Different storage reservoirs[32,72,151] are used with fully automated instruments. They not only permit the fully automatic operation of the analyzer, but also contribute to more precise results as the whole series of samples are equally conditioned. Volatile or subliming samples must be sealed in glass or closed in metal capillaries (*e.g.*, silver).

The sample being analyzed is transferred into the pyrolytic zone of the reaction tube in two ways. In the vertical arrangement, it falls by its own weight into a heated reaction tube after the revolution of the sampling disc[32,151]. In the horizontal arrangement, the sample is introduced into the pyrolytic zone with the aid of a quartz rod[72]. Further development of the sampling systems can be expected in the near future as current efforts are aimed at automating all the functions of the analyzer.

C. Mineralization of sample

The present state of elemental analysis was no doubt affected by the long systematic development of combustion processes and particularly by the development of oxidative catalysts[76,80,154]. The process of combustion of the sample has been the subject of substantial changes, and it is useful to mention at least the principal developments.

Combustion "in an empty tube", re-introduced by Belcher and Spooner[8], did not find wide application in spite of later improvements[7,81,85,104,127,141]. Nevertheless, combustion in an empty tube in the atmosphere of oxygen under the static conditions suggested by Ingram[75] is interesting.

Tremendous interest was devoted to the development of oxidants. The use of automated elemental analyzers required the combustion of all types of organic compounds to be as rapid as possible, with reliable removal of interfering substances. The traditionally used CuO is not always sufficiently active and higher temperatures (minimum 900°) or longer reaction times are required. The decomposition product of $AgMnO_4$[95], with an optimum operating temperature of 550°, and that of Co_3O_4[166], with an optimum operating temperature of 700–750°, proved to be more advantageous in many instances. The use of these catalysts permitted the reduction of the combustion period, lower operating temperatures and higher flow-rates of oxygen. The decomposition product of $AgMnO_4$ absorbs halogens and sulphur oxides at the same time, which, although advantageous, also causes a rapid decrease in the activity of the catalyst. The optimum conditions for combustion on Co_3O_4 were studied by Večeřa[164,165].

The pyrograms of organic compounds of different types differ considerably, depending on the catalyst used. The efficiency of the decomposition products of $AgMnO_4$, Co_2O_3, CuO, MgO, V_2O_5, MnO_2 and WO_3 was studied from this viewpoint by Chields[33] who found $AgMnO_4$ to be the most efficient. Of other oxidative catalysts, NiO[38,39] and CeO_2[27], which can be used at relatively high temperatures (900–950° and 1050–1100°, respectively) proved to be efficient. Metallic platinum[85] is also a useful catalyst, particularly when the retention of some oxidation products is undesirable.

A list of papers dealing with oxidative catalysts for the determination of C, H and N is published every year, and these are summarized biannually[102], as are other papers concerning elemental analysis.

Methods of combustion can be divided into two groups:

(*i*) Combustion with catalysts based on metal oxides, which act as oxygen donors both in oxygen and in an inert atmosphere;

(*ii*) combustion with metallic catalysts (*e.g.*, platinum) or without any catalyst in an oxygen atmosphere.

Further possibilities are combustion in a static system (pure oxygen; an inert gas; oxygen plus an inert gas) or in a dynamic system (pure oxygen; mixture of an inert gas with oxygen).

The rapid and total combustion of compounds of all types is achieved satisfactorily by combustion under static conditions in an oxygen atmosphere at high temperature (minimum 900° with CuO) in a long layer of the catalyst. The use of a longer layer results in a longer catalyst life and ensures complete combustion. This

procedure is used in most of the commercial analyzers but a source of very pure oxygen is necessary (if nitrogen is determined simultaneously).

An attractive method is as follows. The combustion is performed in an inert atmosphere under static conditions with the sample covered with a catalyst (MnO_2, Ag_2O, Co_3O_4, WO_3, V_2O_5, CuO) that acts as an oxygen donor, and the oxidation of the decomposition products is completed in a common layer of the oxidative catalyst.

If the prevention of any retention of accompanying elements (such as sulphur or halogens) is required, combustion must be carried out in an oxygen atmosphere without a catalyst at a high temperature (minimum 900°) or with platinum (below 850°, as platinum reacts with halogens at higher temperatures).

The determination of oxygen can essentially be based on two methods: the hydrogenation suggested by Ter Meulen[158] and on the reaction with carbon developed by Schütze[148]. The former method is rarely used as it is suitable for simple compounds only; sulphur and halogens poison the catalyst. The advantage is a relatively low operating temperature of the catalyst (400°). The disadvantage is an unfavourable gravimetric factor O_2/H_2O, the significance of which can be suppressed by using a combination with a non-gravimetric determination. Methods based on reactions with carbon are mainly used for the determination of oxygen at present:

$$\text{Organically bound oxygen} \rightarrow CO + CO_2 + H_2O$$
$$CO_2 + C \rightarrow 2\,CO$$
$$H_2O + C \rightarrow CO + H_2$$
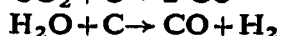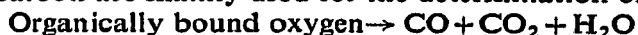
The substance is pyrolysed in a stream of an inert gas (N_2, He, Ar) or hydrogen and is passed through a layer of carbon at 1120°, through a layer of platinized carbon at 900°[123] or through a layer of nickellized carbon at 900°[97,159,170]. Oxygen is determined directly as CO[17,52,159] or as CO_2 after subsequent oxidation (e.g., refs. 17 and 170).

The determination of sulphur is based on both oxidative and reductive methods. In the former method, the determination can be complicated by the formation of of SO_2 and SO_3 (equilibrium). Pure SO_2 is produced only under suitable conditions, such as, for example, oxidation on platinum at 850° in a stream of pure oxygen[10,30], and on a vanadium catalyst at 1200° in pure oxygen[147] or a mixture of helium and oxygen[22]. Reductive conversion of sulphur into hydrogen sulphide proceeds best on metallic platinum at 1000° in a stream of hydrogen[124]. The complications are caused by the carbon that is deposited on the surface of the catalyst and, therefore, must be removed by oxidation when necessary.

Halogens can be determined as such after the oxidation of the sample[9,108] or as hydrogen halides after hydrogenation[37,73]. Fluorine is determined as chlorine after reaction with NaCl[139].

The determinations of arsenic[15] as AsH_3 and phosphorus[29] as PH_3 are also interesting.

D. Separation of reaction products

GC has two interesting features as regards elemental analysis. It permits the rapid separation of the reaction products, and a detection system can be used, particularly a thermal conductivity detector with its accessories (recorder, integrator), such that the whole procedure can easily be automated. These advantages in comparison with classical elemental analysis would not apply if the precision of ±0.3%, accepted

in elemental analysis, could not be satisfied in the determination of every element. This demand can be satisfied in GC only with strict stabilization of all the parameters that affect both the chromatographic process in the column and the operation of the detector with its electrical accessories. Therefore, we shall discuss individually the important parameters in more detail.

The reaction products produced by the degradation of the compound during elemental analysis can be separated chromatographically in three ways: by the elution, displacement or frontal technique.

The *elution* technique is characterized by the instantaneous introduction of a certain amount of the mixture into a column filled with a suitable sorbent. This mixture is carried through the column by a stream of an inert gas. During this process, the components of the mixture are separated between the mobile and stationary phases, and as a result the individual components move towards the column outlet at different rates, *i.e.*, they are separated in the form of zones that leave the column in series. The size of each zone bears a relationship to the quantily of the particular component present and the elution time to the quality of this component.

The reaction mixture is introduced instantaneously also in the *displacement* technique. The reaction mixture moves through the column owing to displacement by a substance (the displacer) being introduced into the column continuously as the pure vapour or as an inert gas saturated with it. The displacer must be adsorbed most, whereas the carrier gas must not be adsorbed at all. The displaced components affect one another in the same way, leaving the column one after another according to their adsorption abilities in individual steps that represent pure components. The period during which any individual component passes through bears a relationship to the amount of the component present.

In the *frontal* technique, the mixture to be analyzed is introduced into the chromatographic column continuously in its original form or after dilution with the carrier gas. Individual components are separated between the mobile and stationary phases with a delay that is proportional to their adsorption abilities. The individual components leave the column in the form of steps. The first step corresponds to the first component, the second step to the first and second components, the third step to the first, second and third components, and so on, according to the increasing adsorption abilities of individual components. The procedure continues until the mixture with the original composition starts to leave the column. The height of each step bears a relationship to the amount of the particular component present.

The elution technique has been applied almost exclusively up to now. The successful application of this technique requires the instantaneous sampling of the reaction products, always under the same conditions. This requirement is obviously contradictory to the demands of the combustion process that takes place during the elemental analysis of compounds of different chemical natures and present in various amounts. The displacement technique, which is not as sensitive to variations in the rate and amount of the sample mixture, has a serious disadvantage in the unavoidable use of a displacer. This has so many drawbacks from the viewpoint of experimental simplicity and repeatability that this technique is unpractical. The frontal technique was also generally believed to have only slight practical value as it is usually accompanied by competitive adsorption and by mutual interactions of the individual components of the mixture during the chromatographic process. However, it can have

certain advantages[135] in comparison with the elution technique under suitable conditions, as will be shown later.

From the viewpoint of the application of the above techniques and the necessity of joining the reaction tube of an elemental analyzer with the chromatographic column of a gas chromatograph, it is useful to investigate the GC response as a function of the sample input profile.

The type of chromatogram obtained is dependent on the profile of the injected sample in chromatography. Although a series of inlet functions is generally possible, only the types shown in Fig. 1 are of practical interest.
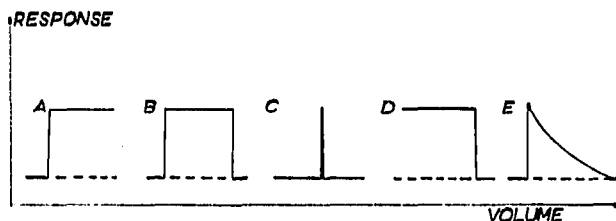

Fig. 1. Input profiles.

In case A, the sample is introduced as a step function, *i.e.*, the concentration of the sample entering the column increases rapidly from zero to a finite value and remains constant at that value (the simplest case of frontal analysis).

Case B represents two stages. The first stage corresponds to A, the second stage is of the same magnitude but negative, and corresponds to an abrupt ending of the sampling into the column.

C is a special case of B. Both concentration steps occur instantaneously on the column inlet (impulse). This is an ideal case of elution chromatography.

The plot in D corresponds to the second stage of B (*e.g.*, the desorption part of frontal analysis).

Case E is an example in which the amount of a component in the carrier gas decreases in a certain manner (exponentially) from the original value to zero (this is caused, for example, by fractionation of the sample in the sampling device, by gradual conversion of the sample in the reactor in a stream of carrier gas (*e.g.*, ref. 131), etc.).

The chromatographic response to the sampled profiles was studied in detail by Reilley *et al.*[134] in Craig's apparatus in connection with several chromatographic processes. The shape of the response profile depending on different lengths of the sample input period in the column is obvious from Fig. 2 for the case of a binary mixture.

Case A represents a large sample input period and is typical of frontal analysis with adsorption and desorption arms. On the other hand, case D is typical for the impulse elution technique. Curves B and C represent intermediate types of both boundary cases and they can be considered as elution chromatograms produced with different sampling periods.

Case B deserves particular attention because of its consequences in quantitative analysis. It represents the injection of the sample for such a time period that the broadening of the central part of the zone of the component during the chromatographic process is of a height that represents the original concentration on the column

outlet (possibility of evaluation from heights). This procedure was called. "step" chromatography by Zhukhovitskii and Turkel'taub[174]. In this case, the sample size must correspond to the condition $V > 3.2\omega$, where ω is the width of the zone (in millilitres) of the elution curve. This method can obviously be applied only when the components can be separated very easily with a sufficient reserve in retention times.
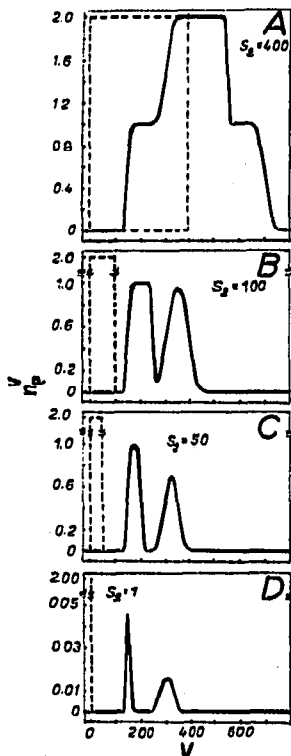

Fig. 2. Input profiles and profiles of the corresponding response for various sampling periods: – – –, input profile; ———, response profile; $s_1 = 0$ in all instances.
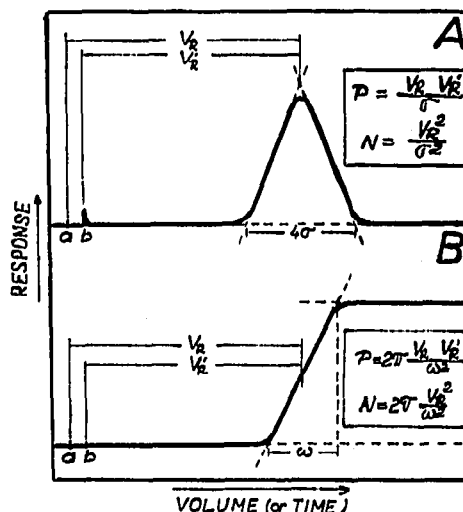
Fig. 3. Schematic diagram of impulse (elution) and stepwise (frontal) response.

The minimum column length for such a separation of two components can be expressed by the relationship

$$L_{min.} = \frac{4H}{K_s^2}$$

where H is the height equivalent to a theoretical plate and K_s is the selectivity coefficient:

$$K_s = 2\frac{V_{g2}^0 - V_{g1}^0}{V_{g2}^0 + V_{g1}^0}$$

Reilley et al.[134] obtained the following relationship for the response for an ideal sampling impulse:

$$R_{(t)} = \sum_j \frac{C_j'}{\sqrt{2\pi}\sigma_j} \cdot \exp\left(\frac{t - t_{Rj}}{\sqrt{2}\sigma_j}\right)^2$$

where C_j' corresponds to $\int C_j dt$ and C_j is the concentration of component j in the sample, $\sum_j$ is the sum of j components and σ_j is a half of the carrier gas volume corresponding to the inflection points of the peak of component j. The response is shown schematically in Fig. 3A for a single component, where

$$N = \frac{t_R^2}{\sigma^2}$$

and N is the column efficiency for a given solute.

The following response to an input step holds in frontal development:

$$R_{(t)} = \sum_j \frac{C_j}{2} + \sum_j \frac{C_j}{2} \cdot \text{erf}\left(\frac{t - t_{Rj}}{2\sigma_j}\right)$$

This relationship is an integrated form of the previous one. Consequently, the profile of the step response is identical in shape with the integral of an impulse response.

The step response for a single component is illustrated in Fig. 3B. If t values are large, the response approaches C_j, the inflexion point occurs at $t = t_R$ and the slope at that point is given by $C_j/\sqrt{2\pi}\sigma$. Hence,

$$\omega = \sqrt{2\pi}\sigma$$

and for the column efficiency for the given solute

$$N = 2\pi\frac{t_R^2}{\omega^2}$$

The response for a double step input (Fig. 1B) when the second step occurs at $t = t_2$ is given by

$$R_{(t,j)} = \sum_j \frac{C_j}{2} \cdot \text{erf}\left(\frac{t - t_{Rj}}{2\sigma_j}\right) - \sum_j \frac{C_j}{2} \cdot \text{erf}\left(\frac{t - t_2 - t_{Rj}}{2\sigma_j}\right)$$

where two steps of impulse are $\sum_j C_j$ and $-\sum_j C_j$.

If the value of t_2 approaches zero, the response to the double step input approaches the response to the impulse that contains the same number of moles.

If $t > t_2 \gg t_R$, the first summation in the preceding relationship approaches the value of $\sum_j C_j/2$; then, for the backstep (Fig. 1D):

$$R_{(t,j)} = \sum_j \frac{C_j}{2} - \sum_j \frac{C_j}{2} \cdot \text{erf}\left(\frac{t - t_{Rj}}{\sqrt{2}\sigma_j}\right)$$

Hence, the backstep for a given component is geometrically symmetrical to the front step. It is supposed that the response to any impulse tends to a Gaussian distribution function in the above examples.

From the preceding evaluation, it can be seen that both frontal and elution developments can provide virtually the same information. If we disregard the identi-

fication aspect and consider the possibilities of quantitative analysis, we arrive at the following conclusions.

(a) Impulse elution method

The impulse elution method permits the evaluation of both peak heights and peak areas. It is rather difficult to express all the effects that influence changes in the concentration of the separated components during their passage through the column. Resulting from this process, in contrast to frontal development, a significant decrease in the concentration in peak maxima takes place. The decrease in peak height h_j for further components sometimes cannot be neglected, in accordance with the following equation:

$$h_j = \sqrt{\frac{N_j}{2\pi}} \cdot t_{R_j}$$

where N_j is the column efficiency.

There is no simple correlation between peak height and the amount of a component present. The correlation of peak height with concentration is generally a linear function in a narrow range of concentrations only. This range is affected not only by the linearity of the adsorption isotherm but also by the geometrical parameters of the column. The peak height is very sensitive to changes in performance, particularly to changes in temperature, carrier gas flow-rate and, of course, in any change in the sample introduction into the column. The last condition can, especially in elemental analysis, play the most decisive role. However, the peak height evaluation will be fully justified in the case mentioned under B in Fig. 2, which can be utilized with advantage particularly in elemental analysis. It should be mentioned that the above drawbacks of the elution impulse analysis (decrease of the concentration maximum with time) do not hold for this case.

The determination by peak area is used most often. Peak area can be expressed mathematically as a time integral of the detector response, which can be directly correlated with the concentration of the component in the carrier gas or with the mass of the component which passes through the detector per unit time. It permits the evaluation of both rapidly and slowly eluted components. The methods used earlier, such as cutting the peaks from the chromatogram and weighing them, further planimetering, multiplying the peak height by the retention time, multiplying the peak height by its width at half-height, etc., are not suitable in the present case. All these methods are time-consuming and introduce considerable errors[4,77]. The same also occurs in the use of mechanical and electromechanical integrators. Electronic digital integrators working independently of recorders are the most suitable means. The combination of a recorder and an integrator usually suffers from the error resulting from the non-linearity of both of the systems[126]. Even though the integrator itself operates with a virtually negligible error, its combination with a detector and a chromatographic column provides results that are less favourable[26].

(b) Frontal analysis

In frontal analysis quantitative results can be obtained relatively easily from the heights of both the adsorption and desorption steps for a given compound, as both of these heights are proportional to the original concentration of the compound.

This, however, holds only under certain conditions: (*i*) The sorption isotherms of solutes must be linear and independent of one another; (*ii*) the detector response must be linear over the whole concentration or mass range; and (*iii*) there must be no interactions among the chromatographed components that would affect the linearity of the detector response. .

These conditions are satisfied only with mixtures that are strongly diluted with an inert gas. However, there is a further reason why it is necessary to use strongly diluted mixtures (maximum concentration <1%). As shown in Fig. 4, which demonstrates the frontal development of a binary mixture of components A and B, the molar fraction of component A (x_A^1) in the first step is enriched in comparison with the original state. This occurs for two reasons[144]. Component B is adsorbed on the boundary of both the steps so that only the mixture of A and T (carrier gas) may keep moving. The enrichment occurs even though the ratio of A to T does not change. As $x_A^1 > x_A^0$, the mass difference must be desorbed during the shift of the boundary and the released fraction of component A increases the ratio of A to carrier gas.
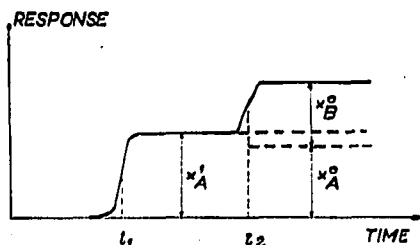

Fig. 4. Frontal chromatogram of a binary mixture.

If both of the components are distributed independently of one another according to their constant partition coefficients, K_A and K_B, then

$$x_A^0 = \frac{\dfrac{x_T^0}{x_T^1} - \dfrac{K_A}{K_B}}{1 - \dfrac{K_A}{K_B}} \cdot x_A^1$$

Hence this enrichment is not the result of any displacement. If A is displaced by B (in the case of multiple mixed adsorption), it appears in an additional increase in x_A^1. The changes in the flow-rate at the column outlet are also connected with the above changes. A similar situation occurs with multicomponent mixtures, although it is, of course, even more complicated. In this respect, it is inherent in frontal development that quantitatively correct results cannot be obtained without complicated corrections of the experimental results. However, for a strongly diluted mixture (total concentration of solute less than 1%), $x_T^0 \approx x_T^1 \approx 1$, so that $x_A^1 \approx x_A^0$; the enrichment effects mentioned are negligibly small, as are the changes in the flow-rate at the column outlet. They can therefore be neglected, particularly if a calibration is carried out with a model substance of a similar composition. Under these conditions, it can be assumed that the concentration of any component remains virtually unchanged during the

passage from one step to another, so that the concentration of the component in the following step may simply be added to the preceding one.

Frontal development necessarily also includes the desorption process. Hence two records, which can be quantitatively treated, are obtained in a single analysis. This fact can sometimes be statistically significant, e.g., in the determination of carbon.

The selection of a suitable sorbent, a sufficiently universal and selective detector, and the most suitable temperature and flow-rate are responsible for optimum column performance.

The reaction products are sometimes diluted with carrier gas under steady-state conditions before the separation itself, and only after the establishment of diffusion equilibrium are they subjected to further analysis[135] or only a small part of those products is analysed[147]. This permits the analysis of even larger amounts of sample (semimicro-analysis) and, to a great extent, the duration of the reaction process for an optional period of time. The latter method allows the reaction process to be carried out in a gaseous medium other than that of the carrier gas without the necessity of removing the rest of the first gas, e.g., by absorption. On the other hand, this necessitates a sampling device that may be a source of error (except for case B in Fig. 2). An example is combustion in oxygen and the sampling of the reaction products simultaneously with the remainder of the oxygen passing into the chromatograph with hydrogen carrier gas.

(c) Selection of carrier gas and sorbent

The selection of the carrier gas is closely related to the type of detector used. As in most instances a katharometer is used, the carrier gas is restricted to helium or hydrogen. Oxygen can be used in exceptional cases and only in combination with a thermistor sensing element. Of other gases, only argon and nitrogen can sometimes be used, if the response to the component being analyzed is favourable, provided that the response to the corresponding components is linear over a wide range of concentrations, e.g., when determining carbon monoxide in nitrogen[89]. In any event, it must be taken into consideration that the use of oxygen, nitrogen or argon as the carrier gas complicates the response of the katharometer because, in addition to thermal conductivity, heat convection plays a significant part and increases the detector time constant of diffusion-type detectors, with practical consequences that will be mentioned later. Table I gives examples of the use of different carrier gases in elemental analysis.

The selection of an appropriate sorbent is determined by the character of the substances produced by oxidation, reduction or reaction with carbon of the compound being analyzed. Interfering reaction products of some elements must often also be separated. This separation is more useful than the use of selectively or specifically absorbing packings (as far as this is possible at all) that must be changed often, and which make the apparatus complicated. Simple low-boiling substances, which are mostly produced in elemental analysis, permit the use of gas–solid chromatography, while gas–liquid chromatography is used only in exceptional cases. In contrast to classical elemental procedures (and also to some modern analyzers), the use of selective and specific adsorbing tubes makes it possible to determine whether the degradation process is quantitative (e.g., CH_4 originating during an incomplete combustion can be separated and determined chromatographically[82,149]). Thus, molecular sieve 5A

TABLE I

SELECTION OF CARRIER GAS

Element determined	Reaction	Reaction products	Carrier gas
C,H	oxidation	CO_2,H_2O (H_2, acetylene)	O_2,He
C,H,N	oxidation	N_2,CO_2,H_2O	He,Ar
O	carbon contact	CO,CH_4,N_2	He,Ar,N_2,H_2
O	carbon contact, oxidation	CO_2,CH_4,N_2	He
O	reduction	H_2O,CH_4,NH_3	H_2
S	oxidation	SO_2,CO_2,H_2O,O_2	He
S	reduction	H_2S,CH_4,H_2O,NH_3	H_2
S,halogens	oxidation	Cl_2,Br_2,I_2,CO_2,SO_2	He
S,halogens	reduction	HCl,HBr,HI,H_2S	H_2
As	reduction	AsH_3	H_2
P	reduction	PH_3	H_2

is suitable for the determination of oxygen by reaction on heated carbon if the oxidation is terminated after the first step (CO). The separation of CO, CH_4 and N_2 is possible —when nitrogen is used as the carrier gas, by the separation of CO and CH_4.

The chromatographic separation of carbon, hydrogen and nitrogen as CO_2, H_2O and N_2 was previously rather a problem. Water, which is a strongly polar and a relatively high-boiling compound, differs substantially in its properties from the other two components, so that a rapid single-step separation was practically impossible. A number of workers solved this problem by the selective adsorption of water and its subsequent desorption[169,172], or by its conversion into H_2 (e.g., refs. 2 and 115) or into C_2H_2 (e.g., ref. 153). The conversion reactions of water were studied in detail by Belcher[6]. From the practical viewpoint, all these reactions are complicated and can be used only with certain restrictions. Another solution was based on the use of two columns[20]; water was separated from N_2 and CO_2 in the one column and N_2 was separated from CO_2 in the other column.

This problem was finally solved by the introduction of new sorbents based on vinylethylbenzene–divinylbenzene copolymers[68,69], which are manufactured under the names Porapak P and Q (Waters Associates, Inc., Framingham, Mass., U.S.A.) or Synachrom (Research Institute of Lacquers and Resins, Pardubice-Rybitví, Czechoslovakia), etc. These sorbents are suitable also for the separation of SO_2, H_2S, CH_4, etc. In some instances, silica gel also proved to be useful for this purpose[124,127].

Gas–liquid chromatography was used for the separation only when the determinations of halogens or HX and SO_2 were concerned. Kel-F silicone oil or grease[108], other halogenated hydrocarbons, dinonyl phthalate[30], etc., were used as stationary phases.

III. QUANTITATIVE DETERMINATION OF REACTION PRODUCTS

A. Detector

The katharometer is the most commonly used detector in elemental analysis.

Its superiority lies in the fact that it gives a signal to all the reaction products that may be produced (CO, CO_2, H_2O, CH_4, N_2, H_2S, SO_2, etc.). Its other valuable properties, such as sufficient sensitivity, simple construction, reliability, commercial availability and cheapness[79], are also important. Of other detectors, the gas density detector[16,109,118] has been used with strongly reactive compounds such as halogens and hydrogen halides and some of the ionization detectors are also useful.

The katharometer can be classified as a concentration detector. Its signal is proportional to the concentration of the effective gas in the carrier gas that flows through the cell and does not depend substantially on the gas flow-rate. Several conditions concerning the construction of the sensing element and the selection of the operating conditions must be fulfilled. When using a katharometer for detection, the changes in resistance of an electrically heated wire round which the gas flows are measured. These changes reflect changes in heat transfer between the wire and its surroundings, due to heat conduction by the gas from the wire to the detector walls, to heat convection, to radiation and/or to parasitic heat conduction by the wire protectors.

If a carrier gas that has a high thermal conductivity, such as hydrogen or helium, is used, then the contribution of heat convection and radiation as well as parasitic heat conduction is negligible[120]. The use of hydrogen or helium leads also to a low time constant of the detector, to a wider range of response linearity and to high sensitivity.

B. Recorder, integrator or digital voltmeter

It is generally assumed that the maximum possible speed of the recorder pen sweep is substantially higher than the change in signal with time and that the time constants of both the detector and the recorder are substantially lower than the passage time of a chromatographic peak or frontal step through the sensing cell. Under these conditions, the response is not distorted by the recorder and the relationship between the signal and response is linear and can be expressed by an apparative constant[120]. However, these conditions are not always fulfilled, particularly in rapid analysis by elution techniques[59,93].

The detector response is regularly registered by a recorder in the form of a chromatogram. Recorders balance the detector signal with an electrical signal of the same value but of the opposite sign. A number of line recorders are manufactured at present, but only recorders with the best parameters are suitable for elemental analysis. Of these parameters, the most important are: high sensitivity, rapid pen sweep (≤ 1 sec over the whole scale), high precision ($\leq 0.2\%$ of the scale range), low inertia, automatic sensitivity reduction or a scale expansion if the pen moves further than the scale range, a linear record over the whole scale range and at different sensitivity values, and a wide record (minimum 250 mm)[61].

Mechanical disc-integrators combined with recorders usually suffer from considerable errors and will be less advantageous for use in elemental analysis. The output signal of the disc-integrator can be converted by means of a transformer into the digital signal that provides the numerical value of the peak area.

Electronic integrators operate on the principle of voltage-to-frequency transformation, have no mechanical working parts, and are rapid in operation, virtually without inertia and easily adaptable to a digital output. Because of their good per-

formance and precision, they are now in general use and are known as digital electronic integrators. The present trend is for the integrator to be separated from the recorder. Most of the modern high-efficiency integrators have a wide dynamic linear range with 10^3–10^6 impulses per sec and are equipped with automatic baseline and baseline drift corrections. The printing device is usually connected to the integrator. The reproducibility of the peak areas is about ± 0.2–0.4%[5,162].

Digital voltmeters can be used directly in frontal analysis, either connected to a recorder (less exact arrangement) or directly independent of the recorder.

C. Accessories

Most accessories are the same as those used in GC. Pneumatic regulation systems, thermostats that enable precise measurements of temperature (better than $\pm 0.1°$) to be made, electrical accessories of the katharometer, Wheatstone bridge, sources of stabilised d.c. voltage, pneumatically controlled valves, etc., are particularly concerned.

The destruction part of the apparatus, of course, is particularly important. It consists mainly of reaction tubes (quartz glass or special metallic alloys), and of ovens whose temperature can be regulated, such as are usually used in classical elemental analysis. Entirely automated instruments are equipped with special sampling devices that are operated automatically in relation to the combustion, separation and registration cycles. The electrical accessories of such instruments usually include a suitable time programmer. Automatic samplers are designed for a greater number of samples so that flushing of the reaction tubes can be omitted and, in addition, samples are conditioned under identical conditions[32,71,151].

IV. CONCEPTS OF INSTRUMENTATION AND COMMERCIAL ELEMENTAL ANALYZERS

There are several possible instrumental arrangements of the individual parts of an elemental analyzer with a gas chromatograph:

(*i*) Direct injection of the sample into a carrier gas stream on the reactor inlet connected directly to the chromatographic column.

(*ii*) Injection of the sample into the reactor by means of a by-pass; degradation is effected under static conditions and the reaction products are then flushed into the chromatographic column.

(*iii*) Injection of the sample into the reactor; degradation is carried out under static or dynamic conditions and the reaction products are then flushed into a dilution chamber where the establishment of steady-state conditions takes place; a certain amount of the sample is then injected into the column.

(*iv*) Injection of the sample into the reactor, followed by degradation under static or dynamic conditions, then elution into a dilution chamber, establishment of steady-state conditions and a continuous introduction of this mixture into the column (frontal development).

Diagrams and the corresponding records demonstrating these cases are shown in Fig. 5.

All the concepts of elemental analyzers are shown below in order to survey and present an instructive comparison, disregarding whether they use a chromatographic separation or not. Most of them have been summarised in the literature[12,40,103,145].
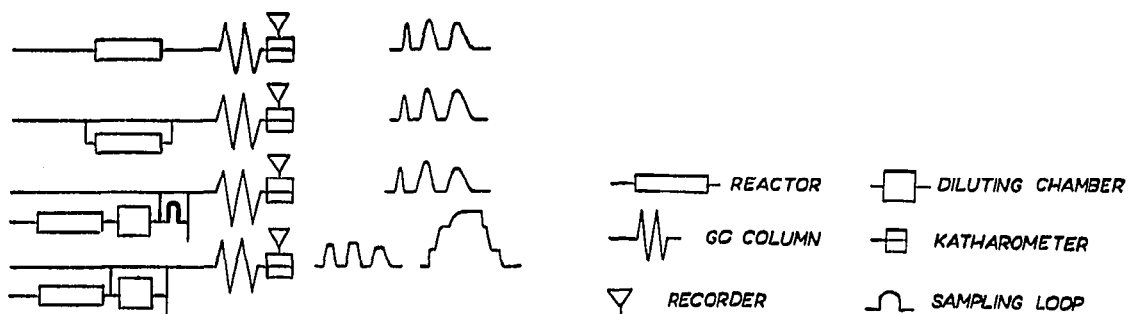
Fig. 5. Arrangement of the key parts of an elemental analyzer using gas chromatographic separation and the shapes of the corresponding chromatographic records.

A. Aminco

In the Aminco analyzer, oxygen is used as the carrier gas[2,114,115], combustion is carried out under dynamic conditions at 1000°, CuO is used as the catalyst and detection is carried out with a thermistor thermal conductivity cell. It can be seen from Fig. 6 that the sample of 0.2–1.0 mg falls from a sampling valve on to the beginning of a packed reaction tube and is immediately burned. A mixture of CO_2 and H_2O in oxygen flows through a layer of silica gel where water is extracted. While CO_2 passes through the katharometer and is registered, H_2O is desorbed by an increase in temperature, converted into H_2 by reaction with CaH_2 and determined. The final
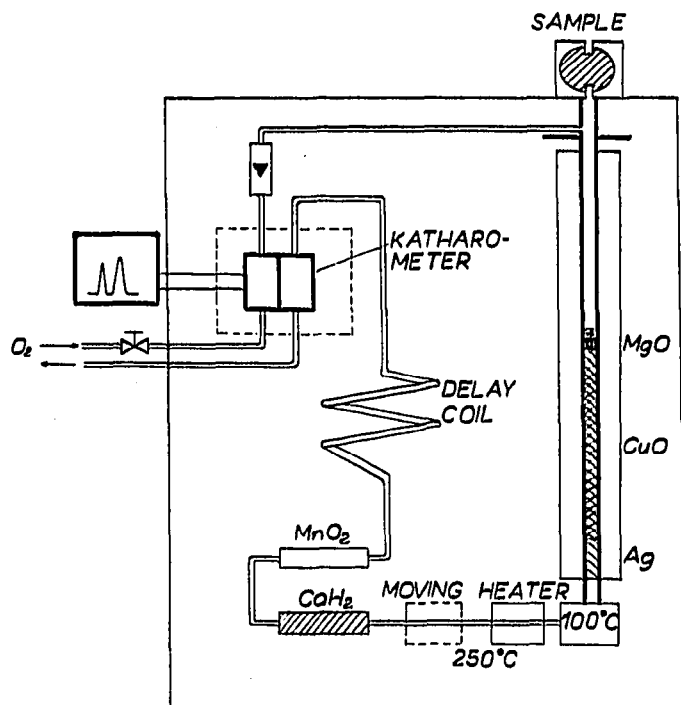

Fig. 6 Aminco analyzer.

evaluation is based on peak height measurements. The total operation time from the introduction of the sample is about 90 sec.

B. Hewlett-Packard[20,21,64].

The C, H and N analyzer is shown in Fig. 7. The sample, preferably 0.25–0.6 mg, is covered with catalyst (WO_3–MnO_2 mixture) and then burned under static conditions in helium at 1050° on CuO. Unreacted oxygen is absorbed and nitrogen oxides are reduced in a tube packed with copper. The mixture of N_2, CO_2 and H_2O is separated in a GC column and simultaneously detected with a katharometer. The evaluation is based on the measurements of peak heights or peak areas. The apparatus is coupled with a Cahn electrobalance and the "ratio-recording" technique is used. The response, proportional to the weighed amount, is registered directly by a recorder and the detector signals are calculated relative to the weighed amount by a compensograph, so that samples with identical compositions give equivalent peak heights (areas) regardless the amount of the sample used.
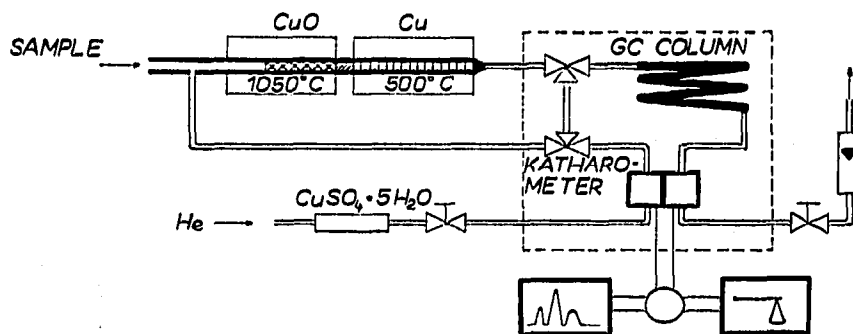

Fig. 7. Hewlett-Packard F&M analyzer.

C. Fisher Scientific

The Fisher Scientific analyzer is shown in Fig. 8. The combustion is based on
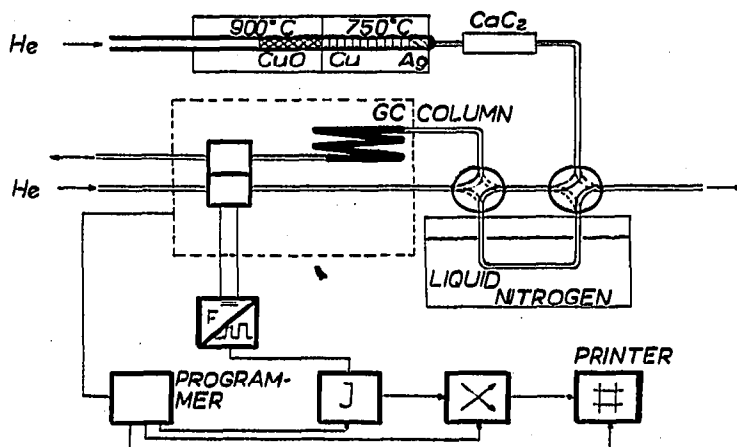

Fig. 8. Fisher Scientific analyzer.

the Dumas principle, H_2O is converted into acetylene, all the reaction products are condensed in a trap cooled with liquid nitrogen, then evaporated immediately, separated by GC and determined with a katharometer in the sequence $N_2-CO_2-C_2H_2$.

D. Technicon and Heraeus

Technicon[157,172] and Heraeus[24,25,62,117] developed analyzers based on Walisch's principle[169]. It can be seen from Fig. 9 that the combustion occurs in a stream of helium
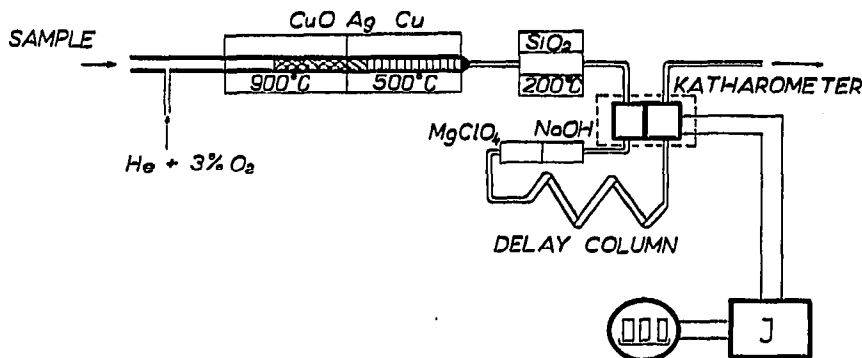

Fig. 9. Analyzer based on Walisch's principle[169] (Technicon and Heraeus analyzers).

plus 3% oxygen; excess of oxygen is extracted in a copper packing, which simultaneously reduces nitrogen oxides to nitrogen. Water is adsorbed on silica gel, and a mixture of CO_2 plus N_2 and later, after the absorption of CO_2, pure nitrogen is detected by means of a katharometer. Finally, H_2O is determined after thermal desorption. The instruments of these two firms differ only in the final treatment of the signal. The Heraeus analyzer also permits the determination of oxygen after pyrolysis of the sample in helium, reaction on a carbon contact and separation of the gases produced (N_2, H_2, CH_4 and CO) on a molecular sieve 5A column.

E. Perkin-Elmer

Perkin-Elmer manufactures an analyzer (Fig. 10) based on the concept of Simon and co-workers[13,151] with certain improvements[14,128] for measuring concentrations of individual components. Samples of up to 3 mg are burned under static condi-
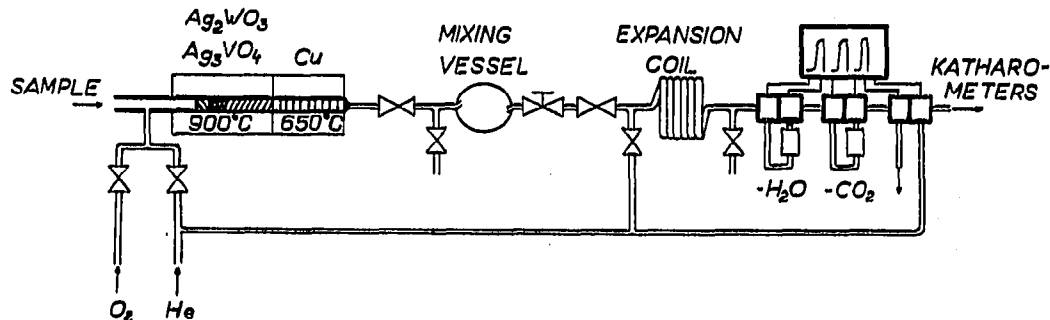

Fig. 10. Perkin-Elmer analyzer.

tions in pure oxygen with common catalysts or on special fillings[19,56]. The mixture of combustion products is purged with a stream of helium through a Cu column (extraction of oxygen, reduction of nitrogen oxides) into a dilution flask where steady-state conditions are established by diffusion. After the establishment of equilibrium, the mixture is allowed to expand into a long spiral tube and then displaced with helium at a constant flow-rate through a system of three katharometers between which selectively absorbing packings are arranged in series to effect the removal of water and CO_2. The concentrations of all the components can therefore be determined from the stepwise measured difference between the individual signals.

F. Carlo Erba

The Carlo Erba analyzer (Fig. 11) permits the analysis of C, H, N and O. It is based on the same principle as the Hewlet-Packard F&M analyzer. It has a special sampling device for 23 samples, which feeds individual samples automatically into a
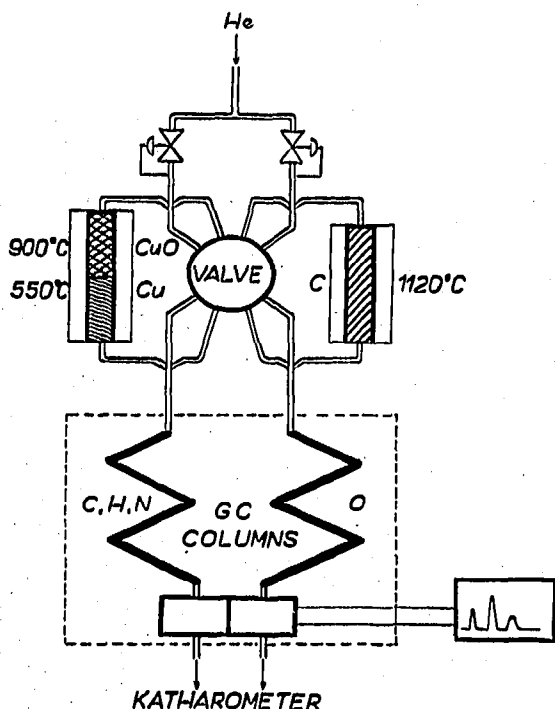
Fig. 11. Carlo Erba analyzer.

combustion space where they are combusted in oxygen under static conditions. The reaction products are separated by GC and detected with a katharometer. An automatic sensitivity selector permits the use of the entire recorder scale. A combination with an electronic integrator and a printer contributes to complete automation. The determination of oxygen is carried out in the same way as for C, H and N analysis. After reaction on a carbon contact, CO is separated on a molecular sieve 5A column.

G. *Yanagimoto*

The Japanese firm of Yanagimoto[173] developed a C, H and N analyzer (Fig. 12) based on the work by Hozumi[70]. In principle, it is similar to the Perkin-Elmer analyzer, the only difference being that the dilution flask and expansion tubes are replaced with a cylindrical chamber with a mechanically controlled piston.
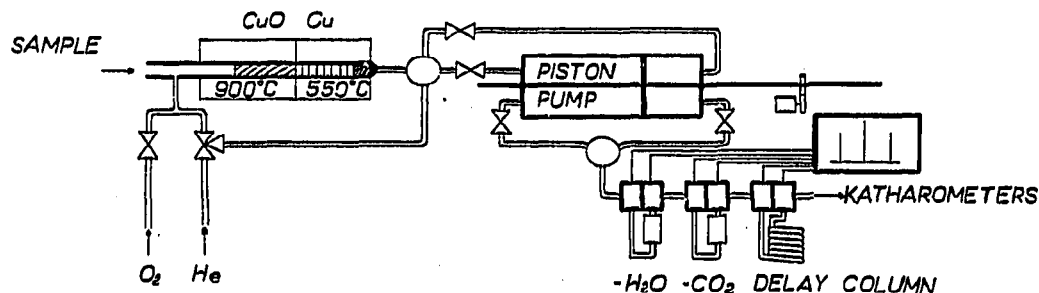
Fig. 12. Yanagimoto analyzer.

H. *Laboratory Instruments N.E.*

Laboratory Instruments N.E. (Pragne, Czechoslovakia) developed a C, H and N analyzer (Fig. 13) based on the GC separation of combustion products by frontal development[135]. The sample, 0.5–2.5 mg, is burned in the usual way under dynamic or static conditions, the mixture of N_2, CO_2 and H_2O produced is diluted with helium and passed into a cylindrical cell with a pneumatically operated piston. After the establishment of steady-state conditions by diffusion equilibrium, the mixture is purged through a chromatographic column packed with Porapak Q and the con-

Fig. 13. Laboratory Instruments analyzer.

centrations of the individual components are detected with a katharometer in the form of frontal steps.

It is evident from this brief survey that only the instruments shown in Figs. 7, 8, 11 and 13 utilise a separation by GC.

V. EVALUATION OF ERRORS IN ELEMENTAL ANALYSIS

Several sources of errors occur in elemental analysis by GC.

Systematic errors rarely occur. It is, for example, an error caused by an imperfect conversion of some samples, such as during the determination of carbon in perfluoro compoun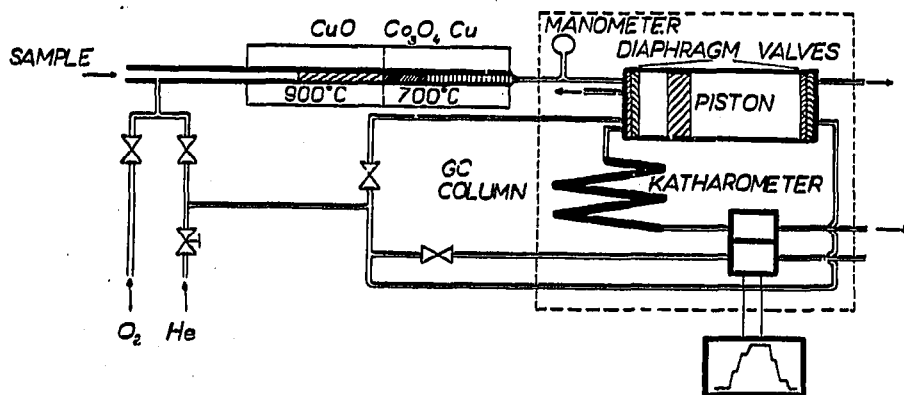ds, thus necessitating the packing of special catalysts. The suitability of catalysts for certain types of substances should be determined first or a universal packing should be used in order to overcome this source of error. Systematic errors also often occur with easily subliming substances if the sample is not adequately treated.

Random errors account for most of the possible sources of errors in the determinations, such as inaccurate weighing, instability of the temperature of chromatographic columns, the carrier gas flow-rate and the katharometer filament voltage, errors due to the recorder (linearity, inertion, distortion by the time constant), errors in peak area measurements (integrator, etc.) or errors in the measurements of peak or front height. If the reaction products are diluted prior to the analysis itself under steady-state conditions, then the effects of drifts and/or fluctuation of the adjusted temperature, pressure and volume must also be considered. The errors caused by manipulations with the sample (covering it with catalyst containing adsorbed water or CO_2; adsorption of CO_2 on quartz walls during the introduction of the sample; imperfect flushing of the combustion space after the introduction of the sample), which are sometimes so significant that they exceed other sources of errors, must be excluded in a reliable analysis. In frontal development, concentration changes must be precisely determined and hence errors that occur during the adsorption and desorption processes and errors due to residual analysed components in the dead volume of the dilution chamber (if interflushing is not carried out) must also be evaluated.

In this and similar instances, a suitable mathematical model can be found for a probable distribution of random errors, which permits the evaluation of their influence on the final result of the analysis by means of parametric methods of mathematical statistics.

When several sources of variance that affect the result are combined, as in the present case, the standard deviation, S, of the result is given by the following relationship[65], if y is a function of a and b and of other variables;

$$S_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 S_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 S_b^2$$

etc., where S_y^2, S_a^2, S_b^2 are the variances (squares of the standard deviations) and $\partial y/\partial a$, $\partial y/\partial b$ are the corresponding partial derivatives of the function y.

Hence, the error of the final determination of individual elements can be estimated if all the conditions are known and if the conditions for the maximum error that is required can be stabilised.

In this way, Clerc et al.[12] studied the influence of the variance of response, weighing, pressure and temperature establishment, and of the fluctuating filament voltage of the katharometer, on the final error of the C, H and N determinations for the suggested analyzer, which became the basis for the Perkin-Elmer analyzer.

Similarly, Shimizu and Hozumi[152] carried out a statistical analysis of the C, H and N determinations with a C–H–N Corder MT-2 analyzer. They considered the

TABLE II

COMPARISON AND EVALUATION OF DIFFERENT COMMERCIAL ANALYZERS

Instrument	Method of measurement	Sample (mg)	Analysis time (min)	Absolute standard deviation (%)			Reference
				C	H	N	
Hewlett-Packard	GC and thermal conductivity	0.5–1.8	15	±0.28	±0.16	±0.13	66, 67
Carlo Erba	GC and thermal conductivity	0.5–1.8	10	±0.30	±0.10	0.20	132
Aminco	Adsorption, GC and thermal conductivity	0.4–1.0	8	±0.15	±0.12	±0.18	58, 99
Technicon	Adsorption and absorption and thermal conductivity	0.2–0.5	16	±0.3	±0.15	±0.4	157
Perkin-Elmer	Absorption and thermal conductivity	1.0–3.0	13	±0.21	±0.15	±0.17	128
Yanagimoto	Absorption and thermal conductivity	2.0–2.5	18	±0.20	±0.20	±0.20	70
Laboratory Instruments N.E.	GC and thermal conductivity (frontal development)	0.5–2.5	10	±0.20	±0.15	±0.20	136, 138
Heraeus	Adsorption and thermal conductivity	3.0–6.0	20	±0.18	±0.08	±0.18	113

following sources of errors: (A) sample weighing, (B) record reading, (C) measurement of atmospheric pressure, (D) detector temperature, (E) response, (F) fluctuation of bridge filament voltage, and (G) the sum of other functions. It was shown that the errors caused by fluctuation of the bridge voltage with those included in the sum of other functions (F and G) contributed several-fold more to the final error than the other sources (A to E). The relative stability of the output voltage from a stabilised source supply increased with increasing voltage. By increasing the bridge voltage from 2.1 to 6.7 V, the precision of the results was improved significantly and the contributions of F and G were thus reduced to a quarter of their original value.

A question that is often discussed is whether or not the precision limits usually stated for elemental analysis, ±0.3% for individual elements, are a correct criterion. This question cannot be answered simply .The precision given is satisfactory in most instances. If elemental analysis is used for testing one of the more likely empirical formulae of an organic compound, this demand on the precision can be too stringent in some instances, and unsatisfactory in others.

The problem of homogeneity of the substances being analysed, which can restrict the size of the weighed sample, is indirectly associated with the question of the analytical precision. In this respect, analyzers with the widest possible performance range (submicro- to semimicro-scale) are, and will be, preferred.

The most important parameters of the analyzers discussed, regarding the precision of the results obtained, are summarized in Table II.

VI. OTHER APPLICATIONS

There are other possibilities of the use of this new instrumentation that are quite different from elemental analysis. All C, H and N analyzers are, in fact, instruments for the determination of N_2, CO_2 and H_2O diluted in an inert gas, e.g., helium. The above components may be determined whatever their origin, if they are introduced in a manner similar to their release during the degradation of an organic compound in a combustion tube.

From the viewpoint of possible applications, the existing concepts of analyzers can be divided into three groups:

(i) Analyzers based on the adsorption or freezing of components and elution chromatographic development on a column and determination of the components with a katharometer. These analyzers can be used with sufficient sensitivity only for the determination of CO_2 and H_2O in the absence of other components.

(ii) Analyzers based on the trapping and storage of gaseous mixture in a dilution chamber and on elution of the equilibrated gaseous mixture into a katharometer. By means of these analyzers, in addition to CO_2 and H_2O, N_2 can also be determined with sufficient sensitivity unless other components are present.

(iii) Analyzers based on the trapping and storage of gaseous mixture in a dilution chamber and on frontal development of components on a column and determination by a katharometer. This type is capable, without additional arrangements, of determining individual components of a gaseous mixture (of any composition) with sufficient sensitivity, provided that suitable partition coefficients and reversible adsorption on the chromatographic packing used occur (e.g., a mixture of H_2, N_2, CH_4, CO, CO_2, H_2O, N_2O, C_2H_4, etc.).

For example, it is possible to analyse the contents of carbonates in rocks (*e.g.*, ref. 121) or in mineral waters by determining CO_2 after its evolution. Similarly, water vapour released from rocks, foodstuffs, etc., gases from the fusion of alloys and glasses, gases produced by microorganisms, plant and animal tissues, and gases produced during the differential thermal analysis of solid substances, etc., can be determined.

There are very many possibilities available for the ingenuity of the analyst, and new fields of application will be opened in the near future. The analysis of gases in steels and alloys can be cited as a good example. The analytical methods being used at present in metallurgical practice involve the evolution of gases bound in metals in a special furnace. The evolved gases (H_2, H_2O, N_2, CO, CO_2, SO_2 and CH_4) are usually flushed into a spectral analyzer. The necessity of transporting a small volume of evolved gases (0.1–0.5 ml) with a relatively large volume of inert gas causes diffusion of the gases, so that the application of classical GC for this purpose is limited[1,44,60,78,88,129,175]. The combination with an analyzer operating with frontal chromatographic development[136], in contrast to this, requires the dilution of the evolved traces of gases with a relatively large volume of an inert gas (helium or argon). Frontal chromatographic development then permits the analysis of such gaseous samples of various compositions without additional modifications to the instrument[137].

VII. CONCLUSIONS

It has been shown that the development of instrumental analytical methods has permitted considerable improvement to be made in the elemental analysis of organic substances in recent years. First, it has permitted progress towards micro- and sub-micro-methods and automation of the procedures involved. The change from the classical scale of elemental analysis to the micro-scale is limited mainly by gravimetry at the beginning (weighing of the sample) and at the end of the analysis (weighing of the produced products, CO_2 and H_2O).

It has been shown that analyzers based on the measurement of the thermal conductivity of the combustion products can completely replace the gravimetric part of elemental analysis, with the exception of isolated cases (*e.g.*, ref. 34). At present, there are not enough reliable statistical data that would enable objective comparisons to be made among all the analyzers based on different concepts. The published statistical data are provided mainly by the manufacturers and there is a lack of critical data obtained by a wide circle of users. On the contrary, the present views of many potential users on different analytical instruments have been influenced by their levels of knowledge of GC, which are not identical and are often insufficient.

Elemental analysis by GC has the advantage of greater flexibility because of the possibility of the simultaneous determination of a larger number of elements. For the time being, the character of combustion procedures has not allowed a flash and quantitative degradation procedure.

An evaluation and critical study of whether further chromatographic detectors of medium and high sensitivity can be applied advantageously in elemental analysis are missing. The cross-section detector[79,98,101] permits, for example, the use of carrier gases other than helium (*e.g.*, oxygen), a fact which can be significant for the further

development of elemental analysis. The gas density balance detector[109,118] is suitable, for example, for use with corrosive and unstable substances such as hydrogen halides, halogens, hydrogen sulphide and PH_3, and its sensitivity to all the components produced by the combustion of organic compounds with suitable modification and/or with the use of a carrier gas of high molecular weight (*e.g.*, SF_6) is relatively very high[54].

The combustion process proceeds more easily as the amount of the substance being combusted is decreased. The trend in the development of elemental analysis to the submicro-scale is limited not only by demands on the purity and homogeneity of the minute amounts of substances used, but even more by the precision of weighing. With volatile compounds, the direct combination of a gas chromatograph with a C, H and N analyzer[138] seems to be possible. Submicro-amounts of a pure substance, which cannot be weighed, can be analysed by elemental analysis with very high precision and in a large number of cases. The significance of such a combination for conformational analysis cannot be overlooked as the extent of the information obtained by this combination is greater than that obtained by either method separately.

The decrease in the amount of sample used to a limit of 10 μg must not represent a substantial obstacle for the sensitivity of a thermal conductivity detector. In this connection, the principle of chemical multipliers[110], which enables the absolute amount of CO_2 or H_2O to be increased by as much as two orders of magnitude, has not yet been used. Its application in GC fails as chemical multipliers cause a substantial broadening of the chromatographic peaks and therefore adversely affect the resolving power of a chromatographic column. In elemental analysis, however, this effect need not play any role.

The prices of GC instruments for elemental analysis are much higher than those of instruments of the classical type. It is therefore necessary to impress on the manufacturers that their instruments should be capable of being operated without being attended by specially trained staff. Such simpler concepts will gain the advantage that they do not require the control of many parameters (mainly flow parameters). Further, the applicability of such instruments to a wider field of varied analyses is an important factor.

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