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ELEMENTAL ANALYSIS OF GAS CHROMATOGRAPHIC EFFLUENTS

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1. INTRODUCTION

The qualitative analysis of organic compounds, particularly of their complex mixtures, is often carried out by gas-chromatography (GC). Retention indices[1], which express the relationship between retention behaviour and molecular structure, are commonly used for this purpose. However, as the differences between retention indices determined on two stationary phases of different polarity result from the combined effects of different structural increments of the molecules, they do not necessarily characterize the substances under analysis unambiguously so that the practical applications of this procedure remain limited.

These are the reasons why combinations of GC with UV, IR, Raman, mass and NMR spectroscopy are also significant. These combinations are expensive, however, not only with respect to the cost of the instruments but also the need for specialist operators. It is therefore desirable to supplement them with a method based on cheaper instrumentation that is less exacting as far as the interpretation of the results is concerned and commonly available. In this respect, a combination of GC with elemental analysis (EA) deserves attention.

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As EA is still one of the most commonly used identification methods in organic chemistry and biochemistry, its combination with GC has already been studied, particularly after the introduction of automated instrumentation. Several procedures have been suggested, but only one has found commercial realization[2–5]. A number of difficulties are involved, *e.g.*, the isolation of the separated components leaving the chromatographic column and the unacceptable precision of EA for 1–100 μg of substance with the use of different methods. The whole problem of combining GC and EA is thus worth analysing in further detail. It is justified to assume that this combination may become a useful and inexpensive tool for the identification of unknown compounds and may find a wider range of application.

2. ANALYSIS OF THE PROBLEM

The following information can be obtained by combining GC with EA: (a) the percentage composition of a compound after its separation by GC; (b) the empirical or molecular formula of the compound after its separation by GC and thus also its molecular mass; (c) the number of double bond equivalents[6]; (d) the parameter that is related to the molecular mass and Kováts retention index[1] or the molecular retention index[7,8].

2.1. Determination of percentage composition

For the determination of the percentages of various elements, the precise mass of the sample under analysis usually must be known. Even in the simplest case of the separate application of GC and EA, *i.e.*, separation of the substance by GC, its isolation, weighing and subsequent EA, the problem sometimes appears to be associated with the isolation of an amount of the sample compound sufficient for precise weighing. If a modern electronic balance is used, this level is 100 μg of the compound at the minimum. With an on-line GC–EA combination, a quantitative signal from the gas chromatographic detector can be utilized, usually with a precision substantially lower than that of weighing.

The isolation of a component represented by a peak at the outlet from the GC column assumes, except if the total effluent trapped in the loop has a sufficiently large volume, that the partial pressure of the eluate after it has entered the condensation device is much lower than that at the column outlet. Usually this is achieved by decreasing the trap temperature, by dissolving the eluate in a solvent with a low vapour tension, by adsorption or by reaction with a suitable reagent. When selecting a particular procedure, it is necessary to take into consideration that the condensation is followed by phenomena associated with the kinetic properties of the gaseous mixture at the outlet from the GC column, such as the passage of the eluate through the trap in the form of a supersaturated vapour or an aerosol. The optimal percentage efficiency of the trap, E, is given by the relationship[9]

$$E = 100\left(\frac{p - P}{p}\right) = 100\left(1 - \frac{P}{p}\right)$$

where p is the partial pressure of the eluate at ambient temperature and P that at the

temperature of the trap in the absence of the condensate. During the peak elution the partial pressure of the eluate varies with time so that the total efficiency, E, at time, t, is given by

$$\bar{E} = \frac{1}{t}\int_0^t E\,\mathrm{d}t$$

It follows that it is impossible in principle to trap the component represented by the peak merely by cooling. Further, with small peaks for which p will be smaller than P throughout the whole peak, $\bar{E} = 0$; however, this will apply even when p at the peak maximum (p_{max}) is equal to P and also when it is greater. In the last case, the isolation of the component can be performed only near p_{max}, so that re-evaporation of the condensate will not occur. In practice, the situation is further complicated by the formation of a supersaturated vapour or aerosol, as mentioned earlier. This may be avoided to a considerable extent if a trap of a suitable type is selected.

An unpacked U-trap is the simplest device, suitable for the isolation of larger amounts of sample only, being available on semi-preparative and preparative scales; all of the preceding considerations apply to it.

The formation of aerosols can be avoided by various procedures, involving temperature gradient, turbulent flow of electrostatic precipitators[9]. The formation of aerosols is suppressed considerably if the U-trap is packed with an inert material with a large surface area, *e.g.*, with glass-wool, crushed material, or deactivated support for the GC column, so that the adsorption of the isolated component may be reversible.

A suitable support coated with a stationary phase, as suggested by Desty *et al.*[10], is the most efficient GC column packing. Under suitable conditions, no loss of the isolated material occurs with these traps and, moreover, the material is concentrated. Although cooling is not applied, a considerable decrease in the vapour tension occurs as a result of the distribution of the eluate between the gaseous and the liquid phases. When the length of this trap is selected, it is necessary for the fact that the substances with short retention times and narrow peaks occupy, as consequence of low solubility in the liquid phase, a longer section on the column, to be considered. This method is suitable for trapping microgram or even smaller amounts of samples[11]; packed capillary columns have been used to trap amounts sample down to 10^{-11} mol[12].

As a rule, the procedure starts with the trapping of the component of the peak in the trap with cooling and continues with its retention, followed after a suitable period by its release for subsequent analysis by heating the trap in a stream of the carrier gas. An example of a suitable device is shown in Fig. 1 (Ref. 13).

By selecting a suitable material and with appropriate connection of the trap, an arrangement is obtained that permits differential weighing before and after the isolation of the component, *i.e.*, it makes it possible to determine its amount, which is of importance in EA.

A trap represented by a large free volume (a coiled tube of stainless steel, glass or PTFE) for trapping the entire peak together with an appropriate volume of the carrier gas or for trapping a peak section near its maximum is also of interest for EA.

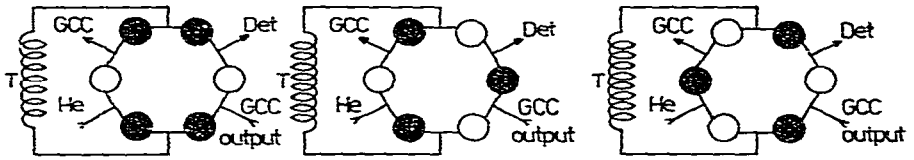

Fig. 1. Device for the isolation and sampling of GC eluates. GCC = GC column.

Isolation of this type is suitable for methods involving dilution of the products from the sample reaction after the reactor under defined conditions; it is less suitable for dynamic systems based on elution GC or selective absorption.

If there is a possibility of performing EA on all the elements contained in the molecule of a sample substance, a method in which it is not necessary to know the mass of the sample substance[14–16] can be used, but of course it requires the use of a reference substance with a known composition. As the determination of C, H, N, O and S, which represents the composition of most of the substances that can be examined by GC, can thus be carried out relatively easily, as will be shown later, this procedure is of great importance for combined GC–EA. At the same time, the determination of the empirical or molecular formula of the sample compound and of its molecular mass can also be effected.

The procedure is based on the determination of the empiricial formula $C_rH_pN_qO_uS_v$ by a common method, *i.e.*, by determining the mutual ratios of the various elements (stoichiometric coefficients r, p, q, u and v) by substituting percentage contents of the sample and the reference substances from eqn. 1.

$$\%X = \frac{K_X (E_X - e_X)}{w} \tag{1}$$

where K_X is the response factor obtained with the aid of a reference compound with a known composition:

$$K_X = \frac{\%X_{ref} \cdot w_{ref}}{(E_X - e_X)_{ref}} \tag{2}$$

E is the height of the frontal step or the peak, or is the area of the peak of the corresponding element, e is the corresponding response of a blank experiment and w is the sample weight.

In the classical procedure, the determined percentage contents of various elements are divided by the corresponding atomic weights and the results are divided by the smallest value or by one of the smallest values and, if it is necessary, they are then multiplied by a small integer (2 and 3 are the most frequent) in order to obtain stoichiometric coefficients of the empirical formula practically in the form of integers. In the present case, using eqns. 1 and 2, the sample weight, w, is cancelled out. Atomic

ratios are derived for the analysed samples directly from the corresponding signals and by means of the response factors determined with the aid of a reference substance. Hence in the analysis of carbon and hydrogen, if $r = 1$ then p is given by the relationship

$$p = \frac{\%H \cdot 12.012}{1.008 \cdot \%C} = 11.92 \cdot \frac{(E_H - e_H)K_H}{(E_C - e_C)K_C}$$

and because

$$\frac{K_H}{K_C} = \frac{\%H_{ref}\,(E_C - e_C)_{ref}}{\%C_{ref}\,(E_H - e_H)_{ref}}$$

then

$$r = 1$$

$$p = 11.92 \cdot \frac{(E_H - e_H)\ \%H_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_H - e_H)_{ref}}$$

Similarly, in C, H and N analysis (related to N which usually possesses the lowest stoichiometric coefficient in the empirical formula),

$$r = 1.17\,\frac{(E_C - e_C)\ \%C_{ref}(E_N - e_N)_{ref}}{(E_N - e_N)\ \%N_{ref}(E_C - e_C)_{ref}}$$

$$p = 13.90 \cdot \frac{(E_H - e_H)\ \%H_{ref}(E_N - e_N)_{ref}}{(E_N - e_N)\ \%N_{ref}(E_H - e_H)_{ref}}$$

$$q = 1$$

It is more advantageous, of course, to relate to C even in C, H, N determinations, as the programming is simplified when a mini- or microcomputer or a programmable calculator is used (this also applies to the determination of C, H and C, H, N or C, N, S and C, H, N, S). Then,

$$r = 1$$

$$p = 11.92 \cdot \frac{(E_H - e_H)\ \%H_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_H - e_H)_{ref}}$$

$$q = 0.86 \cdot \frac{(E_N - e_N)\ \%N_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_N - e_N)_{ref}}$$

As one reference compound is mostly used, the calculation is simplified con-

siderably as the parameters concerning the reference compound are transferred into a numerical constant, so that

$$r = 1$$

$$p = k_1 \cdot \frac{(E_H - e_H)}{(E_C - e_C)}$$

$$q = k_2 \cdot \frac{(E_N - e_N)}{(E_C - e_C)}$$

The same procedure is applied in C, H, S and C, H, N, S determinations:

$$r = 1$$

$$p = 11.92 \cdot \frac{(E_H - e_H)\ \%H_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_H - e_H)_{ref}}$$

$$v = 0.375 \cdot \frac{(E_S - e_S)\ \%S_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_S - e_S)_{ref}}$$

so that eventually

$$r = 1$$

$$p = k_1 \cdot \frac{(E_H - e_H)}{(E_C - e_C)}$$

$$v = k_3 \cdot \frac{(E_S - e_S)}{(E_C - e_C)}$$

and

$$r = 1$$

$$p = 11.92 \cdot \frac{(E_H - e_H)\ \%H_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_H - e_H)_{ref}}$$

$$q = 0.857 \cdot \frac{(E_N - e_N)\ \%N_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_N - e_N)_{ref}}$$

$$v = 0.375 \cdot \frac{(E_S - e_S)\ \%S_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_S - e_S)_{ref}}$$

or

$$r = 1$$

$$p = k_1 \cdot \frac{(E_H - e_H)}{(E_C - e_C)}$$

$$q = k_2 \cdot \frac{(E_N - e_N)}{(E_C - e_C)}$$

$$v = k_3 \cdot \frac{(E_S - e_S)}{(E_C - e_C)}$$

As the determination of O is based on a different reaction principle, *viz.*, hydrogenation pyrolysis of the sample or its reductive conversion on a carbon packing, it is necessary, if coefficient u is to be determined, that together with O one of C, H, N or S elements is also determined simultaneously. As C and H are present in almost all sample compounds, they are of the greatest practical interest. If O/C or O/H atomic ratios and, simultaneously, C/H, C/H/N, C/H/S or C/H/N/S is known, u can be determined.

The simultaneous determination of O and C can be achieved by hydrogenation pyrolysis of the sample over a nickel catalyst, C being determined as CH_4 and O as H_2O (ref. 15); O and H are then determined by the reductive conversion of the sample pyrolysis products on a carbon packing (the best is that catalysed with nickel or platinum) and by subsequent oxidation, *e.g.*, over CuO, so that O is determined as CO_2 and H as H_2O)[16].

In the first case (related to C):

$$r = 1$$

$$u = 0.75 \cdot \frac{(E_O - e_O)\ \%O_{ref}(E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}(E_O - e_O)_{ref}}$$

and, as follows from the above considerations,

$$u = \left[0.75 \cdot \frac{(E_O - e_O)\ \%O_{ref}\ (E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}\ (E_O - e_O)_{ref}}\right] r_{(CHN)}$$

or

$$u = \left[k_4 \cdot \frac{(E_O - e_O)}{(E_C - e_C)}\right] r_{(CHN)}$$

where $r_{(CHN)}$ is the value of the empirical coefficient r determined in the C, H, N determination (it is unity if related to C).

In the second case (related to H):

$$p = 1$$

$$u = 0.063 \cdot \frac{(E_O - e_O)\ \%O_{ref}(E_H)_{ref}}{E_H\ \%H_{ref}(E_O - e_O)_{ref}}$$

so that

$$u = \left[0.063 \cdot \frac{(E_O - e_O)\ \%O_{ref}\ (E_H)_{ref}}{E_H\ \%H_{ref}\ (E_O - e_O)_{ref}}\right] p_{(CHN)}$$

or

$$u = \left[k_5 \cdot \frac{(E_O - e_O)}{E_H}\right] p_{(CHN)}$$

where $p_{(CHN)}$ is the value of empirical coefficient p determined in the C, H, N determination.

In the simultaneous determination of C, N, S[17,18], the calculation can be carried out as in the determination of O. When related to C:

$$r = 1$$

$$v = \left[0.375 \cdot \frac{(E_S)\ \%S_{ref}\ (E_C - e_C)_{ref}}{(E_C - e_C)\ \%C_{ref}\ (E_S)_{ref}}\right] r_{(CHN)}$$

where $r_{(CHN)}$ is the value of the empirical coefficient r determined in the determination of C, H, N, or

$$v = \left[k_6 \cdot \frac{E_S}{(E_C - e_C)}\right] r_{(CHN)}$$

The calculation of the percentage contents of various elements starts from the ratio of the empirical coefficients obtained by the described procedure and the corresponding molecular mass. If the compounds under analysis also contain other elements (*e.g.*, halogens and P) the contents of these must be known or determined by another procedure. In association with this, the utilization of the response of selective detectors[9] is promising.

2.2. Determination of empirical and molecular formulae

The determination of a molecular formula by multiplying the coefficients of the empirical formula by a small integer is possible in the present instance by comparing

the retention data of the analysed compound with the retention data of a compound of similar composition the molecular mass[19] of which is known.

The requirement of the precision of the determination of the empirical formula is governed by the requirement of the unambiguity of the determination of the number of atoms of individual elements, and it is not identical for all of them. It is the most exacting for H, which has the lowest atomic mass. In questionable cases, the rule that a compound that contains in its molecule an even number of atoms with odd valency cannot contain an odd number of H atoms is valid.

The above procedure provides some advantages that are worth mentioning:

(a) precise weighing and careful manipulation of the sample are eliminated;

(b) as the error due to weighing is avoided, EA can be performed with advantage on the microgram scale;

(c) provided that short-term significant changes in physical parameters of the analyser do not arise, it can be assumed that the results of the determination are not influenced by their changes as the ratio of the detector signals for various pairs of elements remains the same.

2.3. *Number of double bond equivalents*

The number of double bond equivalents, *i.e.*, the unsaturation number, R, is an aid in the deduction of the structural formula from the empirical formula. It is determined according to the relationship

$$R = 1 - N + \tfrac{1}{2}\Sigma i\, n_i V_i$$

where n_i are the numbers of individual atoms in the empirical formula, V_i is the valency of element i (the concept of valency here denotes the sum of homopolar and heteropolar bonds) and N is the total number of the atoms present, $N = \Sigma i\, n_i$. A double bond corresponds to one ring and a triple bond to two double bonds[6].

2.4. *Parameter W*

A method for the identification of an unknown compound has recently been described that, combines retention increments compatible with the empirical formula, with the retention of this compound[8]. The parameter W, relating the molecular mass, M, and the Kováts retention index, I, or molecular retention index, Me, is defined as

$$W = Me - M = 0.14\, I - M + 2$$

In this way the limits of the value of W can be determined for certain structural groups on different stationary phases.

3. COMBINATION OF GAS CHROMATOGRAPHY AND ELEMENTAL ANALYSES

GC and EA can be combined by (a) separate use of GC and EA, necessarily involving the isolation of the sample compound (trapping) or (b) on-line connection of GC and EA with or without the trapping of individual peaks.

The former procedure offers universal application without particular requirements for special instrumentation; however, it assumes that a gas chromatograph and an automated elemental analyser, permitting C, H, N, O and also S determinations, are available. It is the type of elemental analyser applied that determines the amount of sample that must be isolated. Usually, this amount is much larger than in an on-line combination, but it represents 100 μg of the sample at the minimum. The problem of the selection of the type of trap is closely associated with the principle of the elemental analyser used[20], systems involving a dilution chamber between the reactor and the separation part can make use of traps of any type, whereas those working under continuous dynamic conditions require the compound to be isolated in the pure state.

However, the weighing, which in general follows the isolation of the compound (with the exception of the procedure without weighing), again restricts the procedure of trapping to isolation in the pure state or to isolation in the packing with a suitable sorbent (differential weighing before and after desorption, which is more suitable with a classical type of microbalance owing to the considerable weight of the trap).

A number of variants of the fundamental arrangement offer in the latter instance an on-line GC–EA combination. They can be classified, with regard to the function of the GC column, into the following systems: (a) with the GC column operating without changing the carrier gas flow; and (b) with the GC column operating as "stop flow" system[21,22].

In the former instance, the GC column outlet must be equipped with a suitable trap if the EA proper is not to be limited to the only peak from the whole chromatogram, whereas in the latter the peaks following the peak under analysis are "preserved" in the GC column after the interruption of the chromatographic process by switching off the carrier gas feed; more attention will be devoted to the realization of individual variants later. Hence the "stop-flow" system does not require any trap and makes it possible to continue chromatographing or subsequent EA after the analysis of the selected peak.

Both chromatographic versions can be connected to different EA systems. As these do not provide results with the same accuracy and may differ in other parameters, it is necessary that these circumstances should be taken into consideration when the type of EA is selected. The following systems can be considered.

4. ELEMENTAL ANALYSIS SYSTEMS FOR ON-LINE CONNECTION WITH THE GAS CHROMATOGRAPHIC COLUMN

The continuously operating GC column is connected to either (a) reactor–elution GC; (b) reactor–detector–selective absorber–detector; (c) reactor–dilution chamber–combination of detectors and selective absorbers; (d) reactor–dilution chamber–frontal GC; (e) reactor–dilution chamber–sampling loop–elution GC.

The following is charachteristic of individual combinations:

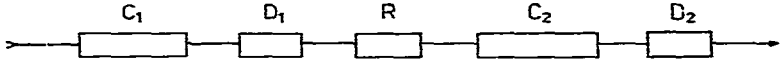

Fig. 2. Flow diagram of a GC column – reactor – EA system by elution GC.

4.1. Reactor–elution gas chromatography

The simplest arrangement[23] is obvious from Fig. 2.

The carrier gas passes through a GC column, C_1, a non-destructive detector, D_1, a reactor, R, a second chromatographic column, C_2, and a detector, D_2. The analysed peak is thus recorded in the detector D_1 first, allowed to react (*e.g.*, oxidation), in reactor R, and the reaction products are separated in column C_2 and detected by detector D_2. Disadvantages of this arrangement are obvious. The direct dependence of individual parts of the arrangement on the flow-rate of the carrier gas restricts this procedure to well separated peaks[24,25] leaving the GC column within relatively short elution times. Sorption phenomena and diffusion then occur in the reactor and, as a result, the zones of reaction products are broadened with adverse effects on the subsequent chromatographic separation.

The system with independent control of the flow-rate of the carrier gas in both the chromatographs and reactor[26], suggested initially for pyrolysis GC, is of greater practical interest. However, even here peaks that follow each other closely cannot be analysed without using a trap or "stop flow" conditions. The function of this device is shown in Fig. 3.

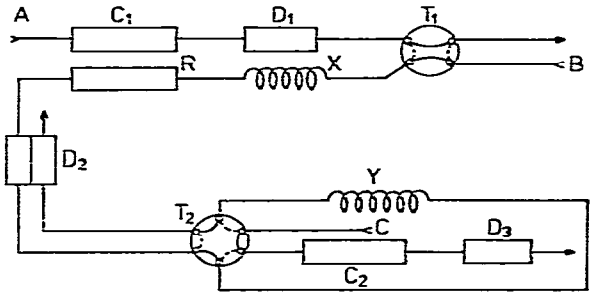

Fig. 3. Arrangement of GC column – reactor – elution GC system with independent control of the flow-rates of gases.

The separation proper proceeds in column C_1, and individual peaks are registered by means of a non-destructive detector, D_1 (this can be replaced with a splitter and a destructive detector) and pass through a valve, T_1, to ambient air. At the same time, the carrier gas is introduced from a source B, via valve T_1, free volume of a delay coil, X, a reactor, R, a non-destructive detector, D_2, a multi-port valve, T_2, and a transfer coil Y, a valve, T_2, again to detector D_2 and to ambient air. In addition, the carrier gas streams from a source, C, via T_2, a column, C_2, and a detector, D_3. If the peak that has just been registered by means of detector D_1 is to be analysed, valve T_1 is turned and the component of the peak together with the carrier gas is introduced into the coil X, reactor R, detector D_2, valve T_2, transfer coil Y, valve T_2 and through the reference section of detector D_2 and out. After completion of the peak registration by detector D_1, valve T_1 is again turned, and further transport of the peak into the reactor is executed by the carrier gas from source B. Detector D_2 plays an auxiliary role, serving to indicate reaction products leaving reactor R or to prevent their elution from transfer coil Y. It can therefore be omitted as it is sufficient if the carrier gas flow-rate from B and the free volume of circuit X, R, Y are known. The analysis

proper of the reaction products is performed by turning valve T_2 and sampling the contents of the coil Y into the column C_2.

4.2. Reactor–detector–selective absorber–detector

A flow diagram of a typical arrangement applied to the determination of C/H ratio[27] is shown in Fig. 4.

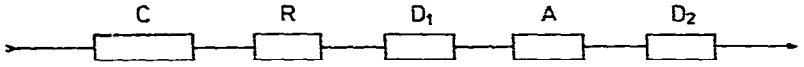

Fig. 4. GC column – reactor – detector – selective absorber – detector system.

The peaks leaving the GC column, C, pass through a reactor, R, where they are oxidized to carbon dioxide and water and the latter is converted to hydrogen. The mixture passes through a detector, D_1, and an absorber, A, where carbon dioxide is trapped, and then through a detector, D_2, where hydrogen is determined. The amount of carbon dioxide is determined from the difference of the responses of the two detectors.

It is obvious that by selecting a suitable packing and temperature of the reactor and using a selective absorber or by inserting more detector–absorber couples, various elements, *e.g.*, C, H, N, O and S, can be determined. An advantage of this arrangement is that it is not necessary for a trap or a "stop flow" arrangement of the GC column to be used, provided that the peaks leaving the column are well separated.

The same does not apply, however, to the different arrangement shown in Fig. 5, used for the determination of C, H, N[28,29]. It differs from Fig. 4 in that the component represented by the peak is oxidized in the reactor into a mixture nitrogen, carbon dioxide and water and freed from water in the absorber, where it is retained until carbon dioxide or nitrogen is detected (by the same procedure as shown in Fig. 4), and only then thermally desorbed and registered with the aid of a detector, D_1. Carbon dioxide is absorbed in an absorber, AB, and nitrogen is registered by a detector D_2. The amount of carbon dioxide is determined from the difference between the data from detectors D_1 and D_2.

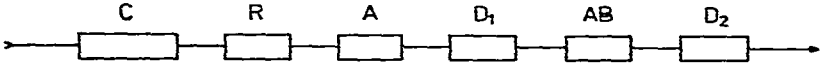

Fig. 5. GC column – reactor – absorber – detector – absorber – detector system.

To compare the dynamic systems described so far, based on separation by elution GC and selective absorption, it must be taken into consideration that component S passes the GC column under repeatedly established equilibrium and that its concentration in the gaseous phase varies[30]. If N_S is the number of moles of component S, then its instantaneous concentration at the column outlet can be expressed as

$$c_S = \frac{N_S}{v\, t_R} \sqrt{\frac{L}{2\pi H}} \cdot \exp\left[-\frac{L}{2H}\left(1 - \frac{t}{t_R}\right)^2 \right]$$

where v is the volumetric flow-rate of the gas, t the elution time (the time period during which concentration c_S is eluted), t_R the retention time, L the column length and H the height equivalent to a theoretical plate.

For the maximal concentration of the eluted component $t = t_R$, so that

$$c_S^{max} = \frac{N_S}{v\, t_R} \sqrt{\frac{L}{2\pi H}}$$

and the integral of the time function of the concentration distribution of the eluted component satisfies the condition of the Gaussian random distribution

$$\int_{-\infty}^{+\infty} c_S dt = Y$$

and has a maximum c_S^{max} at time $t = t_R$ and two points of inflection at time t_{inf}, situated symmetrically on both the sides of t_R:

$$t_{inf} = t_R \pm \sqrt{\frac{L}{H}}$$

The separation of the eluted component in the column is influenced by simultaneous dissolution and absorption processes, shifts in the equilibrium in the presence of inert components and by the amounts of the eluate and the eluted component.

With a change in the concentration of the eluted component a change also occurs in the concentration of the carrier gas. These changes can be expressed in terms of variations in partial pressures as the total pressure in an open chromatographic system remains constant. As long as the pure carrier gas C streams in the column, its partial pressure at the column outlet is $p_C = p$. After the introduction of a substance S into the column, the partial pressure of the carrier gas is changed. As the total pressure remains unchanged, then

$$p = p_C + p_S$$

With all the dynamic systems described so far, component S, leaving the GC column, passes through the reactor where it is converted into the mixture of reaction products, e.g., nitrogen, carbon dioxide and water if C, H, N are determined and, in the next step, this mixture is separated either chromatographically or by selective sorption.

In GC separation, all of the preceding considerations are valid. Provided that the chromatographic separation is good, in the course of the analysis with a defined time sequence the following relationships are valid for the total pressure at the column outlet and in the measuring section of the sensing element:

$$p = p_C$$

or

$$p = p_C + p_{N_2}$$

or

$$p = p_C + p_{CO_2}$$

or

$$p = p_C + p_{H_2O}$$

With selective sorption the situation is different. Having left the reactor, the whole mixture of reaction products passes through the sensing element so that

$$p = p_C + p_{N_2} + p_{CO_2} + p_{H_2O}$$

After the conversion of water into hydrogen,

$$p = p_C + p_{N_2} + p_{CO_2} + p_{H_2}$$

and having passed the absorption layer, where carbon dioxide is trapped, the mixture enters the second sensing element at the total pressure in the profile of the zone of the reaction products:

$$p = (p_C + p_{N_2} + p_{CO_2} + p_{H_2}) - p_{CO_2}$$

i.e., the initial partial pressure of the carrier gas does not change and, as a consequence, the individual partial pressures of the components present vary.

From the viewpoint of the use of the detector of the concentration type (katharometer), in the profile of the peak being analysed concentration changes occur, which are not negligible, particularly in carbon dioxide absorption (carbon dioxide concentrations in the carrier gas of the order of 10% should be taken into account). These changes are the reason for the non-linearity of the detector response, which can be defined only with difficulty as it is affected by a number of factors: (1) variations in the concentrations of the components present; (2) non-linearity of the dependence of the change in the thermal conductivity on the concentration of the components present; (3) non-linearity of the dependence of bridge unbalance signal on the change in the thermal conductivity; (4) variations in the flow-rate of the gaseous mixture in the peak profile and thus also the non-linearity of the detector response depending on the flow-rate of the analysed mixture; and (5) changes in the viscosity of the gaseous mixture in the profile of the peak being analysed.

The phenomena mentioned above are responsible for the fact that this method is suitable for semi-quantitative applications only. The same factors arise in systems using the dilution chamber. However, in this instance the concentrations of the reaction products being determined are lower by an order of magnitude, and also the resulting errors in the determination caused by non-linearity of the detector response are negligible. A more detailed discussion of these phenomena is given in the sections dealing with individual methods.

Finally, a combined case[28,29] can be considered, which is mentioned, *e.g.*, in Fig. 5, where the considerations concerning GC apply to the determination of water.

4.3. Reactor–dilution chamber–combination of detectors and selective absorbes

In this instance the possibility is considered of connecting a GC column on-line to elemental analysers of the Perkin-Elmer Model 240 and Yanaco types[31–35], which differ in the shape and function of the dilution chamber, *i.e.*, the former uses a glass flask with an auxiliary sampling loop and the latter a cylinder with a mechanically controlled piston.

In the first instance, as follows from the flow diagram in Fig. 6, the components from the GC column pass through valve T_1 into ambient air or, in peak analysis, into reactor R, via the three-way valve S_1 into dilution chamber CH, where the reaction products are diluted and homogenized under steady-state conditions after closing the chamber with the aid of valves S_1 and S_2.

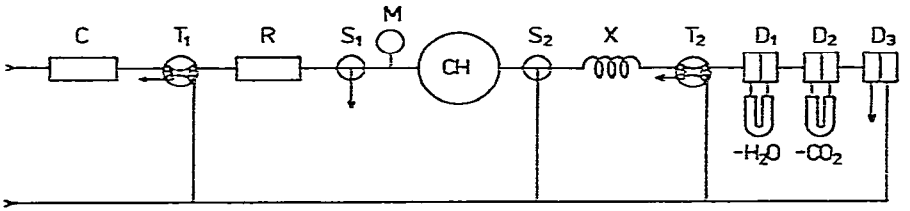

Fig. 6. Arrangement of GC column – reactor – dilution system: separation of individual components by selective absorption and differential measurement of thermal conductivities.

After finishing the peak sampling, the system is fed with the pure carrier gas (helium) via T_1, R and S_1 and the pressure is increased to an overpressure, determined in advance, by means of a manometer, M. After finishing the homogenization, the mixture from CH is allowed to expand via S_2, a sampling loop, X, and a valve, T_2, and out. Meanwhile, the carrier gas streams via T_2 into a system of absorbers and thermal conductivity detectors D_1, D_2 and D_3 (the baseline is registered). Subsequently, by switching valves S_2 and T_2 the contents of loop X are purged via T_2 into the system of detectors and absorbers. In C, H, N determination, water is trapped in the first absorber (packed with Anhydrone) and the difference in the corresponding thermal conductivities is registered by a detector, D_1, carbon dioxide is trapped in the second absorber (Ascarite) and D_2 again registers the difference in the thermal conductivities of the mixtures. The difference between the thermal conductivity of the remaining mixture and the pure carrier gas is measured in a third detector, D_3. When the analysis is finished, chamber CH is washed with the carrier gas via S_2 and S_1 and out.

The second case, using the cylindrical dilution chamber and the mechanically controlled piston, is analogous.

The dilution chamber, which apparently makes the whole process complicated and affects adversely the time of analysis (dilution of the reaction products and their homogenization for about 1.5 min), in addition to some smaller drawbacks [adsorption on the walls, particularly in the analysis of small amounts of the sample (below 50 μg), or the dead volume], has a number of important advantages:

(1) It acts as an integrator and thus simplifies the electronic components of the analyser.

(2) It virtually eliminates difficulties associated with sorption of the reaction products in the reactor, or those complicating the subsequent separation.

(3) It makes it possible to vary the flow-rate through the reactor almost at will.

(4) It permits the use of larger amounts of sample compound for the analysis as it makes it possible, to a considerable extent, to avoid non-linearity of the katharometer response caused by its concentration dependence.

(5) It makes it possible to use large-volume traps of any type.

(6) The frontal GC technique can be used in connection with the dilution chamber, giving higher column efficiency, and enables shorter columns to be used, yielding shorter analysis times, thus compensating for the time necessary for homogenization of the gas mixture in the dilution chamber.

It is the following three factors that contribute to the errors caused by non-linearity of the detector with the systems described above:

(a) The relationship between the component concentration and the change in thermal conductivity is linear at low concentrations or in a narrow range of the concentrations. The effect of the non-linearity can be neglected provided that the molar fraction is less than 0.01; hence follows one of the advantages of the dilution of the components.

(b) The other source of error is associated with the presumption of direct proportionality between the change in the thermal conductivity and the signal of the bridge unbalance. It was proved[28] that the relationship between the molar fraction, x, of the component and the signal of the bridge unbalance, ΔE, has the following form

$$\Delta E \sim x(1 - x)$$

and, in contrast to the case of elution GC, it is therefore very small with dilution and gives rise to errors that do not exceed 0.05% if it is diluted to $x \leqslant 0.01$ (ref. 31).

On the other hand, with systems using elution GC a function-generating device must be used to obtain a linear approximation and thus also the possibility of performing the analysis with a wider range of the weighed amounts.

The application of a later version of the katharometer, operating with a constant temperature of the filaments, provides a wider range of linearity of response[30].

(c) With the systems described above it is necessary to take into account the third deviation from the linear relationship between the amount of the component of interest in the sample, and hence the concentration in the dilution chamber of the products of its specific reaction and the change in its thermal conductivity in a separation section after absorption of individual components. The deviation takes the form of an increase in the initial concentrations of the reaction products after homogenization in the dilution chamber as soon as one of the components of the mixture is absorbed.

If the most frequent application, *i.e.*, C, H, N determination, is taken as an example, then, provided that the Pregl–Dumas reaction system is used, after reaction of the sample and equilibration of the mixture of the reaction products the mixture of helium, nitrogen, carbon dioxide and water remains in the dilution chamber, so that

$$x_{HE} + x_{N_2} + x_{CO_2} + x_{H_2O} = 1$$

where x_i is the molar fraction of an individual component and is calculated according to the relationship

$$x_i = \frac{G_i T \cdot 22.4 \cdot 760}{M_i V P \cdot 273} \cdot 10^{-3}$$

where M_i (μg) and G_i (μg) are the molecular mass and the mass of component i, respectively, and V (ml), T (°K) and P (Pa) are the volume, temperature and pressure, respectively, in the dilution chamber.

Then, with a simplifying assumption[31,32] of linear additivity of the katharometer response to the concentrations of individual components in the case of multicomponent mixtures and of the estimate or the calculation of the corresponding thermal conductivity, λ_i, it is possible to start from the presumption that after the absorption of the first component, *i.e.*, water,

$$x_{H_2O} = 0$$

and

$$x_{He} + x_{N_2} + x_{CO_2} = 1$$

so that in the measuring section of the katharometer (*viz.*, Fig. 6)

$$\lambda^M = x_{He}\lambda_{He} + x_{N_2}\lambda_{N_2} + x_{CO_2}\lambda_{CO_2} + x_{H_2O}\lambda_{H_2O}$$

and in the reference section

$$\lambda^R = \frac{x_{He}}{1 - x_{H_2O}} \cdot \lambda_{He} + \frac{x_{N_2}}{1 - x_{H_2O}} \cdot \lambda_{N_2} + \frac{x_{CO_2}}{1 - x_{H_2O}} \cdot \lambda_{CO_2}$$

and from the difference between the two thermal conductivities, before and after the absorption of water,

$$\Delta\lambda_{H_2O} = x_{H_2O}\lambda_{H_2O} - \frac{x_{H_2O}}{1 - x_{H_2O}} \cdot (x_{He}\lambda_{He} + x_{N_2}\lambda_{N_2} + x_{CO_2}\lambda_{CO_2})$$

and analogously after the absorption of carbon dioxide,

$$\Delta\lambda_{CO_2} = \frac{x_{CO_2}}{1 - x_{H_2O}} \cdot \lambda_{CO_2} - \frac{x_{CO_2}}{(1 - x_{H_2O})\ [1 - (x_{H_2O} + x_{CO_2})]} \cdot (x_{N_2}\lambda_{N_2} + x_{He}\lambda_{He})$$

and finally, by comparing with pure helium,

$$\Delta\lambda_{N_2} = \frac{x_{N_2}}{1 - (x_{H_2O} + x_{CO_2})} \cdot (\lambda_{N_2} - \lambda_{He})$$

Strictly, generally linear additivity of the thermal conductivity cannot be assumed for multi-component mixtures of gases and therefore for the calculation of the thermal conductivity in the individual katharometer cells after the absorption of the components of the mixture it is more exact to use more complicated relationships, the best being that according to Lindsay and Bromley[36]:

$$\lambda_m = \sum_{i=1}^{n} \frac{x_i}{1 + \frac{1}{x_i} \sum_{\substack{i=1 \\ j=1}}^{n} A_{ij} x_j}$$

where

$$A_{ij} = \frac{1}{4}\left\{1 + \left[\frac{\mu_i}{\mu_j} \cdot \left(\frac{M_j}{M_i}\right)^{3/4} \cdot \frac{1 + \frac{S_i}{T}}{1 + \frac{S_j}{T}}\right]^{1/2}\right\}^2 \cdot \frac{1 + \frac{S_{ij}}{T}}{1 + \frac{S_i}{T}}$$

where μ_i and μ_j are viscosities of gases i and j, respectively, M_i and M_j are the molecular masses of i and j, respectively, S_i and S_j are the Sutherland's constants of i and j, respectively, x_i and x_j are the molar fractions of i and j, respectively, and T is absolute temperature (°K).

For practical reasons, it is advantageous that correction factors, f_i, can be calculated for the conditions given for the analyser and that the differences in the thermal conductivities measured for individual components, $\Delta\lambda_i$, can be corrected with the respective factors. The values obtained in this way vary linearly with the change in concentration i (ref. 32):

$$\frac{\Delta\lambda_i}{f_i} = \Delta\lambda_{i,\text{corr.}} = \Delta\lambda_{i,L}$$

For a binary system with thermal conductivities λ_i and λ_{He} (carrier gas) it is possible to write, as a particular case,

$$\Delta\lambda_{i,L} = x_i (\lambda_i - \lambda_{He})$$

The dependence between $\Delta\lambda_{i,L}$ and x_i is linear, so that from the above relationships we have

$$f_i = \frac{\Delta\lambda_i}{\Delta\lambda_{i,L}} = \frac{\Delta\lambda_i}{x_i (\lambda_i - \lambda_{He})}$$

Factors f_i can be calculated from the corresponding relationships, which is impractical. It is more advantageous to tabulate them in relation to the amounts of other components present, which is valid to a first approximation. These corrections need not be performed in practice because, as a rule, the errors that arise do not exceed $\pm$ 0.2% absolute for each element to be determined.

4.4. Reactor–dilution chamber–frontal gas chromatography

Fig. 7 shows a flow diagram of a device suitable for the realization of reaction frontal GC[15,37], and also reaction elution GC, or a combination of both[18].

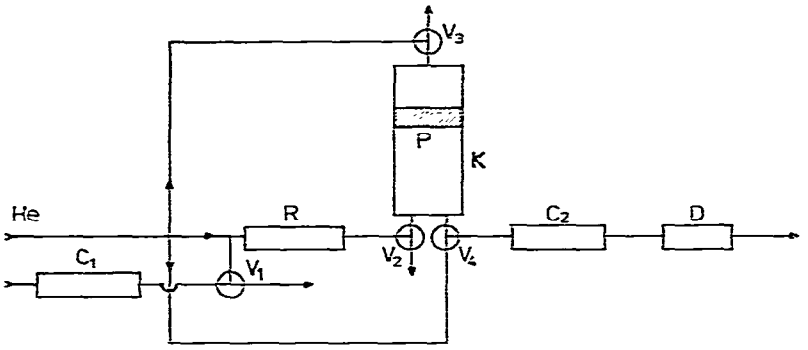

Fig. 7. GC column – reaction frontal GC system.

The substance under analysis, leaving the GC column, C_1, or having been captured in a trap first, is introduced into a reactor, R, via a valve, V_1, reacts with the formation of the defined products, which are carried by the carrier gas via a valve, V_2, into a cylindric dilution chamber, K, equipped with a loosely moving piston, P. At the same time, the piston slides towards the opposite face with a valve, V_3, opened to the atmosphere. The piston having reached the face, the pressure in the chamber increases to a value adjusted in advance, then the chamber is closed for about 1.5 min in order to allow for homogenization of the gaseous mixture by diffusion. Simultaneously valve V_3 is switched and the carrier gas is introduced behind the piston under an overpressure which is at the inlet of the chromatographic column. Valve V_4 is switched, the entry of the carrier gas into a GC column, C_2, is interrupted and, at the same time, the inlet into the dilution chamber is opened. The piston of the chamber purges the equilibrated mixture from the dilution chamber into the GC column, filled with a suitable sorbent (*e.g.*, Porapak Q or QS). Frontal chromatographic development occurs provided that the sampling is performed for a sufficiently long period. By selection of the sampling time, combined frontal elution separation[18], having some advantages over a purely frontal process, can be achieved. The residue from the dilution chamber is blown off into the ambient atmosphere and the next analysis can be started.

This system combines some properties of all of the above arrangements. A bypass arrangement of the reactor–dilution chamber system provides all the advantages of the dilution chamber, as mentioned earlier.

On the other hand, some disadvantages of the application of the dilution chamber, particularly in the analysis of amounts of sample less than 50 μg, cannot be disregarded: (1) existence of dead volumes and large surface areas (surfaces of the piston, inside walls of the dilution chamber), the dimensions and the sorption properties of which must be suppressed (*e.g.*, by silane treatment); and (2) demands on smooth piston sliding.

Strictly, no direct linear proportion exists in frontal GC between the concentration of the component in the dilution chamber after the equilibration and the corresponding katharometer response in the course of the adsorption chromatographic process. The concentration established in the dilution chamber initially varies during the adsorption development.

If C, H, N determination is considered, the concentrations of carbon dioxide, nitrogen and water in helium (carrier gas) reach $x = 0.001$–0.01 when competitive sorption in the chromatographic process can be neglected. This mixture is led from the dilution chamber into the chromatographic column packed with Porapak Q or QS and individual components are sorbed until equilibrium is established. The least sorbed component, nitrogen, appears at the column outlet first as a concentration step, the height of which should correspond to the concentration introduced from the dilution chamber. In fact, it is higher as the remaining components, carbon dioxide and water, were sorbed from the initial mixture. The molar fractions of nitrogen and helium are therefore changed. The situation is similar after the elution of carbon dioxide. Only after elution of water do the initial concentrations established in the dilution chamber leave the column.

These concentration changes are equivalent to those described in further detail in the preceding section, on separation by selective absorption.

Moreover, the concentration changes in this instance result from desorption of the less sorbed component by the components proceeding more slowly (in the present instance by carbon dioxide and water). It is a new establishment of the sorption equilibrium, based on the concentration changes over the sorbent, that is relevant here. With respect to low concentrations of substances, this phenomenon can be neglected.

The situation is different in the desorption part of the frontal chromatographic process. Here no concentration changes occur and the component eluted by the sorbent is immediately replaced with the same molar fraction of helium (carrier gas).

A combined frontal elution separation is obtained if the contents of the dilution chamber are sampled into the GC column within a shorter period of time. It is advantageous as any eventual concentration corrections, discussed above, will be omitted for the last component (in the present instance this is water) and the total analysis time will be shortened by about 2 min[18].

The resulting precision of the determination by the above method, as with all other instrumental methods, is complex. In addition to the separation process proper, the parameters of various elements of the instrument, such as the precision of the temperature control in the thermostat, the precision of the stabilization of the katharometer filament voltage and of the carrier gas pressure, the sensitivity and the precision of the pressure establishment in the dilution chamber, the perfectness of the reaction process, the magnitudes of the dead volumes of the valve system, the sorption properties of the inner surface on the connections and the walls of the dilution chamber affect this precision.

Practical experience suggests that the main sources of errors are sorption of reaction products on the inner surface of the dilution chamber and in the inlets (bore holes towards membrane valves in the face of the dilution chamber) and the concentration changes that occur in the course of adsorption–frontal GC development.

The precision of the results also depends, to a considerable extent, on the initial

amount of the sample. A precision of ± 0.2% absolute can be obtained for individual elements with samples of 100–1000 μg. With decreasing amounts of sample, the effects associated with concentration changes and non-linearity of the katharometer response lose their significance and sorption phenomena predominate. The smallest amount of sample that can be analysed is about 10 μg for systems with a dilution chamber, and about 1 μg for based on elution GC.

More precise results are obtained with larger amounts of sample (100 μg) when the conditions are optimal for easy and rapid selective reactions and the ratio of the sample signal to the blank value for a given element remains sufficiently great.

4.5. Reactor–dilution chamber–sampling loop–elution gas chromatography

A suitable instrumental arrangement for this case can be based, *e.g.*, on Fig. 6, the only difference being that the sampling tube X is replaced with a loop and the system of absorbents and detectors with a chromatographic column and one detector. The advantage of this arrangement over that described in Section 4.1 is the possibility of performing an independent reaction and eliminating sorption phenomena in the reactor. On the other hand, the sampling itself with the aid of the loop suffers from an error that is not negligible and restricts the practical applicability of this arrangement.

Use of a loop with a sufficiently large volume is a particular case when the sampling into the chromatographic column is prolonged; during the chromatographic process, the initial concentration in the centre of the zone of the component being separated will be maintained until leaving the chromatographic column, and the resulting chromatogram will consist of stepwise peaks, the height of which will correspond to the concentrations established originally in the dilution chamber[20]. However, this presumes that a simple mixture of gases is produced by the reaction and that the individual components are separated well with a sufficient reserve with respect to elution time. This case does not suffer from the error caused by the sampling loop and is advantageous in practice. It is substantially identical with the case described in Section 4.4.

5. ELEMENTAL ANALYSIS SYSTEMS FOR ON-LINE CONNECTION WITH THE GAS CHROMATOGRAPHIC COLUMN, USING A "STOP FLOW" SYSTEM

EA systems for connection to the GC column operating as a "stop flow" system differ only in that they do not require trapping. The interruption of the carrier gas flow through the GC column for 8 min, which is necessary to perform, *e.g.*, C, H, N analysis, is said[4] not to have any negative effects on the subsequent separation.

6. REACTION CONDITIONS FOR INDIVIDUAL DETERMINATIONS

6.1. Determination of C, H, N

Most instrumental methods determine C, H, N simultaneously. The reaction principle is very simple and can be expressed schematically as follows:

$$\text{Organic N compound} \xrightarrow{(O)} CO_2 + H_2O + N_2 + \text{N oxides} \xrightarrow{(Cu)} CO_2 + H_2O + N_2$$

In general, however, the mechanism of the oxidation process is complicated and it is not always easy to satisfy the requirements of the reaction scheme. In the reaction of chromatographic effluents, however, the situation is usually much simpler as compounds are involved that are relatively volatile or convertible into the gaseous state and, moreover, have a relatively simple qualitative composition.

Sample compounds are mostly combusted with addition of oxygen and the gaseous reaction products pass additionally through an oxidative packing (mostly oxygen donors) in order to be completely oxidized. Copper (II) oxide still has a wide range of application, although a number of others, such as the decomposition product of $AgMnO_4$[35], Co_3O_4[39] and others, described in detail in textbooks on organic elemental analysis[40–44], have been proposed.

In separate determination by GC–EA, the reaction conditions of EA are determined by the instrumentation that is applied.

Various commercial analysers operate on the basis of different reaction principles, which are usually optimal for the given system[40,41]. Retention of unreacted oxygen and reduction of nitrogen oxides are generally performed over copper at 500–650°C, whereas the oxidation packings and pyrolysis section are mostly at 950–1050°C.

Various forms of metallic silver (silver-wool, silver deposited on an inert support, mixture of silver with Co_3O_4, SnO_2, etc.) at 500–800°C[40–42] are used to absorb interfering elements, such as halogens and sulphur.

All of these methods employ relatively high temperatures (1000 ± 50°C) in the pyrolysis section and the combustion packing in order to effect virtually instantaneous destruction of all types of substances; however, significant corrosion of the quartz tube should not occur. This also results from the fact that, in contrast to classical elemental analysis, reactions are mostly carried out in an inert medium of the carrier gas (helium) with the addition of only a small amount of oxygen in order to prevent rapid exhaustion of the copper packing. Classical donors of oxygen, such as CuO, Co_3O_4 and decomposition product of $AgMnO_4$, are no longer used because at these temperatures they have a high oxygen tension and lose their efficiency (the maximum usable temperatures are 850–900, 750–800 and 500–550°C for CuO, Co_3O_4 and the decomposition product of $AgMnO_4$, respectively). With on-line connection of the GC column to EA, however, it is advantageous to use classical oxygen donors for the oxidative conversion of the sample compound, CuO being the best, or no addition of oxygen, particularly if smaller amounts of compounds (100 μg and less) are analysed.

6.2. Determination of O; C, O; H, O

Oxygen determination is theoretically possible by two reaction procedures:

(a) By pyrolysis of the sample in an inert gas and reductive conversion of the pyrolysis products by passing them through the layer of carbon packing, or nickelized or platinized carbon packing, at a sufficiently high temperature (1120, 950–1050 and 900°C with non-catalysed, nickel-containing and 50% of platinum-containing packings, respectively). Oxygen from the sample is converted quantitatively into carbon monoxide, which is determined as such or converted into carbon dioxide prior to the determination proper. Hydrogen, nitrogen and also methane (if the conversion is performed at temperatures below 1050°C[16,40,41]) are by-products of the reaction.

(b)By pyrolysis of the sample in the stream of hydrogen or hydrogen in a mixture with helium and by conversion of the pyrolysis products on a nickel catalyst at a relatively low temperature 450°C[15]. Oxygen is converted into water and carbon into methane. As the interfering elements, such as halogens and sulphur, poison the catalyst, the application of this reaction procedure, in contrast to the above, is restricted to compounds of qualitatively simple composition.

It follows from the above that in classical elemental analysis, reductive conversion on a carbon packing is used explicitly to determine oxygen. In the present instance it will be used analogously for separate applications of GC and EA, as all the instrumental methods are also based on this principle[40,41].

With on-line systems, hydrogenation cleavage on a nickel catalyst is also possible, as substances that are simple from the viewpoint of qualitative composition are mostly involved[15]. If application to the determination of the empirical formula without weighing is taken into consideration, it is necessary for simultaneous determination of oxygen and carbon, or oxygen and hydrogen, to be obtained[15,16].

In the first instance hydrogenation cleavage of the sample into methane and water can be used successfully, so that methane corresponds to carbon and water to oxygen. This method is particularly suitable for on-line connection[15]. Unreacted hydrogen can be removed by diffusion through a heated capillary made of paladium and silver.

Reductive conversion of the sample on a carbon packing permits the simultaneous determination of oxygen and hydrogen, preferably in the form of carbon dioxide and water after oxidation of the reaction products[16]. With respect to retention of hydrogen on the carbon packing, this procedure is suitable for EA systems with a dilution chamber.

6.3. Determination of S; C, H, N, S; C, N, S

All contemporary instrumental methods can be used for the determination of S or the simultaneous determination of S, C, N or together with H upon total oxidation of the sample[17,45–48]. In contrast to the reaction conditions in C, H, N determinations, it is necessary for some other problems to be solved. Granular WO_3[45,48] and SnO_2[17] at 1000°C, which do not show substantial retention of sulphur oxides, are suitable as combustion packings. Sulphur oxides must be converted into a uniform product, sulphur dioxide. A short layer of copper or copper(I) oxide at 850 ± 20°C was suggested to this purpose, where sulphur trioxide reacts to give copper(II) sulphate in order that the latter may be decomposed into copper(II) oxide and sulphur dioxide. This layer serves simultaneously for the absorption of unreacted oxygen and for reduction of nitrogen oxides, both reactions being accelerated by the presence of sulphur dioxide[49]. It is probable that in this layer [in fact in a mixture of copper(I) and -(II) oxides and copper] partial sorption of sulphur dioxide occurs even at the optimal temperature; however, it can be suppressed to a considerable extent by practical measures[50]. As the method is relative, sufficiently precise the results are obtained in this determination.

With on-line connection of GC and EA, reductive conversion of the sample in a stream of hydrogen over a platinum catalyst to give hydrogen sulphide, methane and water[51] can be considered, as with the determination of oxygen. This reaction is,

moreover, promising for the determination of phosphorus and arsenic as phosphine and arsine, respectively.

7. CONCLUSION

In the identification of unknown compounds leaving the chromatographic column, the determination of their empirical or molecular formulae and hence their molecular masses provides valuable information, which in most instances is sufficient if other chemical properties of the mixture under separation or relative elution data are also known. In practice, combined GC–MS, which moreover provides further information on molecular fragments and thus also on the structure of the compound under study, is mainly used for this purpose. This instrumentation is, however, still expensive and not available in many laboratories. The aim of this present review has been to indicate different ways of acquiring the information mentioned above with the aid of much simpler and less expensive means.

The separate application of GC and EA to the collection of the peak under analysis in a suitable trap can be recommended. The procedure without sample weighing is applicable in most instances, especially in GC. The procedure involving sample weighing is limited to larger amounts of sample (minimum 100 μg), as it is restricted by the sensitivity of currently available ultramicrobalances.

On-line GC–EA connection can be achieved most easily in the form of an adapter for the gas chromatograph (such as a replaceable thermostat head, likewise in the case of exchangeable detectors), providing the possibility of using an electronic modulus of the GC katharometer. The concept using a dilution chamber is advantageous, particularly for the determination of samples with a minimal mass of 50 μg; the possibility of using a trap of any type is an additional advantage. The combination of a GC column operating as a "stop flow" system with elution GC is suitable for samples with masses less than 50 μg.

The application of computers will make data processing and calculation of the empirical or molecular formulae substantially easier[52–54].

8. SUMMARY

General conditions and possibilities are discussed for the identification of GC effluents by determining their elemental composition, thus making it possible to calculate empirical and molecular formulae. Attention is paid to the trapping of GC peaks, to various methods for the direct combination of GC and EA, to elemental analysis without weighing and to the reaction conditions for the EA of GC column effluents, especially for the determination of C,H,N; O; C,O; H,O; S; C,N,S; and C,H,N,S. Individual instrumental methods of EA are discussed in detail, and sources of errors are pointed out.

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