U.D.C. 543.544

Qualitative Analysis in Gas Chromatography

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This review presents the most rational and widely employed methods of qualitative gas-chromatographic analysis of complex organic mixtures.
The bibliography includes 147 references.

I. INTRODUCTION

During the eighteen years of its development, gas–liquid chromatography has become one of the most widely used methods for the analysis of substances, in particular organic compounds. The greatest advances have been achieved using this method to separate complex mixtures of substances having low reactivity, the determination of which by other chemical and physicochemical methods involves considerable difficulties. For example, the problem of analysing petroleum fractions was solved by combining various chromatographic procedures. According to the latest data half the analyses of mixtures of organic substances in the U.S.A. are performed by gas chromatography and every seventh analytical chemist regards gas chromatography as his speciality. The comparatively simple equipment (available in many versions), the automatic recording of the results of separation, and the simple analytical procedure have attracted many investigators to gas-chromatographic methods. In the technological control of industrial processes this method is irreplaceable because of the ease with which the determination may be automated.

The advances in gas chromatography, as in all methods of separation, are associated primarily with the exceptionally high separating power of the chromatographic column. The high linear flow rate of the carrier gas and the small spreading of the chromatographic zone make it possible, in principle, to separate any mixture whose components differ, if only slightly, in their sorbability by the packing of the chromatographic column. However, for the analytical chemist it is important not only to separate the mixture into its components but also to evaluate the percentage present and in many cases also to determine their nature, i.e. to carry out qualitative and quantitative analyses. The methods for calculations on chromatograms, the estimation of the maximum accuracy of the chromatographic analysis, and the correlation of the readings of chromatographic detectors with the physicochemical properties of the substances separated are problems which have been successfully solved in many practical applications and here too no fundamental difficulties have been encountered.

The problems of qualitative analysis by gas-chromatographic methods have been investigated much less, although without a preliminary identification of the mixture components a complete quantitative analysis is impossible. It is paradoxical that in gas chromatography a situation has arisen where the final stage of analysis (the quantitative stage) has been developed to a higher degree than the first (the qualitative determination). Until recently hardly any attention was devoted to the problems of systematic identification of the components of the test mixture; the published data deal largely with specific problems.

The first stage of both qualitative and quantitative chromatographic analysis involves an attempt at the most complete separation of all the components of the test mixture. For such separation, use is made of a high-efficiency column preferably combined, with a programmed column temperature control during analysis. If it is known beforehand which components are present in the mixture, then for a qualitative analysis it is sufficient to employ a column which would yield a chromatogram with the number of peaks equal to the number of expected mixture components. In all other cases it is particularly desirable to employ temperature programming to detect the entire range of products. Only after it has been shown that all the components of the test mixture emerge from the column over a fairly short period, is it possible to abandon temperature programming and to employ isothermal analytical conditions. In order to obtain highly effective columns, capillary gas chromatography may be employed, but packed columns with lengths up to 50 m and having efficiencies equivalent to 50 000 theoretical plates have also been described[1]. In preliminary tests it is usually desirable to employ comparatively short packed chromatographic columns, 1–2 m in length, with temperature programming and only then to proceed to highly efficient columns to check the completeness of the separation of the mixture components. Satisfactory results are obtained when 2–3 high-efficiency columns (3–5 000 theoretical plates) with stationary phases of different types are employed. If there are no *a priori* reasons for a particular procedure, one chooses for qualitative analysis the columns which yielded the greatest number of peaks in preliminary tests. Usually columns with stationary phases of moderate or low polarity prove to be the most effective.

After a preliminary separation chromatogram has been obtained, it is necessary to make sure that each peak contains only one substance. For this purpose, the form of each peak in the chromatogram is analysed in the initial stage: a sharp distortion of peak symmetry and anomalous broadening of the bands are frequently indications of incomplete separation of the substances[2]. The most reliable results are obtained when each peak is collected in a trap and the eluate is subsequently separated on a column with a stationary phase of a markedly different type. Sometimes it is useful to treat the eluate chemically in order to obtain derivatives which can then be separated on the chromatographic column. However, in the separation of structural isomers and substances with similar physicochemical properties the above method may prove to be unsuccessful. To separate such isomers, use is made of selective sorbents or high-efficiency columns under isothermal conditions at several different temperatures.

The scheme for successive systematic qualitative analysis is as follows (see Scheme). The test mixture is

Scheme for systematic qualitative analysis by gas chromatography.

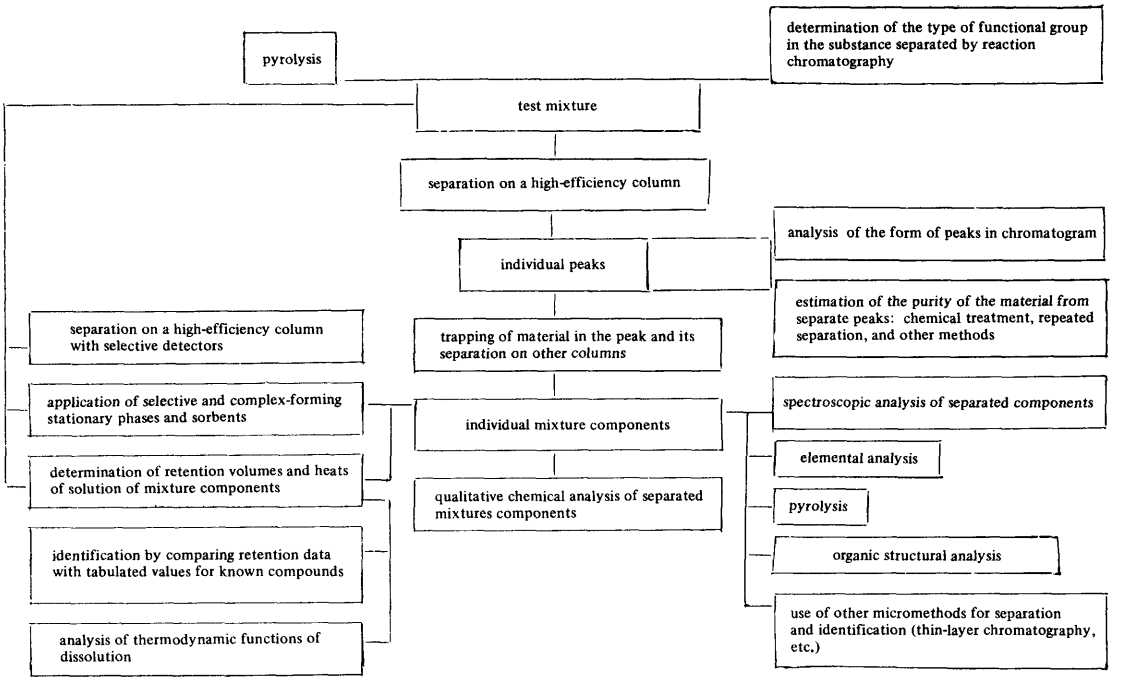


Table of principal methods for identification employed in qualitative gas-chromatographic analysis.

Method	Purpose and range of applicability	Advantages	Disadvantages
Use of stationary phases of different polarity and complex-forming sorbents	detection of individual structural groups and bonds in the molecule and overall estimation of polarity	simplicity of method (moderately laborious)	except when complex-forming sorbents are used, the method yields only approximate information about the polarity of the molecules
Reaction gas chromatography	determination of the functional groups of the compounds in initial mixture	does not require preliminary mixture separation	necessity for modifications of chromatographic apparatus. The functional groups and their position in the molecule are not always determined
Qualititative chemical analysis of separated substances	determination of the functional groups of the compounds after chromatographic separation	possibility of employing a large number of methods in the tests	necessity for complete separation of components investigated; sometimes comparatively large amounts of the substances are required
Organic structural analysis with chromatographic identifiaction of reaction products	determination of the carbon skeleton and the positions of the functional groups in the molecule	high reliability	necessity for the isolation of the pure substances. Laborious procedure
Pyrolysis	analysis of solid substances and high-boiling liquids	high sensitivity to slight changes in molecular structure	special aparatus and pure substances required
Comparison of the retention volumes and heats of solution of the test substances with data for known compounds	applicable to all compounds apart from pairs of isomers difficult or impossible to separate	simplicity of method (moderately laborious)	all the retention data for the substances whose presence is postulated in the mixture must be known or accurate relations for homologous series of these compounds are required
Analysis of thermodynamic functions of dissolution	applicable to all compounds; the molecular size and the number and positions of the functional groups are established	data for the retention of the substances whose presence in the mixture is postulated are not required	the use of semiempirical relations for the given chemical class of compounds; trained investigators needed
Selective detection	in the presence of C, O, Cl, and P atoms and of an aromatic ring in the compounds analysed	preliminary separation not required; high sensitivity	limited number of selectively determined characteristics of the molecules
Spectroscopic analytical methods	determination of the type of functional groups and their distribution and molecular size	extensive information about various molecular properties	need for the pure substances separated, sometimes in large amounts, complexity of the interpretation of the spectra, and the high cost of equipment
Elemental analysis	determination of the relative amounts of the elements in the substance separated	reliable information about elemental composition	need for special equipment and for the purity of the substances separated
Thin-layer and liquid chromatography, determination of physicochemical constants	identification on the basis of tabulated data for known substances	simplicity of method	neeed for the substances separated in pure form, sometimes large amounts; need for data for all the substances which may be present in the mixture

subjected to chemical reactions whereby it is possible to remove or transform chemically certain classes of compounds. Tests of this kind in combination with qualitative tests for functional groups of the separated substances collected in traps make it possible to assign the compounds to particular chemical classes and in many cases to obtain indications of the distribution of the functional groups in the molecule. When literature data are available on the retention of compounds in the same chemical classes as those detected in chemical tests, an attempt is made to compare the relative retention volumes and the heats of solution of the test substances with the tabulated data using 2–3 stationary phases of different types. If the test mixture contains components for which there are no published retention data and the postulated substances are not available in a pure form, then more complex methods of qualitative analysis are employed. The study of the thermodynamic functions of solutions in standard stationary phases makes it possible to elucidate the distribution of the functional groups in the molecule of the test compounds, the size of the molecule, and the structure of its carbon skeleton. The problems can also be solved with the aid of traditional methods of structural organic microanalysis and with the aid of various physicochemical procedures: infrared spectroscopy, mass spectrometry, nuclear magnetic resonance (NMR), determination of the melting and boiling points, and also in combination with other methods of separation, in particular thin-layer chromatography (see Table). Valuable information about the nature of the molecules of the components is provided by selective chromatographic detectors, elemental analysis, and pyrolytic gas chromatography. The main aim of this review is to describe various aspects of the application of these methods in qualitative analysis by gas chromatography.

II. APPLICATION OF QUALITATIVE CHEMICAL REACTIONS FOR THE DETERMINATION OF FUNCTIONAL GROUPS

The purpose of this method of identification in gas chromatography is to determine the type of functional groups in the test substance. Qualitative chemical reactions constitute the simplest and most reliable procedure for solving this problem [3] and such tests are possible both with the entire initial mixture and with the components separated. It is desirable to carry out the reactions with the initial mixture when all or the majority of the components are unknown. On the other hand, when only a few of the components are to be identified, it is more reasonable to establish the chemical nature of their functional groups by qualitative chemical tests on the separated substances.

The initial mixture is treated in reactors incorporated in the gas system of the chromatograph (less often) or functioning separately (more usual procedure). The first method requires a number of precautions in carrying out the reaction: the reaction time and the volume of the reactor must be sufficiently small so as not to affect the retention time or the form of the peaks for the substances separated and the reactor temperature chosen must be close to the temperature of the column or of the metering device. The stream of carrier gas is blown through the reactor during the entire period of the experiment and the chemical nature of the gas should promote the occurrence of the required reactions. In some cases, for example in hydrogenation reactions, the carrier gas must be pure hydrogen or its mixture with an inert gas. The design of the reactors not included in the gas system of the chromatograph can be of any kind. Such a reactor can consist of a tube with an outlet arm, which is closed by a self-sealing rubber system [4]. The outlet arm is connected to the chromatograph via a tap. Volatile reaction products are blown out via the outlet arm of the reactor into the column and the liquid products are collected with a syringe and introduced into the metering device of the chromatograph. The reactor incorporated in the gas circuit of the chromatograph usually consists of a metallic (less often glass) tube filled with a reagent and inserted between the metering device and the beginning of the chromatographic column.

Comparison of the composition of the initial mixture and the reaction products can be made most simply using two identical parallel columns in the same chromatograph with the reactor inserted before one of the columns. After evaporation and metering, the initial mixture is passed through a stream divider, which directs the two parts of the sample into the parallel columns; the ends of these columns are connected to the opposite chambers of the katharometer or differential flame-ionisation detector. In this scheme the pen recorder records only the peaks of the components which have fully or partially reacted, since the detector signals due to the unchanged peaks emerging simultaneously from the two columns cancel out. The reaction products and the composition of the initial mixture can be compared on different apparatus with the same columns. A partial decrease of the peak area of a particular mixture component indicates either that the reaction with the given substance is incomplete or that the peak contains two or more unseparated substances one of which has reacted with the reactor material. The disappearance of the peak is evidence that the substance has reacted with the substance in the reactor.

If the reaction yields volatile products (for example in the esterification of aliphatic acids), the retention data for the reaction products must be determined in order to identify them; an effort is made to select a type of chemical reaction which yields well known and readily available substances—for example hydrocarbons in exhaustive hydrogenation. If the reagent is volatile at the column temperature, then the need for a special reactor may be obviated, the reagent being introduced directly into the chromatographic column via the metering device before or immediately after the introduction of the test mixture. For example, alcohols may be acylated with acetic anhydride in this way.

The reaction with microamounts of substances can be carried out directly in the syringe needle, which is filled with Chromosorb for this purpose and the reaction mixture is then drawn in. After this the needle pierces the selfsealing rubber of the metering device, which is heated to the reaction temperature. The reaction reaches completion in several seconds and by moving the piston of the syringe the volatile products are forced into the chromatographic column where the substances are separated [5].

The methods of reaction gas chromatography enumerated above are based on the fact that they make it possible to compare the compositions of the reaction mixtures and the initial substances on various chromatographic columns. However, it is possible to modify the apparatus in such a way that a comparison may be made using the same chromatographic column with a flow divider [6]. The latter consists of a capillary passing through the reactor; part of the gas stream together with the unchanged components

of the initial mixture flow through this capillary into the chromatographic column. By altering the cross-section of the capillary, it is possible to regulate the amount of unreacted substance. Comparison of the chromatograms for mixture separation using different capillary cross-sections makes it possible to follow clearly the components whose amount decreases as the capillary diameter is reduced (there is a corresponding decrease in the amount of substance by-passing the reactor).

The reaction most widely used for qualitative analysis in gas chromatography is selective or exhaustive hydrogenation of the mixture components. The latter version permits group analysis in terms of the size and structure of the carbon skeleton of the molecule. The oxygen atoms in the test substance are reduced to water and other heteroatoms are either liberated in a free form or are reduced; exhaustive hydrogenation yields the saturated hydrocarbon corresponding to the carbon chain of the initial substance. If the heteroatoms are located between carbon atoms, then, after exhaustive hydrogenation, the corresponding molecular fragments are produced—a set of hydrocarbons the molecular sizes of which are determined by the size of the carbon radicals. In hydrogenation under gas-chromatographic conditions platinum [6,7], nickel [8], and palladium [9,10] catalysts are employed. The platinum catalyst operates at a relatively low temperature but it is also more sensitive to poisoning by sulphide and diene compounds. It is more convenient to carry out hydrogenation on a palladium catalyst in the temperature range between 150° and 260°C. Hydrogenation reactors are employed not only in combination with packed columns but also in combination with capillaries [11].

Reactions which remove particular classes of chemical compounds are most widely employed in the qualitative determination of unsaturated compounds in complex hydrocarbon mixtures. Olefins may be absorbed by a column containing silica gel impregnated with sulphuric acid [12,13] operated at temperatures between 20° and 50°C. In order to absorb ethylene and acetylene, which are not absorbed quantitatively by concentrated sulphuric acid, a solution of silver sulphate in sulphuric acid is employed. Sulphuric acid removes also aromatic compounds [14]. Apart from sulphuric acid, mercury perchlorate [15] and copper(II) chloride [16] are used to eliminate unsaturated compounds. Maleic anhydride absorbs butadiene [17,18].

Straight-chain alkanes are removed from mixtues by molecular sieves [19,20]. Alcohols react with boric or metaboric acids with formation of involatile compounds [3,21]. Aminoacids are converted by oxidation into volatile aldehydes, ninhydrin being employed for this purpose [22]. Reactors with phosphoric acid are used to decarboxylate aliphatic acids [23]. Aldehydes and ketones are removed with sodium bisulphite [24]. The same paper [24] describes a method for the elimination of sulphur-containing components in a reactor containing mercury(I) chloride. Secondary and tertiary alkylbromides are absorbed by silver nitrate [25] and amines by phosphoric acid [26]. Water vapour reacts with calcium carbide [27] and is retained in a reactor containing potassium carbonate [28].

Esterification is widely used in gas chromatography not only for quantitative analysis but also to convert reactive aliphatic acids into readily separated esters. For this purpose, the reaction is carried out between potassium salts of aliphatic acids and sodium ethyl sulphate [29,30] at 300°C or tetramethylammonium salts are pyrolysed [31]. Alcohols form esters with sodium nitrite [32,33] and with acid anhydrides [34]. Esters may be hydrolysed [35] with subsequent chromatographic determination of the products formed. The position of the double bond in the molecule of an unsaturated compound can be established by ozonolysis [36,37].

A very interesting version of qualitative reactions with the initial sample has been described [38]. This type of test is suitable for mixtures of substances the components of which do not boil above 200°C, since the entire mixture must be evaporated at room temperature in a closed vessel before the test. The gas from this vessel is drawn into a syringe on the walls of which the appropriate reactant has been deposited. After the reaction at room temperature the sample is introduced into the chromatograph by moving the piston of the syringe; the chromatogram indicates the composition of the test mixture after the chemical reactions in the syringe.

Much information about the functional groups of the components may be obtained using qualitative chemical reactions on the separated substances beyond the column, transferring them together with the carrier gas into appropriate reagents or collected in traps. The design of the traps depends on the aim of the experiments: universal traps are employed to condense components in amounts ranging from a fraction of a milligramme to 50 mg and special traps are designed where the condensed substance is subsequently subjected to a particular physicochemical determination, for example the recording of the infrared or mass spectrum. Simple glass U-traps attached to the chromatograph via a seal of heat-resistant rubber are normally used in qualitative analysis. To collect or remove very large amounts of the substance (in excess of 50 mg), various traps employed in comparative chromatography are used [39]. Such large amounts of selected separated substances may be needed in structural organic analysis, in the determination of the boiling and melting points, and in certain spectroscopic analyses. To achieve complete condensation of the separated components emerging from the column, it is necessary to create a turbulent gas stream and prevent an unduly high temperature gradient in the trap. The latter condition is particularly important to prevent the creation of a mist and therefore the use of liquid nitrogen and metallic traps is not recommended for the condensation of high-boiling compounds. Traps for semipreparative purposes may be used both at atmospheric and reduced [40] pressures.

The designs of traps for the collection of very small amounts of substance (down to 0.1 mg) has been described [41,42]. The trapping process in such traps takes place in two stages: initially the eluate is collected in a short section of the chromatographic column at a reduced temperature and then, on heating this section a slow stream of gas transfers the fraction collected into the microtrap. Traps for the collection of microamounts of substances which are simple but not really effective consist of the needle of a syringe or short Teflon capillaries [43] cooled with dry ice. For subsequent use, the condensate in such traps in washed off with a solvent or centrifuged.

A number of special traps have been constructed for subsequent employment in the measurement of infrared spectra. Some of them are first filled with a powder transparent to long-wavelength infrared radiation: potassium bromide or lithium fluoride. The products separated in the chromatographic column are condensed on the surface of these powders [44]. Traps where the condensation of the separated substances is achieved on the surface of a cellulose filter [45], which is then placed in an infrared spectrophotometer, have been described. Traps for the collection of very small amounts of separated sub-

stances are also used for the subsequent determination of the infrared spectra of the condensed substances [41,46]. In order to trap the substances for later determination of their mass spectra, traps with an adsorbent filler (molecular sieves, etc.) are used [47]. The substances emerging from the chromatograph are trapped by the sorbent in the cold, then the sorbent is transferred to a tube sealed to the filling system of the mass spectrometer. On heating, part of the substance is desorbed and passes into the mass spectrometer. Traps filled with powders transparent to infrared light have a low trapping efficiency, which may be enhanced by cooling the trap. Devices with adsorbents can be used only to trap relatively low-boiling substances, since desorption of high-boiling substances and substances with highly polar molecules requires high temperatures; there is then a real risk of the degradation or isomerisation of the adsorbed substance.

Qualitative reactions with the separated substances can be performed either directly in the trap or in a vessel after washing the substance out of the trap with a suitable solvent. The principal requirement which must be met in the application of reactions of this kind is high sensitivity (about 10–20 μg). The most suitable are drop reactions and methods specially tested in chromatographic practice [48].

The determination of the carbon skeleton of the separated compound constitutes a very important operation in qualitative chromatographic analysis. For this purpose, use is made of exhaustive hydrogenation on palladium and platinum catalysts [49–51] and attention is concentrated not on the rapidity of hydrogenation but on the completeness of the process and on the prevention of undesirable side reactions such as dehydrogenation and isomerisation. After separation in the chromatographic column, the substance collected in the trap is passed in a stream of hydrogen through the reactor (length about 24 cm), is again collected in a trap, and transferred for analysis on the chromatograph, where the resulting hydrocarbon is identified by its retention time. In those cases where it is very difficult to determine the particular isomer of the alkane formed, a methylene group is introduced [52]. In the analysis of the separated substance there is a possibility of establishing not only the presence of heteroatoms in the molecule but also, in a number of cases, the nature of the chemical bond between the heteroatom and other parts of the molecule, as has been done, for example, with nitrogen [53,54]. In particularly complex cases use may be made of the classical procedures of organic structural microanalysis.

III. THE USE OF RETENTION DATA ON VARIOUS STATIONARY PHASES AND ADSORBENTS

Certain preliminary information about the nature of the substances separated may be obtained by studying the retention of the mixture components on various stationary phases. Best results are obtained by this method in the determination of the retention volumes of substances which were first separated and collected in traps. On the other hand, when the experiments are performed with the entire initial mixture, it is necessary to separate the principal components, otherwise it is impossible to determine to which component particular retention data on various stationary phases refer.

Comparison of the relative retention volumes of the test substances (using a paraffin as a standard) reveals the relative polarities of their molecules [55,56]. If the test compound has polar or readily polarised functional groups (for example, C=O or C–Cl), then on transition from a non-polar to a polar stationary phase the relative retention volume increases. A quantitative estimate of the polarity of the given compound is obtained by measuring such increase. It should be recalled that the polarity of the component characterises only the general properties of the molecule but cannot serve for an unambiguous determination of its structure and the number and nature of the functional groups. Certain relations between molecular structure and the relative retention volumes on various stationary phases have been discussed in a monograph [55].

More definite information about the nature of the test substances is obtained using complex-forming stationary phases and sorbents. For a successful application of such methods, it is necessary that the mixture analysed contains substances which are selectively retained on the complex-forming sorbent. For example, alcohols and phenols are selectively retained on hydroxylated stationary phases. For selective retention of unsaturated compounds, use is made of stationary phases consisting of solutions of silver nitrate in polar liquids (ethylene glycol, benzyl cyanide, *p*-xylyl cyanide, etc.). These stationary phases are used to isolate ammonia [57], olefins [57–60], and other unsaturated hydrocarbons.

The high selectivity of certain adsorbents permits their use in determining the nature of the substances. For example, on silica gel and alumina unsaturated hydrocarbons are selectively separated from saturated hydrocarbons. Bentonites (complex-forming organic clays) with various additives have found the widest application. Isomers of xylene [61], dichlorobenzene [62], dimethoxybenzene, chloroacetophenone, and dimethylnaphthalene [63] are readily separated on these substances. Certain quaternary ammonium bases form complexes with π-donor molecules [64].

1. Identification by Comparing the Retention Data

After the establishment of the presence of particular functional groups in test substances, the compounds can be identified in terms of purely chromatographic quantities—the retention parameters. The retention characteristics are constant only for gas–liquid chromatography and therefore this type of identification is inapplicable to gas adsorption chromatography: in this case the retention volume depends not only on the nature of the compound separated but also on its amount (non-linearity of the adsorption isotherm). Retention parameters such as the relative retention volumes and heats of solution are most widely employed for identification. With the exception of the separation of polar substances on non-polar stationary phases, these quantities are virtually independent of concentration and the amount of the substance separated. If the result of the qualitative chemical reaction depends only on the nature of the functional group of the test compound, then solubility is a function of both the number of chemical groups in the molecule and of the size of the molecule and the structure of its carbon skeleton. Therefore agreement between the retention times of the test and standard compounds on the stationary phase does not constitute an unambiguous proof of their identity: usually in chromatographic practice one compares, for the purpose of identification, the retention volumes on three stationary phases of different types and, when the retention volumes and the relative heats of solution are determined, the

measurements are made on two stationary phases [55]. As a rule at least two liquids (a non-polar and a polar stationary phase) are employed.

For identification, it is most rational to employ relative retention data, since this entails a sharp improvement in the accuracy of the determination and of the agreement between the tabulated data of different authors. The limiting accuracy of the measurements of the relative retention volume is 0.2% and that of the relative molar heat of solution is 0.05 kcal; however, the scatter of the retention data of various authors may reach 5%. The choice of a suitable standard compound plays a major role, since the time required for its emergence must be reliably measured. For a better standardisation of data, it is recommended that the following standard substances be chosen for the measurement of the relative retention parameters: straight-chain alkanes (for non-polar stationary phases), benzene, and carbon tetrachloride; naphthane is suitable at high temperatures. The calculation of the relative retention volume with corrections for the experimental conditions and the determinations of the heats of solution from the temperature variation of the logarithm of the retention volume have been described in a monograph [55]. Identification by comparing the retention parameters can be achieved when pure samples of the substances postulated in the mixture are available (the best procedure) or on the basis of tabulated data [65-68].

If the test mixture is separated at an elevated column temperature, the retention characteristics of the components may be determined in a series of experiments under isothermal conditions with increasing column temperature: at each temperature the retention times are found for those components which are separated within a reasonable time. Then the logarithm of the retention volume is plotted against the reciprocal of the column temperature, the line is extrapolated to the chosen temperature, and the relative retention volumes of all the mixture components at a single temperature are determined from the table of antilogarithms. The determination of the retention volumes and heats of solution of the test substances in mixtures can be recommended only for simple samples containing several peaks of different size. In the general case more reliable results are obtained by collecting the separated substances in traps with subsequent determination of their retention parameters in columns with standard stationary phases.

In a number of studies compounds are identified by a comparison method using the retention indices, but these quantities have no advantages over the relative retention volumes and their use frequently leads to appreciable errors.

If there are no suitable tabulated data for the retention of the compounds thought to be present in the test mixture, it is possible to employ gas-chromatographic correlation methods. Such correlations hold best for the linear relation between the logarithms of the retention volumes of members of a homologous series and the number of carbon atoms in the molecule. The retention volumes for different stationary phases may be calculated by the method of linear correlations [69,70]. The slopes of the lines obtained by plotting the relative volumes for the test and standard substances along the ordinate axes are employed to determine the group to which the component belongs. Although the relation between the retention volumes of the substances separated in non-polar and weakly polar stationary phases and the boiling points has been investigated in a number of studies [70-74], a sufficiently reliable and universal correlation between these quantities has not been established. Such correlations hold only for a narrow range of substances of similar nature but even in optimum cases—solutions of hydrocarbons in hydrocarbon stationary phases—the error exceeds one degree. The boiling point and the logarithm of the retention volume can be unambiguously related only when the components separated and the stationary phase are of a similar type. The plotting of any kind of correlations for aromatic and other highly structured stationary phases, where the entropy factor and the steric hindrance to intermolecular interaction have a significant influence on the retention volume, should be avoided.

The procedure involving the use of various solvents to alter the solubility of the test substance, i.e. the method of determination of the quantity p is extremely promising [75]. The quantity p is the ratio of the solubilities of the test substance in a non-polar and a polar solvent, two immiscible solvents in the same vessel being employed. The values of p are measured for the test substances and then for the compounds whose presence in the mixture is suspected. Since all the measurements are made at room temperature and the choice of solvent is not governed by temperature limitations, it is possible to choose extremely selective solvents whereby the test compounds can be characterised fairly completely. The low temperature in the measurement of solubility favours the occurrence of specific and orientation interactions which make it possible to discover the fine structure of the test compound molecule. Since the amount of solute in each phase is determined chromatographically, the measurement of p is not very laborious. This method has been successfully used to identify isomeric compounds boiling at high temperatures [76-79]. The methods for the comparison of retention data require the availability of all the presumed components or their retention parameters. Certain linear correlations in homologous series may be employed for identification by a comparison method but for this one must be certain that the given test substance belongs to a particular homologous series. At the same time comparison methods have attracted investigators by their extreme simplicity and high reliability of the results. Therefore, when the experimenter has at his disposal the retention data for all the substances postulated in the mixture on 2–3 stationary phases, it is reasonable to employ the comparison method in combination with qualitative chemical analysis.

2. Analysis of the Thermodynamic Functions of Dissolution

If the use of qualitative reactions combined with a comparison of tabulated retention data cannot ensure a convincing identification, it is recommended that the method involving the analysis of the thermodynamic functions for the solution of the substances in standard stationary phases be employed [55]. This procedure has been used with particular success in those cases where there is no information about the substances postulated in the mixture and their physicochemical properties. This method of identification is perhaps simplest for the qualitative analysis of mixtures of polyfunctional compounds and high-boiling isomers, in particular hydrocarbons. An advantage of this procedure is less stringent requirements for the degree of separation of mixture components, since retention data can be determined also for incomplete separation of the components. The main principle of the thermodynamic method of identification consists in the calculation of the thermodynamic functions for the solution of the

postulated substances on the basis of the following characteristics of the molecules: molar refraction, van der Waals radii of the atoms and atomic groups, and the number of internal and external rotational degrees of freedom. The agreement between the calculated and experimental thermodynamic functions of the dissolution of substances in various stationary phases indicates a particular structure of the test substance molecule.

The semiempirical calculation of the heats of solution of various compounds in a non-polar stationary phase is simplest [80]. It is then possible to establish the size of the molecule and the structure of its carbon skeleton; the use of polar stationary phases provides evidence about the number and positions of polar functional groups in the molecule. Analysis of the entropy of solution permits conclusions concerning the rigidity of the molecular structure, the branching of the carbon skeleton, and the number of degrees of freedom associated with rotation—properties which characterise the molecule as a whole. The combination of qualitative chemical tests with the thermodynamic method of identification has been used to determine the products of various chemical reactions—oxidation of olefinic hydrocarbons [81,82], photochemical chlorination of olefins [83], and chlorination of acetone [84] and also for the determination of the composition of industrial mixtures [85].

Identification by the analysis of thermodynamic functions is the only method for the determination of the composition and structure of unknown compounds, particularly those for which no published data are available. However, such identification requires the availability of relations between the thermodynamic functions of solutions and molecular structure. Such relations hold for a fairly wide class of substances, but their use requires prior training of the investigator and a thorough knowledge of the nature of intermolecular forces. The application of this method for identification is possible only in combination with qualitative chemical tests for functional groups.

IV. APPLICATION OF SELECTIVE DETECTORS FOR IDENTIFICATION IN GAS CHROMATOGRAPHY

In a number of studies the high separating power of the gas-chromatographic column has been combined with the analysis of the fractions obtained on separation by infrared spectroscopic and mass-spectrometric measurements. The former provides information about the presence and location of the functional groups in the molecule and the latter about the size of the molecule. The combination of three types of apparatus—a chromatograph, an infrared spectrophotometer, and a mass spectrometer—permits the identification of up to 95% of all volatile organic compounds [1]. The optimum version of this device includes a high-efficiency chromatographic column [of the order of 50 000 theoretical plates] and a complex attachment for the interruption of the separation process during the determination of the spectra of the substances separated. The use of spectrometers as a means of identification imposes certain requirements on such devices: the capacity to record over a short period (3–10 min) the entire spectrum of the test substance and a very high sensitivity permitting the determination of the spectra of small amounts of the substances separated in the chromatographic column. The disadvantages of this combined apparatus include the necessity to interrupt the separation process during the recording of the spectrum and also the high cost of the spectroscopic devices.

One of the versions of apparatus of this kind involves the combination of a chromatograph with a cheap mass-spectrometer having a low resolving power which provides a continuous record for two mass numbers. An apparatus of this type has been called the "Khrommass". [86–88] The use of continuous recording of chromatograms in terms of the coordinates for various mass numbers permits the identification of the substance from the relative peak heights for various characteristic mass numbers [89], but this method becomes complicated with compounds containing more than five carbon atoms in the molecule. The combination of mass spectrometers with chromatographs allows the identification of a large number of compounds [90–92]. An undoubted advantage of the mass-spectrometric detector is its exceptionally high sensitivity, which permits its use in combination with capillary columns. A number of difficulties associated with the inertia of the mass spectrometer then arise; to eliminate this, short heated capillary junctions are employed between the chromatograph and the mass spectrometer [91,93–95] or the carrier gas is removed from the eluate [95,97]. However, the complexity of the design of the mass spectrometer and the need for highly trained operators for such apparatus limits its applicability in chromatographic practice. Reports have been published on attempts to employ radiofrequency mass spectrometers—the so called *QQ*-detectors [98]—but detectors of this kind have a low sensitivity and can be used to determine substances only up to a mass number of 250.

The application of ultraviolet spectrophotometry as a means of identification in gas chromatography is very limited, since its selectivity with respect to molecules having more than six carbon atoms is low, while such molecules in fact constitute the main bulk of the compounds separated by gas chromatography. The use of this method of identification for the analysis of xylene isomers has been described [99] and cases of the application of far ultraviolet absorption spectra in qualitative analysis have been noted [100,101].

The most sensitive selective spectroscopic detector is the flame photometric detector [102]. Its sensitivity exceeds by 1–2 powers of ten that of the flame-ionisation detector.

Two types of detectors, namely the electron capture and thermionic detectors, may be noted among the commonest detectors for qualitative analysis described recently. The operation of the first detector depends on the absorption of the slow electrons emitted by the radioactive source by the molecules of substances having positive electron affinities [103]. The detector signal depends on the capacity of the substance separated to capture electrons, which may be used as a valuable source of information about the properties of the test compound molecule, derived by comparing the chromatograms obtained using selective and non-selective detectors. All organic compounds may be divided into two classes in terms of their capacity to capture electrons: substances with simple capture and substances with capture by conjugated bonds. The first class includes halogeno-derivatives and the second conjugated aromatic systems. The presence of two and more electron-accepting atoms in the compound to be determined increases by 2–3 powers of ten the signal at the electron capture detector (ECD). This type of detector has been successfully used for the selective determination of halogeno-derivatives [104], polynuclear aromatic hydrocarbons [105], and steroids [103]. Since the sensitivity of the electron-capture detector towards substances having electronophilic groups is higher by several powers of ten than for other compounds, comparison of the chromato-

grams obtained using a universal detector and an electron capture detector determines unambiguously the properties of the test substance.

The thermoionic detector is extremely sensitive to chlorine- and phosphorus-containing compounds [106,107]. It is a modification of the flame-ionisation detector, into the flame of which a pellet compounded with an alkali metal salt is inserted. The conductivity of the hydrogen flame increases sharply only when chlorine- and phosphorus-containing compounds emerge from the column. The sensitivity of the thermionic detector is comparable to that of the flame-ionisation detector.

Halogen-containing substances are also determined by the Beilstein test performed visually [108,109] or automatically [101,110]. However, this test does not yield an unambiguous proof of the presence of a chlorine atom in the molecule, since many other compounds also give the same colour in the flame.

Detectors operating in conjugation with chemical reactions, for example automatic titrators, show the greatest selectivity with respect to a narrow range of compounds. The titrators determine selectivity free aliphatic acids [111] and sulphur-containing substances, which are converted into sulphur dioxide in the reactor beyond the chromatographic column [112]. Microcoulometric detectors for the selective detection of organosulphur compounds in complex mixtures have found wide application in the analysis of petroleums [113,114]. They have a very high sensitivity—down to 10^{-6} g of the substance.

A selective detector with a krypton-85 quinol lathrate evolves radioactive krypton on coming into contact with certain substances: chlorine, bromine, nitrogen dioxide, nitrogen oxychloride, and others [115]. This detector may be used for qualitative detection of halogens in the test compound after its combustion.

A detector operating on the principal of piezoelectric absorption can also be included among specific devices [116]. A vibrating quartz crystal is coated by a layer of liquid which absorbs selectively certain components of the mixture to be separated. The detector signal is proportional to the amount of substance absorbed by the liquid layer. The application of this detector is analogous to the use of two and more selective stationary phases for identification.

Detectors involving combustion on a platinum spiral have some selectivity [117,118]; their signal is proportional to the amount of heat evolved on combustion of the separated substance on the platinum spiral; by varying the temperature to which the platinum wire is heated, it is possible to alter the sensitivity of the detector with respect to various substances.

The molecular weight of the unknown substance may be determined by means of a detector the operation of which is based on the density of the gas (gas-density balance) [119-122]; it is applicable to substances with a not unduly high molecular weight—of the order of 100. The measurements are made with two different carrier gases; the main errors arise due to the inaccuracy of the measurements of the peak areas and the inconstancy of the composition of the standard mixture, amounting to about 5% in the most favourable cases. A more laborious method for the determination of molecular weight with the aid of a gas-density balance has been described [122]; in this case the error did not exceed 0.5%. The methods for the determination of molecular weight with a gas-density balance in gas chromatography have not found wide application, since they are suitable only at low column temperatures (the sensitivity of the detector falls rapidly as the temperature increases); on the other hand, the identification of low-boiling substances is not a difficult analytical problem.

Information about the number of carbon atoms in the test substance may be obtained with the aid of detectors involving the combustion of the separated substances to carbon dioxide [123,124]. The peak area is proportional to the number of carbon atoms in the molecule. When the peaks of the same substance in the mixture are compared first using a katharometer and then a device for its combustion, it is possible to estimate the number of carbon atoms in the molecule. Conversion of the separated products into methane, which is then detected by the katharometer, is employed to determine the number of carbon atoms in the molecule. The use of a detector which determines the amount of oxygen consumed in the combustion of the separated substances is very promising [125]. The amount of oxygen consumed is measured by the current necessary to produce this gas by the electrolysis of water. Analysis of the chromatograms obtained with such a detector permits the determination of the number of carbon atoms in the molecule which are not linked to oxygen atoms.

The use of selective detectors makes it possible to elucidate a number of specific properties of the substances separated—the presence of heteroatoms and certain functional groups and the number of carbon, hydrogen, and oxygen atoms in the molecule. Although spectroscopic detectors yield much information about the properties of the molecule, simple selective detectors have found wide application by virtue of their cheapness, simplicity of operation, and high sensitivity in the continuous recording of the results of separation. A disadvantage of selective detectors is high sensitivity for limited classes of compounds only. If the qualitative analysis is carried out in the laboratory fairly frequently, it is desirable to employ spectroscopic devices for identification. In the qualitative analysis of very small amounts of substances, only selective detectors and a mass spectrometer may be employed.

V. THE USE OF OTHER PHYSICOCHEMICAL METHODS FOR THE INVESTIGATION OF SEPARATED SUBSTANCES

In many cases qualitative analysis in gas chromatography is carried out with the aid of other physicochemical methods, for example thin-layer chromatography. Preliminary separation of very complex mixtures is frequently performed in the analysis of petroleum fractions, which involves liquid-adsorption chromatography. The fractions obtained are analysed by gas-chromatography. The converse procedure is also employed: the substances separated on a gas-chromatographic column are deposited on the starting line of the thin-layer chromatographic plate which moves at a constant rate relative to the output from the detector [126-128]. The separated substances are adsorbed on silica gel along the starting line, their positions on the line corresponding to the positions of the peaks on the chromatogram recorded by the katharometer. The chromatograms on the plate are then developed and the R_f values of the spots are determined. The identification is based on the R_f values for silica gel. The principal advantage of this method is its combination of the separation of the substances in terms of the form and size of the molecules by a non-polar stationary phase and in terms of the characteristics of the molecular structure

and the presence of functional groups by silica gel. The system obtained has an exceptionally high separating capacity. A certain disadvantage of the method consists in the fact that thin-layer chromatography requires a relatively large sample, which necessitates the operation of the gas-chromatographic column under conditions of overloading.

The substances separated chromatographically may be investigated by any micromethod. It is possible to determine their boiling and melting points by a micromethod [129] and to record and analyse the NMR spectrum [130]. These methods require a comparatively large amount of the substance (up to 100 mg), which presents certain difficulties, particularly in those cases where the relevant substance is present in the mixture in small amounts. It is somewhat more convenient to investigate the form and colour of the crystals under the microscope—the crystal may be the separated pure substances or the products of their chemical reactions [131]. The microscopic method for the investigation of crystal form makes it possible to distinguish the components of non-separated mixtures provided that they form crystals of different shapes.

Auxiliary physicochemical methods are comparatively rarely required for qualitative analysis in gas chromatography, since they are not very sensitive and universal.

VI. ELEMENTAL ANALYSIS

An additional source of information about the test substance is elemental analysis—this procedure is carried out by classical micromethods with the pure separated compounds collected in traps. The use of gas chromatography in elemental analysis makes it possible to reduce greatly the amount of labour required and to improve the accuracy of the experiments. The high separating capacity of chromatographic columns permits the determination of several elements in one operation. The first stage of elemental analysis in organic chemistry has remained unchanged and is based on the principle of the oxidation or pyrolysis reactions, but gas chromatography allows the use of extremely small amounts of the substances. Two versions of elemental analysis by chromatographic methods are possible: these involve a combination of the apparatus for the decomposition of the substance with a gas chromatograph or the separate operation of these devices with transfer of the reaction products to the chromatograph.

The combined device for the simultaneous determination of carbon, nitrogen, and sulphur consists of a reactor where the specimen is oxidised over copper(II) oxide in a stream of helium at 850°C and a chromatograph [132]. The reaction products (nitrogen, carbon dioxide, and sulphur dioxide) are separated at room temperature on a 1 m chromatographic column filled with Chromosorb P impregnated by 33% DS-550 silicone oil. The time required for the complete separation of the mixture is 4 min and the error of the analysis is 0.3%. If there is no need to determine sulphur, the substances are combusted on a mixture of copper(II) oxide and manganese dioxide at 600°C and the duration of separation is reduced to 1.5 min. Similar devices are used for the simultaneous determination of carbon, nitrogen, and hydrogen [133]; the water formed on combustion reacts with calcium carbide and is determined from the size of the acetylene peak. A mixture of nitrogen, acetylene, and carbon dioxide has been separated on a column containing 5 Å molecular sieves with a programmed temperature change from room temperature to 400°C at a rate of 6 deg min^{-1}. The duration of the complete analysis is 50 min.

Nitrogen and oxygen are determined simultaneously in the pyrolysis of the test substance over "nickel-plated" carbon black at 900°C. [132] The pyrolysis is carried out in the flame of a gas burner over a period of 5 min, the reaction products being separated at room temperature in a 60 cm column with a 5 Å molecular sieve. The analytical error is not greater than 0.8% and the total time required for the determination is 15 min. In all these methods the substance is decomposed in a stream of carrier gas and the outlet from the reactor is connected throughout to the initial section of the chromatographic column. The reaction products are immediately transferred by the stream of carrier gas to the column. The disadvantages of this method include the impossibility of employing oxygen for combustion and the spreading of the chromatographic zone during the finite period of the decomposition of the substance.

The subdivision of chromatographic elemental analysis into two stages makes it possible, at the expense of a slight increase in the analysis time, to separate the chromatograph from the reactor and to employ any conditions for the decomposition of the test substances. The reaction products are collected in a trap whence they are transferred to the chromatograph for analysis. This method for the determination of carbon and hydrogen in organic compounds has been described by Duswalt and Brandt [134]. The test substance is combusted in a stream of oxygen at a reactor temperature of 750°C over silvered copper needles, copper(II) oxide, and platinum, moisture being converted into acetylene by reaction with calcium carbide; carbon dioxide and acetylene condense in a trap and are then separated in a 90 cm silica gel column. The overall duration of analysis is 20 min and the absolute error is 0.5% with respect to carbon and 0.1% with respect to hydrogen. Similar results were obtained also in other investigations [135,136] with a slight modification of the conditions. By combining a gas-density balance as a detector with combustion of the products it is possible to determine the ratio of hydrogen and carbon atoms in the molecule [137]. However, the complexity of the apparatus in this method is not justified by the amount of information obtained with its aid.

By depositing alkali on an inert carrier, one can determine the number of Si–H groups in the molecule from the amount of hydrogen evolved on hydrolysis [138].

Catalytic hydrogenation of the separated substance at 1000°C leads to its complete conversion into methane [139]. The size of the methane peak after such hydrogenation indicates the number of carbon atoms in the molecule of the test substance. Catalytic hydrogenation of nitrogen-containing substances over nickel or magnesium oxide catalysts yields ammonia, the amount of which can be measured chemically or chromatographically [140].

Elemental chromatographic analysis is one of the auxiliary procedures for identification but it yields only the proportions of the elements in the test substance. The structure of the molecule and the location of functional groups in it are determined by other methods, described above.

VII. PYROLYSIS

One of the new trends in the gas-chromatographic identification of compounds is the use of pyrolytic gas chromatography. The pyrolysis is carried out in special cells

(with the amount of test substance between 0.1 and 1 mg) on a platinum wire or a ferromagnetic material, which may be convered by glass. The pyrolysis temperatures lie between 400° and 1200°C. The pyrolysis is usually performed to identify a single substance and more rarely a binary mixture. Pyrolytic chromatography can be most usefully employed for the identification of high-boiling compounds. Solid substances, in particular polymeric compounds, may be identified by this procedure. The pyrolysis products are carried by the carrier gas directly from the pyrolyser to the chromatographic column, where they are separated. The pyrolysis temperature is chosen in such a way that a number of peaks characteristic of the given compound are obtained on the chromatogram. Then the pyrolysis chromatograms of the unknown and known compounds are compared. The identity of the pyrolysis chromatograms is evidence of the identity of the substances compared. The method is the only one available for the identification of high-boiling compounds having isomers with similar properties. Such isomers are extremely difficult to separate on a chromatographic column at a high temperature, since the selectivity of stationary phases falls as the temperature increases. With a correct choice of reaction conditions, pyrolysis chromatograms are characteristic of a given compound [141-143]. The maintenance of rigorous constancy and reproducibility of the pyrolysis temperature is exceptionally important for identification, since the composition of the pyrolysis products varies as a function of reactor temperature. The study of the pyrolysis products at different process temperatures also helps characterise a pure substance. The pyrolytic method has proved extremely effective for the determination of impurities in solids, for example in the analysis of many substances in the living cell [144-147].

In conclusion we must consider the most rational methods for the identification of substances present in the mixture in different proportions. For substances whose concentration in the mixture is from 1% upwards, all the methods described above are applicable in principle, up to structural analysis by methods of organic chemistry. On the other hand, if it is necessary to identify impurity components, two procedures are suitable. The first consists in the concentration of the impurities by chemical or physicochemical methods. The concentrate is then analysed by the usual procedures. On the other hand, if such concentration is impossible, the following methods are employed for identification: selective removal or conversion of the mixture components in reactors, comparison of retention data, and thermodynamic analysis of the properties of the solution. Definite information is provided by mass spectrometers and selective detectors.

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