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APPLICATION OF GAS CHROMATOGRAPHY IN PETROCHEMISTRY AND PETROLEUM REFINING

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SUMMARY

Trends in the use of gas chromatography in petrochemistry and petroleum refining are evaluated on the basis of existing information over the past ten years. A critical search for information on and experience in the following topics is made: (i) physical and chemical measurements, (ii) identification of compounds and (iii) efficiency of separation.

INTRODUCTION

Scientific and technological progress in chemistry and the chemical industry is in many ways determined by the efficiency of the analytical methods used. The development and wide application of gas chromatography (GC) has revolutionized the analysis of multi-component mixtures in petrochemistry and petroleum refining. Much of the quantitative analysis which was formerly considered impracticable, because it could be accomplished in no less than a number of days, has now become feasible because GC allows this work to be done in a matter of minutes or even seconds.

The high resolution and sensitivity inherent in chromatography, as well as the rapidity and potential for automation, have contributed greatly to the extensive application of GC both in research and industry. GC is used with considerable success in measuring the physical and chemical characteristics of a wide variety of substances and in studying chemical reactions. As a matter of fact, GC is at present one of the most widely applied methods in analysis and physicochemical experimentation.

Generally, the development of a branch of science can be most fully characterized by the number and content of publications appearing, and by their dynamics in the course of time. Though widely applied, GC is still developing dramatically and the number of papers appearing on the subject each year amounts to 1500 now, according to the bibliographical data regularly published in the *Journal of Chromatography*.

The development of GC is due partly to its widening field of application and partly to the introduction of new methods, apparatus and theoretical concepts. In this connection, it is interesting to define (on the basis of a statistical analysis of existing literature) the trends of this development as compared to other analytical methods. Such an approach to studying the development of a branch of science is not new[1–4].

With this object in view, a statistical analysis has been performed on papers that appeared in the most important journals on analytical chemistry, published in the U.S.S.R. and abroad[5-9] in 1962, 1967 and 1972, as well as in those on chromatography in the same years[10-12].

Naturally, it had to be firstly found out how often GC was used over the decade from 1962 to 1972 for solving new analytical problems within the subject of all these papers. Tn Table I comparative data are given on the relative frequency of use of various analytical methods. It can be inferred that the number of GC methods has slowly but steadily increased over the decade under consideration, and in 1972 accounted for 12.5% of all the chromatographic methods then in use. The data given in Table I for 1967 are in good agreement with the results of similar studies conducted by

TABLE I

DISTRIBUTION OF PAPERS ON METHODS OF ANALYSIS*

Method	Papers (%)		
	1962	1967	1972
All kinds of chromatography	17.2	19.0	17.8
Gas chromatography	10.1	10.8	12.5
Spectral analysis (spectroscopy, photometry, NMR, etc.)	48.5	47.4	47.8
Gravimetric, volumetric and other methods	18.4	11.5	8.6
Electrochemical methods	15.8	22.1	25.8

* The table lists papers published in refs. 5–9.

Fisher in 1965[4]. According to him, in 1965 GC accounted for 9.5% of the analytical work described, and visual–titrimetric methods for 14.2%. It can also be seen from Table I that the relative number of newly developed methods based on classical analytical methods (gravimetric, volumetric, etc.) has decreased over the past ten years by more than half, which can most probably be accounted for by the wide application of new, more accurate and less strenuous instrumental methods of physical and chemical analysis. At the same time, electrochemical analysis methods have found much wider application.

Table I also suggests that chromatography ranks third among analytical methods. In conducting such studies, however, account must be taken of the specific features of GC. Therefore, additional comparisons should only be made for those papers that deal with methods of analysing gases and organic compounds only, for it is in this field that GC is most widely used. In the above-cited publications, the analysis of gas and organic compounds accounted for about 27% of all the papers in 1962, and about 22% of all the papers in 1967 and 1972.

Table II shows the distribution of the papers dealing with the analysis of gases and organic compounds. It can be inferred that chromatography accounts for almost one half of the entire analytical work performed on organic compounds in 1967 to 1972, with GC constituting almost 75% of this half. The dynamics of publication indicates that the relative number of papers covering all the chromatographic methods

TABLE II

DISTRIBUTION OF PAPERS ON ANALYSIS OF GASES AND ORGANIC COMPOUNDS*

Method	Papers (%)		
	1962	1967	1972
All kinds of chromatography	33.6	47.4	45.7
Gas chromatography (included)	23.3	34.1	34.6
Spectral analysis (spectroscopy, photometry, NMR, etc.)	41.7	31.3	35
Volumetric, gravimetric and other methods	6.7	6.4	3.5
Electrochemical methods	18	14.9	15.7

* The table lists papers published in refs. 5–9

substantially increased from 1962 to 1967 (almost one and a half times) and slightly decreased in 1972 (mainly due to a reduction in the number of papers on paper chromatography, which will be discussed below). The total number of papers dealing exclusively with GC also showed a 150% increase over the period from 1962 to 1967 and a slight increase from 1967 to 1972. However, both in 1967 and 1972, GC was an undisputed leader among other methods of analysing organic compounds. Extensive application of chromatography in the analysis of organic compounds from 1962 to 1967 was largely due to a relative decline of other methods, particularly spectrophotometry. The decrease in the number of papers dealing with GC which was observed in 1967 to 1972 was not unexpected. Similar phenomena are characteristic of the development of other branches of science as well[1]. Generally, a substantial theoretical or methodical "boom" is followed by a sharp increase in the number of papers on a given subject.

Thus, the rapid development and dominant role of GC over the past decade is a characteristic feature of the progress in analytical chemistry of gases and organic compounds.

The development of GC is particularly spectacular in petroleum refining and petrochemistry[13]. Tabulated in Table III are papers concerned with GC or, more particularly, with the applications of GC in petrochemistry. Table III suggests that the number of papers on the subject is steadily growing. GC plays a particularly important part in scientific research. Thus, 69% of all the papers that appeared in 1972 in

TABLE III

DYNAMICS OF PUBLICATION OF PAPERS ON GAS CHROMATOGRAPHY—DEVELOPMENT AND APPLICATION OF THE METHOD

Journals on	Papers on gas chromatography (%)		
	1960	1965	1972
Petrochemistry	13 (1961)	37	69
Chemistry and production of fuels and oils	5	9	10 (1970)
Petroleum refining and petrochemistry	1.5	6	15

TABLE IV

CLASSIFICATION OF CHROMATOGRAPHIC ANALYSES, BASED ON THE STATES OF AGGREGATION OF MOBILE AND STATIONARY PHASES

Mobile phase		Stationary phase								
		Monophasic systems			Diphasic systems					
		Gas (G)	Liquid (L)	Solid support (S)	Gas–gas (G–G)	Gas–liquid (G–L)	Gas–solid support (G–S)	Liquid–liquid (L–L)	Liquid–solid (L–S)	Solid support–solid support (S–S)
Monophasic systems	Gas (G)	G/G	G/L	G/S	G/G-G	G/G-L	G/G-S	G/L-L	G/L-S	G/S-S
	Liquid (L)	L/G	L/L	L/S	L/G-G	L/G-L	L/G-S	L/L-L	L/L-S	L/S-S
	Solid support (S)	S/G	S/L	S/S	S/G-G	S/G-L	S/G-S	S/L-L	S/L-S	S/S-S
Some diphasic systems	Gas–liquid (G–L)	G-L/G	G-L/L	G-L/S	G-L/G-G	G-L/G-L	G-L/G-S	G-L/L-L	G-L/L-S	G-L/S-S
	Gas–solid support (G–S)	G-S/G	G-S/L	G-S/S	G-S/G-G	G-S/G-L	G-S/G-S	G-S/L-L	G-S/L-S	G-S/S-S
	Liquid–liquid (L–L)	L-L/G	L-L/L	L-L/S	L-L/G-G	L-L/G-L	L-L/G-S	L-L/L-L	L-L/L-S	L-L/S-S
	Liquid–solid support (L–S)	L-S/G	L-S/L	L-S/S	L-S/G-G	L-S/G-L	L-S/G-S	L-S/L-L	L-S/L-S	L-S/S-S
	Solid support–solid support (S–S)	S-S/G	S-S/L	S-S/S	S-S/G-G	S-S/G-L	S-S/G-S	S-S/L-L	S-S/L-S	S-S/S-S

Neftekhimiya, a journal on petrochemistry published by the U.S.S.R. Academy of Sciences were concerned with the development of application of GC.

The present paper has for its aim a somewhat closer scrutiny of what are believed to be the most promising trends in the development of GC over the past few years, as applied to petrochemistry and petroleum refining.

DEVELOPMENT OF GAS CHROMATOGRAPHY IN PHYSICAL AND CHEMICAL MEASUREMENTS

Recent years have been marked by a rapid growth in the number of new methods and their variants for measuring various physical and chemical characteristics. As a result of surveying the literature on GC, a bibliography of which regularly appears[10], it can be inferred that over the past five years (1967–1972) the relative number of papers on the applications of GC in physical and chemical measurements has shown a fourfold increase. This can be accounted for by the facts that (a) chemists and physicochemists display a greater interest in GC and regard it as a simple and effective method of physical and chemical measurements, and (b) a number of new trends have appeared in the field.

When considering new physicochemical methods, attention should be given first to those directly associated with two equally important characteristics of the chromatographic process, *viz.* (1) determination of the adsorption characteristics of the gas–stationary liquid phase (SLP) and SLP–solid support interfaces, and (2) determination of the properties of the SLP by using the methods of reverse GC.

Determination of adsorption characteristics in gas–liquid–solid phase chromatography

After first being introduced by Tsvet[14], adsorption processes have been widely used in various methods of chromatographic separation. Even in partition chromatography (*e.g.* in liquid–liquid and gas–liquid chromatography), adsorption processes occur alongside those of dissolution. This is due to the polyphase nature of the sorbents used in conventional partition chromatography. In gas–liquid and liquid–liquid chromatography, the sorbent has at least three phases which are capable of retaining the substance being chromatographed; firstly, the SLP, which dissolves (adsorbs) the substances being separated; secondly, the mobile phase–SLP interface, which adsorbs the substances being separated; and, thirdly, the SLP–solid support interface which also adsorbs the substances being separated.

Thus, the solid support may produce a tangible effect on the chromatographic separation. Therefore, such variants of chromatography as gas/liquid or liquid/liquid may be regarded, in my opinion, more properly as modifications of gas/liquid–solid and liquid/liquid–solid chromatography, respectively. A more detailed classification of various types of chromatography, with due consideration being given to the aggregation state of the mobile and stationary phases, is shown in Table IV.

The polyphase nature of the sorbents in partition chromatography should also be taken into account in theoretical chromatography. Previously, it has been shown within the framework of ideal non-linear chromatography (*i.e.*, under conditions assuming the state of equilibrium to be attained instantaneously, and in the absence of diffusive action) that the net retention volume V_N on a real polyphase sorbent is equal to the sum of the partial retention volumes V_{lt} and V_{sj}, which are due to the absorp-

tion or adsorption, respectively, of the substance being chromatographed on various phases of the sorbent[15,16]:

$$V_N = \sum_{i=1}^{m} V_{li} + \sum_{j=1}^{n} V_{sj} \qquad (1)$$

or

$$V_N = \sum_{i=1}^{m} K_{li} \mathscr{V}_{li} + \Sigma K_{sj} \cdot S_{sj} \qquad (2)$$

where K_{li} is the equilibrium constant of the substance in a mobile phase–SLP system of the i-type, $\mathscr{V}_{li}$ is the volume of an j-type SLP in the column (e.g. SLP in a macrolayer, SLP in a microlayer, SLP in fine capillaries, etc.), K_{sj} is the equilibrium constant of the substance between the stationary phase and a j-type interfacial area, and S_{sj} is the area of the j-type surface in the column (e.g., gas–solid support, SLP–solid support, gas–SLP and other interfaces).

Eqns. 1 and 2 are sufficiently general. It can be shown that the known retention volume equations are particular cases of the above equations.

The following relationships are true for the equilibrium constants:

$$K_{li} = \frac{\partial V_N}{\partial \mathscr{V}_{li}} = \frac{dC_{li}}{dC} \qquad (3)$$

$$K_{sj} = \frac{\partial V_N}{\partial S_{sj}} = \frac{dC_{sj}}{dC} \qquad (4)$$

where C_{li} and C_{sj} are the volume concentrations of the chromatographed substance in the i-type and j-type stationary phases, respectively, and C is the volume concentration of the substance in the mobile phase.

If the adsorption isotherm is given by a non-linear equation, eqns. 1 and 2 are only true within the framework of ideal non-linear chromatography, which substantially limits the field of their application. It should be pointed out, however, that elution GC methods of determining non-linear adsorption isotherms, developed on the bais of ideal non-linear chromatography, are used with great success in chromatography, and the results obtained by these methods are independent of the carrier gas flow-rate, sample size, etc. The adsorption isotherms in gas–solid chromatography, measured by the above GC and statistical methods, are in good agreement with one another[17,18]. Therefore, the field of application of eqns. 1 and 2 for the case of non-linear isotherms can be considered sufficiently extensive. Needless to say, further development of more rigorous methods based on a non-equilibrium theory of chromatography[19–22] will make possible a more coherent explanation of the mechanism of the chromatographic process and will help develop more accurate methods of measuring the adsorption characteristics of polyphase sorbents.

As partial retention volumes are known in gas/liquid–solid chromatography, by using eqns. 3 and 4, which are similar to those used in gas–solid chromatography, one can determine the absorption or adsorption isotherm as follows:

$$C_{li} = \frac{1}{\mathscr{V}_{li}} \int_0^c V_{li}(C) dC \qquad (5)$$

$$C_{sj} = \frac{1}{S_{sj}} \int_0^c V_{sj}(C) dC \qquad (6)$$

These equations open up new possibilities for conducting physical and chemical measurements by means of partition chromatographic methods. They will help determine not only partition isotherms but also adsorption isotherms of chromatographed compounds at interfaces.

It should be noted that in some cases the parameters of adsorption isotherms can be measured directly without using eqns. 5 and 6. To illustrate this, let us now consider the practical case when retention is only determined by dissolution of the substance in SLP and its adsorption at the SLP–solid support interface.

In accordance with the general equations 1–4, the net retention volume in the case under consideration is given by:

$$V_N = V_l + V_s = K_l \mathscr{V}_l + \frac{dC_s}{dC} S_s \tag{7}$$

Dividing both sides of the equation by the weight of the solid support in the column and assuming that $C_s = f(C_l)$:

$$V_{Ns} = K_l \mathscr{V}_{ls} + \frac{dC_s}{dC_l} \cdot \frac{dC_l}{dC} \cdot S_{ss} \tag{8}$$

or

$$V_{Ns} = K_l \mathscr{V}_{ls} + K_l \frac{dC_{ss}}{dC_l} \tag{9}$$

where $C_{ss} = C_s \cdot S_{ss}$ is the concentration of the substance adsorbed at the liquid–solid interface and calculated per unit weight of the solid support, and V_{Ns} and $\mathscr{V}_{ls}$ are the net retention volume and the SLP volume calculated per gram of the solid support, respectively.

Consider now the case when the adsorption isotherm is expressed by the Langmuir equation[23]:

$$C_{ss} = \frac{A_m \cdot K \cdot C_l}{1 + K \cdot C_l} = \frac{A_m \cdot K \cdot K_l \cdot C}{1 + K \cdot K_l \cdot C} \tag{10}$$

where A_m and K are the Langmuir equation constants. In this case, the net retention volume depends on concentration, as follows[24]:

$$V_{Ns}(C) = K_l \mathscr{V}_{ls} + V_{ss} = K_l \cdot \mathscr{V}_{ls} + \frac{A_m \cdot K \cdot K_l}{(1 + K \cdot K_l \cdot C)^2} \tag{11}$$

where

$$V_{ss} = \frac{A_m \cdot K \cdot K_l}{(1 + K \cdot K_l \cdot C)^2}$$

A number of methods can be used to determine the parameters of the Langmuir equation.

If the value of K_l is known from independent chromatographic or statistical measurements, these parameters are determined with one known substrate leading, by using the following equation:

$$V_s(C) = V_N(C) - K_l \mathscr{V}_l = \frac{K_l \cdot A_m \cdot K \cdot P}{(1 + K \cdot K_l \cdot C)^2} \tag{12}$$
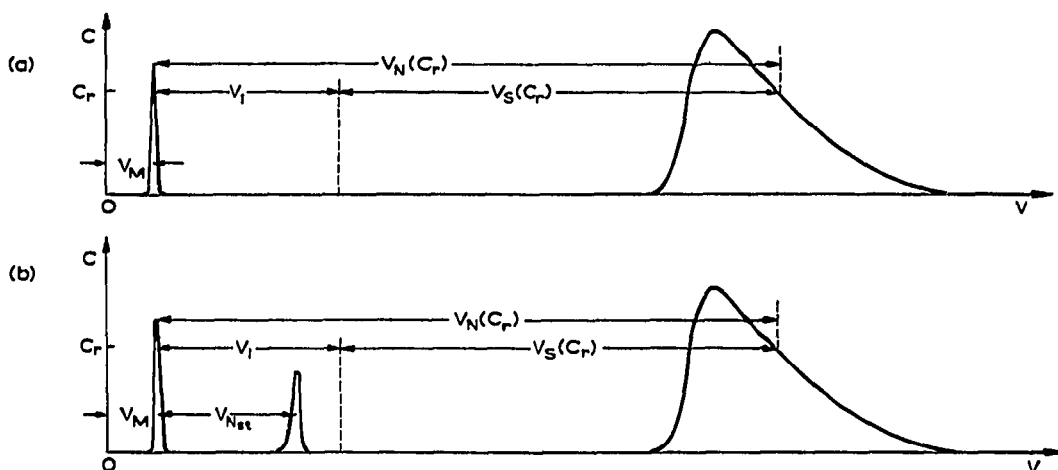
Fig. 1. Determination of the retention volume conditioned by adsorption on the SLP–solid support interface and dissolution in the SLP of the chromatographed compound. (a) Retention volume conditioned by dissolution of the compound in the SLP (V_l) determined by independent measurements. (b) Retention volumes conditioned by dissolution of the compound in the SLP (V_l) determined by the relative method with the use of a standard reference compound the adsorption whereof in the system under consideration can be ignored. V_M is dead volume.

where P is the weight of the solid support. The calculation is made as in the case of gas–solid chromatography[17,18]; however, the value of $V_l = K_l \mathscr{V}_l$ (Fig. 1a) is used as the origin. If it is possible to select a compound for the system under consideration for which the retention is only determined by its dissolution in the SLP, then it is expedient to use a relative method (Fig. 1b) to determine the retention volume, which in this case is determined solely by the dissolution of the compound in the SLP, i.e. V_l:

$$V_l = V_{Nst} \frac{K_l}{K_{lst}} \tag{13}$$

To facilitate the measurement of the parameters of the Langmuir isotherms, with $V_{ss} = \mathscr{V}_s/P = f(C)$, use should be made of the following equation:

$$\frac{1}{\sqrt{V_{ss}(C)}} = \frac{1}{\sqrt{A_m \cdot K \cdot K_l}} + \sqrt{\frac{K \cdot K_l}{A_m}} \cdot C \tag{14}$$

Another method can be used to determine the parameters of the adsorption isotherm, based on measuring the dependence of the retention volume on the substrate loading, with fixed concentrations of the substance being chromatographed:

$$V_{Ns}(C_r) = K_l \mathscr{V}_{ls} + V_{ss}(C_r) \tag{15}$$

where $C_r = C_1, C_2, \ldots \ldots C_n$. This method is similar to that previously described in refs. 15, 25 and 26. As a result of the calculation made on the basis of the above measurements it is possible to determine the value of K_l and the relationship $V_{ss} = V_{ss}(C)$, which is then used as a basis for determining the parameters of the adsorption isotherm equation by means of eqn. 6 or 13.

It should be noted here that the parameters of the adsorption isotherm can also be determined by means of the following equations:

$$\frac{d V_{Ns}}{dC} = \frac{d \mathscr{V}_{ss}}{dC} = -\frac{2 A_m \cdot K^2 \cdot K_l^2}{(1 + K \cdot K_l \cdot C)^3} \tag{16}$$

$$-\frac{1}{\sqrt[3]{\frac{d V_{Ns}}{dC}}} = \frac{1}{\sqrt[3]{(2 A_m \cdot K^2 \cdot K_l^2)}} + \frac{1}{\sqrt[3]{\frac{2 A_m}{K \cdot K_l}}} \cdot C \tag{17}$$

These methods were used to determine experimentally the adsorption isotherm of p-xylene on a dimethyldioctadecylammonium derivative of vermiculite impregnated with diisooctyl sebacate. At the same time the adsorption isotherm of n-xylene was statistically determined from the adsorption process studied in glass ampoules; by this means, the equilibrium concentration of xylene in the liquid phase was determined by means of GC. In Fig. 2 the adsorption isotherm (63°) of n-xylene is shown, the parameters of which have been determined by processing the GC data
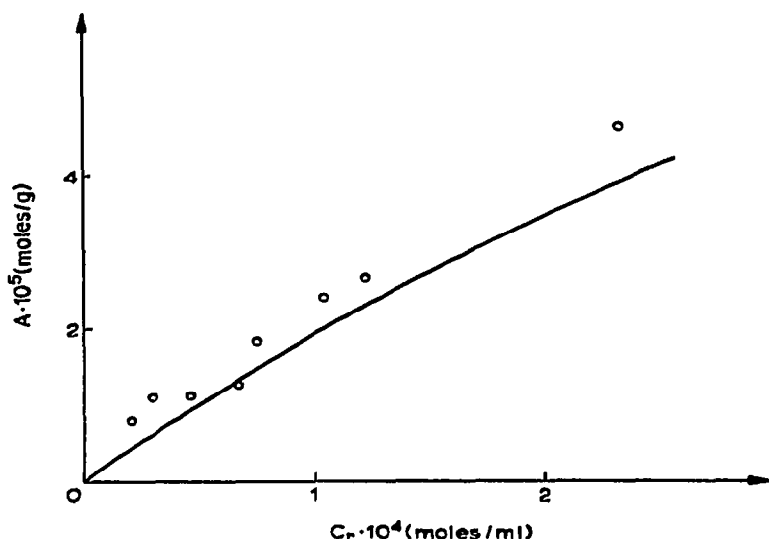

Fig. 2. Measurement of the adsorption of n-xylene on dimethyldioctadecylammonium vermiculite from solutions in diisooctyl sebacate. Solid line, adsorption isotherm based on GC data; dots, data obtained statistically.

with the aid of eqn. 17, as well as points obtained as a result of a statistical analysis of the same system. As can be seen from the graph, the results of GC and statistical analysis correlate well. As far as we know, these were the first studies conducted with the sole aim of checking how effective chromatography may be in measuring the non-linear SLP–solid support adsorption isotherms. Special experiments have proved that the parameters of the adsorption isotherm determined by chromatography are independent of the carrier gas flow-rate within the range 10–76 ml/min, which indicates that the lack of equilibrium in the process can be neglected. It should also be noted that GC methods of determining the equilibrium constant (for the system SLP–solid sup-

port) in the case of a non-linear isotherm have been developed earlier[15,25,27]. When the coefficients K_i and K_j of eqns. 1–4 are constants independent of the concentration, the interpretation and determination of the sorption characteristics are substantially simplified, particularly in the area of substrate loading sufficient for the solid support to be fully coated with a continuous film of the SLP[28]. In this case, the equation for the net retention volume is simplified and can be written as follows[15].

$$V_N = K_l \mathscr{V}_l + K_{gl} S_l + K_l K_s S_s \tag{18}$$

where K_l, K_{gl} and K_s are the coefficients of partition of the chromatographed substance between the gas–SLP and SLP–solid support interfaces, respectively, $\mathscr{V}_l$ is the volume of the SLP and S_s is the SLP–solid support interface area.

Note that eqn. 18 was later used with great success by a number of investigators, for example Conder and co-workers[29–31], Karger *et al.*[32], Urone *et al.*[33], Gritchina and Dreving[34] and Hauch-Liang Liao and Mortire[35] in the analysis and study of adsorption phenomena in gas–liquid chromatography.

Various methods of determining sorption characteristics by using this equation have been developed[15,16,36]. Conder has proposed a method based on eqn. 18 of accurately determining the constant of partition of volatile substances in the gas–SLP system under conditions of adsorptive interaction[29,30]. Ref. 37 deals with a method of determining the adsorption heat on the SLP–solid interface, based on the temperature dependence of K_s. This method is illustrated in Table V, which gives the heats of solution of hydrocarbons on Apiezon K and heats of their adsorption in the system Apiezon K–solid support.

TABLE V

HEATS OF SOLUTION AND ADSORPTION ON THE SURFACE OF THE SOLID SUPPORT OF ALKANES AND ALKYNES IN THE SYSTEM APIEZON K–INZ-600

Component	Heat of solution (kcal/mole)	Heat of adsorption (kcal/mole)
n-Hexane	5.8	4.55
1-Hexyne	5.2	10.9
n-Heptane	6.6	7.6
2-Heptyne	8.6	17.8

As can be inferred from Table V, the heats of adsorption of alkynes are substantially higher than their heats of solution, while in the case of *n*-alkanes the difference is insignificant. By taking the adsorption on the surface of the solid support into account, one can obtain more accurate values for the constants of adsorption on the gas–SLP interface as well[36].

Chromatography, as compared to statistical methods, offers the advantages of high speed, the possibility of using small amounts of the substance to be analysed and the possibility of measuring minor adsorption phenomena. The results yielded by these methods indicate that studies in this direction hold much promise, particularly insofar as the use of adsorption-active solids as the solid support is concerned [38–41].

Studies of phase interfaces using gas chromatography

Studies of liquid–solid and solid–solid interfaces, as well as the associated crystallization phenomena, determination of purity of various compounds, etc., are of great scientific and practical interest[42,43]. The known methods of studying phase interfaces are for the most part based on measuring the time dependence of temperature variations in a sample, this depending on the phase transfer heat, content of impurities, conditions of the experiment, etc. The sensitivity and accuracy of such methods decrease with the interface temperature, as well as with the rate of temperature variation. In this connection, the development of new methods based on an entirely different principle of measurement, free of the above disadvantages, arouses particular interest. The retention volume (in some cases, the width of the chromatographic zone) as well as such chromatographic characteristics as partition coefficient, sorption heat, height equivalent to a theoretical plate, etc., should depend on the state of the stationary phase in GC. Therefore, phase interfaces can be studied by means of reverse gas chromatography (RGC).

In RGC, unlike classical chromatography, it is the stationary phase that is subjected to analysis, and it is on this stationary phase that the known volatile compounds (reference samples) are separated. RGC is based on direct interactions between the reference compounds being chromatographed and the sorbent being examined, as well as on establishing a certain correlation between the values of the chromatographic characteristics of the reference compounds and the composition, structure and other properties of the stationary phase. The term "reverse gas chromatography" was proposed in 1966[44,45].

As a result of a phase transformation a new stationary phase (sorbent) appears in the chromatographic column instead of the initial stationary phase, and in general it possesses physicochemical properties different from those of the initial phase. This feature is expected to result in an alteration of the chromatographic characteristics of the volatile reference compounds in the phase transition region of the stationary phase. Therefore, RGC can be used for studying phase transitions.

Some investigators have long noted a pronounced dependence of the retention values on the temperature in the melting region of the SLP[46,51]. Attention, however, was generally directed not to studying the phase transition phenomenon, but to the effect it produces or to its applications in analytical chromatography. So, for example, the effect of a sharp decrease in the retention values of the compounds being analysed when the column is cooled to a temperature below the melting point of eicosane SLP has been used[46] as a method of rapid elution of heavy hydrocarbons from the column after having analysed the lighter components.

It has been shown, *e.g.* with carbon tetrabromide[52], that RGC can be applied advantageously to study phase transformations when one crystal modification is transformed into another. Later, this method was used with great success by Guran and Rogers in their studies on phase transitions in thallium nitrate crystals[53,54]. In all the above-mentioned cases, the results of GC experiments were in good agreement with the data on phase transitions obtained by other methods.

According to Guillet and Stein[55], RGC, as specially applied to studies of phase transitions in polymers, was first mentioned by Alishoev *et al.*[52]. In this case, stereospecific polymers with a high degree of crystallinity, such as polyethylene or polypropylene, were used. A mechanical mixture with glass beads of the powdered poly-

mer studied (1 %) was charged into a column (100 × 0.4 cm) which was connected to
a chromatograph and heated at a rate of 0.2 to 0.5°/min. Periodically, samples of the
reference compound were introduced into the column and their chromatograms were
obtained. In the cases under consideration, maxima were observed in the temperature
region of the phase transition on the curves representing the temperature dependences
of the retention time and the peak width. Such maxima are due to variations in the
partition and diffusion coefficients of the volatile reference substance as a result of the
phase transition. The study with polypropylene suggested that this method is sensitive
to the history of the sample. A similar phenomenon has been observed in studying
phase transformations of univalent thallium nitrate crystals[53].

A particularly significant contribution to the development of RGC as applied
to studies of phase transitions in high-molecular-weight compounds and their quanti-
tative interpretation has been made by Guillet and co-workers[55–59]. Unfortunately, in
their calculations no account has been taken of any possible adsorption of the volatile
reference compounds at the boundary between the crystalline and amorphous regions,
as well as on the gas–polymer and polymer–solid support interfaces.

The new method of studying the structure and physical state of polymers based
on the temperature dependence of retention volumes has been termed by Guillet the
"molecular sampling" method[58]. This method is used to determine the degree of crys-
tallinity of high-density polyethylene at various temperatures[59]. Results from the above
two methods agree quite well.

Given in Table VI[57] are vitrification temperature values obtained by differential
thermal analysis and reverse chromatography. The agreement between both methods is

TABLE VI

DETERMINATION OF VITRIFICATION TEMPERATURE BY RGC

Characteristic	Polyvinyl chloride		Polystyrene	Polymethyl-methacryl-ate
	A	B		
Molecular weight	68,000	35,500	31,000	48,000
Standard volatile substance	Dodecane	Dodecane	Dodecane	Hexadecane
Vitrification tem-perature, °C (DTA)	75 ± 2	75 ± 2	95 ± 2	100 ± 2
Temperature of pri-mary deviation from linear, T_1, °C	81	81	88	97
Temperature of the first minimum, T_2, °C	91	91	100	105

quite satisfactory, and it should be borne in mind that when the vitrification tempera-
ture of a polymer is determined by means of GC, it is most expedient to use as the
characteristic value the temperature of the first deviation from linear of the plot of log
retention volume *versus* inverse of the temperature.

RGC has also been used with great success in studying the kinetics of crystalli-
zation of organic substances from a melt. The application of this method to polymeric

compounds has been described by Gray and Guillet[59] and to monomeric compounds by Andreev et al.[60].

It is as well to point out certain specific features and limitations of GC in determining phase transitions, which are related to the effect of the solid support on the state of the stationary phase.

The above phenomena were first observed and carefully studied by Serpinet and Robin[61-64]. The effect of the solid support can be drastically reduced by using thick layers of SLP and inert pore-free carriers, as well as capillary columns.

Reverse chromatography applied to the study of phase transitions is advantageous in that it enables the experiment to be simplified, ensures rapid measurement of the chromatographic characteristics of reference volatile compounds and permits the polymers being studied to be used in small amounts. Another advantage of RGC, as compared to other widely used methods based on measuring the thermal effect of a phase transition, is the possibility of studying slow phase transitions.

DEVELOPMENT OF GAS CHROMATOGRAPHY IN THE IDENTIFICATION OF CHROMATOGRAPHIC ZONES

Despite the successful and steadily developing application of combined methods[44,45], chromatographic identification methods proper, based on the experimental determination of retention values and comparison of the obtained values with the data recorded in literature, have not lost their significance.

Adsorption phenomena in partition chromatography have been the object of research by a great number of investigators in recent years[15-41] and have suggested a new view of the identification of chromatographic zones. Until very recently, it has been widely accepted in gas–liquid and liquid–liquid chromatography that the value of the relative retention is dermined only by the ratio between the partition constants of given and reference compounds, hence this value has been generally considered as a chromatographic constant of the chemical compound in question. Therefore, the identification of chromatographic zones, i.e. qualitative chromatographic analysis of separated compounds, was usually performed on the basis of relative retention values[66,67].

The adsorption of chromatographed compounds on phase interfaces in the course of chromatographic partition results in the absolute and relative retention values being in general determined not only by the ratio between the partition constants of given and reference compounds, as was believed earlier, but also by the adsorptive properties of the solid support, substrate loading and phase characteristics of the sorbent, which depend on how it has been prepared, etc.[15,68,69]. Fig. 3 shows, by way of example, the dependence of the relative retention volume on the substrate loading, calculated by us in accordance with the data disclosed in ref. 70. It can be inferred that the relative retention value obtained from adsorption occurring in the chromatographic process in the system gas/liquid–solid support is not a chromatographic constant of the compound in question.

To deduce a general equation for the relative retention volume, in which account is taken both of the dissolution and adsorption of the chromatographed compounds, use is made of eqn. 3 above for the net retention volumes of the given and reference compounds. The following equation for the relative retention volume applies.

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} \cdot \frac{1 + \left(\sum_{l=2}^{m} K_{ll} \cdot \mathscr{V}_{ll} + \sum_{j=1}^{n} K_{sj} \cdot S_{sj}\right)\dfrac{1}{K_l \cdot \mathscr{V}_l}}{1 + \left(\sum_{l=2}^{m} K_{llst} \cdot \mathscr{V}_{ll} + \sum_{j=1}^{n} K_{sjst} \cdot S_{sj}\right)\dfrac{1}{K_{lst} \cdot \mathscr{V}_l}} \qquad (19)$$

It can be seen from this equation that the relative retention volume is not a constant of the chromatographed compound, hence it cannot be widely used for identifying compounds on the basis of data recorded in literature. It should be noted that despite the application of the known methods of modifying solid diatomite supports or the use of polymeric supports, the contribution of adsorption to the relative retention volume is often still significant[27,31]. Adsorption phenomena are particularly evident in the high-temperature chromatography of polar compounds. Therefore, for
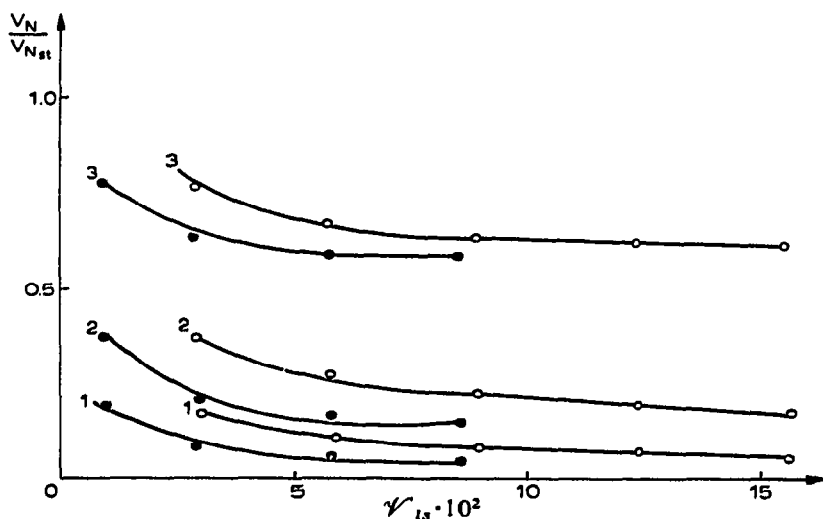
Fig. 3. Dependence of the relative retention volume (reference compound, methyl ethyl ketone) on the SLP volume (per gram of the solid support). Calculations are based on data disclosed in ref. 70). Experimental conditions: SLP, β, β'-thiodipropionitrile; temperature, 25°; solid supports, Chromosorb W (●) and firebrick (○). 1 = Ethyl acetate; 2 = n-butyl ethyl ether; 3 = n-heptane.

a more extensive application of GC as a method of qualitative analysis, new methods of determining the ratio between the partition constants K_l and K_{lst} had to be developed on the basis of the relative retention values obtained from the adsorption of the chromatographed compounds[69].

If the retention volume depends only on the dissolution of the chromatographed compound in the SLP and the linear adsorption isotherm on the SLP–mobile phase and SLP–solid support interfaces, eqn. 19 is simplified and the relative retention volume can be expressed by the following equation,

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} \cdot \frac{1 + \dfrac{K_{gl}S_{ls} + K_l \cdot K_s \cdot S_{ss}}{K_l} \cdot \dfrac{1}{\mathscr{V}_{ls}}}{1 + \dfrac{K_{glst} \cdot S_{ls} + K_{lst} \cdot K_{sst} \cdot S_{ss}}{K_{lst}} \cdot \dfrac{1}{\mathscr{V}_{ls}}} \qquad (20)$$

where $\mathscr{V}_{ls}$, S_{ls} and S_{ss} are the SLP volume, gas–SLP interface and SLP–solid support interface, respectively, each calculated per gram of solid support. By expanding this equation into Maclaurin's series using variable $\mathscr{V}_{ls}$, we obtain the following linear equation relative to the reverse substrate loading,

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} + \lambda \cdot \frac{1}{\mathscr{V}_{ls}} \tag{21}$$

where

$$\lambda = \frac{(K_{gl} \cdot K_{lst} - K_{glst} \cdot K_l)S_{ls} + (K_s - K_{sst}) \cdot K_l \cdot K_{lst} \cdot S_{ss}}{K_{lst}^2} \tag{22}$$

It should be noted that a similar relationship is obtained from the more general eqn. 2 if an increase in the substrate loading brings about an increase only in the thickness of the SLP film, while the contents of other phases in the sorbent remain practically the same. In Figs. 4 and 5, the experimental data in refs. 70 and 31 are represented in accordance with eqn. 21. As can be seen from the above data, the use of eqn. 21 permits the value of the ratio between the partition constants (which is independent of the experimental conditions) to be determined.
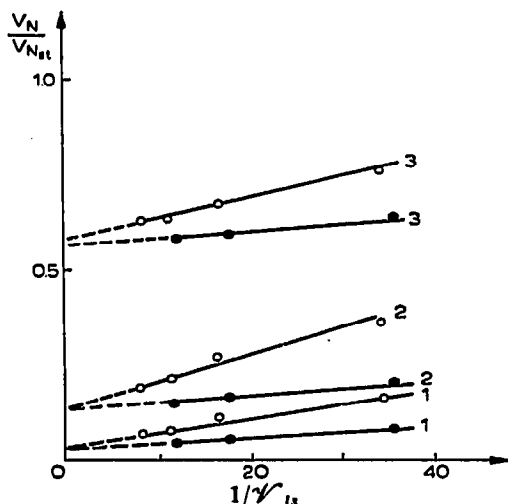

Fig. 4. Dependence of the relative retention volume (reference compound, methyl ethyl ketone) on the inverse of SLP volume (per gram of the solid support). Calculations are based on data disclosed in ref. 70. Experimental conditions are the same as in Fig. 3. 1 = n-Heptane; 2 = n-butyl ethyl ether; 3 = ethyl acetate.

It is desirable that a compound should be used as a reference sample whose retention is only determined by dissolution, i.e.:

$$V_{Nst} = K_{lst} \cdot \mathscr{V}_{ls}, \quad \lambda_1 = \frac{K_{gl}S_{ls} + K_l \cdot K_s \cdot S_{ss}}{K_{lst}}$$

In some cases, the percentage content of the SLP in the column is preferably used as the SLP content characteristic. In this particular case, we obtain by performing
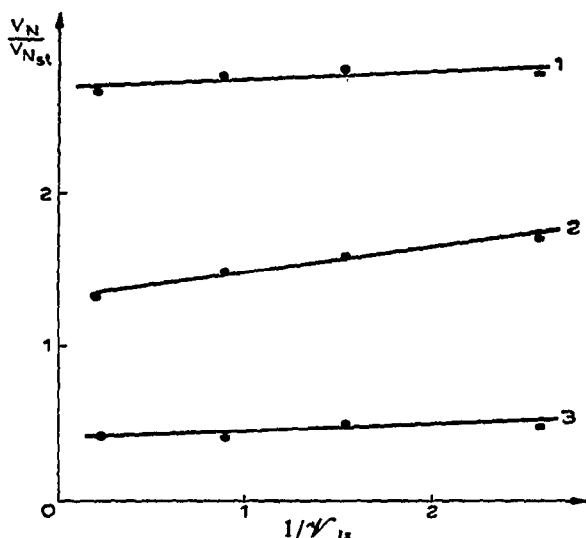
Fig. 5. Dependence of the relative retention volume (reference compound, ethanol) on the inverse of SLP volume (per gram of the solid support). Calculations are based on data disclosed in ref. 31. Experimental conditions: SLP, dinonylphthalate; temperature, 86°; solid support, PTFE. 1 = n-Butylamine; 2 = n-hexane; 3 = water.

adequate transformations the following equation similar to eqn. 21,

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} + 3\,\frac{1}{P_l} \tag{23}$$

where P_l is the percentage content of the SLP on the solid support (percentage substrate loading), the weight of the solid substrate being taken as 100%.

Eqn. 23 can be used in cases when the determination of $\mathscr{V}_{ls}$ presents certain difficulties (e.g. the SLP density at the experimental temperature is not known). Fig. 6
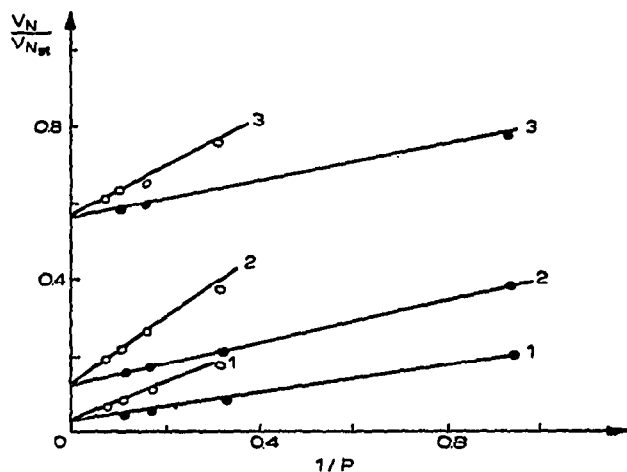

Fig. 6. Dependence of the relative retention volume (reference compound, methyl ethyl ketone) on the inverse of percentage substrate loading. Calculations are based on data disclosed in ref. 7. Experimental conditions are the same as in Fig. 3. 1 = n-Heptane; 2 = n-butyl ethyl ether; 3 = ethyl acetate.

represents the relative retention volume *versus* the inverse of the percentage substrate loading. As can be inferred from this graph, eqn. 23 corresponds well with the experimental results. The proposed methods can be used to utmost advantage for determining the partition constant ratio, which is a thermodynamic characteristic of the compound being examined and, therefore, may be used as the basis on which the compound can be identified. The obtained values of K_{lc}/K_{lest} are independent of the substrate loading and of the type of solid support used.

Identification by methods of GC makes extensive use, along with relative retention values, of Kováts' system of indices[71],

$$I = 100z + 100 \frac{\log V_N/V_{Nz}}{V_N(z+1)/V_{Nz}} \tag{24}$$

where V_{Nz} is the net retention volume of an *n*-alkane whose molecule contains z carbon atoms, $V_{N(z+1)}$ is the net retention volume of an *n*-alkane whose molecule contains $(z+1)$ carbon atoms and V_N is the net retention volume of the compound being analysed.

$$V_{Nz} \leqslant V_N \leqslant V_{N(z+1)}$$

It is advisable to use as reference compounds those in which retention is only determined by dissolution in the SLP. In this case, by extending the numerator of the
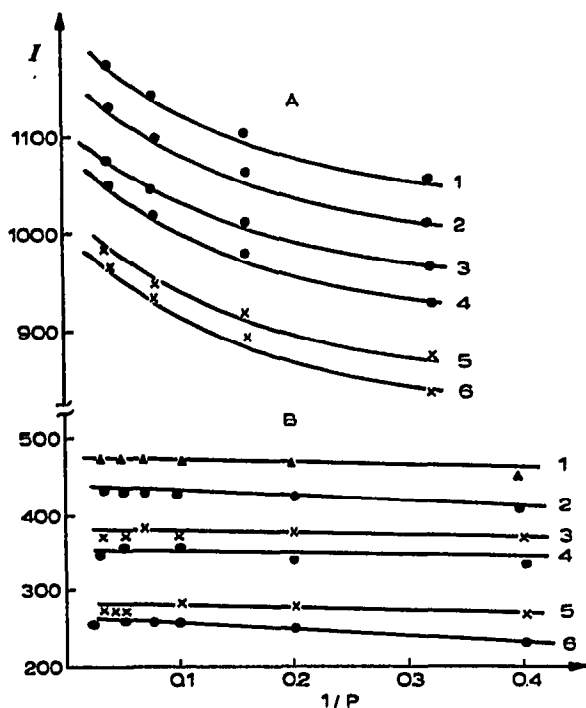

Fig. 7. Effect of selection of reference compounds on the dependence of retention indices on the inverse of percentage substrate loading. Calculations are based on data disclosed in ref. 72. Experimental conditions: SLP, Carbowax 20M; temperature, 120°; solid support, Chromosorb P. 1 = 2-Heptanone; 2 = ethylbenzene; 3 = 2-hexanone; 4 = toluene; 5 = 2-pentanone; 6 = benzene.

second term of eqn. 24 into Maclaurin's series, using $\mathcal{V}_{ls}$ with restriction to the first two terms, we obtain

$$\log \frac{V_N}{V_{N_z}} = \log \left(\frac{K_l}{K_{lz}} + \lambda \frac{1}{\mathcal{V}_{ls}} \right) = \log \frac{K_l}{K_{lz}} + 0.43 \, \lambda_4 \cdot \frac{1}{\mathcal{V}_{ls}} \qquad (25)$$

where

$$\lambda_4 = \lambda^{K_{lz}/K_l}.$$

Taking into account eqn. 25. eqn. 24 transforms into

$$l = 100z + 100 \frac{\log\left\{\frac{K_l}{K_{lz}}\right.}{\log \frac{K_{l(z+1)}}{K_{lz}}} + \frac{43 \, \lambda_3}{\log \frac{K_{l(z+1)}}{K_{lz}}} \cdot \frac{1}{\mathcal{V}_{ls}} \qquad (26)$$

or

$$I = I_0 + \lambda_4 \frac{1}{\mathcal{V}_{ls}} \qquad (27)$$

where

$$I_0 = 100z + \frac{100 \left(\log \frac{K_l}{K_{lz}} \right)}{\log \frac{K_{l(z+1)}}{K_{lz}}}$$

$$\lambda_4 = \frac{43 \, \lambda \, K_{lz}}{K_l \cdot \log \frac{K_{l(z+1)}}{K_{lz}}}$$

As has already been mentioned above, the reference compounds used are those in which retention is determined mainly by dissolution in the SLP. In the case of non-polar phases and phases of average polarity, it are normally n-alkanes that comply with this requirement; however, in the case of polar stationary liquid phases, preference should be given to polar compounds (e.g. n-alcohols) as reference compounds (Fig. 7).

Fig. 8 illustrates the determination of the values of I_0, invariant under the experimental conditions, for the methyl esters of myristic acid and n-dodecanol. As can be inferred from these data, the use of a sufficiently inert Chromosorb G treated with acid and dimethyldichlorosilane does not necessarily preclude adsorption processes in gas–liquid chromatography.

Thus, in partition (gas–liquid and most probably liquid–liquid) chromatography, there is a linear relationship between the relative retention value and the substrate loading, which can be successfully used for determining the partition constant ratio of chromatographed compounds, thereby permitting a reliable identification of chromatographic zones even in the presence of adsorption phenomena during chromatographic separation.

INCREASING THE EFFICIENCY OF CHROMATOGRAPHIC SEPARATION

The best and most commonly used method of improving chromatographic separations is to enhance the efficiency of the column. Therefore, the attention of most investigators has been directed throughout the entire period of development of GC to
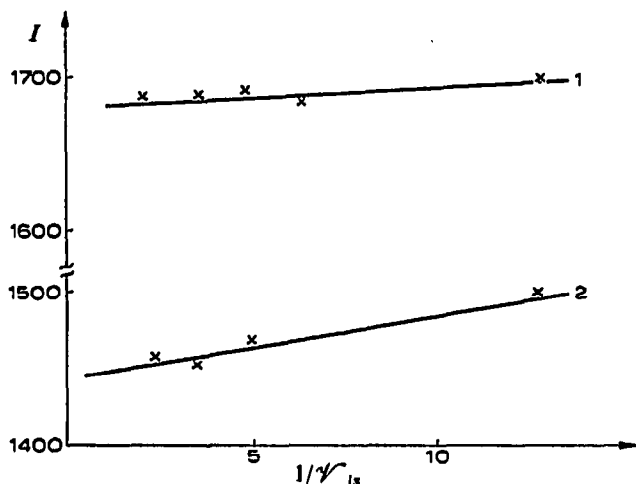
Fig. 8. Dependence of retention indices of the methyl esters of myristic acid (1) and n-dodecanol (2) on the inverse of SLP volume in the column. Experimental conditions: SLP, Apiezon L; temperature, 150°; solid support, Chromosorb G treated with acid and modified with dimethyldichlorosilane; column, 100 × 0.3 cm.

elaborating reproducible methods of providing highly effective chromatographic columns. The capillary columns introduced by Golay have substantially widened the scope of application of GC in the analysis of complex compounds. However, the practical application of capillary chromatography is less than that of chromatography with columns of greater diameter. Thus, for example, only 7% of the papers that appeared in 1972 in most journals on analytical chemistry and chromatography published in the Soviet Union and abroad were concerned with the development and application of capillary columns. This can be accounted for by the following reasons: limited choice of SLP (generally non-polar liquid phases are used), difficulties in making columns of reproducible properties and low sorbent capacity per unit length, which places stringent requirements on the sample introduction system and the detector, etc. As a result of research by some investigators[73-76], there have been developed new types of capillary columns free of some of the above disadvantages. The greatest promise, in our opinion, is shown by micropacked columns in which the advantages of capillary and packed columns are well combined.

As to their diameter, micropacked columns may be grouped with classical capillary columns, whereas the possible size of a sample that can be packed therein places them into the category of analytical packed columns.

The low column diameter produces a tangible effect on the diffusion of chromatographic zones. In capillary packed columns, sorption processes at the fronts of the chromatographic zones occur at distances as small as 0.4 to 0.8 mm, which provides for most favourable conditions for equalizing transverse concentration of the chromatographed compound as a result of diffusion, as the molecular diffusion time at a distance equal to the column diameter is substantially lower than the time of passage of the chromatographed zone[77]. The height equivalent to a theoretical plate (HETP) is, in the case of a capillary packed column, practically the same as that in the case of a classical capillary column.

   A major advantage of capillary packed columns is the lower mass-transfer co-
efficient in the Van Deemter equation[78] as compared to conventional packed columns.
This makes it possible to have high carrier gas rates in these columns without material-
ly affecting their performance, *i.e.* micropacked columns can be used to their utmost
advantage in rapid analyses. In micropacked columns, as distinct from capillary
columns, the partition coefficient increases at the expense of a reduction in the sorbent-
to-gaseous phase volume ratio, which is why in separating the light components of
complex compounds preference is given to micropacked columns.

   Another advantage of capillary packed columns is the possibility of using sub-
stantially larger samples for analysis, as compared to classical capillary columns, this
being due to the presence of a sorbent and, consequently, to the higher sorption capac-
ity of these columns. This feature makes it possible to use larger samples in the analysis
of impurities and to record the results of the separation not only by a highly sensitive
ionization detector, but also by a less sensitive and simpler microkatharometer (be-
cause conventional katharometers used for recording the results of separation on
high-performance micropacked columns are unsuitable). Fig. 9 shows chromatograms
of heptane cracking products obtained by means of a microkatharometer, a flame
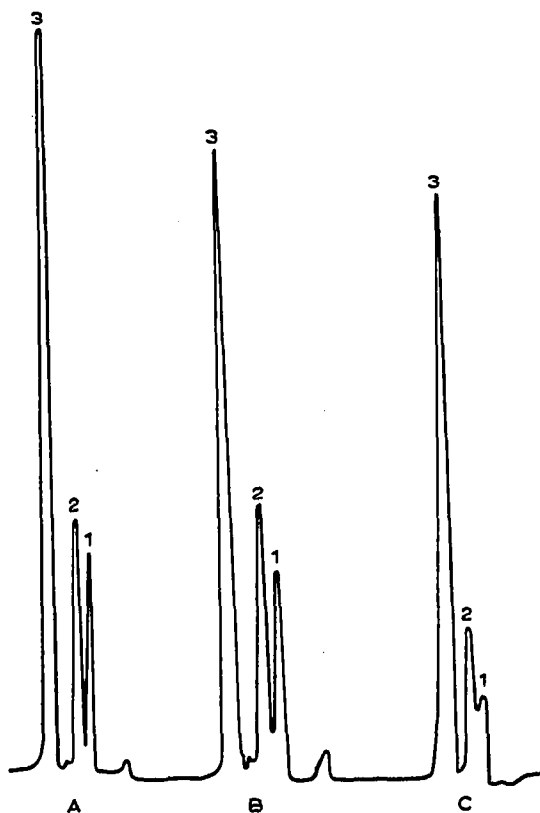ionization detector and a katharometer of the semidiffusive type. These chromato-

Fig. 9. Analysis of products of cracking of *n*-heptane on a micropacked column with various detectors.
(A) microkatharometer, (B) flame ionization detector, and (C) semidiffusion katharometer. 1 = 2-
Methylhexane; 2 = 3-methylhexane; 3 = *n*-heptane.

grams suggest that the use of a microkatharometer (40-ml capacity) for recording the results of the separation of a mixture on a micropacked column yields the same results as that of a flame ionization detector. It should be taken into consideration that a katharometer is more versatile, simpler both in design and in operation and more reliable than a flame ionization detector. In the case of common separations, preference should be given to a microkatharometer. It is as well to point out that the use of micropacked columns allows for a substantial reduction in the weight and size of the chromatographic equipment.

Still another advantage of micropacked columns is the possibility of using sorbents of different polarity and type both for gas–solid and gas–liquid chromatography. However, the general methods of preparing micropacked columns used so far do not give long columns characterized by better performance (the number of theoretical plates exceeding ten thousand).

The latest trend in the development of micropacked columns is associated with the elaboration of methods of obtaining sufficiently long (10–50 m) high-performance columns.

In 1971, at a conference held in Bratislava, Cramers *et al.*[70] reported methods of preparing and employing glass micropacked capillary columns up to 15 m long and having an efficiency of up to fifty thousand theoretical plates. However, the columns were packed with the sorbent in an ultrasonic bath under pressurized nitrogen, *i.e.* this method necessitates complex equipment.

Let us now consider the main fields of application of capillary packed columns.

Analysis of multicomponent mixtures

Capillary micropacked columns are characterized by a high total efficiency ($45 \cdot 10^3$ to $50 \cdot 10^3$ theoretical plates for columns 16 m long) and specific efficiency (2500 to 3000 theoretical plates per meter; HETP = 0.3 to 0.5 mm). Therefore, these columns can solve complex problems in analytical separations. It should be noted that capillary micropacked columns may be packed with sorbents of any kind: solid absorbents, polymeric absorbents, sorbents obtained by applying an SLP to a solid support, etc. The amount of sorbent necessary to prepare columns of this type is small because the required amount of sorbent for a 16 m × 0.8 mm column is less than 7.5 cm³. As an example, Fig. 10 shows the separation of alcohols and Fig. 11 illustrates the separation of hydrocarbon gases. These columns also look promising for rapid analysis and the analysis of impurities.

Measurement of the physicochemical properties of the products of reactions

At present, GC is extensively applied in determining various characteristics of a substance[80], particularly in determining the characteristics of dissolution of chromatographed compounds in the SLP, as well as in conducting analytical measurements. The high efficiency and the possibility of making measurements with small amounts of samples suggest that capillary micropacked columns are one of the most promising trends in physicochemical applications of GC. Examples of the use of such columns for determining adsorption heats are given in ref. 81.

Micropreparative separation

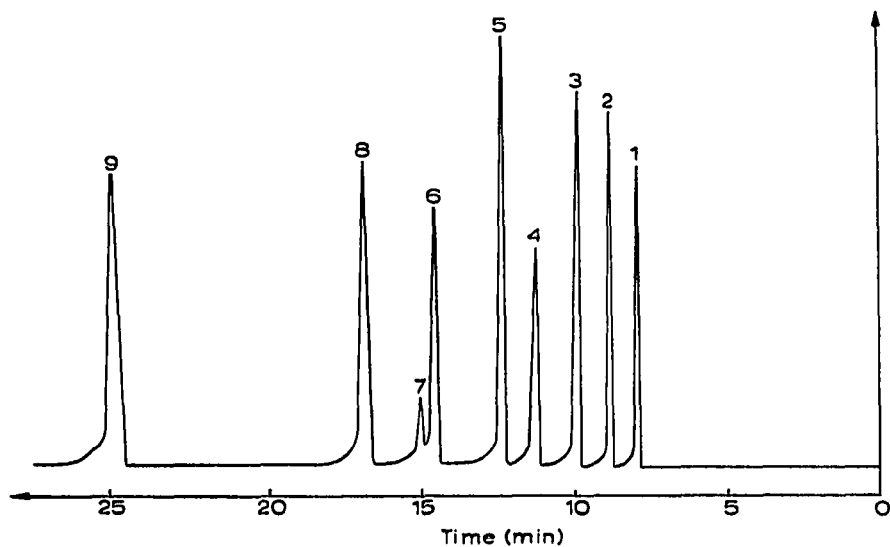Capillary micropacked columns can be employed with greater success, as com-

Fig. 10. Separation of aliphatic alcohols. Analysis conditions: column, 16.5 m × 0.8 mm with poly-phenyl ester (5%) on Chromosorb W; temperature, 120°. 1 = Isopropanol; 2 = 2-butanol; 3 = 1-butanol; 4 = 2-methyl-1-butanol; 5 = pentanol; 6 = 2-methyl-1-pentanol; 7 = 2-ethyl-1-butanol; 8 = hexanol; 9 = heptanol.
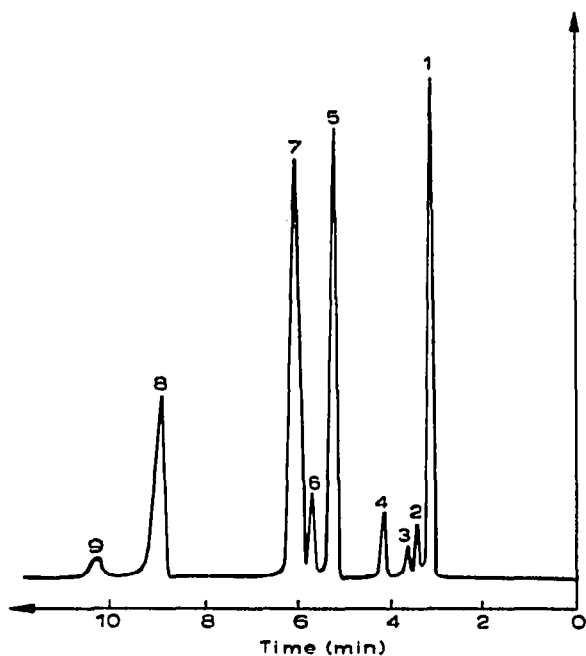

Fig. 11. Separation of hydrocarbon gases. Analysis conditions: column, 5.3 m × 0.8 mm with silica gel MC-A-1; temperature, 60°. 1 = Methane; 2 = ethane; 3 = ethylene; 4 = propane; 5 = pro-pylene; 6 = isobutane; 7 = n-butane; 8 = trans-butylene; 9 = cis-butylene.

pared to conventional capillary columns, for separating individual components of complex compounds with the aim of identifying these compounds, etc. Unfortunately, we know of no papers concerned with this problem.

On the strength of the foregoing, it can be inferred that the reproducible methods of preparing micropacked columns developed so far ensure their high efficiency.

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