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THE ANALYSIS OF COMPLEX ORGANIC MIXTURES BY GAS CHROMATOGRAPHY

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CONTENTS

Introduction 35

1. The identification of chromatographic peaks 35

2. Scheme for the separation of complex organic mixtures 41

3. A review of work on the analysis of hydrocarbons 45

INTRODUCTION

Gas chromatography is now one of the most effective methods of analysing organic substances. The following represents a far from complete list of mixtures which can be studied by gas chromatography: petroleum and petroleum products boiling at up to 600°, organic fluorine- and chlorine-containing compounds, the combustion products from internal combustion engines, essential oils, resins, solvents for plastics and lacquers, fruit and vegetable components, tobacco smoke, the products of the Fischer–Tropsch synthesis, air, paraffin waxes, etc.

The present review is devoted to the problems of the analysis of complex mixtures by gas chromatography, with particular reference to methods for the analysis of the liquid hydrocarbons present in various natural products.

1. THE IDENTIFICATION OF CHROMATOGRAPHIC PEAKS

In the analysis of different mixtures by gas chromatography, an extremely important problem is the identification of the resulting chromatographic peaks. This is often made much more difficult by lack of the pure individual substances thought to be present in the mixtures being analysed. In this case it is necessary to use the various relationships between the elution characteristics of the components and their other properties.

Retention volume. A characteristic property of a component being analysed by gas chromatography is its retention volume, which corresponds to the quantity of carrier gas passing through the column before elution of the peak maximum. Extensive collections of data for the retention volumes of hydrocarbons and other organic substances for different sorbents and temperatures are now available[1-3]. In addition, extensive use is also made of the relationship between retention volume and other characteristics of the components.

From elementary theory[4] it is known that the retention volume (V) is proportional to the Henry coefficient (Γ), since

$$V = LS\Gamma \qquad (1)$$

where L is the length of the column and S its cross-section.

In addition,

$$\Gamma = Ae^{Q/RT}, \qquad (2)$$

where Q is the heat of sorption, T the absolute temperature of the system, R the universal gas constant, and A a constant.

Since the change in the heat of sorption when the number of carbon atoms in the molecule increases by one is a constant for a homologous series, the following relationships apply:

$$\log V = an_C + b \qquad (3)$$

for a homologous series at constant temperature, and

$$\log V = c\frac{1}{T} + d \qquad (4)$$

for any component. Here, n_C is the number of carbon atoms in the molecule and a, b, c, and d are constants.

The applicability of these relationships is confirmed by appropriate plots, obtained in experiments with a wide variety of substances.

James and Martin[5], who analysed normal and iso-acids on a column containing a mixture of silicone and stearic acid, were the first to obtain the relationship between the logarithm of the retention volume and the number of carbon atoms. The plots for normal and for iso-acids were found to be parallel and approximately straight lines (Fig. 1).

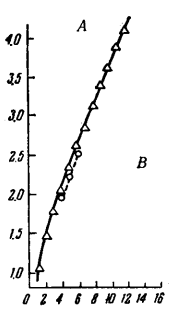


Fig. 1. Relationship between the logarithm of the retention volume (ordinate) and the number of carbon atoms (abscissa). Stationary phase: silicone and stearic acid. Temperature 137°: *A*) normal acids; *B*) iso-acids.

Analogous graphs were obtained by Hawke *et al.*[6] for esters of normal, branched, and unsaturated aliphatic acids, and by Ray[7] for normal paraffins, alcohols, ethers, and ketones (with dinonyl phthalate as stationary phase).

A method for calculating corrected retention volumes reduced to one gramme of stationary phase has been given by Littlewood *et al.*[8]

The retention time is a function of the nature of the substance, the nature of the stationary phase, and the column temperature, and also depends on the quantity of carrier gas used, the free volume between the point of admission of the specimen and the detector, the pressure drop, and the weight of stationary phase. The difference between the retention times of a given component and of hydrogen is multiplied by the quantity of carrier gas used and a coefficient which allows for the pressure drop[5,9]. If the flowmeter is calibrated at 0°, it is necessary to multiply by the quantity $T/273$, where T is the absolute temperature of the column. Division of the resulting product by the weight of stationary phase gives the retention volume reduced to one gramme.

In the work cited, Littlewood *et al.* give graphs of the relationship between the logarithm of the reduced retention volume and the number of carbon atoms for normal alcohols (column with Silicone 702) and of the relationship between the logarithm of the retention volume and the quantity $10^4/T$, for alcohols, acetates, and aromatic hydrocarbons. The last of these graphs is shown in Fig. 2.

Similar graphs have been constructed for organic compounds of boron by Seely *et al.*[10] and for light gases and normal paraffins by Janák (sorbents silica gel and zeolite)[11,12].

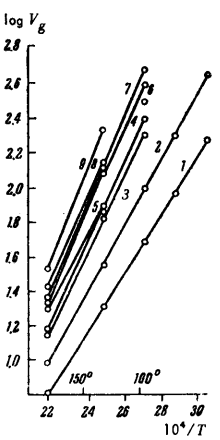


Fig. 2. Relationship between the logarithm of the reduced retention volume and the quantity $10^4/T$ for aromatic hydrocarbons on tritolyl phosphate: 1) benzene; 2) toluene; 3) *p*-xylene; 4) *o*-xylene; 5) isopropylbenzene; 6) mesitylene; 7) s-butylbenzene; 8) *p*-cymene; 9) t-pentylbenzene.

A recent paper[13] gives a generalised formula for calculating the retention volume reduced to one gramme of stationary phase:

$$V_g = \frac{z}{U} \cdot \frac{273}{T_m} \frac{p_0 - p_w}{760} \frac{F}{W} \cdot \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right], \quad (5)$$

where z is the distance between the peaks for air and the given component, U the velocity of the recorder chart, T_m the absolute temperature of the flowmeter, p_i the pressure at the column inlet, p_0 the pressure at the column outlet, p_w the vapour pressure of water at T_m, F the carrier-gas velocity, recorded by the flowmeter at the column outlet, and W the weight of stationary liquid.

At present, use is generally made of the relative retention volume, obtained by dividing the retention volume of the given component by the retention volume of a standard substance, which is often n-pentane. This characteristic is very convenient since it can be calculated without reduction to standard experimental conditions.

The Nomenclature Committee of the Symposium on Vapour-Phase Chromatography[14] recommended the following substances as standards: n-butane, isooctane, benzene, *p*-xylene, naphthalene, methyl ethyl ketone, and cyclohexanol.

Graphical interpretation of the relationship between the retention volume and the boiling point is often used. When the graphs are drawn on semi-logarithmic coordinates, various homologous series give almost straight lines. In the separation, for example, of hydrocarbons on a column with a polar phase, the straight lines corresponding to paraffins and alkylbenzenes will lie at a considerable distance from one another, but when a nonpolar liquid is used the straight lines will be extremely close together. Using these graphs it is possible to determine by two analyses the boiling point of an unknown substance and to find whether it belongs to a particular homologous series.

Graphical relationships for a wide range of organic compounds have been obtained by Tenney[15] — stationary phases: the unsaturated hydrocarbon oil "Convoil-20" †, squalane, di-(2-propionitrile) ether, the chlorinated oil "Convachlor-12" †, di(ethylhexyl) sebacate, the chlorotrifluorovinyl polymer "Fluorolube S" ‡, triethylene glycol, and a saturated solution of $AgNO_3$ in triethylene glycol — and by Bayer[16] — stationary phases: hexatriacontane, a mixture of polyethylene oxide and "Lubrol MO" §, di(ethylhexyl)sebacate, and dinonyl phthalate. Bayer used the graphs to determine the selectivity coefficients of the various liquid phases.

Lo Chang *et al.*[17] were able to identify 52 aromatic hydrocarbons in coal tar, by means of these graphs and infra-red spectrometry. Grant and Vaughan[18] constructed analogous graphs for paraffins and aromatic hydrocarbons in a study of the distribution of the latter in coal tar (stationary phases: dinonyl phthalate and tricresyl phosphate). Eggertsen and Knight[19] and McFadden[20] constructed curves for the direct graphical relationship between the retention time and the boiling point (stationary phases: glycol, squalane, and Silicone SF-96).

A number of authors have used the relationship between the logarithms of the retention volume and the vapour pressure. It is known[21] that the retention volumes v_1 and v_2 of the components being separated are inversely proportional to their vapour pressures p_1 and p_2 at the temperature of the experiment:

$$\frac{v_2}{v_1} = \frac{\gamma_1 p_1}{\gamma_2 p_2}, \quad (6)$$

where γ_1 and γ_2 are the activity coefficients. Within a homologous series the values of γ are close to one another (as is usual for non-polar substances in non-polar solvents), or vary linearly, so that the following relationship, given by Purnell[22], applies:

$$\log v = -a \cdot \log p + b, \quad (7)$$

where a is the ratio of the molar heat of solution at infinite dilution to the molar latent heat of volatilisation, and b is a constant. The graphs constructed on the basis of this equation were used by Purnell to discuss problems related to the choice of solvents. Jentzsch and Bergmann[23] studied the applicability of this relationship to aromatic hydrocarbons and used the graphs to identify the components. The relationship between the logarithms of the retention volume and of the vapour pressure has also been used in other work[24,25].

James *et al.*[26] proposed a graphical representation of the relationship between the retention volumes in different stationary phases (for example paraffin and benzylbiphenyl). The straight lines for the various homologous series intersect at a point. The existence of a relationship between the elution characteristics in polar and non-polar phases makes it possible to determine the chemical character of unknown substances. The diagram constructed by these authors is shown in Fig. 3.

Phillips[27] has given similar graphs for amines, alcohols, ketones, and hydrocarbons, with "Lubrol MO", liquid paraffin, zinc stearate, and Silicone 702 as stationary phases.

Construction of the relationship between the logarithms of the retention volumes gives almost parallel lines. Fig. 4 gives the graphs used by Desty and Whyman[28] to identify 81 hydrocarbons and 7 sulphur compounds by analysis on

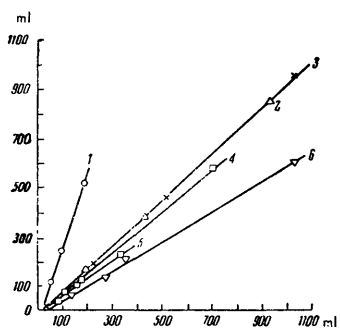


Fig. 3. Relationship between the retention volume in benzylbiphenyl (abscissa) and the retention volume in paraffin (ordinate):
1) normal aliphatic hydrocarbons; 2) aromatic hydrocarbons; 3) isoiodides; 4) normal iodides; 5) alcohols; 6) ketones.

† Made by Consolidated Electrodynamics Corp., USA (Ed. of Translation).

‡ Made by Hooker Chemical Corp., USA (Ed. of Translation).

§ An emulsifying agent made by Imperial Chemical Industries Ltd. (Ed. of Translation).

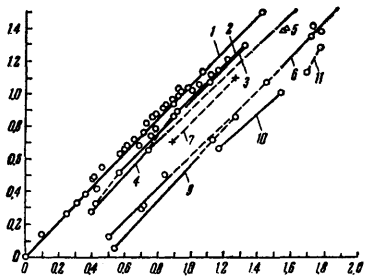


Fig.4. Relationship between the logarithms of the retention volumes (n-pentane = 1):
on ordinate axis: stationary phase n-hexatriacontane;
on abscissa stationary phase benzylbiphenyl:
1) paraffins; 2) alkenes; 3) cyclopentanes;
4) cyclohexanes; 5) bicyclic naphthenes; 6) aromatic hydrocarbons; 7) cyclic monoolefines; 8) cyclic diolefines; 9) sulphides; 10) thiophenes; 11) cyclic sulphides.

columns with n-hexatriacontane and benzylbiphenyl (in conjunction with mass-spectrometric data). The same authors gave the graphs of $\log v$ *vs.* n_C and $\log v$ *vs.* (boiling point) for these phases.

James[29] used graphical relationships to determine the degree of unsaturation of fatty acids. The graph which he constructed consists of a net: one family of straight lines correspond to the number of double bonds in the molecule and the family of straight lines intersecting these (dotted lines) correspond to the number of carbon atoms.

Hudy[30] constructed a graph showing the relationship between the logarithms of the retention volumes for the methyl esters of various acids (stationary phases: "Apiezon"¶ and succinate polyester), and Pierotti *et al.*[31] did the same for alkanes, alcohols, and ketones (in "Triol" and diisodecyl phthalate). [Triol, made by Union Carbide and Carbon Co., USA, is 2,4-dimethyl-2-(2-hydroxyethoxy)-pentane--1,5-diol (Ed. of Translation.)] Desty and Harborn[32] suggested the use of a detergent containing an alkyl aryl sulphonate as packing for chromatographic columns and gave a graph for the relationship between the retention volume and molecular weight for different hydrocarbons. Homologous series give straight lines on the graph. An analogous diagram was constructed from data obtained on a column with "Apiezon L".

Extensive work is at present being done on the determination of the retention volumes of various individual substances and their dependence on other physicochemical properties, to facilitate their identification in real mixtures. In this connection, the following have been proposed as standard stationary phases[14] (the temperature limits are given in brackets): n-hexadecane (20°–50°), dinonyl phthalate (20°–100°), squalane (20°–150°), dimethylformamide (-20° to +20°), benzylbiphenyl (80°–150°), and diglycerol (20°–100°). The use of a mixture of 20 parts by weight of liquid and 80 parts by weight of inert carrier — preferably "Celite 545"† — is recommended.

¶ Made by James G. Biddle Co., USA (Ed. of Translation).

† Highly porous filter aid made from diatomaceous earth by Johns-Manville Corp., USA (Ed. of Translation).

Determination of molecular weight. In the identification of various substances, a knowledge of their molecular weights is extremely important. In this connection, the development of methods capable of giving rapid, accurate, and reliable data is of considerable interest. The usual methods of determining molecular weights are time-consuming and require highly-trained personnel. A fairly large specimen is also required. Gas chromatography[33,34] makes possible a rapid and sufficiently accurate determination. An important advantage of this method is that it is possible to carry out the continuous identification of the components of a complex mixture being separated on a chromatographic column.

The determination is based on the addition, to the mixture of unknown composition, of a pure substance of known molecular weight to act as "internal standard". Two chromatographic analyses are then carried out on the same apparatus but with different carrier gases. The detector used is a Martin gas density balance which compares the densities of the gas streams leaving the separating and reference columns, the density difference being converted to an e.m.f. by means of a sensitive thermocouple.

Let us assume that an "internal standard" k with molecular weight M_k is added to an unknown component with molecular weight M_x and that the resulting mixture is eluted from a chromatographic column by a gas with molecular weight M_1. If another gas with molecular weight M_2 is used, the retention volumes will, of course, be analogous to those obtained in the first case, but even for identical velocities, the heights and areas of the peaks will be different, due not only to the difference in the size of the specimen being analysed, but also to the effect of the nature of the eluant.

The densities of the gas streams leaving the reference (d_1) and chromatographic (d_x) columns can be obtained from the Clapeyron equation:

$$d_1 = \frac{M_1 p}{RT};\quad d_x = \frac{(n_1 M_1 + n_x M_x)\,p}{RT}, \tag{8}$$

where n_1 and n_x are the mole fractions of the eluant and the substance being analysed. From this the density difference is

$$\Delta d_{x-1} = \frac{n_x (M_x - M_1) p}{RT}. \tag{9}$$

Similarly, for an eluant with molecular weight M_2

$$\Delta d_{x-1} = \frac{n_x (M_x - M_2) p}{RT}. \tag{10}$$

The quantity Q_x of the component being analysed may be written

$$Q_x = \int_0^\infty \frac{n_x M_x p}{RT}\, dv, \tag{11}$$

where v is the volume of gas mixture leaving the chromatographic column. Alternatively, substituting Eqn. (9):

$$Q_x = \frac{M_x}{M_x - M_1} \int_0^\infty \Delta d_{x-1} dv.$$

Similarly, the quantity q_k for the standard used during the same experiment is equal to

$$q_k = \frac{M_k}{M_k - M_1} \int_0^\infty \Delta d_{k-1} dv.$$

Here Δd_{k-1} is the difference between the densities of the gas streams at the moment when the standard passes through the detector. Similar relationships are obtained for the quantities Q'_x and q'_k obtained when a gas with molecular weight M_2 is used as eluant.

Since for sufficiently small specimens (several microlitres) the e.m.f. E of the detector thermocouple is proportional to the density difference, the relationship $\int_0^\infty \Delta d dv = k\int_0^\infty \Delta E dv$ applies; the value of this integral is, of course, proportional to the area of the corresponding peak on the chromatogram.

Since $\frac{Q_x}{q_k} = \frac{Q'_x}{q'_k}$, we obtain for the peak areas the relationship:

$$\frac{A_x}{a_k}\left(\frac{M_k - M_1}{M_x - M_1}\right) = \frac{A'_x}{a'_k}\left(\frac{M_k - M_2}{M_x - M_2}\right), \qquad (12)$$

where A_x, A'_x, a_k, and a'_k are the corresponding areas.

This last relationship is used to find the desired value of M_x. The accuracy of the determination is ~4%.

Determination of the elementary composition. There are two papers[35,36] devoted to the determination of the elementary composition of hydrocarbons by gas chromatography. This method has an accuracy comparable with that of Pregl's method and possesses a number of advantages over the latter; the time required for the analysis is small (< 10 min) and it is possible to work with very small amounts of specimen.

The specimen is ignited in a tubular furnace either in a current of dry oxygen or with cupric oxide and the resulting products are passed through a tube containing calcium carbide to convert the water into acetylene and then collected in a trap cooled with liquid nitrogen. The acetylene and carbon dioxide are then volatilised and passed in a current of argon or helium to a chromatographic column containing silica gel. A thermal-conductivity detector is placed after the column. Such an apparatus is illustrated in Fig. 5.

The areas of the resulting chromatographic peaks for acetylene and carbon dioxide are proportional to the percentage concentrations of hydrogen and carbon in the specimen being analysed. The elementary composition can be calculated by multiplying the peak areas by appropriate calibration coefficients.

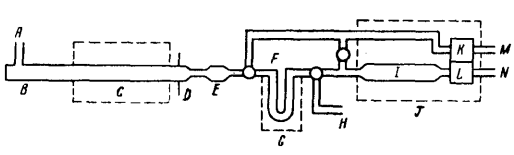


Fig. 5. Apparatus for the elementary analysis of hydrocarbons:
A) oxygen inlet; *B*) ignition tube; *C*) tubular furnace; *D*) aluminium shield; *E*) tube with calcium carbide; *F*) cold trap; *G*) Dewar vessel containing liquid nitrogen; *H*) vacuum connection; *I*) chromatographic column; *J*) insulating jacket; *K*) reference cell of detector; *L*) measuring cell of detector; *M*) helium inlet; *N*) outlet to gas meter.

The accuracy of the method is ~0.5% for carbon and 0.1–0.2% for hydrogen. Milligramme specimens are used and the quantities can be reduced considerably by using more sensitive detectors.

The use of molecular sieves. The molecular sieves normally used to separate light gases exhibit selective adsorption for certain homologous series; this is determined by the size and shape of the molecules. This has made it possible to use molecular sieves as an additional means of identifying the components being analysed[37,38]. It has been established that on passage through a column containing a molecular sieve, some components are not retained by the latter while others are irreversibly adsorbed. This property of molecular sieves can be used to remove certain groups of substances for identification "by difference". The assembly includes a column 50 cm long and 6.35 mm in diameter, filled with a 5 Å molecular sieve (pore diameter 5 Å) connected in series with an ordinary 2 metre column operating on the principle of gas-liquid partition chromatography.

When a mixture of normal paraffins, isoparaffins, cycloparaffins, and aromatic hydrocarbons was passed through the system, it was found that the C_3-C_{11} n-paraffins were irreversibly adsorbed by the molecular sieve, whereas the other classes of hydrocarbon gave appropriate peaks on the chromatogram. A number of other compounds were also found to be irreversibly adsorbed.

Table 1 gives components which pass readily through a column of 5 Å molecular sieve and Table 2 gives compounds which are irreversibly adsorbed.

It has been established that other types of molecular sieve do not behave in exactly the same way as the 5 Å sieves, due to their different pore diameters. Thus the

TABLE 1. Components passing through a column of 5 Å molecular sieve.

Group	Hydrocarbons studied
Isoparaffins	isobutane, isopentane, 2,3-dimethylbutane
Aromatic hydrocarbons	benzene, toluene, *m*-xylene
Cycloparaffins	cyclopentane, cyclohexane
Isoolefines	2-methylpropene, 2-methylbuta-1,3-diene
Esters	pentyl formate, ethyl acetate, ethyl propionate
Ketones	acetone, methyl ethyl ketone, mesityl oxide
Halogenated hydrocarbons	chloromethane, chloroform
Isoalcohols	isopropyl and isoamyl alcohols
Ethers	diethyl ether, diisopropyl ether
Other compounds	carbon monoxide, oxygen, nitrogen, the inert gases, methane, nitromethane, carbon disulphide, dimethyl sulphide, thiophen

TABLE 2. Components completely adsorbed by a column of 5 Å molecular sieve.

Group	Components studied
Normal paraffins (except methane)	propane, n-butane, n-hexane
Normal olefines	ethylene, propene, hex-2-ene
Normal alcohols	methanol, ethanol, n-butanol
Aldehydes	acetaldehyde, propionaldehyde, isovaleric aldehyde
Acids	formic acid, propionic acid

4 Å molecular sieve adsorbs only ethane from the normal paraffins and ethylene and propylene from the normal olefines. In the analysis of complex mixtures containing different homologous series, it is possible to simplify the identification of the components by using these properties of molecular sieves to remove one member of the series. Removal of a component from a system may also be useful when it is necessary to measure superimposed peaks.

Fig. 6 illustrates the removal of normal paraffins from mixtures. The upper chromatogram was obtained after passage of the specimen through a column filled with di-(2-propionitrile) ether deposited on "Chromosorb" ‡ and the lower one after passage through a system consisting of the same column and a column containing a molecular sieve.

Use of the chromatographic-detector characteristics. Components can be identified on the basis of measurement of the peak areas, using an ordinary katharometer. Quantitative determination of the composition of the mixture being analysed is carried out by normalisation of the peak areas, correcting for the thermal conductivity[39-43].

By carrying out a parallel analysis with chemical conversion of the chromatographic peaks before passage through the katharometer, it is possible to determine the carbon number of a component by combined calculations on the two chromatograms. There are now a number of methods involving conversion for the chromatographic analysis of mixtures. For instance, Norem[44] ignited the components to CO_2, removed the water formed, and determined the CO_2 by means of a katharometer. Green[45] passed the substances leaving the column through a layer of CuO to give CO_2 and H_2O, and then through iron powder to convert the water into hydrogen, which was passed to the katharometer cell. Zlatkis *et al.*[46,47], using hydrogen as carrier-gas, converted the components into methane and water over a nickel catalyst. The water was removed and the methane passed to the katharometer. In the analysis of hydrocarbons, of course, no water is formed.

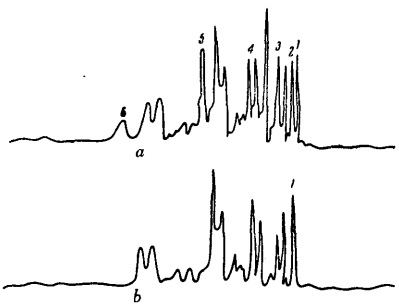


Fig. 6. Removal of normal paraffins by means of molecular sieves:
a) separation on a column of di-(2-propionitrile) ether; b) chromatogram of mixture after removal of normal paraffins by means of a molecular sieve: 1) isopentane; 2) n-pentane; 3) n-hexane; 4) n-heptane; 5) n-octane; 6) n-nonane.

The area of the peak obtained after conversion of the components is proportional not only to its concentration but also to the number of carbon (or hydrogen) atoms present, and it is possible to determine the latter by combined calculations on a given chromatogram and the chromatogram obtained without conversion. Instead of using the katharometer, it is possible to determine the CO_2 with an infra-red spectrometer[48-50], by titration with potassium methoxide[51], or coulometrically (carrier gas: oxygen; the CO_2 and O_2 are bubbled through $BaCl_2$ solution in a cell containing a platinum spiral which acts as an oxygen electrode)[52].

The components can also be identified by an ionisation detector[53,54] since the ionisation current is proportional to the "effective ionisation cross-section of the molecule" — a molecular characteristic[55].

It is also possible to use a flame detector[56,57] since the increase in the temperature of the thermocouple on combustion is proportional to the quantity of heat evolved, and hence for one carbon bond, *i.e.* to the peak area. The use of a micro-flame emission detector, which measures the luminescence of the flame[18,58] is also of interest, since in this case the response depends markedly on the nature of the substance. In particular, the response is much greater for aromatic substances than that for paraffins.

The use of infra-red and mass spectrometry. There are many examples of the identification of chromatographic peaks with the aid of infra-red or mass spectrometry. The simplest method used in these cases involves trapping the fractions leaving the gas chromatograph in cooled traps and then transferring, for example, to a cell for analysis by infra-red spectrometry.

The American firm of Beckman now produces a system consisting of a GC-2 gas chromatograph and IR-5 infra-red spectrometer[59]. The cell for the infra-red analysis has a very small volume, only 0.0002 cm^3, which ensures extremely accurate data in the determination of impurities in chromatographic bands. The same firm also produces a "Megachrom" gas chromatograph combined with an IR-4 infra-red spectrometer[60], which makes it possible to carry out the spectrographic analysis of the large fractions obtained in preparative work (the volume of the specimen separated by the "Megachrom" is ~20 ml). A serious disadvantage of these systems is the time required for the spectrographic analysis. Thus, for example, 16 min are required to record the spectrum of benzaldehyde on an IR-5 apparatus. When the chromatogram contains a large number of peaks, the time required for their identification naturally becomes very great.

Analogous schemes are used for the identification of peaks by mass spectrometry. In work by Desty and Whyman[28] and Bradford *et al.*[61], this method was used as an additional means of determining the composition of various light petroleum products. Whitham[62] identified the heavy $C_{10}-C_{14}$ hydrocarbons in kerosene fractions by freezing the chromatographic fractions with subsequent mass-spectrometric analysis.

The firm of Consolidated Electrodynamics (USA) produces a system consisting of a 26-201 A laboratory chromatograph and 21-620 mass spectrometer with mass range from 2 to 150 and a response of 1 sec.[63] This system is suitable for the comparatively rapid analysis of mixtures of hydrocarbons and other organic substances.

‡ Closely-graded calcined diatomite, made by Johns-Manville Corp., USA (Ed. of Translation).

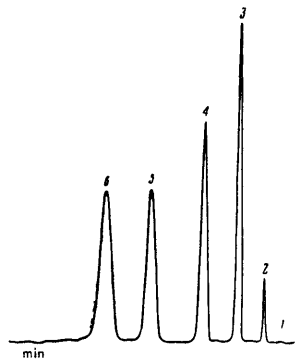


Fig. 7. Chromatogram for the separation of a mixture of acetone, benzene, toluene, ethylbenzene, and styrene:
1) air; 2) acetone; 3) benzene; 4) toluene; 5) ethylbenzene; 6) styrene.

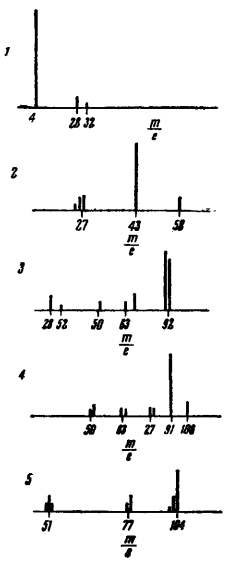


Fig. 8. Mass spectra corresponding to the chromatographic peaks:
1) helium with a trace of air; 2) benzene; 3) toluene; 4) ethylbenzene; 5) styrene.

The use of a time-of-flight mass spectrometer for the direct observation of a chromatographic process is of considerable interest[64]. The mass spectrometer is connected to the chromatograph at a point between the column and the thermal conductivity detector and makes it possible to obtain on an oscillograph 2000 mass spectra per second (m/e from 1 to 6000), thus achieving continuous identification and determination of the degree of purity of the components corresponding to the chromatographic peaks.

Fig. 7 shows the chromatogram for the separation of a mixture containing acetone, benzene, toluene, ethylbenzene, and styrene, and Fig. 8 gives the mass spectra corresponding to the peaks obtained.

One possible method of combining mass spectrometry and chromatography is by carrying out parallel analyses on both instruments with subsequent combined calculation of the results. This method has been used, in particular, by Eggertsen and Knight[19] in the analysis of C_5-C_7 hydrocarbons. Howard and Ferguson[65] carried out the mass-spectrometric analysis of petrols without preliminary removal of pentanes and introduced into the mass spectra corrections based on the chromatographic analysis of hydrocarbons up to and including C_5.

2. SCHEME FOR THE SEPARATION OF COMPLEX ORGANIC MIXTURES

The complex mixtures of hydrocarbons and other organic compounds normally encountered in various real products can seldom be analysed in detail on an ordinary chromatographic apparatus consisting of one column, since various peaks are superimposed. This is due to the fact that the retention volumes of some isomers, or of substances of different type with different molecular weights, are equal. Thus in the analysis of the C_3-C_5 hydrocarbons on a column of diisodecyl phthalate, which is weakly polar, the components are separated according to their boiling points[66]. n-Butane, 2-methylpropene, and but-1-ene, however, appear as one peak, since their boiling points are very close. In addition, propane and propene, *cis*- and *trans*-but-2-ene, n-pentane and pent-1-ene, are not separated. When the more polar triethyleneglycol n-butyric ester[67] is used, the the olefines have retention volumes slightly higher than the corresponding paraffins, but in this case some of the C_4 olefines are superimposed on C_5 components. Analysis on a column of the strongly polar dimethylsulpholane§ [66] gave good separation of paraffins and olefines with the same number of carbon atoms, but the olefines were retained by the column to such an extent that they were superimposed on the peaks of paraffins with one more carbon atom in the molecule.

These features show the necessity for developing different schemes for the chromatographic analysis of complex mixtures, either by using several columns or by using supplementary techniques such as liquid chromatography, distillation, hydrogenation, sulphonation, infra-red, and mass spectrometry, etc.

The simplest version of multi-stage chromatography involves the use of two columns with different sorbents. All the components of the mixture being analysed are passed first through one and then through the other. With the correct combination of sorbents and column lengths, good separation of a large number of components can be achieved. Thus for the separation of hydrocarbons up to and including C_5, for example, Fredericks and Brooks[66] used columns of diisodecyl phthalate and dimethylsulpholane, and Zhukhovitskii *et al.*[68] used a column of alumina and a gas-liquid column with dibutyl phthalate. Single-stage columns with mixed stationary phases can also be used[20,69]. Of course, such schemes are of very limited application, since the degree of separation of any two components

§ 3,4-Dimethyltetrahydrothiophene-*S*-dioxide (Ed. of Translation).

achieved on the first sorbent may be reduced or eliminated completely on passage through the second sorbent.

A number of papers have been devoted to the problems of analysing the C_5-C_7 hydrocarbons. Thus a sorbent consisting of "Pelletex" furnace black¶, modified with 1.5% squalane[19,70], has been proposed for the separation of saturated hydrocarbons according to the number of carbon atoms. This packing, like solid adsorbents, has a slightly higher selectivity towards paraffins compared with naphthenes of similar boiling point, and this causes it to yield combined peaks according to carbon number. Modification by means of squalane eliminates tailing of the chromatographic peaks. A column of this sorbent has been used to separate the saturated C_5 and C_6 hydrocarbons.

For the analysis of the saturated C_5-C_7 hydrocarbons, Eggertsen and Groennings[71] suggested using three columns: one with 3% squalane on C-22 firebrick† (non-polar), one with 40% di-(2-propionitrile) ether on C-22 (polar), and one with 1.5% squalane on "Pelletex" (which separates according to the number of carbon atoms). Combination of the three chromatograms made it possible to determine all paraffinic and naphthenic C_5 and C_7 hydrocarbons except 3-ethylpentane. In the analysis of the raw material of catalytic reforming, containing C_8 hydrocarbons, whose peaks often overlap the C_7 peaks, these compounds can be removed beforehand on the third column of squalane on "Pelletex" and the C_5-C_7 fraction is analysed on the other two. Use can also be made of mass-spectrometric data.

Simmons and Snyder[72] analysed the products of platforming by means of a two-stage chromatographic column constructed in such a way that only the desired fractions passed from the first stage to the second for further separation. Thus the sections of the column can operate either in series or in parallel. Such a scheme, using squalane on "Pelletex" and silicone on firebrick as sorbents, is illustrated in Fig. 9; with this it was possible to separate paraffinic, naphthenic, and aromatic hydrocarbons containing up to 8 carbon atoms. An analogous scheme with silica gel and n-octadecane on "Celite 545" as sorbents was used by Amberg *et al.*[73] to analyse the products of the oxidation of ethylene.

Knight[74] has shown, by comparing the activity coefficients of hydrocarbons of different structure, that a column of 1.5% squalane on "Pelletex", which achieves greater retention of paraffins relative to naphthenes with similar boiling points, has the same effect on aliphatic olefines relative to cycloolefines, and it is therefore possible to separate unsaturated hydrocarbons according to the number of carbon atoms. On this basis a method has been developed for determining pentenes and hexenes in petrol from catalytic cracking. This involves liquid chromatography with fluorescent indicators to obtain an olefinic–aromatic fraction, distillation of the latter to obtain the pentene and hexene fractions, and analysis of the latter by gas chromatography. The pentene fraction was first analysed on a column of squalane on "Pelletex" to remove traces of hexenes and then on a dimethylsulpholane column; the hexene fraction was also analysed first on a column of squalane on "Pelletex" and then on di-(2-propionitrile) ether. In addition, the C_6 monoolefines were analysed on dimethylsulpholane, the C_6 cycloolefines on firebrick C-22 with 3% squalane, and the C_5 olefines on diisodecyl phthalate.

¶ Granulated carbon with an active surface of 21 $m^2\ g^{-1}$, made by Cabot Corp., USA (Ed. of Translation).

† Made by Johns-Manville Corp., USA (Ed. of Translation).

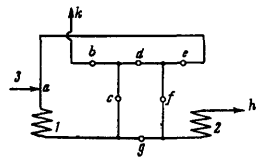


Fig. 9. Two-stage apparatus for analysis by gas chromatography:
1) column 1; 2) column 2; 3) carrier gas; *a–g*) valves; *h*, *k*) outlets to detector.

Combination of all these chromatograms makes it possible to determine 15 C_5 olefines (including cyclic olefines and dienes) and all 17 C_6 monoolefines (except 3- and 4-methylpent-1-enes) and also to obtain certain data on the cyclic olefines and C_6 dienes. The analytical scheme for the olefines is shown in Fig. 10 and the chromatograms for the separation on the various columns in Fig. 11. A serious disadvantage of this method is that it is cumbersome and time-consuming (the analysis of the C_5 compounds by gas chromatography requires 5 h, and that of the C_6 compounds 10–12 h).

A paper by Henschkel *et al.*[75] on the determination of traces of methylacetylene and allene in cracking gases is of interest. On a column of silicone oil, the peaks for these compounds come between the propane–propene and isobutane peaks. The polar phase diethylformamide holds back methylacetylene and propadiene to a greater extent than the saturated C_4 hydrocarbons. This has been used to carry out a two-stage analysis. The fraction containing the C_3 components and isobutane was taken from the first column and analysed on the polar column: this gave good separation of the peaks for the two trace substances being determined.

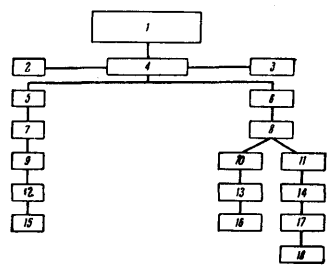


Fig. 10. Scheme for the analysis of C_5 and C_6 olefines by gas chromatography:
1) olefines; 2) hydrocarbons lighter than C_5; 3) hydrocarbons heavier than C_6; 4) 1.5% squalane on "Pelletex"; 5) C_5 hydrocarbons; 6) C_6 hydrocarbons; 7) 20% dimethylsulpholane on C-22; 8) 40% di-(2-propionitrile) ether on C-22; 9) some vapour undergoes further separation; 10) 13 out of 17 possible monoolefine peaks; 11) cycloolefines and dienes; 12) 10% diisodecyl phthalate on C-22; 13) 20% dimethylsulpholane on C-22; 14) 3% squalane on C-22; 15) all 14 possible components; 16) all components except the vapours of 3- and 4-methylpent-1-enes; 17) cycloolefines; 18) dienes.

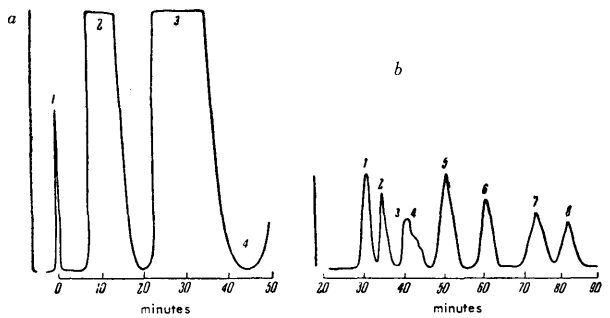


Fig. 11. Separation of olefines on various columns.
a) Separation on a column of squalene on "Pelletex":
1) air; 2) C_5 hydrocarbons; 3) C_6 hydrocarbons;
4) C_7 hydrocarbons.
b) Separation of the pentene mixture on a column of 10% diisodecyl phthalate on C-22 firebrick:
1) pent-1-ene; 2) 2-methylbut-1-ene; 3) and 4) *cis*- and pent-*trans*-2-ene and 3,3-dimethylbut-1-ene;
5) 2-methylbut-2-ene and 3-methylbuta-1,3-diene;
6) 3-methylbuta-1,2-diene; 7) penta-1,2-diene;
8) cyclopentene.

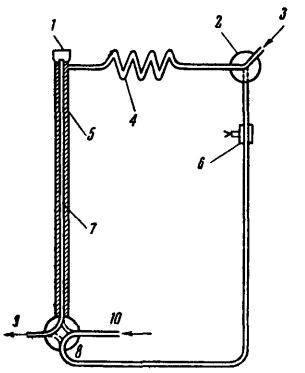


Fig. 12. System of preliminary fractionation for the analysis of the C_3-C_7 components present in petroleum:
1) silicone film; 2) three-way tap; 3) nitrogen;
4) nitrogen heater; 5) specimen inlet zone; 6) needle valve; 7) preliminary fractionation column; 8) four-way tap; 9) to analytical column; 10) nitrogen for blow-back.

The analysis of straight-run petrols by a combination of liquid chromatography (to separate the naphthene–paraffin fraction from the aromatic fraction) and gas chromatography with precise rectification, first used by Bradford *et al.*[61] and Lichtenfels *et al.*[76], was further developed by Kerenyi and Keszthelyi[77], who used a column of cetane on crushed 63 brick to analyse narrow naphthene–paraffin fractions of petrol, boiling up to 150°. This made it possible to carry out gas–liquid chromatography without using the pure components, since the fractions either had constant boiling point or were transitional. This method has been used for the analysis of petrols from eastern oils of the Soviet Union and has made it possible to determine the concentrations, in these materials, of a large number of hydrocarbons up to and including C_9.

Martin and Winters[78] used gas chromatography for the direct determination of the composition of petroleum up to and including the C_7 hydrocarbons, by means of a system of preliminary fractionation (Fig. 12).

A column containing "Apiezon" grease was used to separate the C_2-C_7 fraction, which was then passed to analytical columns containing isoquinoline and chloronaphthalene. The preliminary separation column was blown back to remove heavy components. Combined calculation on the two chromatograms makes it possible to determine 35 paraffinic, naphthenic, and aromatic hydrocarbons. This has been done for 20 Asiatic and American oils from different sources and has revealed a number of interesting features.

It is known that a large number of real hydrocarbon mixtures contain components of different classes, and this makes it difficult to develop methods for their chromatographic analysis. Methods have been proposed, based on the utilisation of the chemical reactions of given classes of substance. Thus Ray[79], in the analysis of non-olefinic trace impurities in ethylene, removed the latter beforehand on a column of carbon impregnated with bromine. Martin[80] used this "removal method" to analyse the C_3-C_6 hydrocarbons in cracking petrols. To absorb olefines he used an absorber containing sulphuric acid on silica gel. The analysis involved two runs on a column of isoquinoline, with and without the absorber connected in series. Combined calculations on the two chromatograms made it possible to determine 45 components in petrols from catalytic cracking and coking, and in commercial petrol (except for four groups of two to three components, which could not be separated). An analogous scheme is used with molecular sieves as separating agents, which irreversibly adsorb certain groups of substances, as mentioned above in connection with the problems associated with the identification of chromatographic peaks[37,38].

O'Connor and Norris[81] carried out a group analysis of petroleum distillates by a similar method, combining it with liquid chromatography on silica gel and with mass spectrometry. The analytical scheme is shown in Fig. 13. Hydrocarbons of normal structure, adsorbed by the molecular sieve, were extracted and analysed by gas chromatography.

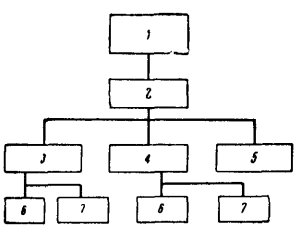


Fig. 13. Scheme for the analysis of petroleum distillates using molecular sieves and mass spectrometry:
1) specimen; 2) separation on silica gel;
3) saturated hydrocarbons; 4) olefines; 5) aromatic hydrocarbons; 6) 5 Å molecular sieves; 7) mass spectrometers.

Bayer *et al.*[24] analysed essential oils by successive separation of aldehydes and ketones (as the 2,4-dinitrophenylhydrazones), alcohols (as the dinitrobenzoates), and acids (as the alkali salts), with chromatographic separation of the residue on a column of silicone grease and $C_5H_{11}COOLi$ on brick.

Another method of using the chemical conversion of substances combined with gas chromatography has been proposed by Scharfe[82] for the analysis of hydrocarbon gases. According to this method, part of the specimen is hydrogenated in the presence of a platinum catalyst and then separated on a column containing 20% diisoheptene on kieselguhr. Another part of the specimen passes through a column of absorbent material (a solution of Ag_2SO_4 in H_2SO_4 on kieselguhr), which removes olefines, and is then subjected to chromatographic analysis. This method, which is applicable to the determination of the composition of C_1-C_5 hydrocarbons, can also be used for the analysis of hydrocarbons of higher molecular weight, if a knowledge of the individual composition of the olefines is not required and if it is possible to restrict the analysis to the determination of the concentration of groups with a given carbon skeleton.

When carrying out various chemical changes combined with gas chromatography, it is convenient to use the modified six-way tap proposed by Ettre and Brenner[83].

These examples illustrate the advantages of using multi-stage assemblies for the chromatographic analysis of complex mixtures.

Hurn *et al.*[84], in the analysis of waste gas consisting of hydrocarbons, the products of their partial oxidation, and other compounds, used a system of three different chromatographic columns connected in such a way that after passage through one column and detector, a fraction can be directed for further separation to either of the other two, and then, if necessary, to a third column. This scheme has been used to achieve good separation of components with 2–10 carbon atoms. In this case all components are passed through the first column (containing silicone oil), components up to and including heptane are passed through the second column (containing benzyl ether), and components up to hexane through the third (containing dibutyl maleate).

The American firm of Perkin–Elmer now produces a three-stage chromatograph[85] for the analysis of complex mixtures operating on the above principle. The apparatus is illustrated schematically in Fig. 14. In the analysis of petrols free from olefines, separation of saturated hydrocarbons from aromatic hydrocarbons and separation of the latter into individual components is achieved on the first column, packed with polyethyleneglycol on firebrick (Fig. 15*a*). The naphthene–paraffin fraction is then separated on a second column containing di-(2-propionitrile) ether as stationary phase (Fig. 15*b*). Finally, the light paraffins are separated on a column containing squalane (Fig. 15*c*). Cracking products cannot be analysed in this way, since they contain olefines.

Martin[86], in a study of the decomposition of α-cellulose, collected the products in a cold trap and separated these into two fractions. The first (light) fraction was then directed to a column of carbon or silica gel and the second to a gas–liquid column.

Madison[87] analysed light gases and C_1-C_4 hydrocarbons by means of columns of active carbon and dimethylsulpholane on firebrick, together with a cold trap containing

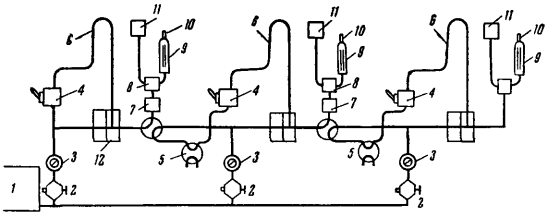


Fig. 14. The Perkin-Elmer Chromatograph, Model 188: 1) carrier-gas source; 2) pressure regulator; 3) manometer; 4) liquid specimen inlet; 5) tap for introducing gaseous specimen; 6) chromatographic column; 7) needle valve; 8) solenoid valve; 9) flowmeter; 10) outlet; 11) tap for removing specimen; 12) detector.

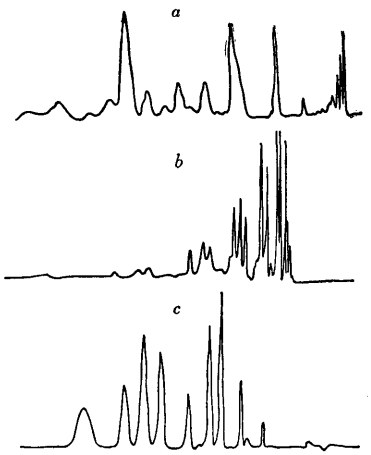


Fig. 15. Analysis of petrol on a Perkin–Elmer Chromatograph, Model 188: *a*) aromatic hydrocarbons, column of polyethylene glycol; *b*) paraffins, column of di-(2-propionitrile) ether; *c*) light paraffins, column of squalane.

carbon. An analysis was first carried out on the gas–liquid column, the light gases being retained in the trap, and the carrier gas (He) passed to the atmosphere *via* a bubbler (*D*). When the recording of the CH_4 was complete, the tap *B* was turned so that the hydrocarbons from C_2 upwards were removed from the system after analysis. The trap was then heated and taps *A*, *B*, *C*, and *D* were turned so that the light gases passed for analysis in a stream of helium from the trap containing carbon to the detector (see Fig. 16).

Cold traps can be used to concentrate trace impurities for analysis[88,89], and also to retain the components after separation for study by the other methods described in the discussion of the problems of component identification.

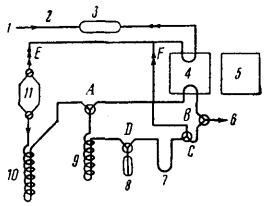


Fig.16. Diagram of a two-stage chromatograph using a cold trap:
1) helium supply; 2) pressure regulator; 3) buffer vessel; 4) thermal-conductivity gauge; 5) recorder; 6) to gas-meter; 7) trap with active carbon; 8) bubbler; 9) 25 foot column with active carbon; 10) 25 foot column with dimethylsulpholane; 11) tube for specimen. *A*–*F*) Taps.

Other useful schemes for the determination of the composition of complex mixtures by chromatographic analysis include: a circulation chromatograph[90-92], which makes it possible to imitate any length of column without significant pressure drop; a rotating column[93] in the form of two concentric cylinders, which makes it possible to separate components according to the lag angle; and the use of various types of chromathermography[94], in particular the method proposed by Nerheim[95], in which a heater producing a temperature gradient passes repeatedly along the column with increasing heater temperature, so that the components or fractions with corresponding characteristic temperatures are eluted in succession as narrow peaks.

3. A REVIEW OF WORK ON THE ANALYSIS OF HYDROCARBONS

In this review particular attention is paid to the problems of analysing hydrocarbons from C_5 upwards. The problems of analysing lighter components are considered only when these components are present in mixtures with C_4 and C_5 hydrocarbons. Moreover, we shall not deal with certain papers considered in the preceding sections.

The analysis of C_5 and lighter hydrocarbons. Systems containing hydrocarbons up to and including C_5 play an important part in various branches of the petrochemical industry, and the development of rapid and accurate methods of analysis is of considerable interest, since these make it possible to achieve control of such processes as cracking, pyrolysis, gas-fractionation, etc. A number of authors have used various polar and non-polar stationary phases to solve these problems. Thus Keulemans and Kwantes[96] used dimethylformamide on brick for the analysis of the butane fraction of cracking products. All the components were separated, except propene and isobutane, which gave a single chromatographic peak. Bradford *et al.*[61] analysed hydrocarbons up to and including C_4 on columns of triisobutene, acetonylacetone, and a saturated solution of silver nitrate in glycol. Buta-1,3-diene, but-1-ene, and 2-methylprop-1-ene gave a common peak on triisobutene, and the last two a common peak on acetonylacetone. When silver nitrate solution was used, the saturated hydrocarbons gave a common peak, and ethylene and propene were not separated.

Armitage[97] used columns of silver nitrate solution and dimethylsulpholane to analyse the products of isoprene production.

Brodskii *et al.*[98,99] put forward a method for determining the individual composition of C_3-C_5 hydrocarbons, involving two parallel analyses on columns of acetonylacetone and diisoamyl phthalate; however, each analysis may take several hours. A chromatogram for the separation of a mixture of C_5 hydrocarbons on a column of diisoamyl phthalate is given in Fig.17.

Taylor and Dunlop[100] have carried out parallel analyses on columns of dimethylformamide and dinonyl phthalate.

Turkel'taub *et al.*[69], selecting stationary phases for the analysis of C_2-C_5 hydrocarbons, found that complete separation of a mixture of C_2-C_4 and saturated C_5 hydrocarbons can be achieved with mixed solvents: 45% dimethylformamide + 1% liquid paraffin on brick or 45% dimethylformamide + 6.5% triisobutene on diatomite.

McKenna and Idleman[101] tested the efficiency of a number of liquids for the separation of C_4 hydrocarbons and found the best to be a 30:70 mixture of glutaronitrile and propylene carbonate. The chromatogram which they obtained showed complete separation of all components. For the same purpose Devyatykh *et al.*[102] used a composite 5 mm diameter column in which 1.5 m of carrier was impregnated with a solution of silver nitrate in glycol and 3 m with furfural.

McEwen[13] separated the C_2-C_7 hydrocarbons using the hexamethyltriamide of phosphoric acid as stationary phase. The 30 components of the mixture being analysed gave 22 chromatographic peaks. 2-Methylprop-1-ene and but-1-ene, n-pentane and buta-1,3-diene, *cis*-, and *trans*-pent-2-ene, and others were not separated.

Recently Dement'eva[67,103] proposed triethylene glycol n-butyrate as stationary phase for the analysis of C_3-C_5 hydrocarbons. This gives separation of almost all isomers (but-1-ene and 2-methylprop-1-ene give a common peak). Fig. 18 gives a chromatogram for the analysis of C_5 hydrocarbons and illustrates the high resolving power of this stationary phase.

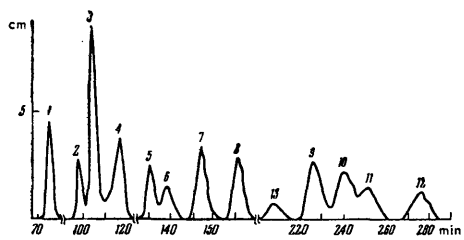


Fig.17. Chromatogram for the separation of a mixture of C_5 hydrocarbons on a column of diisoamyl phthalate on crushed brick:
1) isopentane + 3-methylbut-1-ene; 2) n-pentane; 3) pent-1-ene; 4) 2-methylbut-1-ene; 5) pent-*trans*-2-ene; 6) pent-*cis*-2-ene; 7) 2-methylbut-2-ene; 8) isoprene; 9) *trans*-piperylene + cyclopentane; 10) cyclopentene; 11) *cis*-piperylene; 12) cyclopentadiene.

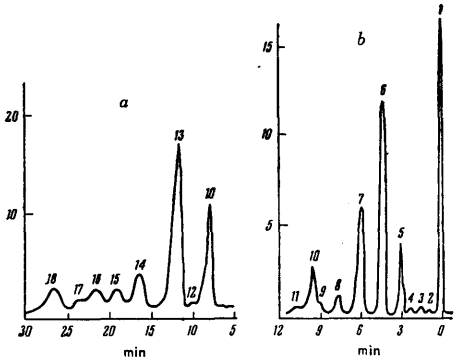


Fig. 18. Chromatograms for the separation of C_4 and C_5 hydrocarbons on a column of triethylene glycol n-butyrate: 1) air; 2) ethane; 3) propane; 4) propene; 5) isobutane; 6) n-butane; 7) isobutene + but-1-ene; 8) but-*trans*-2-ene; 9) but-*cis*-2-ene; 10) isopentane; 11) buta-1,3-diene; 12) 3-methylbut-1-ene; 13) n-pentane; 14) pent-1-ene; 15) 2-methylbut-1-ene; 16) pent-*trans*-2-ene; 17) pent-*cis*-2-ene; 18) 2-methylbut-2-ene.

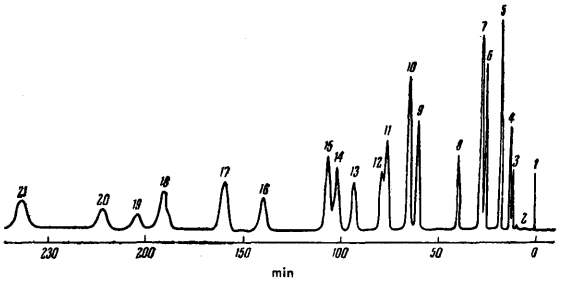


Fig. 19. Separation of a mixture of C_2-C_5 hydrocarbons on a column of dimethylsulpholane at 0°: 1) start of experiment; 2) air; 3) ethane; 4) ethylene; 5) propane; 6) propene; 7) isobutane; 8) n-butane; 9) but-1-ene; 10) 2-methylprop-1-ene; 11) isopentane; 12) but-*trans*-2-ene; 13) but-*cis*-2-ene; 14) n-pentane; 15) 3-methylbut-1-ene; 16) buta-1,3-diene; 17) pent-1-ene; 18) 2-methylbut-1-ene; 19) pent-*trans*-2-ene; 20) pent-*cis*-2-ene; 21) 2-methylbut-2-ene.

Complete separation of the C_2-C_5 hydrocarbons normally encountered has been achieved only by Fredericks and Brooks[66], who used a 15 m column of dimethylsulpholane at 0°. Analysis up to 2-methylbut-2-ene, however, required ~4.5 h. Isoprene comes out 390 min after insertion of the specimen. This is naturally a serious disadvantage of the method.

The C_3-C_5 hydrocarbons have also been separated by gas-adsorption chromatography on alumina. Scott's data[104] show that in this case 2-methylprop-1-ene comes off with but-*trans*-2-ene, and butadiene with isopentane. The last two hydrocarbons can be separated by treating the adsorbent with 2% silicone oil.

Greene *et al.*[105] have also obtained separate peaks for all unsaturated and monoolefinic C_1-C_4 hydrocarbons on alumina.

Zhukhovitskii *et al.*[68,106,107] analysed hydrocarbons up to and including C_5 by means of a universal chromathermographic apparatus including a column of alumina working on the chromatographic principle and a gas–liquid column of dibutyl phthalate on diatomite. The peaks for 3-methylbut-1-ene and isopentane coincide and to determine these compounds it is necessary to carry out a parallel analysis on a single column of alumina. *cis*- and *trans*-pent-2-ene are also obtained as a single peak.

In the VNIINP‡, a sorbent consisting of Zikeevskii tripoli treated with sodium carbonate and liquid paraffin has been proposed for the separation of C_3-C_5 hydrocarbons. This sorbent achieves separation of most components, but the peaks for butadiene and but-*cis*-2-ene, and for pent-*trans*-2-ene and 2-methylbut-1-ene coincide. A chromatogram obtained with this sorbent is shown in Fig. 20.

‡ Vsesoyuznyi Nauchno-Issledovatel'skii Institut po Pererabotke Nefti i Gazovi Polucheniyu Iskusstvennogo Zhidkogo Topliva (All-Union Scientific Research Institute for the Treatment of Petroleum and Gases and the Production of Synthetic Liquid Fuel) (Ed. of Translation).

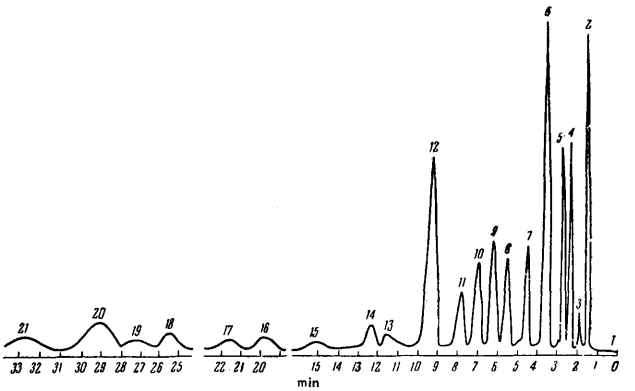


Fig. 20. Chromatogram for the separation of hydrocarbon gas on the VNIINP adsorbent: 1) specimen inserted; 2) methane; 3) ethane + ethylene; 4) propane; 5) propene; 6) 2-methylprop-1-ene; 7) n-butane; 8) but-1-ene; 9) 2-methylprop-1-ene; 10) but-*trans*-2-ene; 11) but-*cis*-2-ene; 12) isopentane; 13) 3-methylbut-1-ene; 14) n-pentane; 15) pent-1-ene; 16) pent-*trans*-2-ene + 2-methylbut-1-ene; 17) pent-*cis*-2-ene; 18) 2-methylbut-2-ene; 19) 2-methylpentane + + 2,2-dimethylbutane; 20) 3-methylpentane; 21) n-hexane.

Thus only one paper[66] reports the complete separation, in a single analysis, of the C_2-C_5 hydrocarbons normally encountered, up to 2-methylbut-2-ene, but in this case the time needed is a serious disadvantage. The method also requires that the column be cooled to 0°, and this is not always possible.

The analysis of saturated hydrocarbons. The development of methods for the analysis of saturated hydrocarbons is of considerable interest for the determination of the composition of light petroleum fractions, paraffins, and other products.

Although the choice of stationary phases for the analysis of normal paraffins is a fairly simple problem, considerable difficulty is introduced by marked difference in vapour pressures, since this makes analysis time-consuming under isothermal conditions. In this connection use is made of temperature programming [116,117] and chromathermography [95,110-113], which achieve separation fairly rapidly.

The analysis of mixtures containing both normal and isoparaffins as well as naphthenes is a more complex problem and cannot be achieved on a single column for hydrocarbons above C_6. Various natural mixtures of saturated hydrocarbons have been analysed by James and Martin [114], Lichtenfels *et al.* [76,120], and others, with substances such as phthalates, sebacates, high-boiling paraffinic hydrocarbons, polyethylene glycol, benzylbiphenyl, etc. as stationary phases. Table 3 gives some examples of the analysis of saturated hydrocarbons.

In the analysis of saturated and other hydrocarbons, use should be made of the extensive data given by Tenney [15], Bayer [16], Desty and Whyman [28], Desty and Harborn [32], and others, who have determined the elution characteristics of a large number of components on a wide variety of stationary phases.

TABLE 3. Analysis of saturated hydrocarbons.

Components being analysed	Stationary phase, temperature, °C	References
Normal paraffins C_3-C_7	diatomite, kaolin, natrolite* gradual heating to 100°–120° (chromathermography)	110–113
Normal paraffins C_2-C_7	sodium zeolite 20°–80°	12
Paraffins and naphthenes C_4-C_{10}	n-octadecane, 65°; solid paraffin, 78.6°; polyglycol, 78.6°; benzylbiphenyl, 78.6° (40% stationary phase on 100 g firebrick)	114
Paraffins and naphthenes C_5-C_7	1.5% squalane on "Pelletex", 40°, 75°; 3% squalane on firebrick, 25°; 40% β, β′-di-(2-propionitrile) ether on firebrick, 25°	70, 71
Paraffins and naphthenes C_5-C_7	13.4% isoquinoline on firebrick; 3.1% chloronaphthalene on firebrick	78
Paraffins and naphthenes C_5-C_6	40% heterocyclic amines on "Chromosorb"	115
Normal paraffins C_5-C_{36}	20–30% high-vacuum silicone grease on firebrick. Linear temperature programming up to 400°	116, 117
Normal paraffins $C_{20}-C_{27}$	asphaltenes on firebrick, 280°–320°	118
Normal paraffins C_5-C_6, isopentane	45% silicone oil on firebrick. Chromathermography with heater temperature rising to 217°	95
Hexane isomers	12% isoquinoline on firebrick	119
Paraffins and naphthenes C_5-C_8	dioctyl phthalate on "Celite", 65°; dioctyl sebacate on firebrick, 45°	76, 120
Paraffins and naphthenes C_5-C_9	paraffin, 78.5°	121

* The zeolite $Na_2O.Al_2O_3.3SiO_2.2H_2O$ (Ed. of Translation).

TABLE 4. Analysis of aromatic hydrocarbons.

Components being analysed	Stationary phase, temperature, °C	References
C_6-C_{11}	40% silicone 702 on firebrick, 132°	8, 61
Benzene, toluene, ethylbenzene, styrene	"Tide" detergent, 133°	64
Ethylbenzene, isopropylbenzene	liquid paraffin	122, 123
Xylenes	benzylbiphenyl, 78°, 100°; 7,8-benzoquinoline, 78.5°, 110.8°; phenanthrene, 110.8°; substituted montmorillonite, 80°; tetrahalogenophthalates; a mixture of ethylene carbonate and chloronaphthalene, 50°; dimethylsulpholane, 50°; chloronaphthalene, 40°, 50°	130, 131, 132, 133, 134, 135
Benzene, naphthalene, methylnaphthalene	silicone oil, dinonyl phthalate, 78.5°, 200°	136
Toluene, *p*- and *o*-*xylenes*, *mesitylene*, pseudocumene	silicone oil, 130°–220°	23
Benzene, ethylbenzene, xylenes, naphthalene, methylnaphthalene, biphenyl, dimethylnaphthalene	polyoxyalkylene adipate (Reoplex 400), 110°, 200°, etc.	125, 126, 137, 138
Cumene, n-propylbenzene, *p*-ethyltoluene, mesitylene, pseudocumene, etc.	dinonyl phthalate, tricresyl phosphate, 130°	18
High-boiling aromatic hydrocarbons	"Apiezon", high-vacuum silicone grease, polyethylene, asphaltenes, polyphenyl resins, 375°–445°	17, 124, 127
Impurities in commercial benzene, toluene, and xylene	*squalane, tetrapentylsilane, p-nitroaniline picrate,* fluorene picrate, picric acid with dibutyl phthalate, didecyl phthalate, β, β′-di-)2-propionitrile) ether, 2,4,7-trinitrofluoren-9-one	139, 140

The analysis of aromatic hydrocarbons. Aromatic hydrocarbons are of considerable importance as motor-fuel components and as raw material for various chemical processes. The aromatic hydrocarbons present in petrol can be analysed comparatively simply with various stationary phases [8,61]. The separation of *m*- and *p*-xylenes, whose boiling points are extremely close, is not always achieved, and a number of studies [124-129] have been devoted to the selection of conditions for their separation. This procedure is now relatively trivial.

A number of papers have been devoted to the determination of trace components in the commercial products: benzene, toluene, xylene, and cumene [122-125], which contain saturated hydrocarbons as well as aromatics.

As a result of the development of high-temperature chromatography, it has become possible to analyse the polynuclear aromatic hydrocarbons present in various natural products [17,126-129]. The temperature of the column may reach 475°.

Table 4 gives some typical examples of the analysis of aromatic hydrocarbons. These examples, with the work previously cited, give an idea of the possible uses of gas chromatography for determining the composition of hydrocarbons of this class, present in various products.

TABLE 5. Analysis of unsaturated hydrocarbons.

Components analysed	Stationary phase	References
C_5-C_6 olefines (mono-, di- and cyclo-)	1.5% squalane on "Pelletex"; 40% β,β'-di-(2-propionitrile) ether on firebrick, 10% diisodecyl phthalate on firebrick; 20% dimethylsulpholane on firebrick; 3% squalane on firebrick	74
Isomeric hexenes	phthalate esters	142
Cycloolefines	solution of $AgNO_3$ in glycol, on firebrick	143–145
Cyclopentadiene and methylcyclopentadiene	30% polyethylene glycol on firebrick	146
3- and 4-methylpent--1-ene	solution of $AgNO_3$ in glycol, on firebrick	141
Terpenes	tricresyl phosphate on crushed tile	150

The analysis of unsaturated hydrocarbons. Knight[74] has separated a mixture of C_5 and C_6 olefines of different structures. In particular, all 15 C_5 olefines and all 17 possible C_6 monoolefines except 3- and 4-methylpent-1-enes have been determined. Smith and Ohlson[141] studied the separation of this last pair of compounds, using a 17% solution of silver nitrate in glycol as stationary phase.

The analysis of the isomeric hexanes and hexenes has been studied by Sullivan *et al.*[142], who examined the possibility of using phthalate esters for this purpose.

Shabtai *et al.* have published a number of papers[143-145] on the problems of analysing alkylcyclopentanes, alkylcyclohexenes, and also cyclopentanes and cyclohexanes with unsaturated side chains. A solution of silver nitrate in glycol proved extremely effective for these and other purposes.

Since cyclopentadiene and its derivatives are present in a number of products, a method developed by Dahmen and van der Laarse[146] for the analysis of cyclopentadiene and methylcyclopentadiene is of considerable interest.

The analysis of the terpenes present in many natural products[147-149] is made difficult by the catalytic action of the solid carrier. To avoid this, Czechoslovak workers have used an unglazed brick ("porovin")[150] which is catalytically inert. This has made it possible to carry out the chromatographic process at high temperatures (136°); this is impossible when ordinary carriers are used[147].

Capillary chromatography. In the last few years, extensive development of capillary chromatography has taken place; this technique readily achieves certain separations which are extremely difficult when ordinary columns are used. Thus xylenes can be separated rapidly at various temperatures between room temperature and 80° on the weakly polar phases didecyl phthalate[151] and dinonyl phthalate[152].

Using a capillary column containing squalane, Zlatkis and Lovelock[153] separated a mixture of C_5-C_8 hydrocarbons containing 25 individual components, in 90 min.

Desty *et al.*[154] examined the problems of the theory and construction of apparatus for capillary chromatography and concluded that this method can be used for the analysis of petrols, lubricating oils, and other oil products.

Condon[155] used capillary columns 0.006–0.055 inch in diameter to separate a variety of hydrocarbon mixtures, including mixtures of C_6 isomers (40°, 150 ft column of diisodecyl phthalate), terpenes (125°, 175 ft column of polypropylene glycol), reforming products (115°, 150 ft column of diisodecyl phthalate), and a mixture of C_5-C_8 paraffins and naphthenes (33°, 175 ft column of polypropylene glycol).

A synthetic mixture of C_2-C_5 hydrocarbons has also been analysed at 33° on a composite column (200 ft of dimethylsulpholane and 100 ft of polypropylene glycol). In this case, however, but-1-ene and 2-methylprop-1-ene, and ethane and ethylene, gave common peaks.

Analytical distillation by gas chromatography. Eggertsen *et al.*[156] have achieved analytical distillation using a gas chromatograph instead of a fractionating column. The method makes it possible to separate petroleum products boiling in the range 40°–400°. A 6 inch long, $\frac{1}{4}$ inch internal diameter chromatographic column was filled with insulating brick impregnated with 20% silicone oil, and had an efficiency of 200 theoretical plates, which corresponds to 20 plates in a fractionating column. Programming of the column temperature from 2° to 280° makes it possible to distil a mixture boiling up to 400°, in 30 min. Fig. 21 gives graphs for the relationship between the temperature and times of leaving the column and the boiling points of paraffins, olefines, naphthenes, and aromatic hydrocarbons. These curves and the chromatograms obtained can be used to construct distillation curves.

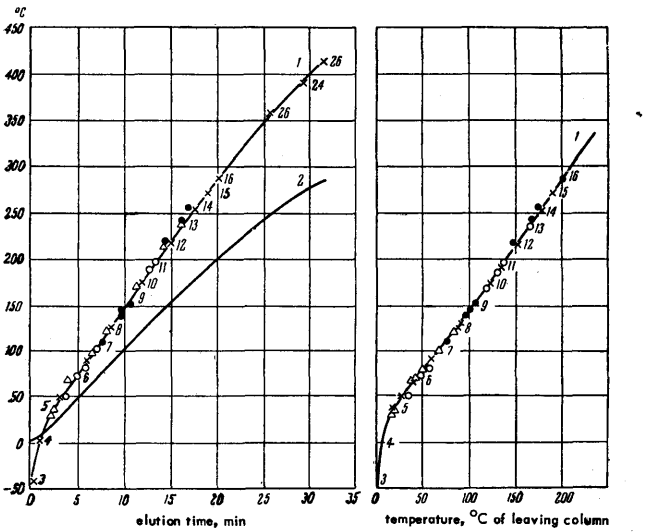


Fig. 21. Curves giving the relationship between the temperature and elution time and boiling point for hydrocarbons during analytical distillation by the gas-chromatography method:
1) boiling points of the substances; 2) column temperature.

Such curves have been obtained for the catalytic cracking products and have shown good agreement with distillation curves.

Analysis of mixtures of gaseous and liquid hydrocarbons. Some of the most complex hydrocarbon mixtures, containing a very large number of individual components, are the liquid raw material and products of pyrolysis. In a number of cases, in order to direct industrial plant conditions, it is necessary to know the individual components of the light fractions of the pyrolysis gas and the group composition of the heavier fractions. As shown above, these problems can be solved by means of an ordinary two-stage analytical scheme.

The method which we have developed for the analysis of the C_1-C_{10} hydrocarbons and hydrogen in pyrolysis gas makes it possible to determine the individual composition of the C_1-C_3 fraction, the concentration of C_4, C_5, and C_6 components, and the total concentration of heavier hydrocarbons[157]. The 3 m long, 4 mm internal diameter column of the first stage is filled with inzenskii brick impregnated with 20% liquid paraffin. This is placed in an air thermostat at 70°. The sorbent used makes it possible to separate the pyrolysis gas into a number of fractions, which are recorded by means of a thermal-conductivity detector and appropriate recording apparatus.

The first fraction containing hydrogen and the C_1-C_3 components is then directed to the column of the second stage for further separation. The fractions containing the C_4, C_5, and C_6 hydrocarbons are eluted directly to the atmosphere. After the components with six carbon atoms have been eluted, the carrier-gas (air) stream is blown back to elute the C_7 and heavier hydrocarbons. The consumption of carrier gas increases in this stage.

The 3 m long, 4 mm diameter column of the second stage is filled with KSK silica gel modified with 1–2% liquid paraffin and is placed in an air thermostat at 25°–40°. A detector responding to the heat of combustion is placed at the column outlet. This second column separates hydrogen, methane, ethane, ethylene, propane, acetylene, and propene with close degrees of separation between neighbouring peaks.

When necessary, the fractions eluted from the first column to the atmosphere can be analysed further in an additional section with suitably chosen sorbents, for example Zikeevskii tripoli or inzenskii brick impregnated with triethylene glycol n-butyrate. Pyrolysis tars have been analysed on columns of silicone elastomer and triethylene glycol, deposited on "Celite": The components were identified either by comparing the retention volumes of the components with those of standard substances or by using the "removal method" described above.

The petrols used as liquid raw material for pyrolysis are extremely complex mixtures and cannot be analysed on a single column due to superposition of the peaks. The petrols have therefore been separated by means of a chromatographic assembly including one column in the first stage, three columns in a second stage, and a system for redirecting the gas streams. After the first column, a small part of the stream is directed to a flame-ionisation detector. Flame-ionisation detectors and katharometers are also placed after the columns of the second stage. The device for redirecting the streams is constructed in such a way that if the eluate after the first stage is directed to one of the columns of the second stage, pure carrier gas passes to the other sections. By means of this system it is possible to carry out in the second stage a detailed separation of the narrow fractions produced in the first column.

The use of gas chromatography makes it possible to carry out a detailed analysis of complex mixtures, the study of whose composition previously seemed almost impossible.

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ISOTOPE EFFECT IN VAPOUR PRESSURE

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CONTENTS

A. Experimental data 52

1. Vapour pressure of monatomic isotopic substances 53

2. Vapour pressure of diatomic isotopic substances 54

(a) Isotopes of hydrogen 54
(b) Diatomic substances differing in isotopic composition with respect to carbon, nitrogen, oxygen, hydrogen, and chlorine 55

3. Polyatomic isotopic substances not associated by hydrogen bonds (compounds isotopic with respect to hydrogen, boron, carbon, nitrogen, silicon, chlorine, and germanium) 58

(a) Negative isotope effect 58
(b) Positive isotope effect and mixed cases 58

4. Polyatomic isotopic molecules associated by hydrogen bonds 62

(a) Compounds showing little or no association in the gas phase (alcohols, ammonia, amines, water, and hydrogen cyanide) 62
(b) Isotopic compounds which are strongly associated in both liquid and gaseous phases (hydrogen fluoride, carboxylic acids) 66