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Group Identification of Hydrocarbons by Reaction Gas-chromatography

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Methods for the group identification of hydrocarbons of the following classes have been examined: paraffins, olefins, conjugated dienes, acetylenes, naphthenes, and aromatic hydrocarbons. Methods of consecutive group analysis of complex industrial mixtures have been specially considered.
The bibliography includes 118 references.

CONTENTS

I. Classification of chemical-chromatographic methods of analysis 1048
II. "Elimination" or "subtraction" methods 1048
III. "Transformation" or "peak shift" methods 1052
IV. Schemes for the consecutive group analysis of hydrocarbon mixtures 1057

I. CLASSIFICATION OF CHEMICAL-CHROMATOGRAPHIC METHODS OF ANALYSIS

The use of chemical reactions specific to substances with a particular functional group greatly simplifies the identification of the components of mixtures analysed by gas-chromatography. Therefore, soon after the publication of substances, studies were made where chemical reactions were employed for identification in gas-chromatography. Up to 1960 there were only a few studies of this kind: bromination was employed to determine multiple bonds[2], alcohols were determined with the aid of 3,5-dinitrobenzoyl chloride or acetic anhydride, and carbonyl compounds were determined by treatment with semicarbazide or 2,4-dinitrophenylhydrazine[3]. The structures of involatile organic compounds were established by preliminary pyrolytic[4] or oxidative decomposition[5].

Since 1960 the combination of the two methods of analysis has greatly developed and more than a thousand original studies and a number of reviews and monographs[6-13] dealing with methods of identification based on the results of chemical and chromatographic analyses have now been published.

Drawert et al.[14] were the first to combine in a separate group the methods of chromatographic analysis in which a reactor is placed in the carrier gas system of the chromatograph and which they called "reaction gas-chromatography".

Despite the recognition of Drawert's term by other authors of original studies and reviews[7-10], there is no complete unanimity concerning terminology. Thus methods in which a transformation of the specimen is combined with chromatographic separation have been included in reaction gas-chromatography in some reviews[6,11,12] regardless of the analytical procedure.

"Elimination" or "subtraction" methods, "transformation" or "peak shift" methods, as well as analytical methods which do not give rise to changes in the chromatogram can be distinguished on the basis of the changes in the chromatogram after chemical or physical modification of the specimen.

"Subtraction" or "elimination" consist in the conversion of compounds of a particular chemical type into involatile or undetectable products. The peaks corresponding to these transformed substances disappear (are "subtracted") in the chromatogram beyond the reactor. This method of identification was employed for the first time by Martin[15], who absorbed olefins in a reactor with sulphuric acid.

"Transformation" or "peak shift" are distinguished by the fact that the disappearance of the peaks from the chromatogram after treatment with the reagent is accompanied by the appearance of new peaks due to volatile reaction products. The term "peak shift" was employed for the first time by Langer and Pantages[16], who described the conversion of alcohols into trimethylsilyl ethers in the presence of hydrocarbons.

When the reactions are carried out after chromatographic analysis, there are no changes in the initial chromatograms. An example of this kind is provided by the qualitative group tests carried out at the instant of isolation of the substance from the chromatograph[17,18].

This review deals with methods for the analysis of hydrocarbons combining chromatographic separation with chemical and physicochemical processes, which lead to a change in the composition of the sample. Special identification procedures, such as pyrolysis and elemental analysis, have been excluded from consideration. Regardless of the experimental technique employed (using a divided or continuous scheme), the analytical methods have been grouped on the basis of the changes induced in the chromatogram after the transformation of the specimen. "Elimination" or "subtraction" methods are considered first and then the "transformation" or "peak shift" methods. Apart from the analytical methods applicable exclusively to hydrocarbons, methods of identification developed for mixtures of different classes of compounds, including hydrocarbons, are also quoted. Consecutive group analysis is treated separately, since this has become particularly important recently in the petrochemical industry.

II. "SUBTRACTION" OR "ELIMINATION" METHODS

"Subtraction" methods are most suitable for the group identification of complex mixtures, since in the assessment of the changes in the chromatograms after the transformation of a specimen the interpretation of the results is not complicated by the appearance of new peaks due to reaction products. A general disadvantage of the "subtraction" methods consists in the low accuracy of the

analysis at low concentrations of the components constituting the unresolved peaks.

1. Overall Determination of Unsaturated Hydrocarbons

Martin[15] was the first to employ an absorber with sulphuric acid in a single system with chromatographic separation and tested the effect of the reagent on model C_3–C_6 hydrocarbon mixtures. Sulphuric acid (98%) was deposited on silica gel in proportions of 3 : 2 by weight. The height of the reagent layer (2 cm) was sufficient for the quantitative absorption of unsaturated hydrocarbons of all classes, except ethylene, acetylene, and benzene. In order to remove ethylene and acetylene, it was necessary to add silver sulphate to sulphuric acid. A mixture of hydrocarbons could be analysed in two ways: either by comparing the chromatograms recorded before and after the reactor or by single-stage chromatography on apparatus with two katharometers and a reactor with sulphuric acid placed between them. The first detector recorded all the components of the initial mixture and the second only paraffins and naphthenes. The error of the method in the group determination of olefins amounted to 2–9%.

The reagent (98% sulphuric acid) has been used most widely in the gas-chromatographic analysis of petroleum fractions and of pyrolytic petrol[19–22].

Hines and Smith[19] employed sulphonation and dehydrogenation in a divided system with chromatographic separation for the group analysis of a petroleum fraction containing aromatic hydrocarbons, naphthenes, and paraffins. After the first sulphonation in order to remove aromatic hydrocarbons, the residue was subjected to dehydrocyclisation and the dehydrogenated product was again sulphonated. At each stage of the treatment the reaction product was chromatographed on a capillary column with squalane and the changes which had occurred in the mixture composition were inferred from the chromatograms.

Sulphuric acid at different concentrations was employed for the successive removal of unsaturated hydrocarbons of different classes[22]. Initially olefins were adsorbed with 80% sulphuric acid and then aromatic hydrocarbons with 98% sulphuric acid. The fraction of unsaturated hydrocarbons of each class was determined by comparing chromatograms obtained on a column with Apiezon L without complete separation of the components.

In the group analysis of petrols described below, Rowan[23] employed a reactor with sulphuric acid deposited on glass fibres. He noted that the absorption of olefins is accompanied by the evolution from the acid of hydrocarbons, which he did not identify.

Similar observations were made in another study[24]. In the absorption of olefinic admixtures in ethylene , an increase of the height of the isobutane peaks was observed together with the appearance of peaks due to new substances, which had been absent from the initial mixtures. The above investigators[23,24] did not consider the mechanism of the formation of new substances as a result of reaction.

Ipat'ev[25], who carried out a special investigation of the action of sulphuric acid on olefins, made the following important remark: "The determination of olefins with the aid of sulphuric acid in the presence of paraffins and naphthenes must be performed with caution using an excess of the acid and over a short period, since, on standing, olefin polymers which are sparingly soluble in sulphuric acid with the $d = 1.86$ are separated from it".

It is noteworthy that, in contact with sulphuric acid under optimal conditions (10–50°C), paraffins containing a tertiary carbon atom can also isomerise[26].

A novel location for the reactor with sulphuric acid in the chromatograph detector was proposed by Berezkin et al.[27] They placed the absorber between two katharometer chambers. A mixture of hydrogen and paraffins was not recorded by the detector, since the signals of the sensor elements cancelled out and the overall signal was proportional to the concentration of the olefin. Thus the concentration of olefins in a mixture with paraffins was established from a single chromatogram and not by comparing two chromatograms.

In the identification of atmospheric impurities, Williams[28] employed an absorber with sulphuric acid, deposited on Chromosorb in proportions of 1 : 4, designed for the absorption of unsaturated hydrocarbons. The impurities concentrated from air were either passed directly through the analytical column or through the absorber.

A separate investigation of the absorption properties of sulphuric acid at different concentrations was undertaken by Innes et al.[29], who found that, when the acid is diluted to 80%, the absorption of olefins became incomplete and at a concentration of 60% ceased completely.

Table 1. Absorption of hydrocarbons by chemical absorbents[29].

Hydrocarbon	Degree of absorption, %					
	20% $HgSO_4$ in 20% H_2SO_4	$Hg(CH_3COO)_2$	4% Ag_2SO_4 in 95% H_2SO_4	H_2SO_4		
				95%	80%	60%
Methane	0	0	0	0	0	0
Ethane	0	0	0	0	0	0
Propane	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0
n-Hexane	0	0	0	0	0	0
n-Octane	0	0	0	0	0	0
Cyclohexane	0	0	0	0	0	0
Ethylene	100	94	100	11	6	0
Propene	100	100	100	100	67	0
Isobutene	100	100	100	100	100	100
Pent-2-ene	100	67	100	100	88	0
Hex-3-ene	100	60	100	100	85	0
4-Methylcyclohexene	100	70	100	100	70	0
Benzene	5	46	100	94	32	13
Toluene	0	22	100	100	33	0
p-Xylene	0	0	100	100	0	0
Acetylene	100	100	100	16	11	0

Apart from sulphuric acid, Innes et al.[29] investigated the absorption properties of a number of other reagents. They noted that liquid absorbers are less active than those deposited on a solid carrier. They prepared absorbers 10 cm long containing diatomaceous earth impregnated with liquid reagents and compared the degrees of absorption of hydrocarbons of different classes present in air at a concentration of 0.5% and contained in a sample having a volume of 5 ml (Table 1). Table 1 shows that mercury sulphate removed olefins quantitatively, while sulphuric acid with added silver sulphate eliminated in addition aromatic hydrocarbons. However, the latter reagent suffered from the disadvantage that ethylene was evolved for a long time after its absorption. The authors also established that nitric and hydrochloric acids and bromine water are ineffective. On the basis of their

investigation, they recommended that mercury sulphate be employed for the removal of olefins in gas-chromatographic analysis[30,31]. They developed a model of an industrial exhaust gas analyser[30], which consists of a chromatograph with two parallel columns and two flame-ionisation detectors with a reactor containing mercury sulphate placed in front of one of the columns.

It has been found[24] that the rate of reaction of olefins with mercury sulphate depends on the steric configuration of the olefins. The reaction is greatly retarded for the *trans*-isomers of β-olefins and fails to reach completion under the conditions of the stream of carrier gas.

In the chromatographic analysis of petrols[23,32,33] and exhaust gases[34], mercury perchlorate deposited on a solid carrier was also employed. This reagent absorbed olefins and partly aromatic hydrocarbons. For a quantitative elimination of aromatic hydrocarbons, it was necessary to add perchloric acid to mercury perchlorate. However, this led to the retention of branched paraffins in the absorber. The use of this reagent required special precautions. At room temperature high-boiling components were strongly absorbed, while on heating above 65°C the olefins were incompletely absorbed and side reactions with unsaturated hydrocarbons took place to a greater extent.

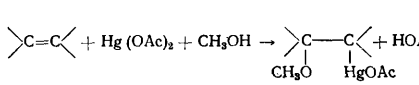
Albert[33] placed the absorber in the thermostat of the chromatogram in front of the analytical column and recommended that the absorber be back-flushed after each analysis in order to avoid the access of side products into the column in subsequent analyses.

Soulages and Briewa[35] investigated the interaction of olefins and aromatic hydrocarbons with mercury perchlorate. They found that the degree of reaction in the absence of side processes depends on the extent to which the optimal conditions are maintained: the amount of absorbent, the contact time, temperature, and the moisture content of the carrier gas. The last factor is particularly important. The moisture content in the gas must be equivalent to the vapour pressure of the absorbent; only then does the concentration of perchloric acid remain constant. Since in previous investigations the moisture content of the gas was not taken into account, dilution or increase of the acid concentration might have been a likely source of secondary phenomena.

It has been suggested that an absorber with mercury perchlorate be employed for the type analysis of liquid industrial mixtures. Analytical schemes[35-37] are discussed below.

Kerr and Trotman-Dickenson[38] suggested that a paste of mercury acetate and nitrate in ethylene glycol deposited on a refractory brick be used to absorb olefins under flow conditions.

Doring and Hauthal[39] investigated the kinetics of the competing reaction of olefins with mercury acetate in methanol:



They established that the rate of esterification with mercury acetate decreases in a series of olefins with different structures in the following proportions: α-olefins: β-olefins: γ-olefins = 100 : 10 : 1, *cis*-isomers reacting faster than their *trans*-analogues. In order to identify C_6–C_8 olefins, the authors removed samples from the reaction mixture at different times after the start of the reaction and subjected them to chromatographic analysis. The degree of conversion of the unknown component was calculated from the decrease of its peak height and its structure was established.

As already noted earlier, Innes et al.[29] found that bromine water is ineffective for the absorption of olefins under flow conditions. However, bromination in a stream has been carried out with bromine deposited on activated charcoal, which was capable of the stable retention of up to 40 wt.% of bromine. Wirth[40] achieved a quantitative separation of a mixture of ethylene, acetylene, and ethane. At −78°C only ethylene reacted with the bromine and at 0°C acetylene reacted as well. The gases which failed to react were desorbed with evacuation, and were collected in a measuring burette. Ray[41] used this method to establish the content of light impurities in ethylene. Ethylene was brominated at room temperature. Non-olefinic impurities were removed from the charcoal column in a stream of carbon dioxide and were collected in a nitrometer over aqueous alkali.

Bromination under flow conditions was carried out separately from the subsequent chromatographic analysis in some investigations[24,42]. In order to reduce the volatility of bromine, its solution in aqueous sodium bromide was employed. The reagent, deposited on Chromosorb in proportions of 1 : 1 by weight, eliminated quantitatively olefins and C_2–C_8 dienes from vapour–gas mixtures.

Hoff and Feit[43] used a saturated solution of bromine water under static conditions to absorb the vapours of olefins and certain oxygen-containing compounds.

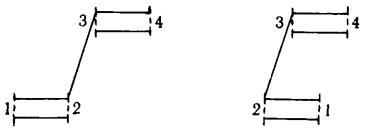
In this section of the review, it is useful to consider the analytical method described by James and Martin[2] and Hoff and Feit[43]. Although aliphatic acids and not hydrocarbons were the object of investigation, this procedure may be of wider applicability. The authors brominated the methyl esters of saturated and unsaturated aliphatic acids in the liquid phase and compared the chromatograms of the initial mixture and the reaction products. James and Martin[2] carried out the chromatographic separation of such products on Apiezon L as the stationary phase. By subtracting the peaks of the bromides of the unsaturated components, they were able to distinguish the esters of acids of two types—saturated and unsaturated. Landown and Lipski[44] improved this method by using for the separation a more polar phase—diethylene glycol glutarate. After bromination, the peaks due to the dibromides (which the authors identified component by component) were seen on the chromatograms obtained with the aid of this phase, in addition to the peaks due to the saturated acid esters. Thus they established that the esters belonged to three groups of compounds: (1) saturated compounds whose peaks remained unchanged under bromination; (2) mono-olefins the disappearance of whose peaks was accompanied by the appearance of those of the dibromides; (3) polyolefins the removal of which after bromination did not entail the appearance of the peaks of the corresponding tetra- and hexa-bromides owing to the low vapour pressures of the latter.

2. Identification of Conjugated Dienes and Acetylenes

Janak and Novak[45,46] used maleic anhydride to retain the main mixture component (butadiene) and to determine in the latter the admixtures of light hydrocarbons. Maleic anhydride deposited on Kieselguhr was placed in the reactor in front of the analytical column. The authors noted the following disadvantages of the method: solubility

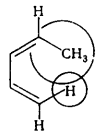
of light hydrocarbons in maleic anhydride and the catalytic effect of traces of maleic acid on the polymerisation of isobutene. The degree of absorption of butadiene increased with catalyst temperature and it was difficult to maintain the optimal temperature because the anhydride sublimed readily and blocked the gas channels in the apparatus.

The reactivity of dienes in Diels–Alder reactions depends on the structure, configuration, and the nature of substituents in the conjugation chain [47]. In the two possible coplanar systems [(I) and (II)], the reacting 1,4-carbon atoms approach one another sufficiently closely for diene condensation only in dienes with a cisoid disposition of the carbon bonds [system (II)]:



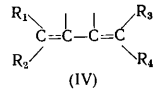
(I) (II)

The transoid conformation (I) is characteristic of the *cis*-piperylene molecule. In the cisoid form (III) the distance between CH_3 and H would be less than the sum of the van der Waals radii of these groups. This would lead to a considerable internal strain, as a result of which the cisoid conformation is hindered.



(III)

Dienes with fully substituted terminal C atoms of the conjugated system (IV) are likewise incapable of undergoing the Diels–Alder reaction.



(IV)

Gil-Av and Herzberg-Minzly [48,49] investigated by gas chromatography the kinetics of the reaction of dienes with chloromaleic anhydride. They employed chloromaleic anhydride as the stationary phase and chromatographed the mixture of dienes at different flow rates of the carrier gas. Since in the presence of an excess of anhydride the reaction became pseudomonomolecular, its rate was directly proportional to the contact time. Therefore the decrease of the peak areas for dienes with the cisoid conformation, reacting with the anhydride [47], depended on the flow rate of the carrier gas, while for other dienes the peak areas remained constant. The authors employed these findings for the identification of dienes [48]. *cis*- and *trans*-Piperylenes and 2,4-hexadienes were identified in this way.

Berezkin and coworkers [50–52] also made a chromatographic study of the kinetics of the reactions of dienes with maleic anhydride. In order to increase the temperature and the contact time, the reagent (maleic anhydride) was introduced in solution in tricresyl phosphate. The reactor with the anhydride was placed between two detectors. In each analysis the concentrations of the diene before and after absorption were obtained. The authors suggested that this method be used to calculate the rate constants for bimolecular reactions at variable concentrations of the anhydride. In addition, the method may be useful in the determination of the initial concentrations of unstable compounds [52]. It has been shown for butadiene that the error of the method is 3–4 rel.%.

Kugucheva and Alekseeva [24,53] used the reaction with maleic anhydride to identify the dienes present in vapour–gas mixtures in microconcentrations. The analytical scheme with separate steps made it possible to raise the reactor temperature to 135°C and to increase sharply the absorption of dienes (Table 2).

Table 2. Absorption of hydrocarbons by maleic anhydride [53].

Hydrocarbon	Degree of absorption, mole %	Hydrocarbon	Degree of absorption, mole %
Butadiene	73	*cis*-Penta-1,3-diene	26
Isoprene	100	Cyclopentadiene	100
trans-Penta-1,3-diene	90	2,3-Dimethylbuta-1,3-diene	100

Together with a high degree of absorption of dienes, an enhanced solubility of compounds, non-specific in relation to the reagents, was noted [24].

An aqueous solution of silver nitrate deposited on Chromosorb has been used [53] to absorb monosubstituted acetylenes. The reaction was quantitative and was not complicated by secondary phenomena.

3. Adsorption of n-Alkanes on a 5 Å Molecular Sieve

Molecular-sieve analysis in gas chromatography was achieved for the first time by Brenner and Coates [55]. They placed the reactor with the 5 Å molecular sieve in front of the analytical column and showed that n-alkanes in a mixture of C_3–C_{11} straight-chains and branched-chain alkanes, cycloalkanes, and aromatic hydrocarbons were retained in the reactor at 60–180°C.

Adlard and Whitham [56] compared the results of liquid-phase and vapour-phase adsorption of n-alkanes on a 5 Å molecular sieve and the results of extraction by urea and obtained similar results. They extended the molecular sieve analysis in chromatography to hydrocarbons with up to 44 carbon atoms [56–58]. In order to prevent the spreading of the chromatographic peaks when the specimen passes through the reactor, the zeolite was impregnated with a small amount of the stationary phase.

Barrall and Baumann [59] investigated the effect of water remaining in the zeolite pores on the accuracy of the molecular-sieve analysis in chromatography. They found that traces of water cause degradation of the zeolite pores, which leads to the breakthrough of the straight-chain hydrocarbons during analysis and a rapid decrease of the adsorption capacity of the sorbent. High-temperature dehydration procedures under various conditions have been proposed for the activation of zeolites: by evacuation [60], in a stream of nitrogen or helium [61], and in an open system [62]. Dehydration by heating to 350–400°C in a stream of dry nitrogen is most frequently employed.

Molecular-sieve analysis in gas chromatography is widely employed in group determination of n-alkanes in petrols, kerosenes, and waxes [23,33,63].

In the determination of small amounts of n-alkanes in a mixture with branched-chain alkanes, Eggertsen and Groennings [63] placed two reactors in the anlytical circuit.

The first analytical cycle included separation on the chromatographic column, absorption of n-alkanes in the reactor with the zeolite placed beyond the analytical column, and the recording of the residual branched-chain alkanes by the katharometer. In the second cycle the n-alkanes retained in the reactor were desorbed and were redirected with the aid of the back-flushing apparatus to the analytical column. In the course of their elution from the column, the n-alkanes entered the second reactor where they were combusted to carbon dioxide and were recorded by the katharometer with a higher sensitivity than the initial alkanes. The method permitted the determination of n-alkanes at concentrations down to 0.01% and branched-chain alkanes present in large amounts did not interfere.

In the first study involving the application of a 5 Å molecular sieve in gas-chromatographic analysis, Brenner and Coates [55] already mentioned the possibility of extending their analytical procedure to compounds of other homologous series. Subsequently they demonstrated for artificial mixtures of hydrocarbons and oxygen- and halogen-containing compounds that straight-chain olefins, alcohols, acids, and aldehydes are also retained in the zeolite pores [69].

However, molecular sieve analysis has not been widely used in the study of compounds belonging to classes other than the paraffins owing to the aluminosilicate catalytic activity of the zeolite [54,70].

Table 3. Isomerisation of olefins on contact with a Linde molecular sieve at 200°C. [75]

Initial substance	Reaction products		Degree of reduction*
	hydrocarbons	content, %	
2-Methylbut-1-ene	2-Methylbut-1-ene	29	71
	2-Methylbut-2-ene	71	
2-Methylpent-1-ene	2-Methylpent-1-ene	24	76
	2-Methylpent-2-ene	76	
2,3-Dimethylbut-1-ene	2,3-Dimethylbut-1-ene	25	75
	2,3-Dimethylbut-2-ene	75	
2,3-Dimethylbut-2-ene	2,3-Dimethylbut-1-ene	25	75
	2,3-Dimethylbut-2-ene	75	
trans-3-Methylpent-2-ene	*trans*-3-Methylpent-2-ene	60	40
	cis-3-Methylpent-2-ene	34	
	2-Ethylbut-1-ene	6	
cis-3-Methylpent-2-ene	*trans*-3-Methylpent-2-ene	60	
	cis-3-Methylpent-2-ene	34	66
	2-Ethylbut-1-ene	6	
2,3,3-Trimethylbut-1-ene	2,3,3,-Trimethylbut-1-ene	100	0

*Calculated relative to the isomerisation products.

There are only isolated reports on the molecular sieve analysis of olefins in gas chromatography [59,67,69]. This is due to the isomerisation of straight-chain olefins during their desorption [56,71,72]. There are also data indicating the isomerisation of iso-olefins on contact with the zeolite [73].

However, there exist contradictory views concerning the nature of the isomerisation of olefins. Norton [74], who characterised the isomerising properties of zeolites of various types, concluded that a 5 Å molecular sieve is inactive in relation to olefins. On the other hand, Baas and Vlugter [73] not only observed the migration of the double bond in the molecular under these conditions but also skeletal isomerisation.

Kugucheva and Aleksseva [75] investigated the behaviour of individual isomeric olefins on contact with a zeolite under flow conditions. Branched-chain olefins did indeed change: instead of a single peak on the initial chromatogram, two or three peaks appeared beyond the reactor. For the olefins listed in Table 3, the transformations consisted in the migration of the double bond and in a change of the steric configuration. There was no skeletal isomerisation, which was specially confirmed in relation to 2,3,3-trimethylbut-1-ene. The migration of the double bond in the molecule of this isomer is impossible due to the presence of the quaternary carbon atom. The results of chromatographic analysis beyond the catalyst with the zeolite confirmed the absence of isomerisation.

Investigators [64,66,75] who used low concentrations of various substances noted that a certain amount of compounds having a critical molecular diameter greater than the pore size of the molecular sieve (5 Å) undergoes irreversible absorption on contact with the zeolite, namely cycloalkanes, branched-chain alkanes or aromatic hydrocarbons. This adsorption is not eliminated when the zeolite is impregnated with a small amount of the stationary phase [66]. The reason for the absorption may be adsorption on the outer surface of the zeolite crystals and, in the case of zeolite granulated with a binder, on the surface of the secondary pores formed by the gaps between the zeolite crystals and the coarse-grained binder [76,77]. The possibility of methyl-substituted alkanes being able to pass into the molecular sieve pores as a result of a change in the pore size and in the critical diameter of the hydrocarbon molecules at a high temperature has been examined [78].

III. "TRANSFORMATION" OR "PEAK SHIFT" METHODS

1. Exhaustive Hydrogenation of Unsaturated Hydrocarbons

The elimination method, a great advantage of which is simplicity of the interpretation of the chromatograms, are of limited applicability because it is possible to make only a group identification of the components of the mixture analysed, involving their assignment to groups of substances which react in the same way with the reagent employed. In the case of hydrogenation, on the other hand, which is one of the transformation methods where the chromatogram shows, instead of the peaks of the initial unsaturated hydrocarbons, those of the saturated analogues, there is a possibility of "skeletal" identification, i.e. one can determine the hydrocarbon skeleton of the initial molecule. However, the positions of the multiple bonds and the *cis–trans* configuration of the olefins remain unknown.

Moreover, in contrast to the elimination method, the reduction method can yield information about the composition of the unresolved peaks corresponding to several unsaturated hydrocarbons. In this case "elimination" makes it possible to infer the presence of multiple bonds in the molecules and hydrogenation can achieve the separate identification of the components in terms of their saturated analogues.

Reduction usually leads to a simplification of the composition of mixtures and to a more complete chromatographic separation. The method has been widely used in the gas-chromatographic analysis of petroleum fractions.

In one of the first studies on the chemical-chromatographic analysis of petroleum, Nelson et al. [79] used a

multistep analytical scheme in which each step was carried out separately. In the first step saturated hydrocarbons were separated by liquid-phase chromatography on silica gel. Paraffins and naphthenes in the isolated fraction were identified component by component. The identification was carried out with the mixture separated on columns with two stationary phases of different polarity—squalane and silicone oil, using a standard mixture of isomers. The corresponding paraffin and naphthene peaks were found on the chromatogram of the initial mixture before the separation on silica gel. After the liquid-phase reduction of the initial mixture in the presence of palladium on charcoal (10% Pd) at 100°C, the content of olefins and their hydrocarbon skeletons were determined from the increments in the peak areas of the known paraffins and naphthenes. The authors estimate the error of the method as ±6%.

Hydrogenation in a microreactor in a stream of hydrogen, which serves at the same time as the carrier gas in the apparatus, has been widely used. The reactor is placed in front of the sample inlet or in front of the analytical column. The advantage of the process carried out in this way consists in a very rapid reaction and a very low consumption of the catalyst, the activity of which hardly changes owing to the small sample volume. Group VIII metals on various carriers have been used as catalysts.

Klesment et al.[80] investigated the properties of catalyst carriers employed for reduction in chromatographic analysis. They found that alumina gives rise to side reactions involving cracking, isomerisation, and cyclisation and activated charcoal and silica gel adsorb organic compounds too strongly. The authors employed platinised diatomaceous earth (2–10% Pt) saturated with hydrogen as the catalyst. The petrol specimens from shale oil which they employed were reduced in a microreactor at 200°C in a stream of hydrogen or helium and were then transferred to the analytical column.

Rowan[23] suggested that olefinic and aromatic hydrocarbons be hydrogenated on a platinum catalyst (Pt/Al_2O_3) at 299°C and that the selective reduction of olefins alone be performed on a palladium catalyst (5% Pd on asbestos) at room temperature.

Nickel, platinum, and palladium catalysts have been used for the vapour-phase hydrogenation and investigation of the composition of shale petrols[81–83] and other petroleum products[21,84,85], including procedures where hydrogenation was combined with pyrolysis[86,87].

An interesting combination of reduction reactions with separation of the products on a capillary column was proposed by Struppe[88]. An aluminium capillary 6 m long with an internal diameter of 0.3 mm was filled with chloroplatinic acid, which was reduced in a stream of hydrogen at 150°C. Platinum black was then deposited on the inner walls of the capillary. The capillary reactor thus obtained was placed between the sample inlet and the separating column. Mono-olefins, dienes, and cyclo-olefins were reduced in the reactor at 125°C. Aromatic hydrocarbons and naphthenes did not react. Individual identification could be achieved by combining the reactor with capillary columns filled with different stationary phases. The author determined the time required by the sample to pass through the capillary reactor and took it into account in the calculation of the retention volumes.

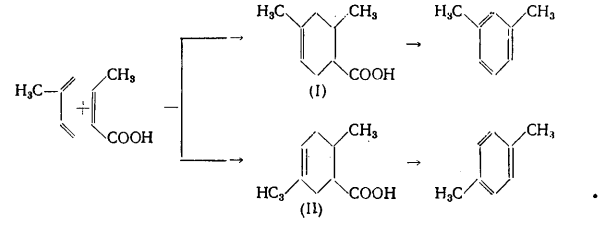
The method involving the reduction of individual compounds of different classes, including unsaturated hydrocarbons, has been investigated systematically by Beroza and coworkers[10,89,90]. The authors developed a model of a standard apparatus for hydrogenation[90], which can be connected to any chromatograph with a katharometer or a flame-ionisation detector. The gas channel scheme was such that the reaction products were transferred by the carrier gas directly to the analytical column. The reduction was carried out on a palladium catalyst (1% Pd on Gas Chrom P) at different temperatures and hydrogen flow rates. Table 4 summarises the results of hydrogenation under conditions leading to the formation of the hydrocarbon with the same number of carbon atoms as in the initial compounds or to a lower homologue.

Table 4. Determination of the carbon skeleton by hydrogenation using Beroza's method[10] (catalyst—1% Pd on Gas Chrom P, temperature 300°C, hydrogen flow rate 20 ml min^{-1}).

Classes of substances yielding a hydrocarbon analogue	Reaction
Paraffins	None
Unsaturated hydrocarbons	Hydrogenation of double bond
Halogeno-derivatives	Dissociation of C-X bond
Secondary and tertiary alcohols	Dissociation of C-O bond
Secondary and tertiary ethers	Dissociation of C-O bond
Ketones	Dissociation of C=O bond
Secondary and tertiary amines	Dissociation of C-N bond
Amides (amine component with a secondary or tertiary carbon atom)	Dissociation of C-N bond
Classes of substances yielding a hydrocarbon analogue and (or) the next lower hydrocarbon homologue	**Reaction**
Aldehydes	$RCHO \rightarrow RH,\ RCH_3^{\alpha}$
Acids	$RCOOH \rightarrow RH,\ RCH_3^{\alpha}$
Anhydrides	$(RCO)_2O \rightarrow RH,\ RCH_3^{\alpha}$
Primary alcohols	$RCH_2OH \rightarrow RH,\ RCH_3^{\alpha}$
Esters, alcoholic component with a primary carbon atom (OCH_2R) and R'CO acid component	$R'COOCH_2R \rightarrow RH,\ RCH_3$; $R'H,\ RCH_3^{\alpha}$
Primary ethers	$RCH_2OCH_2R \rightarrow RH, RCH_3$
Amides, amine component ($NHCH_2R$) at a primary carbon atom, R'CO acid component	$R'CONHCH_2R \rightarrow RH,\ RCH_3$; $R'H,\ R'CH_3^{\alpha}$

*α—slight or none.

The practical application of the method can be clearly demonstrated using as an example the reaction of isoprene with crotonic acid[10]:



In order to identify the product formed in the reaction [(I) or (II)], it was reduced at 330°C. Apart from decarboxylation, the aromatic ring underwent aromatisation at this temperature. *m*-Xylene, corresponding to reaction product (I), was identified on the basis of the retention time. The identification was confirmed by the ultraviolet spectrum. The usual methods for the determination of structure by an oxidation procedure would have been more laborious.

In reduction by Beroza's method, it is necessary to maintain the hydrogenation conditions exactly, since at temperatures intermediate between the optimal values (200°C for hydrogenation and 300°C for dehydrogenation), alicyclic and aromatic derivatives are formed in different proportions.

The reduction is usually accompanied by the formation of intermediates or side products. Beroza [91] suggested, for example, that ketones be identified not only on the basis of the main product of the hydrogenation reaction (the hydrocarbon analogue) but also on the basis of the small amounts of compounds appearing as a result of the dissociation of the bond between the carbon atom and the adjacent carbonyl group. Thus ethane and butane were detected in the reduction of 3-heptanone in addition to n-heptane.

It is difficult to carry out the hydrogenation reaction in a single cycle with chromatographic separation because of the spreading of the chromatographic peaks and the change in the retention times of the components on passing through the reactor. This is caused by adsorption on the catalyst layer and occurs to a particularly marked extent in the analysis of polar or high-boiling substances.

Beroza [10] suggested that, in order to establish the structure of the hydrocarbon skeleton of strongly adsorbed compounds, one should collect initially the reduction products in a cooled trap and then introduce them into the chromatograph.

Langner [92] investigated the influence of various methods of packing of the catalyst in the reactor on the retention times of substances reduced by Beroza's method. He found that the retention times change after filling the reactor with a fresh portion of the catalyst. In order to obtain reproducible relative retention times, it is necessary to carry out a calibration with standard substances directly before or after the analysis.

Even in the reduction of pure substances, the nature of the test substance must be known for a correct interpretation of the results. For example, different chemical compounds such as toluene, benzyl alcohol, benzaldehyde, and benzonitrile give rise to the same product on reduction–methylcyclohexane.

An interesting method for determining the chemical nature of the test substance in the reduction process was proposed by Franc and Kolouskova [93], who investigated the relation between the number of reduced double bonds or the functional group and the ratio of the retention times of the initial and reduced compounds. They found that the logarithm of the ratio of the retention volumes of the corresponding analogues is determined solely by the type of functional group. On the basis of their relation, they identified hydrocarbons and other compounds. They designed a special device for analysis whereby it is possible to record in a single chromatographic cycle both the initial and the reduced compounds. An empty glass capillary was inserted through the reactor containing a platinum catalyst (10% Pt on pumice). The sample introduced was divided in the reactor into two parts. One part passed through the capillary to the analytical column in an unchanged form and the other was reduced on contact with the catalyst.

2. Selective Hydrogenation of Conjugated Dienes and Acetylenes

Beroza and Sarmiento [90], who investigated the reduction of unsaturated acids esters with different numbers of double bonds in different positions, attempted to relate the change in the retention time of the reduced compound to the position of the double bond. By reducing the contact time with the catalyst, they identified the incomplete reduction products on the chromatogram. However, according to their data, the interpretation of the chromatograms did not always lead to unambiguous results and was not developed further in subsequent investigations.

A more successful attempt to employ partial reduction for identification was made by Smith and Ohlson [94]. The pure substances or narrow fractions were isolated on a preparative scale, collected in a U-shaped reactor, and hydrogenated on the Adams catalyst (PtO_2 with added iron) or sodamide. After raising the temperature, hydrogen was passed into the reactor at a pressure of 3 atm and the system was maintained at 80–90°C for 1 min in order to complete the reduction process. After connecting the chromatograph to the device for the introduction of the sample, the volatile reaction product entered the analytical column.

Table 5. Hydrogenation of dienes on the Adams catalyst [94].

Initial hydrocarbon	Unchanged fraction	Composition of catalytic reaction mixture			
		partly reduced products	wt.%	fully reduced products	wt.%
Buta-1,3-diene	82	But-1-ene *cis*-But-2-ene *trans*-But-2-ene	6 1 2	n-Butane	9
Penta-1,4-diene	75	Pent-1-ene	9	n-Pentane	16
cis-Penta-1,3-diene	21	Pent-1-ene *cis*-Pent-2-ene *trans*-Pent-2-ene	4 10 7	n-Pentane	58
trans-Penta-1,3-diene	9	Pent-1-ene *cis*-Pent-2-ene *trans*-Pent-2-ene	4 3 6	n-Pentane	78
Penta-1,2-diene	98	Pent-1-ene *cis*-Pent-2-ene *trans*-Pent-2-ene	0.3 0.6 0.7	n-Pentane	1
Hexa-1,5-diene	68	Hex-1-ene	11	n-Hexane	21
cis, trans-Hexa-2,4-diene	22	*cis*-Hex-2-ene *trans*-Hex-2-ene *cis*-Hex-3-ene *trans*-Hex-3-ene	8 14 3 6	n-Hexane	47
trans, trans-Hexa-2,4-diene	15	*cis*-Hex-2-ene *trans*-Hex-2-ene *cis*-Hex-3-ene *trans*-Hex-3-ene	2 14 3 6	n-Hexane	60
trans-Hexa-1,3-diene	60	*cis*-Hex-2-ene *trans*-Hex-2-ene *trnas*-Hex-3-ene	2 15 3	n-Hexane	20
Cyclopenta-1,3-diene	79	Cyclopentene	8	Cyclopentane	13

On shortening the reaction time, the dienes and acetylenes were not reduced completely. The authors investigated the partial reduction products of certain dienes (Table 5) and acetylenes (Table 6) and suggested that the method be employed for their identification. Tables 5 and 6 show that the catalysts chosen by the authors are not very selective. The reduction either takes place to a very low degree or leads to completely hydrogenated products. The method requires a relatively high content of the components to be separated, which are detected by a katharometer, and is applicable only to pure compounds.

Kugucheva and Alekseeva [60,95] proposed a method for the identification of conjugated dienes and acetylenes mixed with hydrocarbons of other classes. The method consists in the selective reduction of dienes and acetylenes, olefins being involved in the reaction to only a slight extent.

Palladium prepared by Lindlar's method [96] was chosen as the catalyst. The hydrogenation was carried out under flow conditions at room temperature. The conjugated dienes and acetylenes with different structures and steric configurations were reduced to a high degree and selectively to olefins (Table 7). The olefins reacted (reduction and isomerisation) to an extent not greater than 20% (Table 8). The method, which was developed on artificial mixtures, was applied to real products of petrochemical synthesis [85].

Table 6. Hydrogenation of acetylenes [94].

Initial hydrocarbon	Catalyst	Unchanged fraction, %	Composition of catalytic reaction mixture			
			partly reduced products	wt.%	fully reduced products	wt.%
Hex-3-yne	PtO_2	50	*cis*-Hex-3-ene	15	n-Hexane	32
			trans-Hex-3-ene	3		
	$NaNH_2$	90	*trans*-Hex-3-ene	10	„ „	0
Hex-2-yne	PtO_2	55	*cis*-Hex-2-ene	10	„ „	33
			trans-Hex-2-ene	2		
	$NaNH_2$	60	*trans*-Hex-2-ene	40	„ „	traces
	PtO_2	96	Hex-1-ene	3	„ „	1
Hex-1-yne	$NaNH_2$	38	Hex-1-ene	62	„ „	0
	Na	37	Hept-1-ene	63	„ „	0

Table 7. Hydrogenation of dienes and acetylenes on a palladium catalyst [53].

Initial compound	Composition of catalytic reaction mixture		Degree of reaction, %
	hydrocarbon	mole %	
Buta-1,3-diene	n-Butane	3.1	100.0
	But-1-ene	51.3	
	trans-But-2-ene	40.2	
	cis-But-2-ene	5.4	
Isoprene	2-Methylbutane	4.3	100.0
	3-Methylbut-1-ene	21.1	
	2-Methylbut-1-ene	25.1	
	2-Methylbut-2-ene	49.5	
Penta-1,3-diene (70% of *trans*-form and 30% of *cis*-form)	n-Pentane	5.4	100.0
	Pent-1-ene	22.3	
	trans-Pent-2-ene	61.4	
	cis-Pent-2-ene	10.9	
Cyclopentadiene	Cyclopentane	14.9	100.0
	Cyclopentene	85.1	
Penta-1,4-diene	n-Pentane	7.9	51.2
	Pent-1-ene	34.7	
	trans-Pent-2-ene	7.2	
	cis-Pent-2-ene	0.4	
	Penta-1,4-diene	49.8	
Acetylene	Ethane	21.3	100.0
	Ethylene	78.7	
Hex-1-yne	n-Hexane	25.2	100.0
	Hex-1-ene	68.0	
	cis-Hex-2-ene	6.8	
Hex-2-yne	n-Hexane	1.1	8.77
	trans-Hex-2-ene	4.1	
	cis-Hex-2-ene	82.5	
	Hex-2-yne	12.3	

3. Dehydrogenation of Naphthenes

Keulemans and Voge [97] were the first to suggest the dehydrogenation of naphthenes in gas-chromatographic analysis. They were aromatised on a reforming catalyst (platinum on Al_2O_3 containing a halogen) at 350°C in a stream of hydrogen. The reaction products were transferred by the stream of hydrogen to the analytical column. The authors found that cyclohexane derivatives were aromatised to the extent of 96–100% except for the 1,1-dimethyl derivative (66%). Cyclopentanes were converted into benzene derivatives to the extent of only 1.4 to 25%.

Table 8. Reactions of olefins on a palladium catalyst [53].

Hydrocarbon	Degree of reaction, mole %		Hydrocarbon	Degree of reaction, mole %	
	hydrogenation	isomerisation		hydrogenation	isomerisation
Pent-1-ene	12.9	6.9	2-Methylbut-2-ene	0.0	0.0
Hex-1-ene	10.5	7.2	*trans*-Hex-2-ene	0.0	4.7
3-Methylbut-1-ene	0.0	0.0	Cyclopentene	5.3	—
2-Methylbut-1-ene	0.0	0.0			

In order to suppress the aromatisation of cyclopentane hydrocarbons, Rowan [23] carried out the dehydrogenation at 299°C in a stream of helium with a small amount of added hydrogen. Dehydrogenation, which takes place to the extent of 100% for six-membered naphthenes, was used as a method for their group identification in complex hydrocarbon mixtures.

Klesment et al. [80] dehydrogenated petrols in a stream of helium at 325°C on platinum black deposited on diatomaceous earth. The yield of aromatic hydrocarbons from six-membered naphthenes was 87% and above, while five-membered cycloalkanes did not react. The process was complicated by cracking. The catalytic aromatisation of naphthenes and heterocyclic compounds on platinium catalysts was also carried out by Nigam [98].

Ivanova et al. [99] aromatised by the Zelinskii method the fraction of paraffins and naphthenes isolated by liquid–liquid chromatography and deduced the results on the basis of subsequent gas-chromatographic analysis.

The dehydrogenation and sulphonation of the aromatisation products in a system with separate steps involving subsequent chromatographic separation [19] have already been described.

4. The Introduction of the Methylene Group

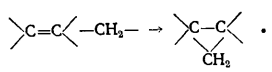
Dvoretzky et al. [100] treated alkanes, cycloalkanes, and olefins with diazomethane and then separated the reaction products on a capillary column with squalane. The treatment with diazomethane was accompanied by short-wavelength irradiation. In order to avoid side reactions between the methylated products and diazomethane, the reaction was carried out with a 50-fold excess of the hydrocarbon.

The methylene group is introduced according to the following scheme:

$$\rangle C{-}H + {-}CH_2{-} \rightarrow \left[\rangle C{-}CH_2{-}H\right] \rightarrow \rangle C{-}CH_3 .$$

This method of introduction is independent of the type of C–H bond: aliphatic vinyl, or allyl. The yield of isomers is directly proportional to the number of primary, secondary, and tertiary C–H bonds in the initial hydrocarbon molecule and can be calculated beforehand.

The reaction with olefins is complicated by the formation of cyclopropane:



The ratio of the contributions of the C=C/C–H reactions varies in the range from 6 to 8 and therefore the corresponding substituted cyclopropane is the main reaction product.

The method has been applied mainly to alkanes. The structure of the unknown component was established on the basis of the number and relative amounts of the methylenation reaction products. Moreover, data for the contents of the isomers obtained may be used to identify unknown mixtures. The retention times of 19 nonanes synthesised from 6 initial octanes have been obtained [101]. By comparing the retention times of the nonanes and the components of a real mixture—the products of the alkylation of isobutane with olefins—the authors determined the mixture composition.

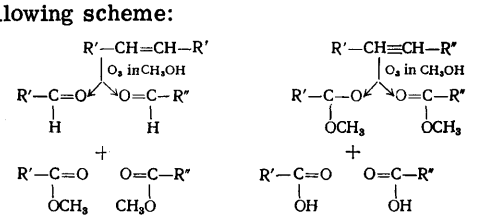
It has been shown for a large number of examples involving alkanes [100] that the ratio of the yields of the isomers coincides with theoretical predictions within the limits of the error of the chromatographic analysis.

5. Ozonolysis

Blumer and Thomas [102] isolated on a preparative scale the olefin fraction from a plankton extract and subjected it to ozonolysis. The ozonides were cleaved in the chromatograph injector and the presence of methylene and vinyl groups as well as conjugated double bonds in the molecule of the initial olefin was inferred on the basis of the identified carbonyl compounds.

Davison and Dutton [103] placed a reactor with zinc oxide beyond the chromatograph injector. Acidic compounds formed on decomposition of the ozonides were retained in the reactor, while aldehydes passed to the analytical column without hindrance.

Spencer et al. [104] used the ozonolysis method for the identification of double and triple bonds. They ozonised hydrocarbons in methanol solution. After subsequent cleavage of the ozonides (also carried out in the chromatograph injector), only olefins gave rise to aldehydes, while esters and acids were obtained from acetylenic hydrocarbons. The reaction was carried out according to the following scheme:



Thus 83% of methyl valerate and 17% of valeric acids were obtained from dec-2-yne, which was completely ozonised after 7 min.

Smith et al. [105] ozonised unsaturated compounds isolated by preparative chromatography. The carbonyl compounds obtained on decomposition of the ozonides were treated with dinitrophenylhydrazine. The dinitrophenylhydrazones isolated were identified by paper chromatography. The ozonolysis method has been used successfully to identify C_6–C_{11} α-olefins, C_5–C_6 dienes, styrene, pentynes, etc. Ozonolysis combined with gas chromatography has also been used in other investigations [106,107].

6. Other Identification Methods

Frank et al. [108] used reductive catalytic cleavage for the identification of alkyl substituents in the aromatic ring. The reaction was carried out at 620°C in a quartz tube filled with the Leuna WK 9063 catalyst (silicon and aluminium oxides in proportions of 60:40, impregnated with 4.5% WO_3 and MoO_3) in a stream of hydrogen, which served as the carrier gas in the apparatus. The reaction tube was connected to the sample injection device, so that the volatile cleavage products entered the analytical column directly. At the above temperature carbon–carbon bonds in the alkyl group were ruptured in all positions and the relative amounts of the hydrocarbons formed remained constant (to within ±3 rel.%). On the basis of the ratios of the reaction products obtained, it was possible to infer whether one or several alkyl groups are split off from the initial alkylbenzene. The authors also established that there are optimal temperatures for the scission of various alkyl groups and suggested that this phenomenon be employed for identification. 5-Isopropyl-1,2,4-trimethylbenzene gives rise to only propane at 200°C, to propane and propene at 300°C, to propane, propene, ethane, and ethylene at 500°C, and to methane as well as the compounds enumerated above at 600°C.

Walsh and Merrit [17] treated the elutate with reagents for qualitative analysis directly at the outlet from the column. A device for dividing the stream into five parts was connected to the outlet tube of the katharometer. This made it possible to carry out five calorimetric reactions for each substance. Reagents were proposed for oxygen-, sulphur-, nitrogen-, and halogen-containing compounds and also for aromatic hydrocarbons and olefins. Having determined the homologues series to which the compound belongs, it was identified with the aid of plots of the logarithm of the retention volume against the number of carbon atoms in the molecule.

Casu and Cavalotti [18] improved the method by suggesting an attachment to the pen recorder of the chromatograph. A glass strip on which a layer of silica gel impregnated with the appropriate reagents has been deposited, moves at the same speed as the paper strip of the pen recorder. A coloured spot appears on the silica gel synchronously with the appearance of a peak on the chromatogram.

The methods described above [17,18] require the application of relatively large samples and the use of detectors which do not decompose the substance, since the lower limit of the sensitivity of the reagent varies from 20 to 100 μg.

Janak [109] employed a similar attachment to the pen recorder for the crystal-chemical identification of substances isolated on a preparative scale. High-boiling compounds, separated in a capillary column at 280°C, were condensed on a thin glass sheet moving at a distance of 1–2 mm from the chromatograph outlet and cooled from inside. These compounds formed bands 3–4 mm wide with characteristic microcrystals. The author investigated the crystals under the microscope and described a method for the preparation of coloured complexes by carrying out the reaction with samples of the substances isolated weighing 10^{-2} μg and having a volume of 10^{-5} ml. Janak [109] investigated the crystals of 15 aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, fluorene, benzopyrene, and other polycyclic hydrocarbon derivatives) as well as certain oxygen-, nitrogen-, and sulphur-containing compounds. Sublimatograms and a colour table of the complexes of the test compounds with tricyanoethylene are quoted.

IV. SCHEMES FOR THE CONSECUTIVE GROUP ANALYSIS OF HYDROCARBON MIXTURES

This section deals with examples of group analysis of hydrocarbon mixtures in which elimination and transformation methods are combined in a single scheme with chromatographic separation at each stage of the treatment.

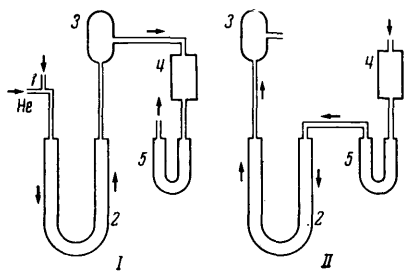


Figure 1. Schematic illustration of Martin's gas-chromatographic apparatus[32]: 1) injector; 2) analytical column; 3) katharometer; 4) absorber with $HgClO_4$; 5) trap.

Martin[32] developed a combined method for the analysis of petrol based on the elimination of substances of certain classes. The gas stream scheme is illustrated in Fig. 1. A column with $\beta\beta'$-oxydipropionitrile retained aromatic hydrocarbons. Naphthenes, paraffins, and olefins were recorded by the detector in the form of a single peak (*A* in Fig. 2). Beyond the katharometer, the sample passed through an absorber with mercury) perchlorate (Fig. 1, position I). Olefins were absorbed in the absorber and paraffins and naphthenes were collected in a cooled trap. By altering the direction of the carrier gas stream (Fig. 1, position II), aromatic hydrocarbons were initially eluted from the column in the form of a single peak *B* and then the trap was warmed and saturated hydrocarbons (peak *C* in Fig. 2) were recorded.

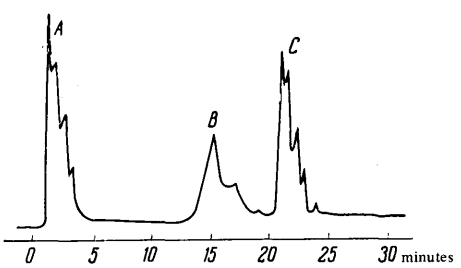


Figure 2. Chromatogram of a hydrocarbon mixture[32]: *A*) naphthenes + paraffins + olefins; *B*) aromatic hydrocarbons; *C*) paraffins + naphthenes.

Albert[33] employed a similar scheme for the analysis of petrol having supplemented it by the elimination of straight-chain paraffins and the interpretation of each peak. Aromatic hydrocarbons were initially retained on a column with *NN'*-bis-(2-cyanoethyl)formamide as the stationary phase and the remaining hydrocarbons were eluted from the column, detected by the katharometer, passed through an absorber with mercury perchlorate and a molecular sieve, and were collected in a trap. After heating the trap, the stream of gas was directed to the column and branched-chain paraffins were separated and detected. Finally the absorber with the molecular sieve was heated for 15 min at 400°C and the gas stream was again switched to the column, whereupon the desorbed straight-chain paraffins were identified component by component.

The most complete method of group analysis of hydrocarbon mixtures by a continuous procedure was proposed by Rowan[23]. The apparatus is illustrated schematically in Fig. 3. As in the examples described previously, its principle involves the switching of the gas stream and chromatography of the sample collected in the trap after preliminary separation. Steps of the following types were employed: retention of straight-chain hydrocarbons on a 5 Å molecular sieve, absorption of olefins by mercury perchlorate, hydrogenation of aromatic hydrocarbons and olefins, hydrogenation of olefins alone, and dehydrogenation of six-membered naphthenes. The analytical scheme illustrated in Fig. 4 combines the operations enumerated above and makes it possible to select the required sequence of steps.

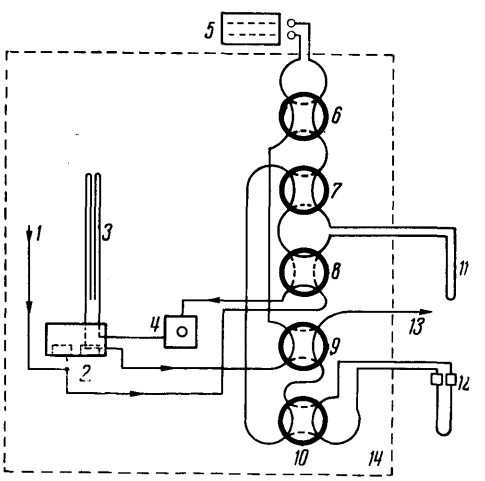


Figure 3. Schematic illustration of Rowan's gas-chromatographic apparatus[23]: 1) carrier gas supply line; 2) katharometer; 3) analytical column; 4) injector; 5) furnace; 6)–10) four-way taps; 11) cooled trap; 12) absorber with sulphuric acid or 5 Å molecular sieve; 13) outlet; 14) chromatograph thermostat.

Reactors with sulphuric acid, mercury perchlorate, and a molecular sieve can be replaced and interchanged. Sulphuric acid was deposited on glass fibre and the absorber temperature was maintained at 54°C. The reactor with mercury perchlorate was constructed by Coulson's method[110]. The water evolved in the reaction with olefins was absorbed by a layer of a 4 Å molecular sieve. Adsorption was carried out with the aid of a 5 Å

molecular sieve at 93° and 165°C, depending on the boiling point range of the fraction analysed. Palladium on asbestos (5% Pt) was employed as the catalyst for the hydrogenation of olefins at room temperature, while the hydrogenation of aromatic hydrocarbons and the dehydrogenation of naphthenes at 299°C were carried out on the platinum–alumina catalyst proposed by Keulemans and Voge[97].

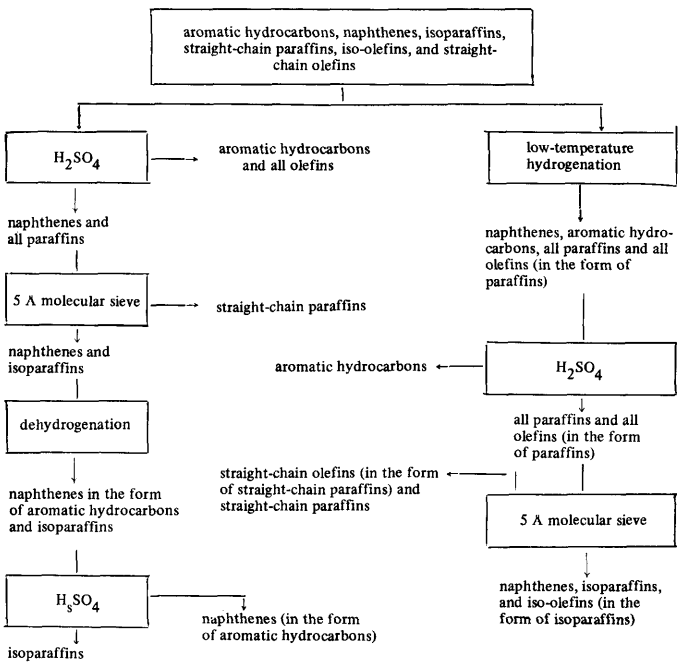


Figure 4. Analytical scheme for the assignment of gas-chromatographic peaks to different classes of hydrocarbons[23].

Fig. 3 shows the taps in the position where the sample, having passed column *3*, proceeds via taps *9* and *6* into the catalytic furnace *5* and is then collected in trap *11* after passing through taps *6* and *7*. After trap *11* has been heated and tap *8* switched over, the concentrated hydrocarbons are again directed to column *3*. The changes which have occurred are recorded by the katharometer and the specimen is returned to the trap via an absorber with the appropriate reagent.

The method was tested on artificial mixtures of hydrocarbons of different classes but without cyclopentane derivatives, acetylenes, and conjugated dienes and also on technical petrol in which the fraction of aromatic components predominated.

Methods for continuous group analysis of hydrocarbons were developed also for exhaust gases[31] and atmospheric contaminants[28].

A scheme of group analysis[24], involving the identification of olefins, conjugated dienes, acetylenes, and straight-chain paraffins, has been developed for hydrocarbons present in gases in microconcentrations.

Hoff and Feit[111,112] described a consecutive functional analysis of a vapour–gas mixture of hydrocarbons and oxygen-containing compounds by the method of "syringe reactions".

Several schemes for the type analysis of liquid hydrocarbon mixtures have been proposed recently. They require an apparatus modified by the introduction of additional valves, by-pass systems, and chambers with various heating devices. In their practical application these schemes differ from those already described by the fact that provision is made for the heating of the taps, in order to prevent adsorption, and cooled traps for the collection of samples for repeated analysis are eliminated. This made the new methods more accurate and faster.

Robinson et al.[37] described a system comprising the two capillary columns and a device which divides the sample into two equal portions. One portion passes through the empty column into the detector, giving rise to a signal corresponding to the size of the entire sample, while the other passes in succession through a column with *NN'*-bis-(2-cyanoethyl)formamide, where aromatic hydrocarbons are retained reversibly, and a reactor with mercury perchlorate for the irreversible retention of olefins. Thus the second chromatogram shows only paraffins and naphthenes. The back-flushing device makes it possible to switch the direction of the stream and to transfer aromatic hydrocarbons from the *NN'*-bis-(2-cyanoethyl)-formamide column to the detector. The third chromatogram shows aromatic hydrocarbons. The olefin content is calculated from the difference between the peak areas on the three chromatograms.

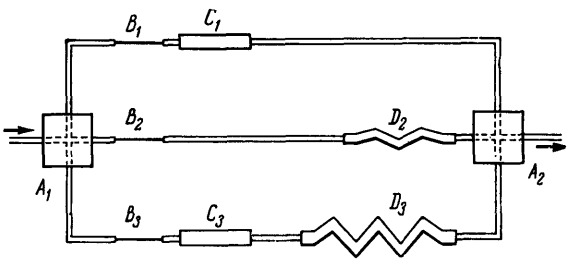


Figure 5. Schematic illustration of the analyser[35]: A_1 and A_2—four-way connecting sleeves; E_1, E_2, and B_3—capillary connections; C_1—absorber with $HgClO_4$.$HClO_4$; C_3—absorber with $HgSO_4.H_2SO_4$; D_2 and D_3 flow retarding devices.

A scheme for analysis in which the sample is divided into three streams (Fig. 5) was proposed by Soulages and Briewa[35]. One part of the sample passes to the detector without hindrance, olefins are subtracted from another in a reactor with H_2SO_4, and olefins and aromatic hydrocarbons in the third are retained in a reactor with $HgClO_4$. In order to avoid the superposition of peaks, capillary sections were fitted in the path of each sample in order to regulate the flow rates. The subdivision of the sample into three [equal] parts was adjusted by introducing pure heptane and comparing the areas of the three peaks. The time required to apply the methods described[35,37] is 5–15 min.

McTaggart and Luke[36] introduced an improvement into type analysis by introducing an additional stage involving the separation of paraffins, naphthenes, and olefins on the

basis of the number of carbon atoms. The method provides for the introduction of two liquid samples of equal size. In the first cycle of the analysis aromatic hydrocarbons are retained on a packed column with *NN'*-bis-(2-cyanoethyl)formamide. The remaining hydrocarbons pass through a reactor with a platinum catalyst (Pt/Al_2O_3), where olefins are reduced quantitatively to the corresponding paraffins and naphthenes. Together with the paraffins and naphthenes present in the initial mixture, they pass to a column with a 13X molecular sieve treated with alkali and are separated on the basis of the number of carbon atoms according to the method of Brunnock and Luke[113]. In the same analytical cycle the aromatic hydrocarbons retained on the column are flushed out with the aid of the back-flushing device and recorded by the detector in the form of a single peak. In the second analytical cycle aromatic hydrocarbons and olefins are retained irreversibly in a reactor with mercury perchlorate and paraffins and naphthenes are separated on the basis of the number of carbon atoms.

By subtracting the areas of the corresponding peaks obtained on the first and second chromatograms after separation on the molecular sieve, the content of olefins is calculated and the results of analysis are produced in the following form:

Paraffins	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Naphthenes	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Olefins	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Cyclo-olefins	C_1	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Aromatic hydrocarbons	Sum							

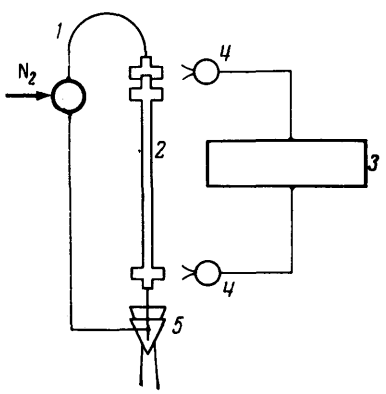


Figure 6. Trap and device for the reintroduction of sample[116]: 1) flexible tube; 2) trap; 3) heater; 4) clamp; 5) injector.

Comparison of reaction chromatographic methods[35-37] with the FIA type method[114] (adsorption separation on a silica gel column in the presence of an indicator, which dyes the boundaries between the following bands: paraffins and naphthenes–olefins–aromatic hydrocarbons), which is widely used for hydrocarbon mixtures, demonstrated a satisfactory agreement between the results. Reaction chromatographic methods require much less time and are applicable to highly coloured specimens.

The analytical methods described have been applied to hydrocarbon fractions boiling up to 180–220°C. An analytical scheme incorporating hydrogenation, molecular sieve analysis, partition and displacement chromatography, and spectroscopic research techniques has been proposed[115] for hydrocarbons boiling in the range 160 to 250°C.

In the present section of the review it is useful to consider the very promising method of "multidimensional chromatography"[116]. In contrast to the methods described earlier, in this case type analysis is not based on the application of chemical reactions but on a consecutive separation on columns with stationary phases of different polarity. While the components are eluted from the nonpolar phase in order of increasing boiling points, the order of their appearance after separation on the polar phase depends mainly on their polarity. The following series in terms of increasing polarity holds for hydrocarbons: paraffins < aliphatic olefins + naphthenes < < aliphatic dienes + cyclo-olefins < acetylenes < cyclodienes < aromatic hydrocarbons.

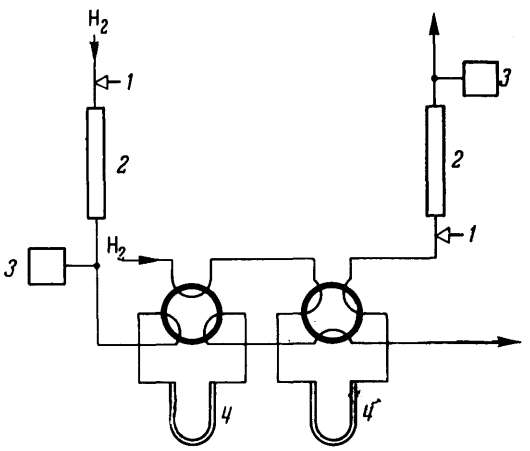


Figure 7. Schematic illustration of the universal two-dimensional chromatograph[116]: 1) injector; 2) analytical column; 3) detector; 4) trap.

Boer[116], who employed successfully the method of multidimensional chromatography for the analysis of complex hydrocarbon mixtures, regards it as "quantitative trapping of the required fraction after separation on the first column and its introduction into the second column". The method can be applied in continuous and discontinuous schemes. The first case has the advantage of the possibility of employing any standard chromatograph. It is only necessary to connect to it via a three-wave tap a heated trap (duration of heating to 250°C 10–15 s) and a device for the reintroduction of the sample (Fig. 6). A universal apparatus for continuous analysis is illustrated in Fig. 7. It consists of two chromatographs connected by a system comprising two traps and several devices, which can be switched in different directions, for the reintroduction of the sample and for back-flushing. Stream dividers are placed before flame-ionisation detectors. One part of the fraction is detected, while the other is directed to further analysis.

Boer[116] describes also more complex schemes with four columns and three traps and a specific example of the analysis of a petroleum fraction. The petroleum fraction was introduced into the first column with a polar phase (cyanoethylsucrose). Saturated hydrocarbons together with benzene and toluene were detected, the results integrated, and the substances collected in trap *1*. The residual aromatic hydrocarbons were flushed out in the opposite direction, detected, the signals integrated, and the substances collected in trap *2*. The contents of trap *1* were introduced into a second column with a non-polar phase (SF-96) and divided, under the conditions of a programmed temperature, into 24 fractions, which were collected alternately in trap *3* and directed one at a time into a third column with a polar phase (picryl chloride). The contents of trap *2* were then introduced into a fourth column (SF-96) and chromatographed under isothermal conditions. The analysis yielded 86 peaks and the weight and molar percentages of isoparaffins, naphthenes, and aromatic hydrocarbons were determined for each group with identical numbers of carbon atoms.

The principles of multidimensional chromatography constitute the basis of a standard apparatus for the analysis of petroleum fractions[117,118]. During an analytical cycle lasting 2–3 h, it is possible to obtain the following data: the individual compounds present in the aromatic hydrocarbons and the distribution of straight-chain paraffins, isoparaffins, and naphthenes among groups corresponding to numbers of carbon atoms ranging from 5 to 12.

Analysis of pyrolytic petrol is more difficult owing to the presence of olefins and dienes. Boer[116] suggests that the specimen be separated on a non-polar phase into very narrow fractions, which are chromatographed in succession on a polar phase.

Attempts are now being made to develop a scheme for the standard analysis of industrial mixtures containing olefins[117].

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