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REACTION GAS CHROMATOGRAPHY IN ANALYSIS

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1. INTRODUCTION

Gas chromatography is now an effective method for the analysis of organic and inorganic compounds. Fairly frequently, however, particularly in the analysis of complex organic mixtures, the oridinary methods of gas chromatography are unsatisfactory.

The efficiency of gas chromatography as an analytical method can be increased considerably by the simultaneous use of chromatographic separation and chemical reactions. Chemical reactions in gas chromatography can be carried out for different purposes, in particular: (1) the analysis of substances for which direct use of the methods of gas chromatography is impossible (e.g. the analysis of polymers, non-volatile compounds, etc.); (2) the reduction of a difficult analytical problem to a simpler problem which has previously been resolved (e.g. the conversion of alcohols into alkenes or alkanes or esters of nitrous acid, followed by chromatographic analysis of the reaction products); (3) the identification of peaks due to unknown components by the use of group (individual) selective absorbers (e.g. sulphuric acid for the absorption of alkenes from hydrocarbons) or group qualitative reactions; and (4) the simplification of quantitative calculations and increase in the sensitivity and accuracy of analysis by the conversion of all the organic compounds being analysed into one or two simple compounds at the outlet from the separating column (e.g. conversion to carbon dioxide and water or hydrogen with the use of a thermal-conductivity detector).

Thus the use of chemical reactions in gas chromatography is extending appreciably the range of the ordinary chromatographic separation and exhibits a number of specific features. It is therefore appropriate to deal with the use of chemical reactions in gas chromatography as a separate field — reaction gas chromatography. This term was first used by Drawert[1,2], who at first, however, gave a too narrow definition of reaction gas chromatography, restricting himself to the case where the substance being analysed undergoes changes in a reaction vessel placed before the separating column (in order to convert the compounds being analysed into definite compounds whose chromatographic analysis presents no difficulties).

In a later paper, Drawert[3] correctly pointed out that in a wider sense the term "reaction gas chromatography" can be taken to mean the use of chemical reactions together with chromatographic separation. It is necessary only to emphasise that the chemical changes should take place in a single chromatographic scheme. The present review considers only the analytical applications of the combined use of chemical reactions and chromatographic separation. Another important independent field of reaction gas chromatography involves the study of the kinetics and mechanism of chemical reactions under chromatographic conditions. Work on these lines, which is now being successfully developed, was begun by Roginskii and coworkers[4,5].

A promising development is the use of the mathematical methods of the theory of reactions under chromatographic conditions to determine the initial concentration of a substance in a specimen, some components of which undergo chemical changes as a result of chemical reactions in the chromatographic column.

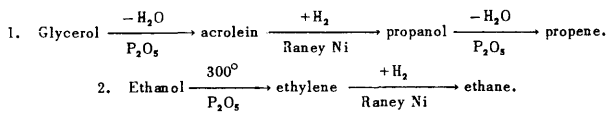
Thus analytical reaction gas chromatography is a form of gas chromatography in which chemical reactions in a single gas-phase chromatographic process are used for analytical purposes. The chemical reactions may take

place in special reaction vessels placed before, after, or directly inside the column or between two chromatographic columns. When a special reaction vessel is introduced into a chromatographic set-up, there is a possibility that the efficiency of separation will be reduced. These fears generally prove groundless, however, since the chromatographic characteristics of the packing of the reaction vessel and column do not generally differ greatly from one another, and the length of the reaction vessel amounts to only a small percentage of the length of the chromatographic column.

No published papers have referred to a decrease in the efficiency of separation. For a quantitative estimate of the decrease in the efficiency using chromatograms obtained with and without a reaction vessel[6], we calculated the number of theoretical plates. The calculation showed that there is no decrease in the efficiency of separation.

Table 1 gives a classification of known reaction gas chromatography procedures according to the given chromatographic set-up (position of reaction vessel) and according to the types of chemical reaction used.

In a number of cases it is convenient to effect different chemical reactions simultaneously in a single analysis by using a multistage reaction vessel. For example, for the determination of alcohol and glycerol in dilute aqueous solutions, Drawert et al.[3] used a complex multistage reaction vessel in which the following chemical changes took place:



The gas-chromatographic determination of the products formed (propene and ethane) presents no difficulties and can be carried out using simpler apparatus than that required for the determination of the original compounds (glycerol and ethanol). The combined use of several chemical reactions has also been described[7]. The fractions leaving the gas chromatograph were oxidised on a platinum catalyst, and the oxidation products were studied by qualitative reactions for sulphur, nitrogen, and halogens. A positive qualitative test indicated the presence of the elements detected in the molecule of the original compound.

TABLE 1. Chemical reactions and chromatographic set-ups*.

Types of chemical change	Position of reaction vessel in gas-chromatographic set-up		
	reaction vessel before column	reaction vessel—column	reaction vessel after column
Pyrolysis	10—30, 31—36		
Hydrogenation and dehydrogenation	1, 2, 3, 8, 39—43		
Dehydration and decarboxylation	2, 3, 39, 40		
Esterification	1, 2, 3, 39, 40, 44	9	
Saponification			45
Formation of non-volatile compounds	6, 48, 49, 46		47
Oxidation	8, 37, 38		52—64
Qualitative reactions			7, 67
Cracking			
Study of reactions under chromatographic conditions		4.5	37—39
Reduction	65, 66		

* The numbers give the literature references.

To detect traces of inorganic gases (carbon monoxide, oxygen, etc.) by means of the highly sensitive flame-ionisation detector, the inorganic gases are converted quantitatively into compounds which can be measured by this detector. An example is the gas-chromatographic method for determining oxygen by means of a flame-ionisation detector after the quantitative conversion of the oxygen to carbon monoxide over carbon and reduction of the carbon monoxide to methane in a current of hydrogen over a nickel catalyst[8].

Different chemical reactions and different set-ups can be used in reaction gas chromatography, depending on the type of problems to be solved. Thus pyrolysis, hydrogenation, dehydration, esterification, and other chemical changes are usually employed for the analysis of non-volatile substances and for the conversion of polar, unstable, or non-volatile substances, which are difficult to study chromatographically, into compounds which are determined more easily. In this case the reaction vessel is generally placed before the chromatographic column.

Reactions involving oxidation, reduction, cracking, and the formation of non-volatile compounds, and also qualitative colour reactions, are often used to simplify quantitative calculations, to increase sensitivity, and for the identification of peaks due to the compounds being studied. In this case the reaction vessel is usually placed after the column, either before the detector or (when qualitative reactions are being carried out) after the detector. In some cases the chromatographic set-up contains no special reaction vessel and the reaction takes place directly in the column. Thus Anders and Mannering[9] introduced acetic or propionic anhydride into a chromatographic column immediately after a specimen of alkaloids and steroids and their derivatives. Under these conditions many of the compounds being analysed formed esters (acetates or propionates) directly in the column.

Thus the aims and purposes of the study determine not only the position of the reaction vessel in the general gas-chromatographic set-up, its shape, and the constructional details, but also the type of chemical reaction used.

The use of various types of chemical reaction in reaction gas chromatography is examined below.

2. PYROLYSIS

Pyrolysis is widely used in reaction gas chromatography for the identification of polymers, the study of the composition of copolymers, the identification of individual functional groups (e.g. benzene nuclei) in the molecules of non-volatile compounds, and the identification of isomeric paraffinic hydrocarbons.

A combination of the controlled pyrolysis of non-volatile compounds with gas-chromatographic determination of the product spectrum opens up the possibility of rapid identification of non-volatile compounds.

It has been shown[10-15] that under certain pyrolysis conditions, solid non-volatile substances decompose in a specific fashion and that analysis of the products enables certain conclusions to be reached regarding the structure and composition of the original substances.

The pyrolysis is carried out in a special assembly mounted before the separating column. The substance being studied is deposited beforehand on a metallic (platinum or, less frequently, nichrome) filament, wound to

form a spiral or mesh. After the spiral carrying the substance has been introduced into the gas stream, the spiral is heated rapidly by an electric current. The resulting pyrolysis products pass to the chromatographic column and are recorded by the detector at the outlet from the column.

Fig. 1 shows a typical pyrolysis cell. In some cases[16-19] the pyrolysis is carried out in a tube heated to high temperature.

The use of a special cell for the rapid pyrolysis of non-volatile substances on an incandescent filament has certain advantages over the method involving prolonged pyrolysis in a heated tube: (1) small quantities of the specimen (milli- or micro-grammes) are required for the analysis; (2) the method is rapid; and (3) the part played by secondary reactions in the formation of pyrolysis products is reduced.

The method of depositing the specimen on the filament is determined by the nature of the specimen. Solid soluble substances are deposited in a thin layer from solution on one or two rings in the centre of the spiral, and insoluble substances are deposited in the form of an aqueous suspension. The spiral with the specimen is then dried by means of an infrared lamp until the solvent is completely removed.

It is not always possible to achieve complete removal of the solvent, and the pyrolysis products of the solvent are generally present in the chromatograms together with the pyrolysis products of the substances being studied[20,21].

In another method[13,14,21,22] pyrolysis is carried out in a special boat of inert material (porcelain or quartz), which is brought rapidly into the hot zone. The quantity of volatile products and the weight of residue are found by weighing the boat.

By carrying out the pyrolysis in a boat, it is also possible to control accurately the pyrolysis process, to analyse liquid and solid specimens, and to determine the resulting products chromatographically. The temperature of pyrolysis is varied over a wide range, from 150° to 950°, depending on the nature of the substances being studied. The optimum pyrolysis temperature is found empirically. The temperature dependence of the yield of pyrolysis products from butyl methacrylate (Fig. 2) shows that, under the given conditions of pyrolysis in the boat, the optimum pyrolysis temperature is ~500°.

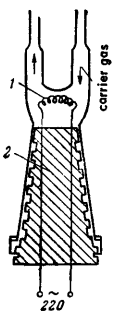


Fig. 1. Pyrolysis cell:
1) nichrome spiral with specimen; 2) Teflon block.

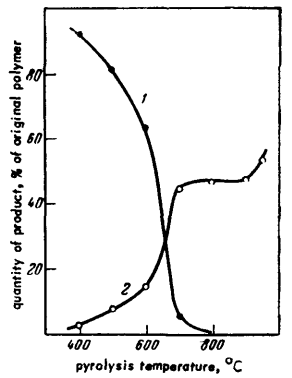


Fig. 2. Dependence of the yield of pyrolysis products from butyl methacrylate on the pyrolysis temperature:
1) butyl methacrylate monomer; 2) gaseous products ($CO + CO_2$).

The method involving pyrolysis can be used successfully to study the structure and composition of solid, liquid, and gaseous substances. For example, in the pyrolysis of polymers of the methyl methacrylate type and other acrylates[14,16,23-25] the original monomers are formed as chief product. The method involving pyrolysis has been used for the analysis of a number of copolymers (of styrene with methyl methacrylate[26] and of ethylene with vinyl acetate and ethyl acrylate[27,28], etc.) and polymers (polyurethane[17], polyethylene, polypropylene[29], etc.). Pyrolysis in gas chromatography has also been used to establish the structure of non-volatile compounds such as natural oils[6-8] and medicinal products[10-12,15,30]. As an example, Fig. 3 gives the chromatograms of the pyrolysis products from natural barbituric acids. It can be seen from Fig. 3 that the compounds of the same class give identical pyrolysis products.

Study of the pyrolysis products from a large number of high-boiling aromatic compounds (~100)[19] showed that a combination of pyrolysis with subsequent chromatographic analysis of the products provides a reliable method for detecting benzene rings in the compounds being analysed,

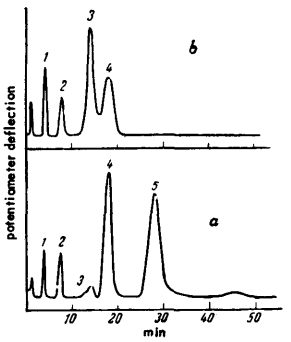


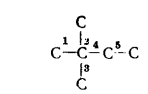
Fig. 3. Chromatograms of the pyrolysis products from the sodium salts of barbituric acid derivatives. Analysis conditions: 30% squalane on Celite 545, 100°:
a) luminal, *b*) eudon; 1) benzene; 2) toluene; 3) ethylbenzene; 4) *o*-xylene; 5) propylbenzene.

since the benzene nuclei are not broken down during the thermal decomposition of the substances, and the decomposition products contain aromatic compounds. Thus, for example, in the pyrolysis of benzyl alcohol, benzyl benzoate, and benzyl phenylacetate, the chief products are benzene, toluene, and carbon dioxide (Fig. 4). The pyrolysis was carried out in a short quartz tube filled with chromosorb (~2 g) and connected to the chromatographic column.

Hyden[31] proposed the use of the pyrolysis method for the gas-chromatographic analysis of thermally unstable compounds. For example, in the water–di-t-butyl peroxide system at 310° the peroxide decomposes almost instantaneously and the thermal decomposition products can be used for its qualitative identification. The method can be used for the quantitative analysis of the peroxide, since it has been established that there is a linear relationship between its concentration in the specimen and the area of the peaks due to the decomposition products (see Table in Ref. 31).

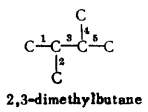
Nishi Sueo[32] showed that the method involving pyrolysis can be used for the qualitative and quantitative analysis of carbonyl compounds. The C_2–C_6 carbonyl compounds are liberated quantitatively from the 2,4-dinitrophenylhydrazones by heating with dicarboxylic acids. A specimen of the dinitrophenylhydrazone being studied is mixed with phthalic acid in the ratio 1 : 10 and introduced into a glass reaction vessel (250 × 0.3 cm) placed directly before the separating column. The dinitrophenylhydrazones of the carbonyl compounds decompose quantitatively at 250° with the liberation of the original compounds, which are then analysed chromatographically.

The use of pyrolysis in reaction gas chromatography is not restricted to the study of the pyrolysis products from polymers and non-volatile compounds. By analysing the pyrolysis products from 2,2- and 2,3-dimethylbutanes, Keulemans and Perry[33] showed that it is possible to identify paraffinic hydrocarbons. The pyrolysis was carried out in an empty quartz tube at 500°. The various possibilities of C–C bond rupture lead us to expect the formation of the following compounds:



2,2-dimethylbutane

Rupture of bond	Probable products
1	2-methylbut-1-ene
2	2-methylbut-2-ene
3	
4	ethylene and isobutene rearrangement
5	



2,3-dimethylbutane

1	3-methylbut-1-ene or 2-methylbut-2-ene
2	
3	
4	
5	
3	propene

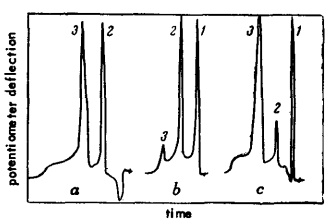


Fig. 4. Chromatogram of pyrolysis products from: *a*) benzyl alcohol; *b*) benzyl benzoate; *c*) benzyl phenylacetate (stationary liquid phase — silicone oil); 1) carbon dioxide; 2) benzene; 3) toluene.

TABLE 2. Chief products of the pyrolysis of 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB).

Products	Composition, %	
	2,2-DMB	2,3-DMB
Propene	1	10
But-1-ene, isobutene	10	3
3-Methylbut-1-ene	0	0.5
2-Methylbut-1-ene	3	traces
2-Methylbut-2-ene	11	16

Data on the composition of the pyrolysis products from the isomeric alkanes 2,2-dimethylbutane and 2,3-dimethylbutane (Table 2) show that the expected products are in fact formed. There is thus a simple relationship between the pyrolysis product and the original compound and this can be used for the identification of the hydrocarbons.

The study of substances by the pyrolysis method is carried out using standard chromatographs fitted with special assemblies for the pyrolysis[34,35] or in specially constructed apparatus[36].

3. CRACKING

Hydro-cracking was first used in gas chromatography by Zlatkis and Ridgway[37] to increase the sensitivity and accuracy of quantitative analysis and to simplify analytical calculations. The fractions leaving the separating column undergo cracking to methane and water at 425° in a reaction vessel containing a catalyst (nickel on kieselguhr). The water is absorbed in a special column and the methane is recorded by a thermal-conductivity detector. This method can be used to record various classes of organic compounds: alkanes, alkenes, aldehydes, ketones, alcohols, etc. In particular, the hydro-cracking of chromatographically separated aldehydes to methane has been described[38,39]. It should be noted that when the high-boiling compounds to be analysed are converted into equivalent quantities of methane, it is possible to use simpler and less expensive detector assemblies operating at room temperature.

4. HYDROGENATION AND DEHYDROGENATION

It is convenient to use hydrogenation and dehydrogenation reactions for the identification and analysis of compounds which give products whose gas-chromatographic separation has been studied in detail (i.e. for the reduction of an unknown problem to a problem which has already been solved) and also for the determination of impurities. In all cases the resulting hydrogenation and dehydrogenation products have properties which differ sharply from those of the original compounds, and this can be used for the qualitative and quantitative analysis of complex mixtures by comparative calculation based on two chromatograms obtained for the original specimen and the hydrogenated specimen. Thus by carrying out the catalytic hydrogenation of oxygen-containing compounds it is possible to identify ketones, esters, aldehydes, alcohols, and acids in a mixture from the hydrocarbons produced.

Drawert and coworkers[39,40] used hydrogenation to determine small quantities of ethanol in aqueous solutions and in blood. The alcohols were converted into hydrocarbons

by hydrogenation in a short tube filled with catalyst (Raney nickel on kieselguhr in the ratio 1 : 10). The hydrogenation is carried out at 160–200° in a current of hydrogen, which is also used as carrier gas. The above ratio of catalyst and inert carrier is an optimum, since large quantities of nickel above 200° lead to sintering of the catalyst, and when the quantity of nickel is decreased the rate of the hydrogenation also decreases. In the analysis of specimens with a high water content the water is removed from the specimen in a tube which contains CaH_2 and is placed after the reaction vessel but before the separating column. This method can be used to determine small quantities of the C_1–C_{10} alcohols in aqueous solutions.

In a number of cases, in the analysis of saturated and unsaturated hydrocarbons, hydrogenation is used for the identification of peaks due to alkenes[41], using platinised asbestos as catalyst. The reaction vessel is placed before the column.

Struppe[42] made use of reaction gas chromatography in capillary chromatography. The reaction vessel was an aluminium capillary tube (600.00 × 0.03 cm) whose inner wall was covered with a thin layer of platinum. The catalyst was deposited on the inner walls of the capillary reaction vessel by the usual method for depositing the stationary liquid phase on a capillary column, i.e. the capillary was filled with an ethereal solution of $H_2[PtCl_4]$, the solution was shaken from one end of the tube to the other for 15 min, and the reaction vessel was dried in a current of hydrogen at 150° to reduce the hydrogen chloroplatinate to platinum. The hydrogenation was carried out in a current of hydrogen at 125°. The method was tested by analysing synthetic mixtures of hydrocarbons with boiling points up to 85°. It was shown that mono-, di-, and cyclo-alkenes add on hydrogen rapidly across the double bonds, whereas the carbon structure of aromatic, naphthenic, and cyclic hydrocarbons remains unchanged during hydrogenation under these conditions.

Keulemans and Voge[43] studied the dehydrogenation of naphthenes on a platinum catalyst (platinum–alumina–halogen). It was shown that under the conditions studied, cyclopentanes show different reactivities. In the reaction vessel, placed before the chromatographic column, cyclohexane is converted to benzene, but cyclopentane is unaffected under these conditions. Cyclopentanes undergo aromatisation to a much smaller extent than cyclohexanes and this can be used for the identification of cyclohexane in complex hydrocarbon mixtures.

From these examples, it can be seen that the use of hydrogenation and dehydrogenation provides a useful means of solving a number of analytical problems. The method has a number of disadvantages, however. In particular, the hydrogenation of various alkenes and alkynes containing the same number of carbon atoms in the molecule gives only one alkane, and the dehydrogenation of the *cis–trans*-isomers of cyclohexane derivatives gives only one aromatic hydrocarbon and this makes detailed qualitative analysis and identification of the original compounds difficult. Certain other reactions used in reaction gas chromatography have the same disadvantage.

5. DEHYDRATION AND DECARBOXYLATION

Dehydration and decarboxylation have been used successfully to determine alcohols and acids in dilute aqueous solutions. The procedure[2,3] does not require the preliminary separation or concentration of the compounds and solutions. The method can be used to analyse mono- and di-hydric alcohols and acids by separating the hydrocarbons which are formed from the oxygen-containing compounds in a reaction vessel placed directly before the chromatographic column. The reaction vessel consists of a stainless steel tube (10–15 × 0.6–1.0 cm) filled with sterchamol impregnated with phosphoric acid (ratio 2 : 1). The reaction temperature is 250–300°. To remove the water present in the specimen and formed during dehydration, a special drying tube containing calcium hydride is placed between the reaction vessel and the separating column. Monobasic organic acids react with phosphoric acid on heating and are decarboxylated to hydrocarbons; the number of carbon atoms per molecule of the latter is one less than that in the original acid.

Dilute aqueous solutions of glycerol and alcohol have been analysed using a multistage reaction vessel in which, in accordance with the scheme described earlier, the original substances undergo quantitative conversion to propene and ethane, whose gas-chromatographic analysis presents no difficulty.

It should be noted that, in the decarboxylation of each acid, only one product is formed, whereas in the dehydration of secondary alcohols, for example, two alkenes may be formed.

6. ESTERIFICATION

Carbonyl compounds, whose determination by ordinary chromatographic methods often presents difficulty, are esterified directly in the column or before the column and are analysed in the form of esters of organic or inorganic acids. Esterification in reaction gas chromatography is also used for the group identification of the individual class of compound in the analysis of complex mixtures.

Drawert and coworkers[1-3,39,40] developed a method for the analysis of alcohols in dilute aqueous solutions in the form of their nitrite esters. The esters are formed in a reaction vessel placed before the chromatographic column in the stream of carrier gas. The water which is present in the specimen and which interferes in the analysis of certain alcohols is absorbed in a drying tube containing calcium hydride. The reaction vessel consists of a stainless steel tube (length 8–12 cm, diameter 10 mm) filled with sterchamol and sodium nitrite (ratio 1 : 1). The nitrite esters are formed at 160–200°. The process of ester formation is improved considerably and takes place quantitatively if the specimen is acidified beforehand with tartaric or oxalic acid. The method was used to determine traces of ethanol (concentration 1×10^{-5}%) in blood.

Anders and Mannering[9] showed that the introduction of acetic or propionic anhydrides into the chromatographic column several seconds before the introduction of specimens of certain organic compounds, such as primary or secondary amines or compounds containing an alcoholic or phenolic hydroxyl, leads to the direct formation, in the column, of propionates or acetates whose retention times are different from those of the original compounds. Comparison of two chromatograms for the esterified and non-esterified specimens gives the necessary information for the qualitative and quantitative analysis of complex compounds of different classes. The use of this method, which is called[44] "the peak displacement method", makes it possible to determine naphth-1-ol, *p*-phenylphenol, ephedrine,

TABLE 3. The use of esterification in the analysis of some mixtures of compounds*.

Compound	Column temperature, °C	Volume of 0.5% solution, ml	Without acetic anhydride: retention time, min (area, cm²)	With acetic anhydride: area for esterified compounds, cm²	With acetic anhydride: retention time, min (area of displaced peaks, cm²)
Amphetamine	125	0.5	2.8(70)	0	18.7(4.8)
Ephedrine	125	4.0	9.2(21.0)	0	63.0(10.8)
Naphth-1-ol	150	0.5	6.8(6.7)	3.4	9.1(2.0)
p-Phenylphenol	150	1.0	16.3(12.1)	2.7	23.1(6.0)
Codeine	215	1.0	14.3(18.2)	16.6	20.9(0.3)
Morphine	215	6.0	16.5(15.8)	0	20.3(22.5) 29.2(11.5)
Testosterone	235	1.0	12.4(10.4)	8.6	16.8 (0.6)
Diosgenin	250	3.0	34.7 (68.4)	11.0	47.7 (5.0)
Digitoxigenin	275	5.0	23.7(21.7)	6.9	28.0 (0.6)

* 0.5% solutions of each compound were prepared in methanol, ethyl acetate, or tetrahydrofuran.

codeine, and their derivatives at temperatures in the range 125–275°. Table 3 shows that the retention times of the esterified compounds are much higher and this can be used for identification purposes.

7. SAPONIFICATION

In the analysis of esters the determination of mixed esters is of interest; this can be carried out by saponification, followed by chromatographic analysis of the alcohols formed.

This method was used successfully by Janak et al.[45] for the identification of esters of malonic acid. The reaction vessel (Fig. 5), placed at the outlet from a laboratory chromatograph with a katharometer, was filled with sterchamol with 40% potassium hydroxide deposited on its surface. Steam from water boiling in flask *D* was passed directly to the reaction vessel. After saponification of the high-boiling ester, a specimen of gas containing the vapour of the corresponding alcohols was collected at the outlet from the reaction vessel. The specimen taken was then introduced into a chromatograph with a flame-ionisation detector, where the alcohols formed on saponification were analysed. As an example, Fig. 6 gives the chromatograms for the products of the saponification of various esters of malonic acid.

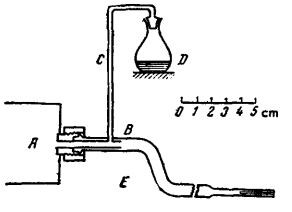


Fig. 5. Assembly for the saponification of ester fractions at the chromatograph outlet: *A*) detector; *B*) reaction vessel; *C*) tube; *D*) flask with boiling water; *E*) reaction vessel thermostat.

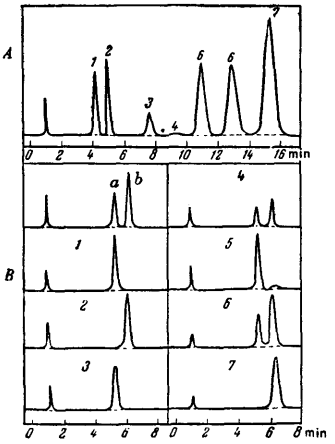


Fig. 6. Identification of esters of malonic acid from the saponification products: *A*) chromatogram of mixture of esters (Apiezon L, 220°); *B*) chromatograms of alcohols in a synthetic mixture [*a*) methanol; *b*) ethanol] and samples of saponified fractions 1–7 (triethanolamine, 60°): 1) methyl phenylacetate; 2) ethyl phenylacetate; 3) dimethyl phenylmalonate; 4) methyl phenylmalonate; 5) dimethyl ethylphenylmalonate + traces of diethyl phenylmalonate; 6) methyl ethyl ethylphenylmalonate; 7) diethyl ethylphenylmalonate.

8. FORMATION OF NON-VOLATILE COMPOUNDS

Of considerable importance in the qualitative and quantitative interpretation of the chromatograms of natural hydrocarbon mixtures are the methods of identification in reaction gas chromatography which involve the selective removal of certain classes of compound from the mixture. Thus sulphuric acid forms non-volatile compounds with alkenes. Martin[6] made use of this property of sulphuric acid in a reaction vessel (20.0 × 0.4 cm) filled with silica gel treated with sulphuric acid (2 : 3). The reaction vessel was placed in the gas-chromatographic set-up before the chromatographic column. It was shown that the absorption of monoalkenes, dialkenes, cycloalkenes, and alkynes, up to at least the C_8 fraction, takes place quantitatively in a stream of carrier gas in the temperature range 20–50°. The chromatograms given in Fig. 7 characterise fairly clearly the "subtraction method", as described by its author.

Mercury(II) perchlorate can also be used successfully for the selective removal of alkenes from a complex mixture[46]. A reaction vessel (25.0 × 0.8 cm) filled with firebrick moistened with a 1 M solution of mercury(II) perchlorate in 2 M perchloric acid (firebrick : solution ratio = = 1 : 1) is placed before the chromatographic column. Unlike the reaction vessel containing sulphuric acid, the vessel containing mercury(II) perchlorate absorbs only alkenes and does not absorb aromatic hydrocarbons.

The ordinary version of the subtraction method suffers from a number of disadvantages, chief of which are the need to obtain two chromatograms and the low accuracy of the determination for the case of a low concentration of component being removed in a general unresolved chromatographic peak. These disadvantages can be avoided by

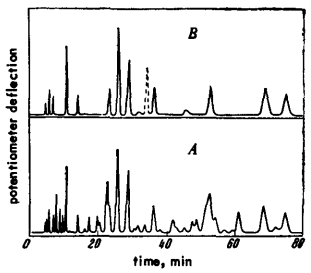


Fig. 7. Chromatograms of petroleum products from catalytic cracking (complex mixture of C_3–C_6 hydrocarbons); experimental conditions: stationary liquid phase — 10% quinoline on brick; length of column 10.5 m; temperature of column 25°; carrier gas velocity (nitrogen) 60 ml min^{-1}; volume of specimen 5 μl: *A*) without reaction vessel containing H_2SO_4; *B*) with reaction vessel containing H_2SO_4 (see Table II in Ref. 43 for interpretation of peaks).

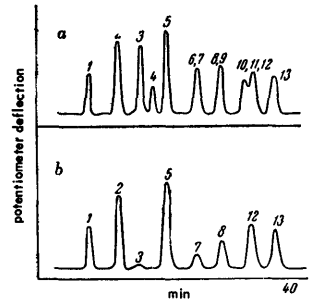


Fig. 8. Chromatograms of mixtures of C_1–C_6 monobromoalkanes on a column containing Tween 60: *a*) reaction vessel without $AgNO_3$; *b*) reaction vessel containing $AgNO_3$:
1) bromomethane; 2) bromoethane; 3) 2-bromopropane; 4) 2-bromo-2-methylpropane; 5) 1-bromopropane; 6) 2-bromobutane; 7) 1-bromo-2-methylpropane; 8) 1-bromobutane; 9) 2-bromo-2-methylbutane; 10) 2-bromopentane; 11) 3-bromopentane; 12) 1-bromo-3-methylbutane; 13) 1-bromopentane.

using the direct method of determining the individual-group composition of complex mixtures, in which the mixture to be analysed is separated on a chromatographic column, after which only those components of the mixture which are absorbed by the selective absorber of a differential analyser are recorded. This is achieved by placing the selective absorber between the katharometer chambers[47].

Since the analyser should record very low, rapidly-changing concentrations of substances in the chromatographic peaks of different compounds against a background of carrier gas and non-absorbed compounds, and also analyse solid and liquid substances in a gaseous phase, it must satisfy special requirements: (1) the dead space in the absorber should be small, relative to the volume of the carrier gas in which the component being analysed is distributed; (2) it is desirable that the sensitivity of the detector be the same for different compounds; and (3) the absorber should have an appreciable capacity and should absorb rapidly compounds of a definite class.

In addition to group reagents, use is also made of specific reagents reacting with one or a few compounds. For example, water is absorbed using compounds such as Anhydrone, calcium chloride, phosphorus pentoxide, etc.

The method of selective absorption has been used successfully to determine the isomeric bromo-hydrocarbons, 2-bromobutane and 1-bromo-2-methylpropane, which are generally eluted as a single peak in chromatographic analysis. The reaction vessel consisted of a 0.8 cm diameter glass tube filled with various reagents: the first layer (3 cm) consisted of silver nitrate on diatomite (1 : 1), the second (2 cm) consisted of sulphuric acid on diatomite, and the third (1 cm) consisted of disodium phosphate on diatomite. The layers in the reaction vessel were separated from one another by a layer of diatomite brick. The reaction vessel was placed before the separating column. At room temperature, 2-bromobutane is absorbed quantitatively by silver nitrate, whereas 1-bromo-2-methylpropane undergoes almost no reaction with this reagent. By comparing the chromatograms (Fig. 8), it is possible to calculate the concentrations of compounds which are not separated by ordinary gas chromatography.

Gil-Av and Herzberg-Minzly[48] extended the range of the subtraction method by proposing for the identification of peaks due to unknown compounds the use of relatively slow chemical reactions, leading not to complete but merely to partial absorption of the peaks ("the partial subtraction method"). As an example, let us consider the reaction between dienes with conjugated bonds (the components absorbed) and a dienophilic stationary liquid phase — chloromaleic anhydride. The reaction products are non-volatile and remain in the reactor column. The compounds being analysed are identified from the retention volume data and also by quantitative estimation of the rates of the chemical reactions with the stationary liquid phases. For example, the determination of the *cis*- and *trans*-isomers of 1,3-dienes is based on the fact that the *trans*-isomer reacts more rapidly with the dienophilic phase than the *cis*-isomer.

Ray[49] was one of the first to use the method of halogenation, leading to the formation of high-boiling compounds in a gas-chromatographic set-up, for the determination of impurities in ethylene. It was shown that removal of ethylene from the mixture being analysed takes place on a column containing 40% liquid bromine deposited on carbon, as a result of the formation of heavy bromo-derivatives of ethylene. The processes of bromination, adsorption (removal), and subsequent volumetric chromatographic separation of the light impurities were combined in a single instrument. The method made possible the quantitative determination of traces of hydrogen, nitrogen, carbon monoxide, methane, and ethane, present in ethylene in very low concentrations.

In reaction gas chromatography impurities accompanying a given compound are sometimes determined using fillers in the separating columns which "selectively retain" certain compounds. The formation of hydrogen bonds can also be regarded as a chemical reaction. Ackman and Burgher[50] made use of the formation of hydrogen bonds between macromolecular alcohols and the stationary liquid phase in a column to determine these impurities. It was shown that at 180–240° higher aliphatic alcohols are completely absorbed and retained by a separating column containing a polyester phase (diethyleneglycol succinate or

diethyleneglycol succinate containing 2% phosphoric acid) on the carrier. The non-alcoholic impurities in the higher aliphatic alcohols are retained on the polyester phase to an insignificant extent.

It is also of interest to supplement the ordinary method involving the selective absorption of certain compounds by subsequent gas-chromatographic analysis of the resulting non-volatile compounds; for this purpose it is necessary either to alter the temperature conditions of the experiment or to carry out new chemical changes.

9. OXIDATION OF ORGANIC COMPOUNDS

The oxidation of organic compounds is used in reaction gas chromatography to increase the sensitivity and accuracy of katharometers, to simplify quantitative calculations on the chromatograms, and also to reduce a complicated analytical problem to a simpler problem which has already been solved. A new method for the analysis of amino--acids was proposed by Zlatkis and Oro[38,51]. The amino--acids are oxidised to volatile aldehydes at 130° in a special reaction vessel placed before the chromatographic column and containing 30% ninhydrin on kieselguhr. The mixture of aldehydes formed was separated on the chromatographic column and passed to a reaction vessel for conversion into methane[37]. This method (where the separating column is placed between two reaction vessels) makes it possible to carry out the quantitative analysis of amino-acids in aqueous solutions at amino-acid concentrations down to 10^{-5}%. The determination was carried out for a mixture of amino-acids containing alanine, α-amino-n-butyric acid, valine, norvaline, leucine, isoleucine, and norleucine. To improve the sensitivity and accuracy of detection, the fractions leaving the separating column are often oxidised and converted into carbon dioxide and water in a special reaction vessel placed before the detector[52]. Quartz or metallic tubes of different lengths (10–20 cm) and diameters (0.6–1.5 cm), filled with copper oxide wire, are used as reaction vessels. At 700–800° the fractions or individual compounds separated by gas chromatography undergo combustion on copper oxide with the formation of CO_2 and H_2O. Water is removed, beyond the oxidation reaction vessel, in absorption tubes containing calcium chloride, phosphorus pentoxide, or other effective absorbents.

The increase in sensitivity when the substances are analysed as carbon dioxide is due to the increase in the number of molecules being analysed, since one molecule of original substance gives several molecules of carbon dioxide. For example, the oxidation of one molecule of heptane gives seven molecules of carbon dioxide, so that the sensitivity of detection increases by a factor of 7. A particularly sharp increase in sensitivity (carrier gas nitrogen) is achieved by using a two-stage reaction vessel in which the organic compound fractions are oxidised to CO_2 and H_2O and the water is reduced to hydrogen[53]. A tube (30.0 × × 0.4 cm) filled with copper oxide and finely-ground reduced iron is used as reaction vessel. The tube is heated to red heat (700–800°). After leaving the reaction vessel, the gases pass through a short soda lime column to remove carbon dioxide.

The chromatogram given in Fig. 9 shows the increase in sensitivity when various methods of converting the mixture of substances, before the latter reaches the katharometer, are used.

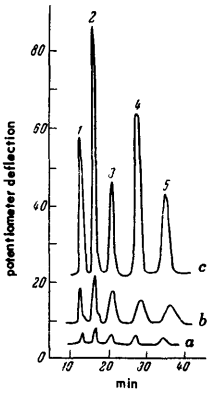


Fig. 9. Change in the sensitivity of the determination of organic compounds when preliminary conversion is used; chromatograms of equal-weight mixtures:
1) cinnamaldehyde; 2) butyl benzoate; 3) coumarin; 4) phenyl propylbutyrate; 5) naphthyl phenyl ketone; experimental conditions: stationary liquid phase — 20% silicone oil on Celite 545; detector — katharometer; carrier gas — nitrogen at 13 ml min^{-1}; column temperature 195°; weight of specimen 1 mg;
a) without conversion; *b*) conversion into carbon dioxide; *c*) conversion into hydrogen.

TABLE 4. C : H ratio in organic compounds, obtained from the peak areas (standard deviations of values given not greater than 3%; benzene used for calibration).

Substance	Peak area, cm^2		Ratio of peak areas (H_2 : CO_2)	C : H ratio	
	H_2	CO_2		calculated	observed
Benzene	634	140	4.53	1.00	1.00
Cyclohexane	515	55.6	9.26	2.00	2.04
Ethyl ether	547	47.9	11.42	2.50	2.52

The oxidation method is used successfully for the elementary analysis of organic compounds[54,55].

A method has been developed[56,57] for the continuous determination of the carbon and hydrogen contents of volatile organic compounds which have previously been separated on a chromatographic column. The conversion is carried out using a two-stage oxidation–reduction reaction vessel (60.0 × 0.6 cm tube) at 725°. After leaving the reaction vessel, the gases were separated on a supplementary column containing acetonylacetone on Celite and detected with a thermal-conductivity detector. The results are shown in Table 4.

In some cases[58,59] quantitative oxidation is used for the continuous radiometric analysis of substances, labelled with ^{14}C and ^{3}H, on leaving the chromatograph. The method involving the detection of the compounds being analysed after their quantitative conversion into CO_2 has been used for the analysis of ethane–ethylene and propane–propene fractions[60], phenylchlorosilanes[61], and other purposes[62–64].

10. DETERMINATION OF WATER

Water is an important component of many systems to be analysed. In the analysis of specimens containing water, two problems arise: (1) the drying of the specimen, and (2) the quantitative determination of the water, The determination of water by the ordinary chromatographic method presents certain difficulties because of its strongly polar character. In some cases, when the water is present in the specimens in sufficient quantities, it can be determined, for example, on columns containing mono- and poly-ethyleneglycol, but the quantitative estimation of the moisture content of specimens with low water content is extremely difficult. The use of reaction gas chromatography makes it possible to analyse specimens containing down to 2×10^{-4}% of water[65].

When a reaction vessel containing calcium carbide is placed before the chromatographic column, the water in the mixtures being studied is converted into acetylene, whose determination by gas chromatography presents no difficulty.

If the calcium carbide in the reaction vessel is replaced by calcium hydride, the reaction of CaH_2 with water gives hydrogen, which is readily determined by chromatographic analysis. The problem of converting water quantitatively into hydrogen and acetylene in heterogeneous systems is not simple and this operation is a source of experimental error. These sources of experimental error are avoided in a method[66,67] for the determination of traces of water in hydrocarbons, based on the gas-chromatographic determination of the quantity of hydrogen liberated as a result of the reaction between the water dissolved in the liquid specimen under study and a solution of sodium aluminium hydride in the dimethyl ether of diethyleneglycol; the sensitivity of the method is 2×10^{-4}%.

11. QUALITATIVE CHEMICAL REACTIONS

The identification of the components of complex mixtures in gas-chromatographic analysis from retention volume data alone does not always give correct results, since many substances of different classes may have the same retention volumes on the same stationary liquid phase.

Fractions separated chromatographically can be identified by making use of the qualitative chemical reactions of group analysis (Table 5).[68]

The components of the specimen were prepared on an ordinary 1.83 mm analytical column packed with squalene on kieselguhr. Beyond the detector (katharometer) the gas stream was split into five separate streams by means of a special device. Each stream was directed into a tube (diameter 1 cm, height 3.5 cm) filled with a suitable reagent for qualitative functional group analysis. The change in the colour in one of the tubes indicated the class of compound being eluted. For the rapid replacement of the tubes containing the reagents (this is particularly important in the identification of chromatographic peaks with similar retention volumes), the gas stream was directed by means of a three-way tap into one of a series of five tubes. After the compound corresponding to a given chromatographic peak had passed through the tubes containing the five reagents, the gas stream was directed to the next series of tubes.

The composition of the specimens was determined from retention volume data and the results of the qualitative functional group analysis. Each substance was determined by comparing the corrected retention volume with the calibration graph for the corresponding homologous series. Since the plot of log V versus n, where V is the retention volume and n the number of carbon atoms in the compound, is linear for two compounds, it is possible to construct this graph when the retention volumes are known.

As an example of the determination of the composition of a complex mixture, let us consider the chromatogram and the results of qualitative analysis given in Fig. 10. Although the chromatogram consists of five peaks, ten compounds were identified. In particular, the first peak corresponds to two compounds — ethanol and propan-2-one.

Thus by using the reagents for qualitative group analysis in chromatography, it is possible to detect substances of a definite class of compound in the fractions leaving the chromatographic column.

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The above examples are evidence of the wide scope and the rapid development of reaction gas chromatography as

TABLE 5. Characteristics of reagents for functional group analysis.

Type of compound	Reagent	Characteristics of positive test; colour of solution or precipitate	Minimum sensitivity, mg	Compounds detected
Alcohols	$K_2Cr_2O_7$–HNO_3 cerium nitrite	pale blue amber	20 100	C_1–C_8 C_1–C_8
Aldehydes	2,4-DNPH Schiff's reagent	yellow precipitate pink	20 50	C_1–C_6
Ketones	2,4-DNPH	yellow precipitate	20	C_3–C_8 (methyl-ketones)
Esters	Fe hydroxamate	red	40	C_1–C_8 (acetates)
Thiols	Na nitroprusside isatin $Pb(OAc)_2$	red green yellow precipitate	50 100 100	C_1–C_9
Sulphides	Na nitroprusside	red	50	C_2–C_{12}
Amines	Ginsberg's reagent Na nitroprusside	orange red, 1° pale blue, 2°	100 50 50	C_1–C_4 C_1–C_4 C_1–C_4 diethyl and dipentyl
Nitriles	Fe hydroxamate–propyleneglycol	red	40	C_2–C_5
Aromatic	HCHO–H_2SO_4	wine red	20	C_6H_6–$C_{10}H_{14}$
Aliphatic	HCHO–H_2SO_4	ditto	40	(C_2H_6)?
Halogeno-derivatives	alcoholic $AgNO_3$ solution	white precipitate	20	C_1–C_5

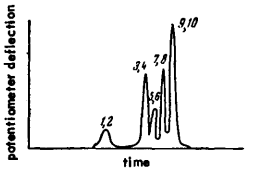


Fig. 10. Identification of compounds in a complex 10-component mixture; experimental conditions: 125°; carrier gas velocity 50 ml min^{-1}; volume of specimen 2.0 μl:
a) alcohol and ketone, ROH, RCOR′; *b*) ketone and ester, RCOR′, RCOOR′; *c*) thiol, RSH; *d*) aldehyde, alcohol, aromatic hydrocarbon, RCHO, ROH, ArR; *e*) aldehyde and aromatic hydrocarbon, RCHO, ArR.

an analytical method. The development of analytical reaction gas chromatography is taking place in two directions: (1) the development of new methods which make it possible to extend the methods of gas chromatography to the analysis of compounds which cannot be analysed by the ordinary form of gas chromatography (e.g. the analysis of polymers, salts of organic acids, etc.); (2) the development of simple convenient practical methods for the analysis of specific systems (particularly in biochemical studies) whose analysis requires complex and expensive equipment (capillary chromatography, electron-capture detectors, etc.). These methods are of particular importance for carrying out specific analyses in industry and in the laboratory.

Thus the introduction of a new "variable" (chemical reactions) into gas chromatography has led to the creation of a promising new form of chromatography — reaction gas chromatography. The skilful use of this "variable" will undoubtedly have a positive influence on the development of practical gas-chromatographic methods for the analysis of a wide variety of mixtures.

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