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USE OF CHEMICAL METHODS FOR THE PREPARATION OF STANDARD MIXTURES FOR QUALITATIVE ANALYSIS BY GAS CHROMATOGRAPHY

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1. INTRODUCTION

The most simple and reliable method for the identification of peaks of unknown substances by gas chromatography is that involving the use of retention data[1–3]. However, the use of this direct method is often complicated as there may be a shortage of the required chemically pure substances (standards), their synthesis may be very difficult or they may be too expensive. These difficulties occur particularly in the gas chromatographic analysis of hydrocarbons and natural substances.

However, this problem may be solved by the careful utilization of chemical reaction methods. These methods are based on the fact that one or several available substances will react under known conditions to yield one compound or a mixture of

compounds the composition of which is described in the literature or can be precisely predicted. The mixture obtained then serves as a standard mixture for comparison in the measurement of the retention data of individual components on a suitable column.

The present survey concerns only one aspect of the use of standard mixtures, *viz.* their use in the qualitative calibration of the chromatograph for practical work, without reference to the problems of quantitative calibration of the instrument with the use of standard mixtures.

The use of reaction methods in order to prepare standard mixtures was first studied by Simmons *et al.*[4] in 1960. Although other efficient methods for the preparation of standard mixtures were suggested later and use of chemical methods has been described in a number of papers, the extent of their utilization has not, in our opinion, made full use of the possibilities available.

Therefore, one of the aims of this review is to increase the interest of researchers working in the field of chromatography in these possibilities.

2. USE OF STANDARD MIXTURES IN GAS CHROMATOGRAPHY

Standard compounds are employed in gas chromatography for solving many problems, the most important of which are:

(1) the identification of unknown components in mixtures being analyzed;

(2) physico-chemical measurements;

(3) the preparation of new sorbents and the development of improved analytical methods.

Owing to the fact that the basic characteristics of the chromatographic process (retention data and broadening of the chromatographic zone) are independent of the presence of other substances[3,5] with a sufficiently small sample, the precision and reliability of the results obtained are independent of whether one substance or a mixture of substances is employed. There are not many exceptions to this rule, and those that do occur can usually be accounted for by a non-linear adsorption isotherm of the chromatographed substances on the surface of the adsorbent or solid support[1,3,6,7] or by the use of too large a sample charge, when the column functions in a "state of oversaturation"[8].

If the sample being chromatographed contains one known compound rather than a mixture of standards, it takes a longer time to measure the retention data of one component and the gas chromatographic instrument must function for a longer time. Also, the price of a mixture is usually lower than the sum of the prices of the pure components that constitute it. A drawback of the method of standard mixtures, however, is its lower versatility: when the retention data of a single component are to be measured, it is necessary to analyze the whole mixture in order to obtain its chromatographic characteristics. However, this drawback can hardly be considered as a serious objection to employing mixtures of known composition in chromatography, as the substantial lengthening of the time of the experiment when this method is used can be avoided or reduced by connecting the columns in series and, after the separation on the first column has been completed, by isolating the uninteresting compounds by backflushing or by using temperature programming[9]. Further, standard mixtures can be added to the sample being analyzed in order to aid in the identification of unknown

components. The identification is then performed by comparing the chromatogram of the initial sample with that of the new sample containing both the initial and the standard mixtures. This method has proved especially suitable in analysis with temperature programming. This method is the reverse of that of subtraction, which is widely used in reaction chromatography (see, for example, refs. 2 and 10). In this instance, the peak areas are calculated by the method described by Berezkin *et al.*[11]. In the analysis of the chromatogram, the characteristic of the compound to be identified is then not only its retention time, but also its content in the mixture. Therefore, the contents of the individual components in the mixture must be significantly different. Although only the application of standard mixtures in qualitative analysis is considered in this review, the use of these mixtures in the quantitative calibration of the chromatogram is also possible, so that the application of standard mixtures in gas chromatography can be very extensive.

3. PREPARATION OF STANDARD MIXTURES BY METHODS INVOLVING CHEMICAL REACTIONS

Standard mixtures for qualitative analysis can be prepared by any chemical reactions which meet the following requirements:

(1) a mixture of products of known composition is produced reproducibly;

(2) the mixture of the products prepared is stable.

In addition, it is desirable that the initial substances should be easily accessible, that the reaction does not take much time, and that non-volatile reaction products, if easily produced, can readily be separated from the volatile products. These conditions are met by a number of reactions[12–14], and it is the task of the researcher to choose the optimum method for a particular synthesis. In order to solve this problem, it is useful to consult an organic synthesis expert.

In order to prepare reaction mixtures of known composition, one can employ:

(1) reactions that proceed almost quantitatively in one direction;

(2) equilibrium reactions, in which the composition of the reaction products can easily be "frozen";

(3) combined reactions with a low degree of conversion;

(4) destructive reactions.

It is expedient that the synthesis be carried out on a micro-scale, as the sensitive detectors that are used in gas chromatography make it possible to analyze samples containing 10^{-6}–10^{-9} g of the components. The pure initial substances for the synthesis of standard compounds can be isolated by high-efficiency preparative gas chromatography[15]. The reactions employed for preparing standard mixtures can take place either outside the gas chromatograph or in a special reactor that is part of the gas chromatographic instrument. In the latter instance, one can use techniques of analytical reaction gas chromatography[10], especially reactions on the chromatographic column and in the syringe.

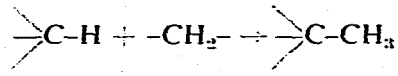
In conclusion, we would like to point out that although reaction methods of preparation of standard mixtures are of general importance, they are particularly useful in the preparation of mixtures of hydrocarbons of known composition.

4. USE OF SOME CHEMICAL METHODS IN THE PREPARATION OF STANDARD MIXTURES

A. Pre-chromatographic methods

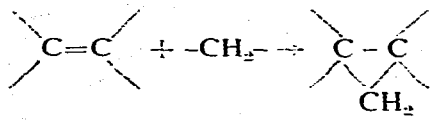
(a) Introduction of a methylene group

At present, the introduction of a methylene group is the most commonly used method in the preparation of standard mixtures in gas chromatography. The introduction of a methylene group was described by Doering *et al.*[16], and the use of this reaction in the preparation of mixtures of hydrocarbons of known structure was suggested by Simmons *et al.*[4] and Dvoretzky *et al.*[17]. The methylene group is attached to a C–H bond, thus producing the next highest member of the homologous series:



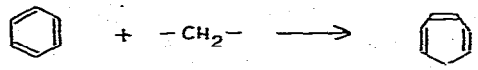
(1)

The addition of a methylene group to a double bond results in cyclopropane derivatives:



(2)

while the reaction of a methylene group with aromatic compounds leads to derivatives of tropylidene:



(3)

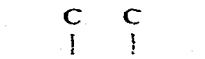
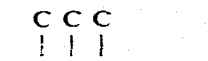
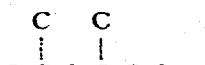
As far as the preparation of standard mixtures is concerned, the first reaction has the greatest significance.

Simmons *et al.*[4] used the following procedure for introducing a methylene group A mixture of 2 ml of pure hydrocarbon and 1 ml of 40% potassium hydroxide solution was cooled in a flask placed in an ice–water bath, 37 mg (0.40 mmole) of N-nitroso-N-methylurea were added to the flask, which should produce 0.25 mmole of diazomethane, and the mixture was stirred until the complete dissolution of the nitrosomethylurea. The diazomethane, which originated in the aqueous phase, passed into the hydrocarbon phase. The hydrocarbon phase was decanted off and dried over solid potassium hydroxide, then this hydrocarbon solution of diazomethane was placed in a flask provided with a drying tube containing calcium sulphate and irradiated with a sun-lamp at a distance of 6 in. The flask was cooled with water during irradiation. As soon as the yellow tint of diazomethane disappeared (in about 1–2 h), the irradiation was stopped and a sample of the reaction mixture was analyzed by gas chromatography. The reaction is of a random, statistical character and its course does not depend on the type of bond (vinyl, alkyl) or the type or carbon atom (primary, secondary) present. The course of the reaction and the origination of the products with isooctane (2,2,4-trimethylpentane) can be considered as an example.

Isooctane has a total of 18 C–H bonds, but some of them are equivalent, which results in the formation of the same products, so that it is possible to group several reactions that give the same products. The products of these reactions together with a statistical estimation of the concentrations and the actual yields of the products are

TABLE 1

COMPARISON OF THE THEORETICAL AND ACTUAL RECOVERIES OF THE INDIVIDUAL PRODUCTS OF INSERTION OF METHYLENE GROUPS INTO 2,2,4-TRIMETHYLPENTANE

Structure of the isomeric products	*Characteristics of the C–H bonds in the initial hydrocarbon*			*Actual recovery of the product (%)*
	Type of bond	*Number of bonds*	*Content of the given bond in the initial hydrocarbon (%) (theoretical recovery)*	
	Primary	9	50.0	50.5
	Secondary	2	11.1	10.4
	Tertiary	1	5.6	3.8
	Primary	6	33.2	35.3

quoted[3] in Table 1. It is apparent that the statistical estimations are close to the actual yields, which permits the identification of these products by gas chromatography, by virtue of their contents in the reaction mixture.

Makarova *et al.*[18] studied the application of the introduction of a methylene group, which was employed in the preparation of open-chain alkanes and the synthesis of derivatives of cyclic hydrocarbons in order to prepare standard mixtures for gas chromatography. It was found that the methylation of C_7–C_9 cycloalkanes with diazomethane follows the usual course of the methylation of saturated hydrocarbons, *i.e.*, the replacement of hydrogen atoms by methylene groups takes place evenly at carbon–hydrogen bonds of any type.

As an example, let us consider the products resulting from the methylation of ethylcyclopentane and methylcyclopentane. Seven isomeric C_8 hydrocarbons should be produced in the following proportions: 3 parts of *n*-propylcyclopentane, 2 parts of isopropylcyclopentane, 1 part of 1,1-methylethylcyclopentane, 2 parts of *cis*-1-methyl-2-ethylcyclopentane, 2 parts of *trans*-1-methyl-2-ethylcyclopentane, 2 parts of *cis*-1-methyl-3-ethylcyclopentane and 2 parts of *trans*-1-methyl-3-ethylcyclopentane. The experimental results of the determination of the products of the methylation of methylcyclohexane[18] are quoted in Table 2. It is evident that the methylation of cyclic hydrocarbons obeys the same regularities as the methylation of open-chain hydro-

TABLE 2

METHYLENE INSERTION REACTIONS OF ETHYLCYCLOPENTANE AND METHYLCYCLOHEXANE

Initial hydrocarbon	*Methylene insertion products*	*Concentration expected (%, w/w)*	*Concentration found (%, w/w)*
Ethylcyclopentane	Propylcyclopentane	21.42	24.9
	Isopropylcyclopentane	14.28	15.8
	1-Methyl-1-ethylcyclopentane	7.14	7.1
	cis-1-Methyl-2-ethylcyclopentane	14.28	14.5
	trans-1-Methyl-2-ethylcyclopentane*	14.28	11.2
	cis-1-Methyl-3-ethylcyclopentane	14.28	15.3
	trans-1-Methyl-3-ethylcyclopentane*	14.28	11.2
Methylcyclohexane	Ethylcyclohexane	21.42	18.8
	1,1-Dimethylcyclohexane	7.14	7.2
	cis-1,2-Dimethylcyclohexane	14.28	15.3
	trans-1,2-Dimethylcyclohexane	14.28	16.0
	cis-1,3-Dimethylcyclohexane	14.28	15.3
	trans-1,3-Dimethylcyclohexane	14.28	19.8**
	cis-1,4-Dimethylcyclohexane	7.14	
	trans-1,4-Dimethylcyclohexane	7.14	7.6

* Separation carried out with the use of a capillary column with dibutyl tetrachlorophthalate as the stationary phase.

** Determined as a sum.

carbons, *i.e.*, it proceeds strictly statistically, and the composition of the products prepared agrees well with expectation. The significance of this method lies in the fact that it can be used to prepare a large number of stereoisomers, the synthesis of which is usually very difficult and not always possible by other methods.

At present, the introduction of a methylene group is widely used for the preparation of standard mixtures. Examples are the preparation of the C_{10} hydrocarbons of the bisbicyclo[3.3.0]octane series[19], methylbicyclo[3.3.1]nonane[20], 1,2,3,4,5-pentamethylcyclohexane and 1,2,3,4,5,6-hexamethylcyclohexane[21], alkyladamantane[22], trialkyl-substituted cyclohexanes[23], 1,2,3-tri- and 1,2,3,4-tetraalkylcyclopentanes[24], monomethylbicyclo[4.3.0]nonane[25] and methylbicyclo[4.4.0]decane[26].

The studies performed prove the universality of the methylene-introduction method in the preparation of mixtures of hydrocarbons that are to be used as standard mixtures.

(b) Isomerization reactions

Petrov and co-workers[27] suggested a reaction method for the preparation of C_6–C_8 alkanes, based on the isomerization of individual, readily available hydrocarbons in the presence of aluminium bromide as follows. A 10–15-ml volume of octane (isooctane or another hydrocarbon) was isomerized in the presence of aluminium bromide (15–20%, w/w) at ambient temperature for 3–12 h in a closed flask with shaking. After the reaction was completed, the reaction mixture was neutralized with 40% sodium hydroxide solution and the supernatant layer was washed, dried and distilled. The mixture of the products prepared was analyzed on a capillary column, employing a flame ionization detector. The chromatographic column was 70 m long

and 0.25 mm I.D. and coated with squalane. The preparation was carried out at temperatures of 30, 50 and 80°.

Starting from the generally accepted scheme of the isomerization of octanes, one can assume that the isomerization proceeds in a stepwise manner:

$$\text{octane} \rightleftarrows \underset{\text{isomers}}{\text{monosubstituted}} \rightleftarrows \underset{\text{isomers}}{\text{disubstituted}} \left(\rightleftarrows \underset{\text{with a quaternary carbon atom}}{\text{disubstituted isomers}} \right) \rightleftarrows \underset{\text{isomers}}{\text{trisubstituted}}$$

When identifying the products, it is necessary to bear in mind that reactions that involve a change in the number of tertiary carbon atoms proceed considerably more slowly than other types of isomerization reactions (*e.g.*, transfer of a radical along the chain). For instance, in the isomerization of octane, one would expect the formation mainly of trisubstituted isomers. As for monosubstituted and disubstituted hydrocarbons (regardless of the degree of conversion of the initial hydrocarbon), an equilibrium can usually be set up. As a result of the stepwise character of isomerization, it is expedient to employ 2,2,4-trimethylpentane for the preparation of trisubstituted hydrocarbons.

As destructive alkylation accompanies the isomerization by aluminium bromide, the octane isomerates contain all of the theoretically possible isomers of heptane, hexane and pentane in amounts sufficient for analysis. Hence, calibration mixtures prepared from octane and isooctane represent a group of all of the possible C_6–C_8 alkanes and can be used in the evaluation of chromatograms of gasoline fractions. Table 3 contains the relative retention data on squalane for 30 alkanes prepared in the above manner[21].

More recently, the method of isomerization has been used in the preparation of standard hydrocarbon mixtures [28–31].

(c) Radiolysis

The use of the products of the radiolysis of organic compounds as standard mixtures was suggested by Berezkin and Polak[32]. It was proved earlier that the dimeric product formed in the radiolysis of hexane in the liquid phase is the result of the recombination of two hexyl radicals[33]:

$$C_6H_{14} \rightarrow C_6H_{13} + H \tag{4}$$

$$C_6H_{13} + C_6H_{13} \rightarrow C_{12}H_{26} \tag{5}$$

Thus, the dimeric product is composed of compounds originating from the combination of two of the three possible hexyl radicals (*cf.* Table 4). Experimental results confirmed the radical mechanism of the formation of the dimeric product[34], the composition of which was completely in accordance with expectation. Therefore, mixtures of dimeric products from the radiolysis of pentane, hexane, heptane and other hydrocarbons can be used as standard mixtures in the determination of retention data of hydrocarbons.

A detailed study of the possibilities of the use of hydrocarbons produced by the radiolysis of *n*-alkanes, as standard substances in qualitative gas chromatography, was made by Armenante *et al.*[35]. The radiolysis was carried out in the following way. Samples of *n*-heptane and *n*-octane were degassed before irradiation by repeating a

TABLE 3

RELATIVE RETENTION DATA OF C_6–C_8 ALKANES ON SQUALANE AS THE STATIONARY PHASE

Hydrocarbon	*B.p. (°C)*	*Column temperature (°C)*		
		30	*50*	*80*
2,2-Dimethylbutane*	49.741	0.47	0.53	0.55
2,3-Dimethylbutane*	57.988	0.65	0.75	0.76
2-Methylpentane*	60.272	0.70	0.75	0.76
3-Methylpentane*	63.282	0.82	0.86	0.89
Hexane*	68.740	1.00	1.00	1.00
2,2-Dimethylpentane*	79.198	1.25	1.25	1.27
2,4-Dimethylpentane*	80.500	1.39	1.31	1.29
2,2,3-Trimethylbutane*	80.883	1.50	1.46	1.45
3,3-Dimethylpentane	86.064	1.80	1.77	1.66
2-Methylhexane*	90.052	2.09	1.90	1.85
2,3-Dimethylpentane*	89.784	2.18	2.10	2.00
3-Methylhexane*	91.851	2.30	2.17	2.04
3-Ethylpentane*	93.475	2.57	2.31	2.24
2,2,4-Trimethylpentane*	99.238	2.64	2.40	2.34
Heptane*	98.428	3.18	2.67	2.50
2,2,3,3-Tetramethylbutane	106.300	—	—	—
2,2-Dimethylhexane*	106.840	3.62	3.20	2.97
2,5-Dimethylhexane*	109.103	4.13	3.50	3.17
2,4-Dimethylhexane*	109.429	4.30	3.64	3.29
2,2,3-Trimethylpentane*	109.841	4.43	3.82	3.52
3,3-Dimethylhexane	111.968	4.45	4.05	3.71
2,3,4-Trimethylpentane*	113.467	4.95	4.45	3.90
2,3,3-Trimethylpentane*	114.760	5.22	4.82	4.22
2,3-Dimethylhexane*	115.607	5.42	4.82	4.22
2-Methyl-3-ethylpentane	115.650	5.42	4.82	4.22
2-Methylheptane*	117.646	5.73	5.0	4.33
4-Methylheptane	117.709	5.92	5.13	4.34
3,4-Dimethylhexane	117.725	5.97	5.32	4.40
3-Methylheptane*	118.925	6.16	5.40	4.40
3-Ethylhexane	118.534	6.44	5.62	4.79
Octane*	125.665	8.17	7.15	5.82

* The individual hydrocarbons used in the analysis of the composition of the standard mixtures.

cycle of freezing, evacuation and melting in a small glass capillary, 45 mm long and 1.5 mm I.D. The ampoules were then sealed under vacuum and irradiated with charges of up to 22 Mrad of γ-radiation from a ^{60}Co source at room temperature. The glass capillary with the radiolysis products was placed in a small bulb-crusher, which re-

TABLE 4

COMPOSITION OF THE DIMERIC PRODUCTS OF THE RADIOLYSIS OF HEXANE RESULTING FROM THE RECOMBINATION OF HEXYL RADICALS

Reacting radical	$CH_3(CH_2)_4CH_2$	$CH_3(CH_2)_3CHCH_3$	$CH_3(CH_2)_2CHCH_2CH_3$
$CH_3(CH_2)_4CH_2$	Dodecane	5-Methylundecane	4-Ethyldecane
$CH_3(CH_2)_3CHCH_3$	—	5,6-Dimethyldecane	4-Ethyl-5-methylnonane
$CH_3(CH_2)_2CHCH_2CH_3$	—	—	4,5-Diethyloctane

placed the usual gas chromatographic inlet port, and crushed in the carrier gas stream. This method of sample introduction prevents the fractionation of the reaction mixture and affords a precise quantitative analysis of a wide range of reaction products. Some of the conditions of the radiolysis, such as the shape of the ampoule, nature of the ionizing radiation and temperature, can be altered without causing a significant change in the composition of the reaction products. It is therefore possible to prepare a wide range of standard hydrocarbons in almost any laboratory by the radiolysis of a suitable *n*-alkane.

Armenante *et al.*[35] presented a general discussion of the radiolytic spectra of *n*-alkanes and, by virtue of extensive experimental experience, formulated regularities that permitted the complete spectrum of the radiolytical products of any *n*-alkane to be predicted and the individual hydrocarbon components of these spectra to be quickly and easily identified.

The radiolysis of a C_n alkane, containing n carbon atoms, yields a number of saturated and unsaturated hydrocarbons C_r, the carbon numbers (r) of the individual reaction products varying from 1 up to $2n$. The complete spectrum of the radiolysis products can be divided into four parts, as follows.

(1) The zone of the "fragmentation products" contains saturated and unsaturated straight-chain C_1–C_{n-1} hydrocarbons. The alkanes are contained in approximately equal molar concentrations, except for methane and the C_{n-1} alkane, the contents of which are lower. The molar content of 1-alkenes is about 30% of that of the corresponding alkanes. 2-Alkenes and acetylene are produced in negligible amounts. Although the "fragmentation products" are commercially available hydrocarbons, the possibility of the rapid and easy preparation of such a wide range of standard hydrocarbons is important.

(2) The zone of "dehydrogenation products" contains all the possible C_n alkenes with one double bond and the same carbon skeleton as that of the parent *n*-alkane. However, these alkenes are not suitable as standard substances for qualitative gas chromatography because they always give two peaks, corresponding to the *cis* and *trans* forms of the alkene, on separation, the relative positions of which are very sensitive to the conditions of separation.

(3) The zone of the "products of synthesis" contains isomeric unsaturated C_{n+1}–C_{2n-1} hydrocarbons. These hydrocarbons arise from the substitution of some of the hydrogen atoms in the molecule of the initial *n*-alkane by alkyl radicals produced by the radiolytical cleavage of C–C bonds.

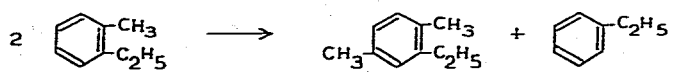
(4) The zone of "dimerization products" contains isomeric C_{2n} alkanes, which originate from combination of the radicals produced by the radiolytic cleavage of C–H bonds in the molecule of the initial *n*-alkane. If n is an even number, $n(n-2)/8$ isomers are obtained from the C_n alkane, and $(n-1)(n-3)/8$ isomers if n is an odd number. Also, the relative proportions of the isomers are characteristic of the individual types of dimer and facilitate their identification. On a non-polar stationary phase, isomeric hydrocarbons are eluted in a sequence according to their boiling points. Armenante *et al.* quoted simple formulae for the simple and rapid calculation of the boiling point of any heavy product of radiolysis. Thus, the "synthesis products" and "dimerization products" form a rarely obtained complete series of isomeric saturated hydrocarbons, which can be employed very well as standard substances in the qualitative gas chromatography of hydrocarbons.

When calibrating chromatographic columns, it is also possible to use products obtained by the action of other types of radiation (*e.g.*, ultraviolet light[36,37] and laser radiation[38,39]).

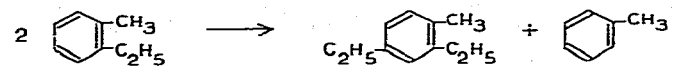
(d) Disproportionation

In addition to alkylation and isomerization reactions for the preparation of mixtures of alkylbenzene isomers, an especially useful technique is that based on disproportionation. Baumann and Csicsery[40] prepared mixtures of selected C_{10} and C_{11} alkylbenzene isomers in this way and used them for identification purposes.

The isomeric alkylbenzenes were prepared by the disproportionation of 1-methyl-2-ethylbenzene in a steel tube of 6 mm I.D., packed with 0.5 ml of silica–alumina cracking catalyst under atmospheric pressure, at a temperature of 400° and with hydrogen as diluent, the reaction period being 65 min. Methyl transfer (eqn. 6) produced ethylbenzene and dimethylbenzenes, and ethyl transfer (eqn. 7) yielded methyldiethylbenzenes and toluene.



(6)



(7)

Retention data of the mixtures of C_{10} and C_{11} alkyl aromatics obtained by the disproportionation of 1-methyl-2-ethylbenzene, separated with temperature programming from 60 to 130° at the rate of 1°/min on a capillary column coated with Ucon LB 550 X, are given in Table 5.

TABLE 5

AROMATIC C_{10}–C_{11} HYDROCARBONS RESULTING FROM THE DISPROPORTIONATION OF 1-METHYL-2-ETHYLBENZENE

r = Relative retentions of the aromatic hydrocarbons relative to 1-methyl-3-isopropylbenzene; I = retention indices of the aromatic hydrocarbons. The retention data were measured on Ucon LB 550 X as the stationary phase with temperature programming from 60 to 130° at 1°/min.

Aromatic hydrocarbon	r	I
1,3-Dimethyl-5-ethylbenzene	1.246	1147
1,4-Dimethyl-2-ethylbenzene	1.333	1163
1,3-Dimethyl-4-ethylbenzene	1.360	1168
1,2-Dimethyl-4-ethylbenzene	1.390	1174
1,3-Dimethyl-2-ethylbenzene	1.422	1180
1,2-Dimethyl-3-ethylbenzene	1.530	1202
1-Methyl-3,5-diethylbenzene	1.662	1225
1-Methyl-3,4-diethylbenzene	1.740	1239
1-Methyl-2,4-diethylbenzene	1.773	1245
1-Methyl-2,5-diethylbenzene	1.837	1256

(e) Catalytic dehydrogenation of n-alkanes

The thermal cleavage of C–C bonds (cracking, dealkylation and depolymerization) takes place in the absence of catalysts. In the presence of catalysts, C–H bonds are also cleaved and dehydrogenation will occur[41]:

$$R\text{–}C_aH_b \rightleftarrows R\text{–}C_aH_{b-2c} + cH_2 \qquad (8)$$

Thus, alkenes ($c = 1$), alkadienes ($c = 2$) and aromatics ($c = 3$), or possibly substances that contain even less hydrogen (carboids is the limiting case) arise from alkanes.

On contact catalysts, dehydrogenation takes place rather than cracking even at high temperatures, *e.g.* at 600°. Alkanes are adsorbed on the active sites of a catalyst X, and the dehydrogenation proceeds according to the scheme:

$$\begin{array}{llll} X \cdots H\text{–}CHR & X\text{–}H \cdots CHR & XH & CHR \\ \vdots & \vdots & & \| \\ X \cdots H\text{–}CH_2 & X\text{–}H \cdots CH_2 & XH & CH_2 \end{array} \qquad (9)$$

Alkenes are the primary products. The reaction is utilized in case of C_3–C_5 alkanes.

C_6 and higher alkanes are dehydrogenated, via alkenes, usually to aromatics (dehydrocyclization). The cyclization probably starts from a double bond, for instance, 1-heptene and 2-heptene are aromatized, with the same ease, to form toluene:

$$\begin{array}{ll} \text{1-heptene} & \cdots C{=}C\text{–}C\text{–}C\text{–}C\text{–}C\text{–}C \cdots \text{toluene} \\ & \quad \vdots \quad\quad\quad\quad\quad \vdots \\ \text{2-heptene} & \cdots C\text{–}C{=}C\text{–}C\text{–}C\text{–}C\text{–}C \cdots \text{toluene} \end{array} \qquad (10)$$

The catalytic dehydrogenation of *n*-alkanes is a suitable source of *n*-alkenes as mixtures of standards for the analysis of straight-chain alkenes and aromatic hydrocarbons, which can also be used as standard mixtures in the analysis of complex mixtures of hydrocarbons.

The initial substances for the preparation of mixed *n*-alkenes are pure individual *n*-alkanes. As for the catalysts, use can be made of various kinds of dehydrogenation catalyst of the oxidation type such as, for example, catalysts with the main dehydrogenation component of the oxides of chromium, molybdenum, etc., deposited on alumina or some other support[42–46]. The dehydrogenation is carried out in an isothermal reactor at temperatures of 400–500°. Deactivation of the catalyst due to coking[42], or by cyclopentadiene or furfural[47], results in the poisoning of its dehydrocyclization ability while preserving its dehydrogenation activity. Hence, the dehydrogenation over a deactivated molybdenum–alumina catalyst at a temperature of 470° with a vapour: *n*-dodecane ratio of 4.0 and a contact time over the catalyst bed of 2.5 sec, Roth *et al.*[42] achieved a 65% selectivity in the conversion to monoolefins at a 12% overall conversion of paraffin.

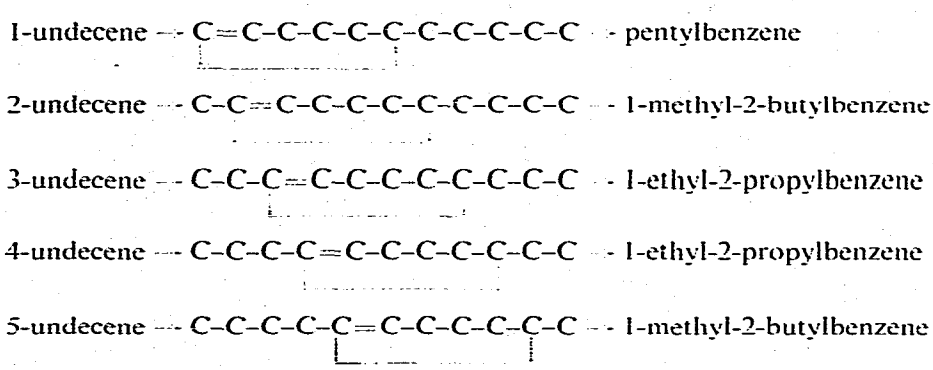
The composition of the dehydrogenation products is determined primarily by catalytic statistics. The dehydrogenation of an *n*-alkane results in a mixture of all of the theoretically possible straight-chain alkenes, particularly *n*-alkenes with internal double bonds[43,48], with a carbon number corresponding to that of the *n*-alkane. The proportions of the individual positional isomers of the alkenes are dependent on the carbon number of the *n*-alkane dehydrogenated. With an even carbon number, there are about half as many isomers with the innermost double bond as those with the double

bond in other inner positions. With *n*-alkenes with an odd carbon number, the proportions of the individual inner positional isomers are about the same (decreasing slightly as the double bond shifts towards the centre of the molecule). The ratio of the amounts of the positional (1- and 2-) isomers is approximately 1:4, and of the geometrical (*trans*- and *cis*-) isomers about 2:1.

Further, the dehydrogenation mixture contains aromatic hydrocarbons, isoalkanes, cracking products, diolefins and triolefins[42]. In order to separate *n*-alkenes from this mixture, it is possible to employ column chromatography on silica gel and to isolate aromatics at the same time. The *n*-alkenes are obtained considerably more rapidly and less laboriously in this manner in comparison with chemical syntheses of individual *n*-alkenes[49,50].

The proportions of the individual straight-chain alkenes are very similar, so that they can be separated only by the use of high-efficiency capillary columns. In the chromatohraphy of *n*-alkenes from the dehydrogenation products of C_6–C_{11} *n*-alkanes, the separation was achieved of all the theoretically possible C_6–C_{11} *n*-alkenes on a 200-m capillary column coated with squalane, the only exception being the pair of 1-decene and *trans*-4-decene[43,48]. The retention indices of the *n*-alkenes, as measured on this column, are summarized in Table 6.

The aromatic hydrocarbons from the dehydrogenation products of *n*-alkanes are mostly further dehydrogenated *n*-alkenes. The composition of the aromatic hydrocarbons from the dehydrogenation of *n*-alkanes is also given mainly by catalytic statistics according to the above cyclization scheme. For example, the dehydrocyclization of the individual positional *n*-undecenes proceeds as follows:



Thus, the following substances were found as the major aromatic components in the dehydrogenation products of *n*-octane, *n*-nonane, *n*-decane, and *n*-undecane, respectively: ethylbenzene and *o*-xylene; 1-methyl-2-ethylbenzene and propylbenzene; 1-methyl-2-propylbenzene, 1,2-diethylbenzene and butylbenzene; and 1-methyl-2-butylbenzene, 1-ethyl-2-propylbenzene and pentylbenzene[43,51]. These mixtures of aromatic hydrocarbons can also be utilized as standard mixtures.

The retention indices of aromatic hydrocarbons from the dehydrogenation of C_6–C_{11} *n*-alkanes, measured on a 200-m squalane capillary column at temperatures of 86, 100 and 115°, are listed in Table 7.

Other cleavage reactions can also be utilized for the preparation of standard mixtures of alkanes and aromatic hydrocarbons. The thermal cracking of higher

TABLE 6

STRAIGHT-CHAIN C_6–C_{11} ALKENES FROM THE CATALYTIC DEHYDROGENATION OF C_6–C_{11} *n*-ALKANES

I^S_{temp} = Retention indices of the alkenes on squalane as the stationary phase at the given column temperature.

Alkene	I^S_{80}	I^S_{100}	I^S_{115}
1-Hexene	583.1	583.6	584.0
trans-3-Hexene	591.4	591.1	590.6
cis-3-Hexene	593.0	593.3	593.7
trans-2-Hexene	596.7	596.5	596.4
cis-2-Hexene	604.6	604.9	605.4
1-Heptene	682.8	683.1	683.5
trans-3-Heptene	687.5	687.4	687.4
cis-3-Heptene	691.7	692.0	692.3
trans-2-Heptene	698.7	698.7	698.7
cis-2-Heptene	704.3	704.7	705.1
1-Octene	782.3	782.6	782.9
trans-4-Octene	784.2	784.1	784.1
cis-4-Octene	787.9	788.2	788.6
trans-3-Octene	788.4	788.2	788.0
cis-3-Octene	789.5	789.8	790.2
trans-2-Octene	797.7	797.5	797.3
cis-2-Octene	802.8	803.2	803.6
1-Nonene	882.2	882.5	882.8
trans-4-Nonene	884.2	883.9	884.4
cis-4-Nonene	884.8	885.4	886.0
trans-3-Nonene	886.6	886.4	886.5
cis-3-Nonene	887.0	887.5	888.1
trans-2-Nonene	896.6	896.4	896.6
cis-2-Nonene	901.5	901.9	902.6
cis-5-Decene	981.0	981.6	982.1
1-Decene	982.2	982.5	982.7
trans-4-Decene	982.2	982.5	982.7
cis-4-Decene	982.2	982.8	983.4
trans-5-Decene	984.0	984.1	984.7
trans-3-Decene	985.4	985.8	985.5
cis-3-Decene	985.4	985.8	986.4
trans-2-Decene	996.7	996.7	996.6
cis-2-Decene	1001.2	1001.7	1002.2
cis-5-Undecene	1077.6	1078.2	1078.9
cis-4-Undecene	1079.9	1080.5	1081.1
trans-4-Undecene	1081.0	1081.1	1081.2
trans-5-Undecene	1081.6	1081.8	1082.0
1-Undecene	1082.2	1082.4	1082.6
cis-3-Undecene	1084.7	1085.3	1085.8
trans-3-Undecene	1085.5	1085.4	1085.3
trans-2-Undecene	1096.6	1096.6	1096.5
cis-2-Undecene	1101.1	1101.5	1101.9

TABLE 7

C_6–C_{11} AROMATIC HYDROCARBONS FROM THE CATALYTIC DEHYDROGENATION OF C_6–C_{11} *n*-ALKANES

I^S_{temp} = Retention indices of the aromatic hydrocarbons on squalane as the stationary phase at the given column temperature.

Aromatic hydrocarbon	I^S_{80}	I^S_{100}	I^S_{115}
Benzene	646.6	650.4	653.6
Toluene	754.2	757.4	760.7
Ethylbenzene	844.3	847.3	851.3
o-Xylene	880.1	883.9	888.1
Propylbenzene	932.6	935.9	940.2
1-Methyl-2-ethylbenzene	961.2	964.7	968.8
Butylbenzene	1033.0	1036.0	1040.0
1,2-Diethylbenzene	1036.0	1039.5	1043.6
1-Methyl-2-propylbenzene	1042.0	1046.1	1050.5
1-Ethyl-2-propylbenzene	1113.9	1118.1	1122.3
Pentylbenzene	1129.5	1133.5	1137.6
1-Methyl-2-butylbenzene	1139.1	1143.7	1148.0

n-alkanes yields mainly 1-alkenes[52]. Through the isomerization of 1-alkenes, it is also possible to prepare mixtures of *n*-alkenes[53]. The product of the catalytic reforming of heavy petrols is a suitable material for obtaining a standard mixture of all C_6–C_{10} aromatic hydrocarbons[54]. Similarly, other products from the processing of crude oil fractions can also serve, after their modification, as useful mixed standards in connection with high-efficiency chromatography and the precise measurement of retention data.

(f) Dehydration

Kugucheva and Alekseeva[55] studied the conditions of the rapid catalytic microsynthesis of some C_5–C_6 hydrocarbons from alcohols. They found conditions under which not more than three components with constant quantitative proportions were obtained. The dehydration was carried out in the vapour phase in a flow-through system, the concentration of the initial alcohols being 10^{-2}–10^{-3}% by volume in nitrogen. Amounts of 0.2–1.0 μl of the initial liquid product were charged into a 100-ml syringe provided with a PTFE disk for mixing. The micro-reactor was a V-shaped glass tube 10 cm long and 0.2–0.4 cm in diameter. The precision of the thermostatic control was ± 3 . The mixture was expelled from the syringe through the reactor at the rate of 10 ml/sec. At the end of the reactor, the gas was taken into another syringe from which it was injected into the chromatograph. The synthesis, including the preparation operations, took 5 min. For the preparation of pentanes, a modified potassium triphosphate and alumina were used as the catalysts. There were significant differences in the concentrations of the isomeric pentanes, as can be seen from Table 8. The reproducibility was ± 10%.

TABLE 8
DEHYDRATION OF AMYL ALCOHOLS

Initial alcohol	*Reaction temperature (°C)*	*Reaction products (%, w/w)**					
		1-Pentene	*trans-2-Pentene*	*cis-2-Pentene*	*3-Methyl-1-butene*	*2-Methyl-1-butene*	*2-Methyl-2-butene*
1-Pentanol	350	70	12	18	—	—	—
2-Pentanol	250	31	21	48	—	—	—
3-Methyl-1-butanol	390	—	—	—	64	25	11
2-Methyl-2-butanol	380	—	—	—	—	64	36

* The amount of unchanged pentanol was not accounted for.

B. Reactions in the chromatographic system

This method of preparing substances is usually applicable only when rapid reactions are used, because (1) slow reactions give low yields and (2) the course of the reaction in a moving chromatographic zone tends to spread the peaks of the compounds[10]. The above requirements are met by reactions such as pyrolysis, catalytic cracking, hydrogenation and dehydrogenation. These reactions are usually performed in special reactors under conditions different from those of the chromatographic separation, but the two procedures can be carried out simultaneously. In such a case, it is necessary that the second reagent be injected a precise time after the injection of the first reagent, and this time has to be taken into account in calculating the retention time of the product. It is necessary that the retention data of both reagents be substantially different from each other and that the reaction be sufficiently rapid. An example is the preparation of acid esters from alcohols, phenols and primary and secondary amines by injecting acetic or propionic anhydride after the injection of a sample containing some of the alcohols etc. The successful application of this method in the identification of various compounds[56-59] demontsrates the possibility of using it for the preparation of standard mixtures.

(a) Pyrolysis

The application of the pyrolysis of non-volatile compounds as a method of preparation of standard mixtures of known composition has a number of advantages: the pyrolysis of polymers usually results in a wide range of products, the method is very simple and rapid, and the experiment is carried out with the use of a conventional chromatograph. The use of volatile products from the pyrolysis of polymers as standard mixtures in the determination of the retention data of organic compounds on gas chromatographic columns was suggested by Berezkin *et al.*[60]. They studied the composition of the volatile products of the pyrolysis of polyethylene and polypropylene, the pyrolysis of which had earlier been studied by Voigt[61], in order to estimate the reproducibility of the method and the possibility of its utilization for the above purposes.

The measurements were carried out on a CVET-I chromatograph equipped with a quartz pyrolytic chamber[62]. The samples of the polymers were pyrolyzed in a mica boat placed inside a nickel-chromium helix heated rapidly by an electric current. The subjects of the study were a polyethylene of the Hostalen GD type and a Soviet polypropylene with a molecular weight of 200,000. The pyrolysis was conducted at a temperature of 550° for a period of 15 sec using a polymer charge of 2 mg. The pyrol-

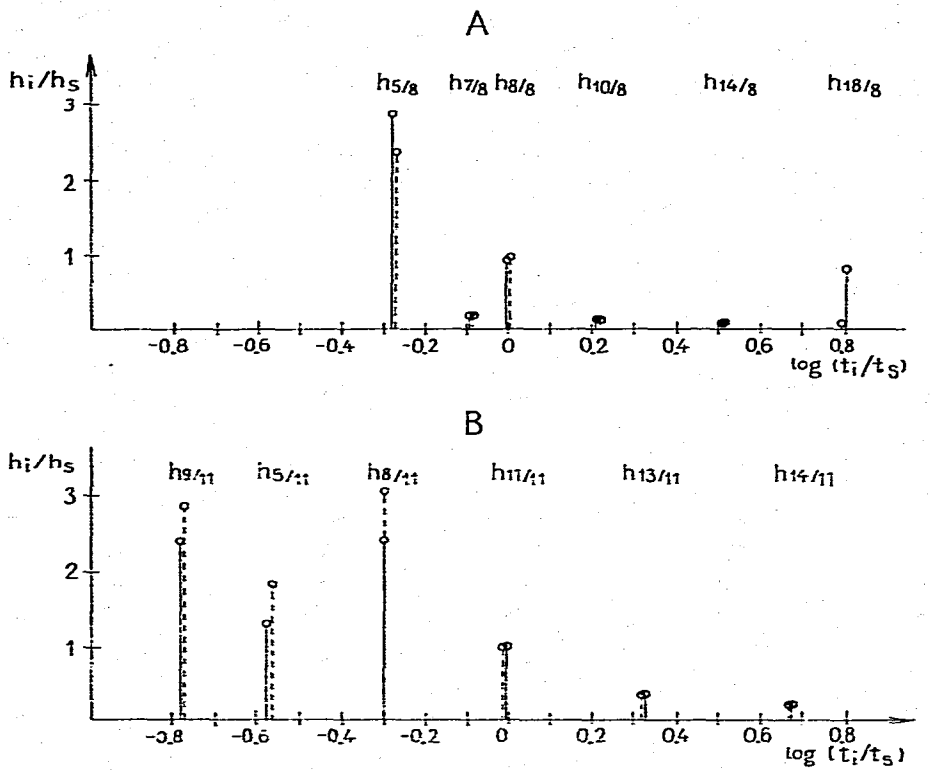


Fig. 1. Products of the pyrolysis of polypropylene (A) and polyethylene (B). h_i/h_s = Relative peak height of product i of the pyrolysis of the given polymer, relative to the height of peak 8 (A) or 11 (B) as a standard, s. Log (t_i/t_s) = logarithm of the relative retention time of the peak of product i of the pyrolysis of the polymer. Broken line, results of Voigt[61]; solid line, results of Berezkin *et al.*[60].

ysis products were separated on a 200 × 0.4 cm I.D. column packed with 8% dinonyl phthalate on Spherochrom at 75°. The results obtained are illustrated in Fig. 1, which shows the logarithms of the relative retention data of the basic products of pyrolysis plotted against the relative heights of the respective peaks. In addition to our results, those for Hostalen GC polyethylene and Hostalen PPN polypropylene, taken from Voigt's paper[61], have been incorporated into the plots. The results are virtually identical. The slight difference in the retention data of the compounds may be due to a difference in the stationary phases employed (Voigt used didecyl phthalate). There are very few variations in the quantitative data except for peak number 18, the difference in which can be explained as being due to losses on the column.

Hence, the mixtures of volatile products produced by the pyrolysis of the polymers are sufficiently reproducible and can be used in the qualitative calibration of gas chromatographic columns. In principle, there are no objections against employing the products of the pyrolysis of volatile substances as standard mixtures[63-66].

(b) Hydrogenation

This reaction is of very great importance in the preparation of hydrocarbons from various derivatives. Beroza and Coad[67], who developed a method for carbon

skeleton determinations, help to widen the applicability of this reaction in gas chromatography. The method can be utilized in the preparation of either individual hydrocarbons or their mixtures. Table 9 shows some complicated reactions in which a reacting substance yields several products.

TABLE 9

PRODUCTS OF THE HYDROGENATION OF SOME DERIVATIVES OF HYDROCARBONS

Catalyst, 1% Pd; temperature, 300°; hydrogen flow-rate, 20 ml/min.

Reacting substance	*Reaction*
Aldehyde	$RCHO \rightarrow RH, RCH_3$*
Carboxylic acid	$RCOOH \rightarrow RH, RCH_3$*
Anhydride	$(RCO)_2O \rightarrow RH, RCH_3$*
Alcohol (primary)	$RCH_2OH \rightarrow RH, RCH_3$*
Ester	$R'COOCH_2R \rightarrow RH, RCH_3$; $R'H, RCH_3$*
Ether	$RCH_2OCH_2R \rightarrow RH, RCH_3$*
Amide	$R'CONHCH_2R \rightarrow RH, RCH_3$; $R'H, RCH_3$*

* These compounds occur in small amounts or not at all.

Unsaturated compounds, halogen-containing compounds, alcohols (secondary or tertiary), ethers (secondary or tertiary), esters (secondary or tertiary alcohol moiety), and amides (NH group bound to a secondary or tertiary carbon atom) yield the parent hydrocarbon upon hydrogenation.

Uhdeová and Janák[68] studied the possibility of utilizing hydrogenation reactions of hydrocarbons, conducted in a reaction gas chromatography apparatus, for the direct preparation of standard hydrocarbons for qualitative gas chromatography. The study was particularly concerned with the qualitative course of the reactions of hydrocarbons of the following basic structural types: aliphatic hydrocarbons (pentane, hexane, heptane, octane), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, styrene) and alicyclic hydrocarbons (cyclopentane, cyclopentene, cyclohexane, cyclohexene). Hydrogen was used as the carrier gas and Raney nickel (10%, w/w, of nickel and 2%, w/w, of Apiezon M on glass beads) as the hydrogenation catalyst.

The properties of Raney nickel depend on the reaction bed temperature, while the hydrogenation, isomerization and hydrogenolytic activity of the hydrogenation packing increase when the temperature of the reaction bed is increased. The conditions of the reaction can be chosen such that the carbon skeleton of the hydrocarbons hydrogenated remain unaltered and do not undergo hydrogenolytic cleavage (at temperatures of 60 and 140°, the hydrogenation of only aromatic and unsaturated alicyclic hydrocarbons, respectively, occurs, while the hydrogenation of styrene and *o*-xylene yields isomeric 1,2-dimethylcyclohexanes), or such that the hydrogenolytic activity of the hydrogenation packing applies (at a temperature of 180°, the hydrogenation packing shows a marked hydrogenolytic activity, a gradual splitting off of methane from the basic aliphatic and aromatic hydrocarbons as well as their reaction products occurs, the alicyclic and aromatic rings are cleaved, and the hydrogenolytic activity of the hydrogenation packing is accompanied by hydrogenation, dehydrogenation and isomerization activity: *cf.* Table 10).

In both instances, the reactions of hydrocarbons over Raney nickel proceed re-

ABLE 10

EACTION PRODUCTS FROM THE CATALYTIC HYDROGENATION AND HYDROGENOLYSIS OF YDROCARBONS

ıtalyst, 10% (w/w) of nickel, 2% (w/w) of Apiezon M and 88% (w/w) of glass beads; reaction temperature, 180°; ydrogen flow-rate, 60 ml/min. The retention data were measured on squalane as the stationary phase at 70°.

ydrocarbon	*Reaction products*																					
	Methane	*Ethane*	*Propane*	*Butane*	*Isopentane*	*Pentane*	*Isohexane*	*Hexane*	*Benzene*	*Cyclohexane*	*Heptane*	*Isooctane*	*Methylcyclohexane*	*Toluene*	*Octane*	*trans-1,2-Dimethylcyclohexane*	*cis-1,2-Dimethylcyclohexane*	*Ethylcyclohexane*	*Ethylbenzene*	*o-Xylene*	*Styrene*
Pentane	+	+	+	+		+															
Hexane	-	-	-	-		-		+													
Heptane	-	-	-	-		-		+			+										
Octane	-	-	-	-		-		+			+				+						
Benzene	-	-	+	-		-	+	+	+	+											
Toluene	-	-	-	-	-	-	+		-	+			+	-							
Ethylbenzene	-	-	-	-	-	-	-		+	-			-	+				+	+		
o-Xylene	+	+	-	-	-					-		+	-	+		+	+			+	
Styrene	+	-	-	-	-	-	-			-		+	-	-		+	+				

producibly and yield the expected range of hydrocarbon products. The retention data of the products were compared by means of the Student *t*-test with those of standard hydrocarbons (the expected reaction products) analyzed on the same analytical column, and no significant differences were found. Thus, it was proved that the reactions of hydrocarbons over Raney nickel in the experimental arrangement described proceed instantaneously from the analytical viewpoint and that no significant sorption of the hydrocarbons in the reaction bed occurs. Hence, hydrogenation, hydrogenolysis and isomerization reactions of selected hydrocarbons or their mixtures, conducted in a reaction gas chromatography apparatus, are suitable for the direct preparation of standard hydrocarbons for qualitative gas chromatography.

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6. SUMMARY

Chemical reaction methods can be used to prepare standard compounds or their mixtures which can serve as standards for the identification of peaks of unknown substances by gas chromatography by means of retention data. The requirements for

the character and course of the chemical reaction chosen for this purpose are specified. In practice, either reactions conducted outside the chromatographic system can be used, or use can be made of techniques of analytical reaction gas chromatography. A survey of the possibilities of utilizing standard mixtures prepared in this way in qualitative gas chromatography and of the basic chemical reaction methods for the preparation of standard hydrocarbon mixtures is presented.

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