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Enhanced possibilities for identification by the use of series-coupled capillary gas chromatographic columns

I. General exposition and application of the retention index concept

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ABSTRACT

After a short survey of the variants of multi-dimensional gas chromatography resulting from the combination of different columns and operating parameters, the possibilities of the use of the retention index concept in systems of series-coupled columns without intermediate trapping for the identification of individual components in complex mixtures are discussed. This technique allows a greater reliability of chromatographic identification by the use of the retention index concept for the simultaneous determination of Kováts retention indices on the two columns, the calculation of isothermal retention indices on the second separation column with temperature-programmed operation of the first column and the predetermination of system retention times of individual components on the basis of known retention indices on either column alone.

INTRODUCTION

In the last few years it has become increasingly necessary to analyse samples consisting of a wide variety of components which may often be distributed over wide boiling-point, polarity and concentration ranges. Classical chromatographic systems are inadequate for the analysis of such samples. Therefore, depending on the particular tasks to be solved, many methods have been developed to cover wider fields of sample application and more effective detection, especially involving the coupling of gas chromatographic (GC) separation with various spectroscopic detection methods such as mass, Fourier transform IR and atomic emission spectrometry. In most instances the spectra resulting from these methods of "multi-dimensional detection" allow an unequivocal identification only if they originate from pure substances and if it can be guaranteed that the preceding separation process led to a complete separation of all components.

The demand for "multi-dimensional" separations led, on the one hand, to the coupling of high-performance liquid chromatography with GC and, on the other, to the many methodological variants of what is known as multi-dimensional GC (MDGC).

Owing to the increasing availability of route-switching devices that are also

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suitable for CGC (Deans switching, Live T-piece, micro-valves), the possibility exists now of making full use of the analytical potential of a switching device between two serially coupled separation columns by the use of high-performance capillary columns.

In many papers (see, *e.g.*, refs. 1–10 and references cited therein) the theory and the advantages of coupled systems has been demonstrated, *e.g.*, the higher resolution, the reduction of the complexity of mixtures by using the cutting technique, the application of the heart-cutting technique to the determination of trace components in the tailing of main components, the backflushing technique for reducing analysis time and a great number of variants of selective sample injection of a precolumn. Often systems with intermediate trapping were used which implies a refocusing of substance zones at the head of the second separation column.

However, in the last few years increasing attention has been paid to series-coupled systems without intermediate trapping, which was especially due to the fundamental work of Sandra *et al.* [7], Hinshaw and Ettre [8,9] and Kaiser and Rieder [10] on the theory of coupled columns and on selectivity tuning. By this means, the selectivity of the system can be selectively varied in a given system of two columns of different selectivity or capacity by varying the flow-rates and/or the column temperatures. The possibilities resulting from this for identification will be described in Part II. After a short survey of the general applications of MDGC systems, this paper discusses the use of the retention index in series-coupled systems without intermediate trapping.

THEORY

Variants of multi-dimensional GC

In Table I, the various possibilities of coupling two GC columns are listed. However, it should be noted that systems of parallel-coupled separation columns do not necessarily give any multi-dimensional separations. For complex mixtures, the serial coupling of two high-resolution capillary separation columns proves to be necessary [5,6,12–14]. However, this serial coupling is only useful if at least one of two conditions is fulfilled: different retention characteristics (selectivity, retention mechanism) or different capacity (film thickness, temperature).

Many workers have used serial coupling with intermediate trapping [13,15]. With this mode of operation, part of the eluate from the first separation column (non-resolved peak groups) is condensed in a trap (indirect coupling) and separated subsequently on the second separation column. The advantage of narrow peak profiles here is accompanied with the disadvantage that the selectivity of the total system is not tunable. The mode of operation without intermediate trapping (direct serial coupling) permits selectivity tuning either by means of different column temperatures or by varying the flow-rates. The latter approach, however, requires a T-piece with an additional carrier gas supply as a coupling device. For this variant, Kaiser and Rieder [10] suggested the term multi-chromatography.

Use of retention indices in series-coupled columns

The retention index is one of the most frequently used means of identification in GC. In comparison with the classical single-column systems, the systems of serially

TABLE I

POSSIBLE VARIATIONS WHEN COUPLING TWO COLUMNS

The different variants cannot be combined with each other at random.

Criterion	Variant
Coupling	On-line or off-line
	Serial or parallel
Type of column	Packed, micropacked, capillary
	Length, inside diameter
	Type (selectivity) and amount (capacity) of stationary phase
Operation mode of coupling	Complete or partial eluate transfer
	With or without intermediate trapping
	With/without monitor detector after the first column
Working parameters	Sequence of columns
	Column temperatures:
	Isothermal, $T_1 = T_2$ or $T_1 \neq T_2$
	Temperature-programmed–isothermal
	Temperature-progr.–temperature-programmed
	Variation of flow-rates either in the total system or separately for each column

coupled separation columns dealt with in this paper offer considerably extended possibilities of using the retention index concept. These possible areas of application can be listed according to the source of the respective necessary information as follows:

(a) Chromatogram of the monitor detector (detector after the first column):

Identification by means of the classical retention index concept for single-column systems.

(b) Chromatogram of the main detector (detector after the second column):

Identification according to the classical retention index concept with the precondition of intermediate trapping and the additional injection of *n*-alkane standards into the trap [13,15].

Use of "system indices" for identification in connection with the different variants of selectivity tuning [10,14,17].

Identification by the prediction of system retention times using tabulated retention indices on both single columns and comparison with measured retention times for different selectivity adjustments of the total system.

(c) Simultaneous use of the information from the main and from the monitor detector in a system without intermediate trapping:

Simultaneous calculation of isothermal retention indices on both separation columns [12], additionally connected with the possibility of using cutting techniques for a clear assignment of peaks.

Operation of the first separation column in the temperatur-programmed mode and of the second separation column isothermally; use of the second column as an "identification column" by determining the isothermal retention indices (possibly again in combination with cutting techniques).

Identification by the combined use of isothermal retention index calculations on the first column, and comparison of calculated and measured system retention times.

The possible applications of the index concept mentioned under (b) are closely connected with the use of selectivity tuning and will be dealt with in Part II [18]. In the following, the possible applications mentioned under (c) and resulting from the simultaneous use of the information from the main and the monitor detectors will be discussed.

The "classical" uses of the retention index concept are of such a type that the *n*-alkanes are chromatographed either simultaneously with the sample or in a separate run. This means that in both instances the same starting point is assumed on the time scale both for the reference substances and for the test substances.

The condition $t_{\text{start }(i)} = t_{\text{start (reference)}} = 0$ results from experimental studies, but is not absolutely essential with the temperature and the flow constancy reached with modern instruments. Now, as before, the decisive precondition is the correct and reproducible determination of retention times. In a system consisting of two series-coupled columns without intermediate trapping, but with a monitor and main detector after the first and second columns, the retention indices for the first column can be calculated in the usual way (all substances have the same starting point) on the basis of the retention times $t_{R(1)}$ measured at the monitor detector.

The retention time $t_{R(S)}$ of any substance registered at the main detector represents the sum of the interaction with the two columns and is composed additively of the retention times $t_{R(1)}$ and $t_{R(2)}$ for the individual columns.

$$t_{R(S)} = t_{R(1)} + t_{R(2)} \tag{1}$$

$$t'_{R(S)} = t'_{R(1)} + t'_{R(2)} \tag{2}$$

On the condition that the dead volumes of the coupling piece and the gas hold-up time in the transfer-line between coupling piece and monitor detector are negligibly small and no adsorptive interactions occur between the substance and the surface of the coupling piece, the retention time of each substance and each *n*-alkane on the second column should, therefore, result from the difference in the corresponding retention times on the main and the monitor detector.

Consequently, a retention index calculation for the second column can be carried out on the basis of the adjusted retention times found according to the following equation, although the individual compounds and bracketing *n*-alkanes are starting at different times on the second column:

$$t'_{R(2)} = t'_{R(S)} - t'_{R(1)} = t_{R(S)} - t_{M(S)} - t_{R(1)} + t_{M(1)} \tag{3}$$

This equation, which was proposed by Rijks *et al.* [12] in 1974, offers enhanced possibilities for identification, but did not find widespread use, perhaps owing to the difficult operation of coupling devices at that time.

RESULTS AND DISCUSSION

The ultilization of eqn. 3 offers the following possibilities for application of the retention index concept.

Determination of two independent sets of retention indices in one run

As in the parallel operation of separation columns with different polarities, the components can be characterized as points in a two-dimensional representation of the retention indices. The advantage is an increased reliability of identification. Compared with the parallel arrangement, serial coupling of the columns offers the additional possibility of selective peak transfer onto the second column (heart cutting) and thus of a clear peak assignment and the recognition of overlapping.

If two columns with the same polarity are operated in a suitable device at different temperatures, the temperature coefficients of the retention indices can be determined simultaneously and used as an identification aid.

Determination of isothermal retention indices in mixtures with a large boiling range by combining two separation columns with the same stationary phase in two separate column thermostats, the first of which is operated in a temperature-programmed mode and the second isothermally at a suitable temperature

The use of temperature-programmed retention indices is limited by the fact that these values, apart from the initial temperature and programming rate, also depend on the wall thickness, the inside diameter and film thickness of the capillary column and the carrier gas flow-rate. The cause of this is the delay in the heat transfer between the column thermostat and the interior of the separation column, which is influenced by the wall thickness and heat capacity of the tubing and by the carrier gas flow-rate. Although few methods for the conversion between isothermal and temperature-programmed retention indices have been published (*e.g.*, [11]) the inter-laboratory reproducibility of retention indices obtained with temperature programming is not as good as that for isothermal retention indices. Therefore, more often than not (especially in analysis with temperature-programmed GC–mass spectrometry, the structural information that can be deduced from the retention values is not made use of, although it would give complementary information in addition to the mass spectra, for example with isomeric compounds.

The use of eqn. 3 should make it possible, with a combination of temperature-programmed and isothermal separation columns, to exploit the second column as an "identification column" for the determination of the isothermal retention indices, and in this way to link temperature-programmed separation with isothermal identification. The results of the experimental verification of this possibility are given in Table II.

The first two columns of data in Table II give the retention indices of compounds found at 100 and 120°C on the OV-1 used for the comparison. In the subsequent columns, the isothermal retention indices on the second column obtained using eqn. 3 at different programming rates of the first column and the differences ΔI from the reference values are listed. These values show that, in principle, the method is useful. In the range 850–1150 I.U. the isothermal retention indices determined at heating rates of up to 4°C/min (of the first column) agree well with the isothermally ascertained reference values. The very large deviations occuring with the first-eluting compounds, benzene and toluene, are obviously due to variations in temperature caused by special features in the temperature regulation of the device used (opening of the lifting casing at low temperatures). Therefore, such measurements should be done in systems with two independently thermostated column ovens.

TABLE II

ISOTHERMAL RETENTION INDICES OF SOME ALKYLBENZENES ON OV-1 OBTAINED BY COUPLING A TEMPERATURE PROGRAMMED AND AN ISOTHERMAL CAPILLARY COLUMN WITHOUT INTERMEDIATE TRAPPING

	Isothermal at		Temperature-programmed from 60 to 120°C at							
Column 1 (OV-1)	100°C	120°C	3°C/min		4°C/min		4°C/min		6°C/min	
Column 2 (OV-1) (isothermal)	100°C	120°C	120°C		100°C		120°C		120°C	
Compound[a]	*I*	*I*	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*
Benzene	663.1	670.7	664.6	6.1	648.6	14.5	658.0	12.7	663.5	7.2
MeB	766.0	771.4	768.0	3.4	760.7	5.3	768.5	2.9	769.0	2.4
EtB	858.4	863.3	862.6	0.7	859.1	0.7	863.3	0.0	862.8	0.5
1,4-DiMeB	866.8	871.3	870.7	0.6	865.6	1.2	871.8	0.5	871.3	0.0
1,2-DiMeB	889.8	895.6	894.8	0.8	888.2	1.6	896.4	0.8	894.9	0.7
1,3,5-TriMeB	962.4	967.3	967.4	0.1	962.6	0.2	968.9	1.6	966.5	0.8
tert.-BuB	986.9	992.5	991.9	0.6	986.4	0.5	993.8	1.3	991.7	0.8
sec.-BuB	1004.9	1010.9	1010.7	0.2	1005.0	0.1	1012.0	1.1	1008.7	2.2
1-Me-4-*i*-PrB	1016.9	1021.9	1021.6	0.3	1017.1	0.2	1023.3	1.4	1020.8	1.1
1,2,3-TriMeB	1014.9	1021.9	1021.9	0.0	1014.6	0.3	1022.9	1.0	1020.5	1.4
1,2-DiEtB	1051.8	1057.9	1057.2	0.7	1051.5	0.3	1058.7	0.8	1055.8	2.1
1,2-DiMe-4-EtB	1074.6	1080.6	1080.2	0.4	1074.8	0.2	1081.6	1.0	1078.1	2.4
1-Et-2-*n*-PrB	1133.8	1139.4	1138.2	1.2	1132.8	1.0	1139.6	0.2	1135.7	3.7
Tetralene	1142.8	1154.0	1152.4	1.6	1142.1	0.7	1152.9	1.1	1149.7	4.3
$t_{M(2)}$			1.09 min		1.07 min		1.1 min		1.09 min	
$a_{(2)}$			− 5.825634		− 5.945178		− 5.899576		− 5.9000063	
$b_{(2)}$			$5.880527 \cdot 10^{-3}$		$6.597449 \cdot 10^{-3}$		$5.934197 \cdot 10^{-3}$		$5.95063 \cdot 10^{-3}$	

[a] Me = Methyl; Et = ethyl; Pr = propyl; Bu = butyl.

At higher programming rates, the heating power and the heat transmission speed are not great enough to follow the temperature programme. This explains the high ΔI values with the late-eluting substances 1,2-dimethyl-4-ethylbenzene, 1,2-ethyl-*n*-propylbenzene and tetralene at a heating rate of 6°C/min, which will be even higher with an increased programming rate.

This method can also be well combined with the cutting technique by transferring certain fractions of complex mixtures with a wide boiling range, which are separated in the temperature-programmed column, onto the isothermal "identification" column. By means of several runs at different temperatures of the second column, the reliability of the findings can be additionally increased.

Predetermination of retention times on the basis of retention indices

The general demand that retention values should be measured on a stationary phase of some other polarity in order to ensure a positive identification will, owing to the many possibilities of overlapping and the great number of peaks with similar areas, lead to problems in recovering the individual components in the chromatograms. This problem also exists with series-coupled separation columns and could be solved by using a costly heart-cutting technique for each peak. Another possibility which implies the inversion of the first principle and is based on the comparison of the measured retention times with the calculated values is dealt with by means of the following example.

Fig. 1 shows the chromatogram of a gasoline which was obtained on a non-polar capillary column. In the marked retention range $I^{OV} = 766–781$ six peaks could registered. The transfer of this peak group to a micropacked column containing graphitized thermal carbon black yielded ten peaks. However, for these peaks the retention indices I_2 cannot be calculated on the basis of the retention time differences according to eqn. 3, as their assignment to the six peaks of the first column is not known. Also, because of the different retention mechanisms of the two columns (see below), a completely changed peak sequence is to be expected in the chromatogram of the main detector. The problem of assigning the ten retention times $t_{R(s)}$ to the six retention times $t_{R(1)}$ could possibly be solved by a repeated application of heart cutting, *i.e.*, by the separate transfer of each peak to the second column, which is, however, costly and difficult to achieve experimentally.

A more elegant and easier method of assignment is the predetermination of retention times by means of available retention indices and making use of the fact that the retention index $I_{(i)}$ for *any* compound i can be calculated by the equation [19]

$$I_{(i)} = 100\,[\log t'_{R(i)} - a]/b \tag{4}$$

where a and b are the intercept and slope, respectively, of the *n*-alkane plot. The constants a and b can be determined from a separate *n*-alkane run at the same temperature and flow-rate at which the retention times are to be determined, according to

$$\log t'_{R(z)} = a + bz \tag{5}$$

where z is the carbon number of the *n*-alkane. By inversion of eqn. 4, the adjusted

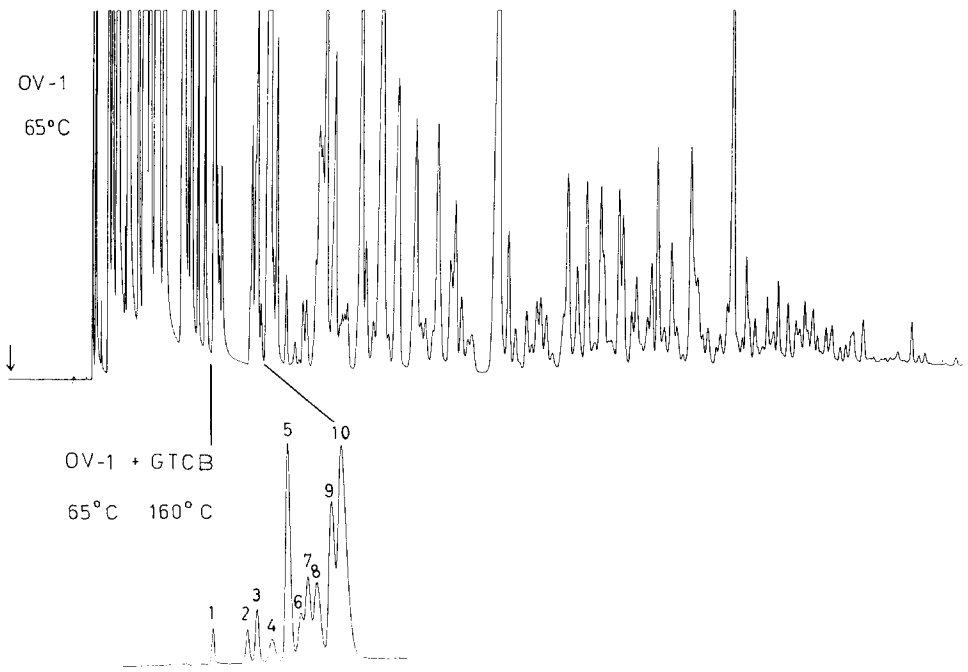

Fig. 1. Chromatogram of a gasoline sample on column system B (for details, see Experimental). Cut of a peak group (marked region) onto the second column and identification by comparision of precalculated and measured system retention times. Peaks: 1 = 1,1,2-trimethylcyclopentane; 2 = 3-ethyl-3-methylpentane; 3 = unknown; 4 = 3,4-dimethylhexane (diastereoisomers); 5 = 1-*cis*,3-dimethylcyclohexane; 6 = 3-ethylhexane; 7 = 1-*trans*,4-dimethylcyclohexane; 8 = 4-methylheptane; 9 = 3-methylheptane; 10 = 2-methylheptane.

retention times $t'_{R(i)}$ of any substance on the separation column used can be calculated using tabulated retention index values according to

$$t'_{R(i)} = \exp [a + 0.01\ b/I_{(i)}] \tag{6}$$

and be compared with the measured retention times.

In our example, the assignment of the peak group is shown in Table III. It was obtained in the following way:

(1) Calculation of the I^{OV} values from the chromatogram after the first column (monitor detector).

(2) Assignment of possible substances by comparison with tabulated values. (here, in some instances, several structural proposals will result).

(3) Search for the relevant I_{GTBC} values in the literature or in the laboratory data collection.

(4) Calculation of adjusted retention time, $t'_{R(2)calc.}$, on the second column from the I_{GTBC} values according to eqn. 6 by using the constants a and b, which are to be ascertained with an n-alkane mixture at a given column temperature and flow-rate according to eqn. 5.

TABLE III

IDENTIFICATION OF A PEAK GROUP IN GASOLINE SAMPLE

OV-1 (65°C)					GTCB (160°C) System				
Peak No.	$t_{R(1)}$ (min)	I^{OV-1}	Proposed structure	I^{OV-1} [21]	I^{GTCB}	$t_{R2\ calc.}$ (min)	$t_{R(S)calc.}$ (min)	$t_{R(S)exp.}$ (min)	Peak No.
1	9.686	765.9	1,1,2-Trimethylcylopentane	765.6	650.0	1.874	11.72	11.728	1
			2-Methylheptane	766.5	770.5	7.564	17.41	17.329	10
2	9.754	767.2	4-Methylheptane	768.2	754.2	6.263	16.177	16.306	8
3	9.895	769.9	3-Ethyl-3-methylpentane	772.9	690.0	2.978	13.033	13.266	2
			3,4-Dimethylhexane (2 diastereomers)	770.9 771.0	718.0	4.118	14.173	14.363	4
4	10.087	773.5	3-Ethylhexane	775.5	737.4	5.156	15.403	15.626	6
			3-Methylheptane	774.3	759.3	6.644	16.891	16.911	9
5	10.409	779.3	1-*cis*,3-dimethylcyclohexane	779.6	724.0	4.415	14.984	15.004	5
6	10.489	780.7	1-*trans*,4-dimethylcyclohexane	781.3	739.0	5.252	15.901	15.912	7
a	−4.144				−6.899				
b	$7.8596 \cdot 10^{-3}$				$1.158 \cdot 10^{-2}$				
t_M	3.16 min				0.16 min				

(5) Calculation of system retention times, $t_{R(s)}$, according to the equation

$$t_{R(s)calc.} = t_{R(1)exp.} + t_{M(s)exp.} - t_{M(1)exp.} + t'_{R(2)calc.} \quad (7)$$

(6) Identification of the peaks by comparing the measured (exp.) and calculated system retention times.

(7) Control by means of peak areas.

With this type of procedure, a good separation and high reliability of assignment are achieved by the combination of two different separation principles, partition and adsorption. On the first column (methylsilicone), a separation of the hydrocarbons takes place according to the vapour pressure (boiling points). On the second column (graphitized thermal carbon black), the retention is mainly determined by the molecular size and shape ("shape selectivity"). This combination of gas–liquid (GLC) and gas–solid chromatography (GSC) with two non-polar columns proved to be more effective for the separation and identification of isomeric non-polar hydrocarbons in the medium carbon number range than a combination of non-polar and slightly polar GLC columns; however, it requires two different column temperatures [20] and thus two separate column ovens.

In cases of doubt, a more reliable assignment can be reached by repeating the sequence with changed column temperatures or flow-rates. This will be discussed in Part II.

EXPERIMENTAL

The instrument used was a Siemens Sichromat 2, equipped with a split injector. The carrier gas was hydrogen.

The live T-piece consisted of a coupling capillary column (18 mm × 0.20 mm O.D.) and two fused-silica-restrictor capillary columns (350 mm × 0.15 mm I.D.) with a flow-rate in the restrictor capillary column 1 of 10 ml/min.

The live T-piece of the Sichromat 2 was normally used in the monitoring mode; thus, the first detector shows which part of the sample is entering the second column. The percentage of sample going to the first detector was adjusted by changing the positive pressure difference. This mode permits the registration of a complete chromatogram of the sample on the monitor detector and also the application of cutting techniques.

System A (temperature-programmed–isothermal) was as follows: columns 1 and 2, both 30 m × 0.32 mm I.D., glass, OV-1; temperature, as indicated in Table III; pressures, P_i = 100 kPa, P_M = 50 kPa. A mixture was used containing some alkylbenzenes and tetralene (boiling point range 80–207°C), which on methylsilicone stationary phases show average temperature coefficients of the retention indices of $\partial I/\partial T$ = 0.2–0.4 I.U./K. Of these compounds, the retention indices at different programming rates (3, 4 or 6°C/min) in the range 60–120°C for the first column were determined at 100°C or at 120°C on the second column.

System B (prediction of retention times; see Fig. 1) was as follows: column 1, 50 m × 0.32 mm I.D., FS-WG-PB-1 (OV-1); column 2, 1.5 m × 1 mm I.D., micropacked, Carbopack C (0.16–0.2 mm); temperatures, T_1 = 65°C, T_2 = 160°C; pressures, P_i = 430 kPa, P_M = 400 kPa. The dead times were calculated from the gross retention times of *n*-alkanes by a regression method.

CONCLUSIONS

The multi-dimensional GC method is mainly used for improving the separation power, shortening the time of analysis and for reliable trace analysis. This technique, however, offers enhanced possibilities also for qualitative analysis. The application of the retention index concept in systems of series-coupled columns without intermediate trapping allows the use of the retention index concept for the simultaneous determination of Kováts retention indices on the two columns, the determination of isothermal retention indices on the second separation column with temperature-programmed operation of the first column and the predetermination of system retention times of individual components on the basis of known retention indices on both the single columns. These applications of the retention index concept enhance the possibilities of the identification of individual components in complex mixtures by chromatographix means.

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