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GAS CHROMATOGRAPHIC SEPARATION OF UNSATURATED HYDROCARBONS, USING $AgNO_3$ SOLUTIONS AS STATIONARY PHASES

1. THE EFFECT OF WORKING PARAMETERS ON COLUMN PERFORMANCE

$AgNO_3$ solutions in various solvents have been successfully used as stationary phases for the analytical and preparative gas chromatographic separation of the *cis-trans*-isomers of normal alkenes, mainly in the C_4—C_9 region [1–6]. There are some papers concerning the separation of *cis-trans*-isomers of normal alkenes C_{10}—C_{13} [6–8]. No references including more detailed gas chromatographic and argentation equilibrium data for higher normal alkenes on stationary phases containing $AgNO_3$ could be found.

While analysing and purifying normal alkenes, we have extended the investigation of the relationship between the structure and gas chromatographic behaviour and the silver-olefin complexation equilibria on stationary phases containing $AgNO_3$ to the *cis-trans*-isomers of internal normal alkenes up to C_{13}.

Some solvents for $AgNO_3$ not examined so far (butane-1,4-diol, etc.) were included. In order to improve the resolution of *cis-trans*-isomers, the effect of working parameters (temperature, carrier gas flow rate, etc.) on column performance was investigated first. The results are as follows.

Experimental

The UH-1 gas chromatograph with a thermal conductivity detector at a current 160 mA and a soap bubble flow-meter was operated at column temperatures of 40, 60, 80 and 100° C with the helium flow rates of 20—100 ml/min. The inlet system was modified so that the inlet pressure could be read on the mercury manometer. Column inlet pressure, atmospheric pressure and room temperature were observed.

The stationary phase was prepared by dissolving the desired amount of silver nitrate in the solvent or its solution in 50 ml ethanol at 40—50° C. The solution was filtered, if necessary, before adding a certain amount of Chromosorb P (usually 30—60 mesh size). As to the column performance, Chromosorb W (30—60 mesh) and Chromosorb P (60—80 mesh) did not show any appreciable difference from Chromosorb P (30—60 mesh). Ethanol was removed by slight warming (not above 50°) under residual pressure 10—20 mm Hg during 70—80 hours, protecting the column packing from light. A weighed amount (ca 20 g) of stationary phase was put into the column. Preliminary experiments with columns of various lengths (1 — 2.5 m) showed the 1 m columns to combine favourably the shot analysis time and a satisfactory resolution of geometric isomers of higher normal alkenes. As a rule, if not indicated otherwise, the 1 m stainless steel columns with an inner diameter of 6 mm were used.

The equilibrium measurements were carried out with mixtures about 1 : 1 by weight of *cis-trans*-pairs of normal alkenes of a single carbon number. Retention times of individual compounds were recorded separately, applying octene-2 or decene-2 as reference substances. Care was taken not to overload the column and to minimize the scatters in the retention values. The recorder range was set to sensitivity 5 mV of full-scale deflection. At this range, sample sizes of 1—9 μl were adopted.

The gas chromatographic nomenclature suggested in [9] was applied. The values of relative retentions (*r*) were fairly well reproducible (±1—3%).

Normal alkenes were prepared by selective hydrogenation of alkynes. If treated with metallic sodium in liquid ammonia, we got *trans*-alkenes [10]. In the presence of the Lindlar catalyst, at a room temperature, mainly *cis*-alkenes resulted.

C_8—C_9 hydrocarbons were purified by rectification through a 40 plate column and by preparative gas liquid chromatography on $AgNO_3$—triethylene glycol columns. Their purity was 97—99.8%, determined as described in [7].

Normal alkenes C_{10}—C_{13} were purified by rectification, and some of them by preparative gas chromatography. Their purity was determined on stationary phases containing $AgNO_3$ and, additionally, on Chrom-2 instrument with open tubular columns (40—80 m long, inner diameter 0.2 mm), coated with squalane or triethylene glycol dibutyrate.

Normal *trans*-alkenes C_{10}—C_{13} contained no *cis*-isomers, and their purity was 98.5—99.9%. The purity of *cis*-alkenes C_{10}—C_{13} was 75—96%, and they contained 1.2—12% *trans*-isomers as the main impurity. *Cis*-isomers of normal undecene-4 and undecene-3 contained, as impurities, 24% and 31% undecyne.

The solvents for silver nitrate used (ethylene glycol, diethylene glycol, polyethylene glycol 400, decane-1,10-diol, hexane-1,6-diol, butane-1,4-, -1,3-, -2,3-diols and 2-butene-1,4-diol) were of reagent grade and commercially available.

Preliminary experiments showed best results when separating geometric isomers on silver nitrate solutions in butane-1,4-diol * and in polyethylene glycol 400 ** as well. The first stationary phase had the highest selectivity compared to others, but at higher temperatures (above 80°) its selectivity diminished rapidly. $AgNO_3$—PG 400 phase had lower selectivity, but it was one of the most stable phases used.

The effects of the gas flow rate on the column efficiency were investigated with these two stationary phases (Table 1).

The results were applied for fixing working conditions for others.

Table 1

Composition of stationary phases

Column No.	Solvent for $AgNO_3$	$AgNO_3$ concentration in solution, %	Content of $AgNO_3$ solution in column packing, %
38	Butane-1,4-diol	5.7	40.0
27	Butane-1,4-diol	32.8	40.0
37	Polyethylene glycol 400	23.0	42.1

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* Later on indicated as B14.

** Later as PG 400.

The effect of temperature on the activity of all above-mentioned stationary phases was revealed, except $AgNO_3$-decane-1,10-diol phase, which yielded very poor resolution in preliminary experiments. Results with $AgNO_3$—B14 and $AgNO_3$—PG 400 stationary phases are to be found in this paper later.

The effect of the solvent, of the $AgNO_3$ concentration and of the olefin structure, will be discussed in the following paper.

Effect of sample size

The optimum sample size depends on retention values which are determined by conditions of gas chromatographic analysis (composition and properties of the stationary phase, working parameters) and by the character of the compound under investigation.

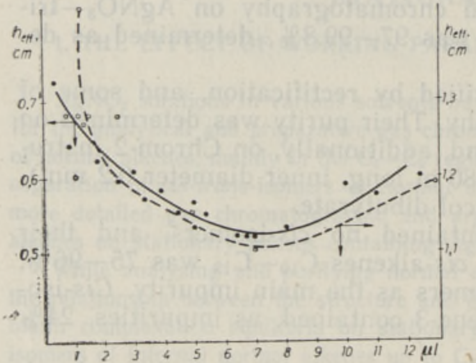

Fig. 1. Variations of h_{eff} with the sample size: column No. 37 (Table 1); temperature 60 and 80° C; helium flow rate — 84 ml/min; sample sizes 0.3—13 l;
———— h_{eff} — height of an effective plate (calculated for *cis*-decene-2)
— — — — h_{eff} — for *cis*-octene-2

It may be seen in Figure I that the optimum sample sizes for *cis*-octene-2 and for *cis*-decene-2 are 4—9 μl. Compared to h_{eff}, there are no principal differences in variations of R_s values for pairs of geometric isomers. When working with various stationary phases and various alkenes, the optimum sample sizes were found for each case. As a rule, these optimum values varied in the region of 1—8 μl for pairs of *n*-alkenes C_8—C_{13} of a single carbon number (at sensitivity scale 5 mV).

Effects of temperature and helium flow rate

As indicated in literature [4, 11, 12], the stationary phases containing $AgNO_3$ inactivate when raising operating temperature above 40—85°. 40° was found to be the upper temperature limit for $AgNO_3$-ethylene glycol columns used most frequently, which was explained as a result of the decrease of stability of Ag-olefin complexes at higher temperatures and by the relatively high volatility of glycol. When analysing higher molecular weight compounds, some higher boiling solvents (di-, triethylene glycols, etc.) were used with success, $AgNO_3$ solutions in polyethylene glycol are indicated to be active at up to 85° [11]. The lack of more detailed data in literature concerning the effect of temperature on the activity of stationary phases containing $AgNO_3$ suggested the optimum separation temperatures for higher normal alkenes to be determined experimentally. So, as a rule, when comparing stationary phases containing $AgNO_3$, variations of selectivity with different temperatures were observed.

Some results are given in Figures 2 and 3, where the values of h_{eff} (calculated for *cis*-isomers) and of R_s (for pairs of geometric isomers) of octene-2, decene-2 and dodecene-2 at 45, 60, 80 and 100° with columns 37 and 38, with helium flow rates 20, 40, 60, 80 and 100 ml/min are shown.

In Figure 4, as an example, some chromatograms of *cis*-*trans*-isomers of decene-2 at various flow rates and temperatures are shown. As it may be seen from the Figures 2—4, the gas flow rate and temperature have

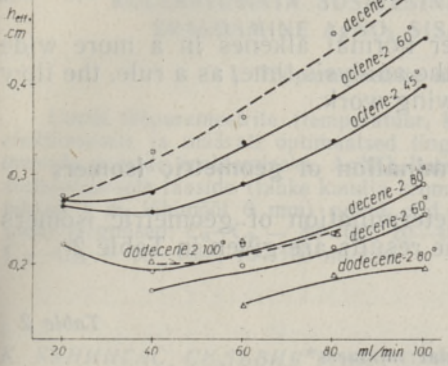

Fig. 2. Variations of h_{eff} with the flow rate and temperature:
——— Column No. 38;
— — — Column No. 37.

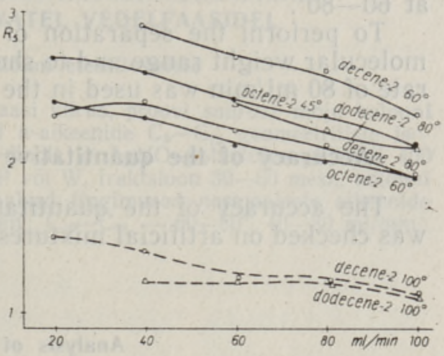

Fig. 3. Variations of R_s with the flow rate and temperature:
——— Column No. 38;
— — — Column No. 37.

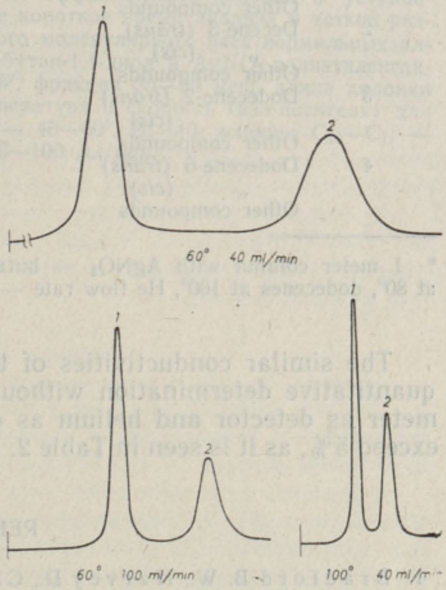

Fig. 4. Separation of *cis-trans*-isomers of decene-2 on $AgNO_3$—B14 stationary phase at various flow rates and temperatures: *1* — *trans*-decene-2; *2* — *cis*-decene-2.

a considerable effect on the resolution of geometric isomers of normal alkenes and their optimum values depend upon the molecular weight of the compounds separated when other conditions remain unchanged.

The data in Figures 2 and 3 show that the optimum temperatures for the separation of geometric isomers are as follows: normal alkenes C_8—C_9 — 40—60°, C_{10}—C_{11} — 60—80°, C_{12}—C_{13} — 80—100°.

The data in Figure 2 show the general regularity in the decrease of efficiency when temperature rises.

The temperature stability of the stationary phases containing $AgNO_3$ used in this work will be discussed in the following paper.

The flow rates 20—40 ml/min were the best for separating isomeric 2-octenes. For separating *cis-trans*-isomers of decene-2 at 80°, the flow rates 40—60 ml/min were found to be the best. With flow rates of 20 ml/min, the dodecene-2-isomers gave very wide diffusive peaks, and the flow rates 40—80 ml/min are recommended in this case. Flow rates above 100 ml/min resulted in a diminishing resolution, and therefore they cannot be recommended.

Though the number of theoretical plates decreases when the gas flow rate increases, the resolution does not change markedly in the 40—80 ml/min range at temperatures 60—80°, when bearing in mind the reproducibility of retentions of ±1—3%, which results in fluctuations of resolution values less than 0.1.

Thus the changes in gas flow rates between 40—80 ml/min do not markedly affect the resolution of *cis-trans*-pairs of normal alkenes C_{10}—C_{12} at 60—80°.

To perform the separation of higher normal alkenes in a more wide molecular weight range and to shorten the analysis time, as a rule, the flow rate of 80 ml/min was used in the following work.

Accuracy of the quantitative determination of geometric isomers

The accuracy of the quantitative determination of geometric isomers was checked on artificial mixtures. Some results are given in Table 2.

Table 2

Analysis of artificial mixtures*

No.	Component	Concentration, %		Absolute error	Relative error
		theoretical	found		
1	Decene-2 (*trans*)	36.7	35.4	—1.3	3.5
	„ (*cis*)	62.2	63.5	+1.3	2.1
	Other compounds	1.1	1.1	—	—
2	Decene-3 (*trans*)	60.5	59.8	—0.7	1.2
	„ (*cis*)	38.7	39.3	+0.6	1.6
	Other compounds	0.8	0.9	—	—
3	Dodecene-2 (*trans*)	46.2	46.3	+0.1	0.2
	„ (*cis*)	49.6	49.6	0.0	0.0
	Other compounds	4.2	4.1	—	—
4	Dodecene-6 (*trans*)	46.6	48.2	+1.6	3.4
	„ (*cis*)	52.7	51.8	—0.9	1.7
	Other compounds	0.7	—	—	—

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* 1 meter column with $AgNO_3$ — butane-1,4-diol stationary phase, C_{10}—C_{11} alkenes at 80°, dodecenes at 100°, He flow rate — 84 ml/min.

The similar conductivities of the pairs of geometric isomers permit a quantitative determination without prior calibration when using katharometer as detector and helium as carrier gas. The relative error does not exceed 5%, as it is seen in Table 2.

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KÜLLASTUMATA SÜSIVESINIKE GAASIKROMATOGRAAFILINE ERALDAMINE $AgNO_3$ SISALDAVATEL VEDELFAASIDEL

1. Tööparameetrite mõju kolonni efektiivsusele

Uuriti tööparameetrite (temperatuur, kandegaasi kiirus, proovi suurus) mõju kolonni efektiivsusele ja määrati optimaalsed tingimused *n*-alkeenide C_8-C_{13} geomeetriliste isomeeride paaride eraldamiseks. $AgNO_3$-butaan-1,4-diooli ja $AgNO_3$-polüetüleenglükooli 400 statsionaarsete faaside (tahke kandja kromosorb P või W, fraktsioon 30—60 mesh, kolonni pikkus 1 m, läbimõõt 6 mm) puhul olid optimaalsed tingimused normaalsete alkeenide jaoks järgmised: C_8—C_9 — 40—60°, 20—40 ml/min.; C_{10}—C_{11} — 60—80°, 40—80 ml/min.; C_{12}—C_{13} — 80—100°, 40—100 ml/min.

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ГАЗОХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ НЕНАСЫЩЕННЫХ СОЕДИНЕНИЙ НА СТАЦИОНАРНЫХ ФАЗАХ, СОДЕРЖАЩИХ $AgNO_3$

1. Влияние рабочих параметров на эффективность колонки

Исследовано влияние рабочих параметров на эффективность колонки и установлены их оптимальные значения, обеспечивающие короткое время анализа и четкое разделение пар геометрических изомеров одинакового молекулярного веса нормальных алкенов C_8—C_{13}. На стационарных фазах $AgNO_3$-бутан-1,4-диол и $AgNO_3$-полиэтиленгликоль 400 (твердый носитель хромосорб *P* или *W*, фракция 30—60 меш, длина колонки 1 *м*, диаметр 6 *мм*) оптимальные условия (температура и скорость газа-носителя) для нормальных алкенов были следующие: C_8—C_9 — 40—60°, 20—40 *мл/мин*; C_{10}—C_{11} — 60—80°, 40—80 *мл/мин*; C_{12}—C_{13} — 80—100°, 40—100 *мл/мин*.