

# Ageing of GC Capillary Columns with Polar Stationary Liquid Phase and Retention Index of Hydrocarbons

<sup>a</sup>L. SOJÁK, <sup>a</sup>I. OSTROVSKÝ, <sup>a</sup>R. KUBINEC, <sup>a</sup>P. KURÁŇ, and <sup>b</sup>V. G. BEREZKIN

<sup>a</sup>*Institute of Chemistry, Faculty of Natural Sciences,  
Comenius University, SK-842 15 Bratislava*

<sup>b</sup>*Institute of Petrochemical Synthesis, Russian Academy of Sciences,  
117912 Moscow, Russia*

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The ageing of capillary column with 1,2,3-tris(cyanoethoxy)propane stationary phase was studied. The study, related to the loss of the stationary phase by evaporation from the column, was based on the column conditioning in the range of maximum allowable operating temperature of used stationary phase (140 °C). The evaluation of the results was based on the changes of benzene retention index and capacity ratio as well as the peak symmetry of chromatographic zones. Benzene retention index significantly decreased with the time of conditioning — 60 index units (i.u.) during 550 h. This effect was explained with the stationary phase evaporation from the front part of conditioned column. Owing to this there is the change in contributions of absorption and adsorption to the retention of separated compounds. The contribution of adsorption is increased for separated n-alkanes, as reference standards for the retention index system, in comparison to that of benzene. The consequence of such effect is the different dependence of benzene retention index on its capacity ratio for fresh and aged columns. This is one of the main reasons of poorer retention index reproducibility of analytes separated on polar stationary phases.

The column ageing is a complex process [1, 2]. One of the reasons of column ageing is the stationary phase evaporation during its using. The evaporation of stationary phase can significantly influence the relative retention (retention index) of analytes in the gas-liquid chromatographic system in which the absorption-adsorption mechanism operates because in such systems the relative retention also depends on the volume of stationary phase in the column [3]. We have studied this effect for some volatile stationary phases previously [4—7], however, the mechanism of ageing was not taken into account.

1,2,3-Tris(cyanoethoxy)propane (TCEP) is one of the most polar stationary phases. That property is employed in the analysis of gasolines for the separation of aromatic hydrocarbons (benzene and alkyl benzenes) from aliphatic hydrocarbons C<sub>1</sub>—C<sub>12</sub>. It is also recommended for the analysis of alcohols in gasoline [8].

In this work we have focused on the study of ageing of capillary column coated with TCEP as stationary phase. As test compounds we have chosen hydrocarbons, the retention of which as nonpolar compounds separated on the polar stationary phase in gas-liquid chromatographic system is determined by the absorption-adsorption retention mechanism [9]. The purpose of this work is to point at the relationship of polar stationary phase evaporation, absorption-adsorption

mechanism of retention, and retention index of hydrocarbons.

## EXPERIMENTAL

Benzene, n-decane, n-undecane, and n-dodecane (Lachema, Brno, Czech Republic) were used as the test mixture. This mixture was injected into gas chromatograph together with methane (without solvent).

Gas chromatograph, model GI 452 with FID and split injector (C. Erba, Milan, Italy) was used for conditioning of columns and GC measurements. Stainless steel capillary columns with the length of 50 m and i.d. of 0.25 mm were dynamically coated with 1,2,3-tris(cyanoethoxy)propane (Eastman Organic Chemicals, Rochester, USA) using the procedure described in Ref. [10]. The film thickness of stationary phase of the prepared columns was in the range 0.08—1.5 μm.

The ageing process was studied on the basis of long-time conditioning of TCEP column (550 h) at 140 °C and nitrogen carrier gas inlet pressure of 0.2 MPa. The changes of benzene retention index (*I*) and its capacity ratio (*k*), resp. the peak symmetry of chromatographic zones, were measured at 50 °C and 0.15 MPa of nitrogen carrier gas inlet pressure. This relatively low temperature was chosen to allow to measure the retention of the model mixture on cut parts of original

column. Namely, after the conditioning the experimental column was cut into the three parts (A, B, and C) with the equal length (16.6 m) in which the values of  $l$  and  $k$  for benzene were measured. Then the front part of original column (A) was gradually shortened with 0.5 m cuts and on the remaining part of the column the values  $l$  and  $k$  of benzene were measured also at 50 °C.

The stainless steel (Laboratorní přístroje, Prague, Czech Republic) was used as the capillary column material because the sorption characteristics of such a column wall are more expressive than those of other capillary column materials. However, it must be mentioned that the novel inert metal capillary columns are a better alternative than fused silica columns for high-temperature and process analysis (less bleeding than fused silica columns) [11].

The different data were published in firm catalogues as the maximum allowable operating temperature values for TCEP columns: Hewlett—Packard 125 °C, Chrompack 150 °C, and Supelco 175 °C. Based on these data the temperature of 140 °C was selected for the study of TCEP column ageing.

## RESULTS AND DISCUSSION

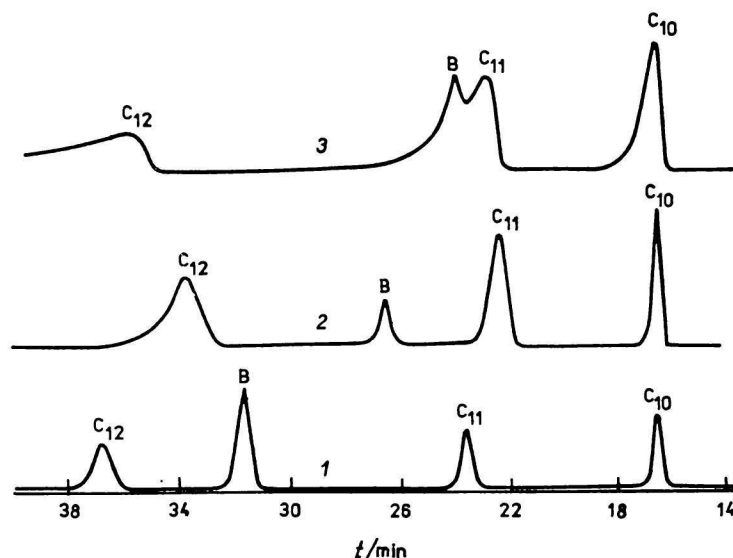
As it is illustrated in Fig. 1, the process of ageing of the column coated with TCEP was very expressive under the used conditioning conditions. The retention of test compounds as well as their peak symmetry has changed during this procedure. TCEP is characteristic by its high surface tension ( $49.2 \times 10^{-3} \text{ N m}^{-1}$  at 25 °C) [2] and therefore the hydrocarbons as nonpolar com-

pounds are adsorbed in contradiction to their polarity on the surface of interface polar stationary phase-carrier gas. The surface of such interface is homogeneous and therefore the chromatographic peaks should be symmetric. The effect of adsorption isotherm non-linearity on this surface manifests itself only at small sorbate concentrations. After the column conditioning the obtained expressive tailing peaks of sorbates point at the sorbate adsorption in the separation system.

We supposed that such effects of column ageing consist in that the stationary phase was evaporated from the front part of the column. For confirmation of that assumption the conditioned column was cut into three equal parts A, B, and C on which the values  $l$  and  $k$  of benzene were measured. The obtained chromatograms are shown in Fig. 2. It is evident from this figure that the biggest changes of retention and symmetry of chromatographic peaks of test compounds were observed in the column A. This result is in accordance with the idea of columns ageing as the process of stationary phase evaporation from the front of column (*e.g.* in the direction of carrier gas flow).

The method of chromatographic scanning was used for determination of the boundary between the stripped and rest parts of conditioned column. The column A was cut from the front in the 0.5 m pieces and chromatographic characteristics were measured on the rest of the column. From chromatograms of those measurements in Fig. 3 it follows that TCEP stationary phase was dominantly evaporated from the short front part of the column. The boundary between aged part and rest of column (in this case in the distance 1.5 m from the column head) is relatively sharp.

The corresponding changes of benzene retention indices at conditioning and following cutting of capil-



**Fig. 1.** Chromatograms of the test mixture on capillary column coated with TCEP as the dependence on the time of column conditioning at 140 °C. 1. 0 h, 2. 250 h, 3. 550 h. Experimental conditions: capillary column 50 m  $\times$  0.25 mm, stationary liquid phase —TCEP, conditioning temperature 140 °C, inlet pressure 0.2 MPa  $\text{N}_2$ , measurement temperature of chromatographic characteristics 50 °C. Peak assignments: B — benzene,  $\text{C}_{10}$ ,  $\text{C}_{11}$ ,  $\text{C}_{12}$  — n-alkanes with the number of carbon atoms in the molecule 10, 11, and 12.

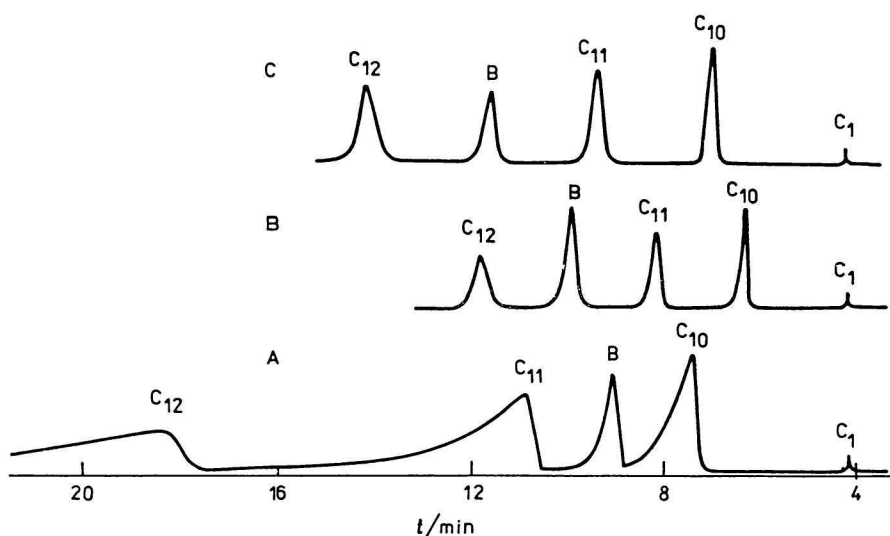


Fig. 2. Chromatograms of the test mixture in three parts of conditioned column after its cutting. A — front, B — middle, and C — rear part (length of each column A, B, and C 16.6 m).

lary column with TCEP are illustrated in Fig. 4. It can be seen that after 550 h of conditioning the retention index of benzene decreased for about 60 i.u. It is related to the fact that by evaporating of the part of the stationary phase from the column the absolute and the relative contribution of adsorption (against absorption) to the retention of n-alkanes, as reference standards in the retention index system, on the surface of interface of stationary phase with carrier gas, resp. capillary column wall, was increased, as well as the contribution of adsorption to the retention of benzene, however less than for n-alkanes, proportionally to the difference in their polarities.

After the cutting of the conditioned column into three equal parts A, B, and C, the measured benzene retention index on the column A was subsequently by 60 i.u. lower than after conditioning of the original column. After 1.5 m piece was cut off from the front of A column, the benzene retention index on the rest part of the column increased to the value which is only moderately lower than those from other two parts (B and C) or those measured in a new prepared column as well. The corresponding benzene capacity ratio values were also lower than those from a new prepared column because of additional saturation of carrier gas with the stationary phase vapours due to its expansion along the column [7]. At the same time another influencing effect could be the nonstandard film thickness of stationary phase along the column, too [10].

The change in the ratio of the contributions of absorption and adsorption to the retention of separated hydrocarbons was relatively small in column A after its front aged part was cut off. The value of benzene retention index in this rest part of A column is similar to that measured in new columns (curve 1 in Fig. 5). Therefore by cutting a piece of the aged column from

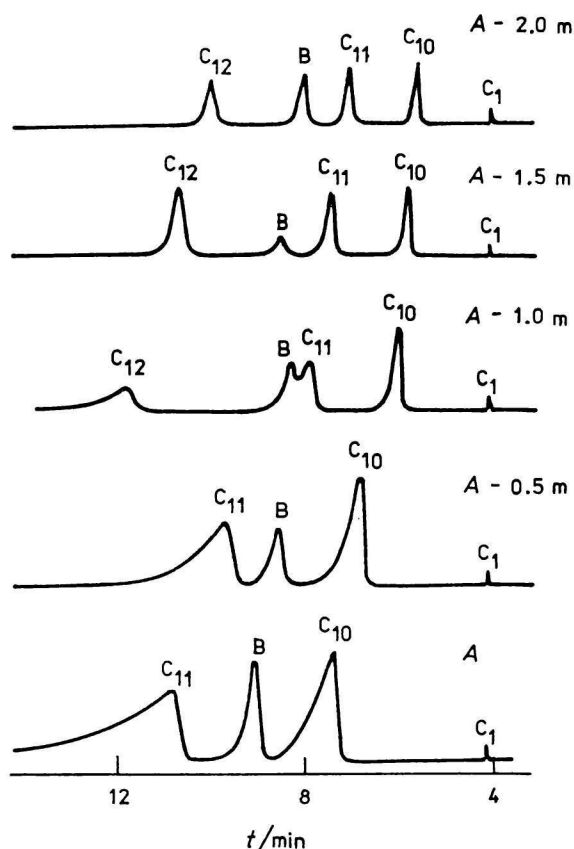


Fig. 3. Chromatograms of the test mixture of compounds measured on the front part of conditioned column (column A). Each chromatogram corresponds to the measurement on column A when its front part was shortened by segment  $a$ . The column length is given on each chromatogram:  $L = A - a$ , where  $A$  is the initial length of column A (16.6 m) and  $a$  the length of column segment by which the column was decreased in this experiment.

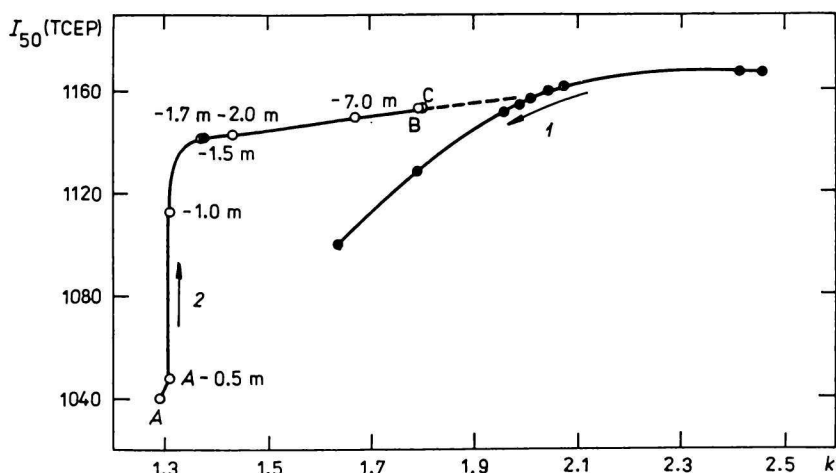


Fig. 4. The dependence of benzene retention index on its capacity ratio in 50 m  $\times$  0.25 mm stainless steel capillary column coated with TCEP obtained by conditioning of the column for 550 h at 140  $^{\circ}$ C and 0.2 MPa  $N_2$ ; A, B, and C are the parts of column (16.6 m long) obtained after cutting of the column. 1. Conditioning, 2. cutting.

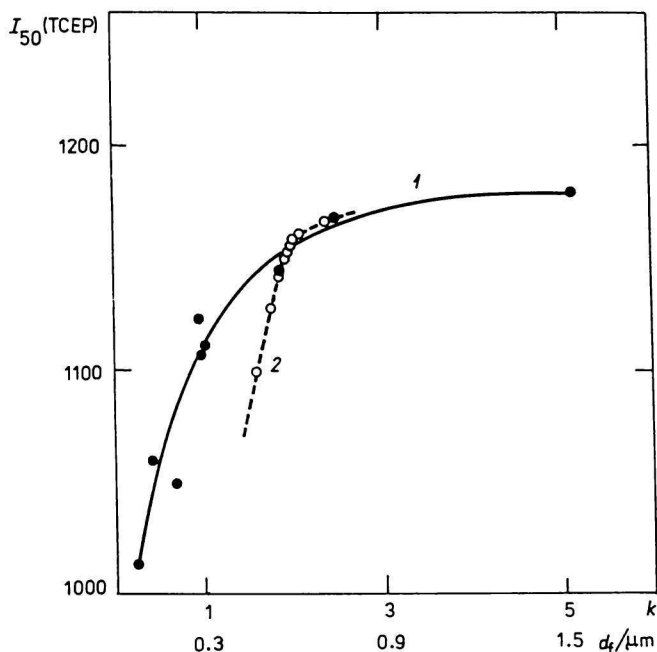


Fig. 5. Change of the retention index  $I$  in dependence on the film thickness of stationary phase ( $d_f$ ) and on the capacity factor ( $k$ ) for benzene in TCEP columns at 50  $^{\circ}$ C. 1. Dependence  $I = f(k)$  for ten fresh prepared columns with different film thickness of stationary phase. 2. Dependence  $I = f(k)$  for one column during its conditioning. Experimental conditions are the same as in Fig. 1.

the front part it is possible to obtain the column with the measured retention indices relatively close to those on a new column. The certain difference in values of benzene retention index is probably related to evaporation of the stationary phase due to carrier gas expansion along the column length.

The relationships for the relative retention of sorbates and absorption-adsorption retention mechanism are valid in the case when the value of the contribution of adsorption to the retention of an analyzed compound at the change of stationary phase volume in the column is not changed [3, 7]. This assumption is not valid for columns aged by the influence of the stationary phase evaporation. After the ageing the properties of the front of such column are basically different from those of the column rest. Because the boundary of the both parts is relatively sharp, the aged column can be considered as a two-column system: the first column is practically adsorption (gas-solid) and the second one is an absorption column (gas-liquid). It is evident from Fig. 5 where the dependences  $I_{50}(\text{TCEP}) = f(k)$  for benzene measured in different columns are illustrated. The first dependence was obtained by measurement on ten new capillary columns with different film thickness of TCEP stationary phase (0.08—1.5  $\mu\text{m}$ ). The second dependence was obtained as a result of conditioning of one (originally fresh) column. It is evident that for values  $k < 2$  both dependences are different because by stationary phase evaporating during column conditioning the change (the increase) of adsorption contribution value to the retention of sorbates occurs. This result shows the limitations of the use of retention indices for identification if they were measured in aged columns due to evaporation of stationary phase in separation systems where the absorption-adsorption retention mechanism operates.

The surface tension of nonpolar stationary phases is approximately two times lesser than that of polar phases, therefore the relationships of stationary phase evaporation, absorption-adsorption retention mechanism, and retention indices of hydrocarbons are less significant than in the case of polar stationary phases.

## CONCLUSION

The ageing of capillary columns with the polar stationary phase (TCEP) causes expressive changes in peak symmetry and retention indices of hydrocarbons (benzene) during their conditioning in the range of maximum allowable operating temperature. These changes are basically the consequence of stationary phase evaporation from the front part of columns. During the evaporation of stationary phase the increase of adsorption and the decrease of absorption contributions to the retention of hydrocarbons are observed. Because there are the differences in adsorption among the analytes and n-alkanes (reference standards in the retention index system) proportional to their polarity difference, the changes in retention indices of analytes occur in time. It is evident that the use of retention indices measured in such aged separation systems is limited for identification. On the other hand, the obtained results emphasize the importance of using stable cross-linked stationary phases.

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