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# GAS CHROMATOGRAPHIC STUDY OF THE TEMPERATURE DEPENDENCE OF THE HYDROGEN BOND ENERGY OF ADSORPTION ON SILICA

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## SUMMARY

The retention of molecules of a homologous series of alkylbenzenes and of polymethylbenzene isomers on a Silochrom surface was studied by gas chromatography in the temperature range 70–170°C. The energy of adsorption of these molecules on the silica adsorbent surface was shown to depend considerably on the temperature. The changes in the differential heats of adsorption at low (zero) surface coverage attain *ca.* 20–30 kJ/mol within the above temperature range and depend on the geometric and electronic structures of the adsorbate molecules. The determination of the contributions of specific interactions (*viz.*, adsorbate–adsorbent interactions via hydrogen bonds) to the total energy of adsorption of these molecules by Silochrom indicates that the observed decrease in the heats of adsorption of substituted benzenes with temperature is mainly due to a decrease in the contribution of specific interactions and related to the weakening of hydrogen bonds formed when molecules are adsorbed on the surface silanol groups.

## INTRODUCTION

The use of gas adsorption chromatography to study adsorption thermodynamics has been successfully developed with the application of the most non-specific and homogeneous adsorbent, *viz.*, graphitized thermal carbon black (GTCB). The adsorption of various classes of molecules on the GTCB surface has been regularly and systematically studied for many years, leading to results that not only are of practical value but also form an experimental basis for a molecular–statistical theory of adsorption on homogeneous surfaces[1]. The use of this method for investigating the thermodynamics of adsorption and intermolecular interactions on specific adsorbents is limited, as it is difficult to obtain adsorbents having chemically and geometrically uniform surfaces with well reproducible properties.

It has been shown previously that among the silicas which, according to Kiselev's classification, are second-type specific adsorbents[2], the Silochroms produced in the U.S.S.R. satisfy the above requirements[3]. Silochroms are uniform macroporous pure silicas with completely hydroxylated surfaces. Many polar substances, including

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oxygen-containing organic compounds, emerge from chromatographic columns as symmetrical peaks[3–5]. This enables one to use gas adsorption chromatography for the investigation of adsorption thermodynamics and intermolecular interactions on the surfaces of these promising but inadequately explored adsorbents.

It is known that the main contribution to the energy of adsortion on a hydroxylated silica surface is due to the interaction of adsorbate molecules with the surface silanol groups[6]. According to the same classification[2], for molecules of groups B and D the energy of specific interactions with an adsorbent is determined by that of hydrogen bonds formed by these molecules with the surface silanol groups. The strength of these bonds depends on the chemical composition, the geometric and electronic structures of the adsorbed molecules and temperature. So far, the effect of temperature on the adsorption interaction energy has not received much attention, because when determining the heats of adsorption of various compounds it is usually assumed that under the conditions of adsorption and gas chromatographic measurements these thermodynamic characteristics are independent of temperature. However, in recent years Kuznetsov *et al.*[7], using calorimetry, have succeeded in demonstrating a noticeable influence of temperature not only on adsorption interactions via the hydrogen bond mechanism (triethylamine–Aerosilogel system), but also on adsorption on non-polar adsorbents (GTCB) when a temperature increase makes the dislocations in the GTCB lattice more accessible to the adsorption of certain molecules. These results indicate a need for greater attention to the experimental study of the problem in order both to enhance our knowledge of the adsorption mechanism and to determine the most specific thermodynamic characteristics of adsorption, and in order to solve practical problems related to the control of the selectivity of gas adsorption columns.

The aim of this work was to study the effect of temperature on the energy of adsorption interactions via hydrogen bonds for a series of aromatic hydrocarbons with different structures. The molecules of isomeric series of substituted benzenes chosen as adsorbates are convenient for studying intermolecular adsorption interactions as the differences in the geometric and electronic structures of these molecules are reflected in their retention behaviour.

## EXPERIMENTAL

Silochrom C-120 macroporous silica adsorbents (Reachim, U.S.S.R.) with a specific surface area, $S$, of *ca.* 120 $m^2/g$, an average pore diameter, $d$, of 350 Å and grain sizes of 0.35–0.5 mm were used. The column (41 × 0.3 mm I.D.) was previously heated at 250°C while being flushed with nitrogen for 16 h. Gas chromatography was performed on a Tsvet-104 chromatograph with a flame ionization detector, using nitrogen as the carrier gas. *n*-Alkanes ($C_6$–$C_{10}$) and various methyl- and alkyl-substituted benzenes of chromatographic-grade purity were employed as adsorbates.

The retention times of the compounds were measured at 10°C intervals in the range 70–170°C. The chromatographic peaks corresponding to all compounds were symmetrical within the above temperature range, the retention times being virtually independent of the amount of sample introduced. The time required for methane to emerge from the column was taken as zero time.

The corrected retention volumes, $V_{g,1}$, were calculated from the experimental retention volumes for all adsorbates. To evaluate the dependence of the differential heats of adsorption on temperature at low (zero) surface coverage, use was made of differentiation with respect to $1/T$ of the empirical equation describing the relationship between $\log V_{g,1}$ and $1/T$ as the trinomial*

$$\log V_{g,1} = A + BX + CX^2 \tag{1}$$

where $X = 1/T$.

## RESULTS AND DISCUSSION

The differences in the geometry and conformational structure of alkylbenzene and polymethylbenzene molecules usually result in a weakening of the dispersion interactions of the alkylbenzenes with the adsorbent surface[8]. An increase in the electronic density of polymethylbenzene rings with increasing number of substituents (methyl groups) and a weak dependence of this parameter on alkyl substituents manifest themselves in stronger specific interactions of polymethylbenzene molecules with polar adsorbents[9–11]. Therefore, polymethylbenzenes are usually retained on various adsorbents more strongly than the corresponding isomeric alkylbenzenes. Silochrom is not an exception and, in accordance with the differences in the geometric and electronic structures, polymethylbenzenes interact with the silanol groups of the adsorbent surfaces with greater energies than alkylbenzenes, having longer retention times than the corresponding alkylbenzenes.

In Fig. 1, where typical $\log V_{g,1}$ dependences of substituted benzenes on the number of carbon atoms, $n_C$, are presented for one value of temperature, a similar relationship is shown for molecules of the *n*-alkane series which is parallel to that for the alkylbenzenes. *n*-Alkanes, being adsorbed on Silochrom basically at the expense of dispersion forces, are more weakly retained by the adsorbent surface than substituted benzenes having the same number of carbon atoms in the molecule. The parallel course of the curves for *n*-alkanes and alkylbenzenes indicates that the additional contribution to the alkylbenzene retention, related to the elongation of the alkyl chain by $CH_2$ groups, is made mainly by the dispersion interaction energy, as the effect of the alkyl chain length on the electronic density of the benzene ring is insignificant. In the polymethylbenzene molecules each new $CH_2$ group not only increases the dispersion component of the adsorption energy, but also changes the magnitude and distribution of the electronic density of the benzene ring, leading to increased specific interaction of ring $\pi$-electrons with surface hydroxyl groups. Fig. 1 shows that the straight line corresponding to the $\log V_{g,1} = f(n_C)$ relationship for *ortho*-substituted polymethylbenzenes is higher and steeper than that for *n*-alkylbenzenes.

In the general case, the adsorption of polar molecules by Silochrom and the sequence of their emergence from a chromatographic column are largely determined by the energy of the hydrogen bond formed by these molecules with surface silanol groups, this energy being dependent on the composition and electronic and geometric

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* A supplementary examination showed that eqn. 1 leads to the same results as the thermodynamic relationship $\ln V_{g,1} = a + (b/T) + c \ln T$ (see Table I). In both instances the correlation coefficients were 0.9996–0.9999.

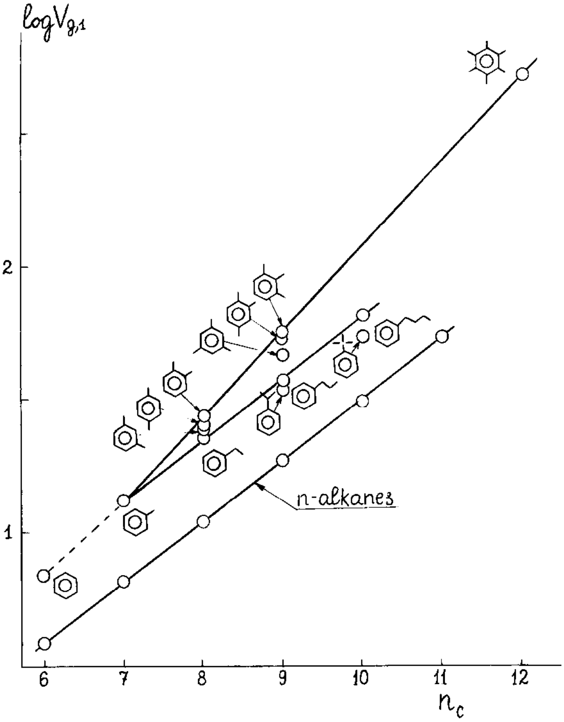


Fig. 1. Dependence of log $V_{g,1}$ on the number of carbon atoms, $n_C$, in molecules of *n*-alkanes and substituted benzenes adsorbed on a Silochrom C-120 surface at 150°C.

structures of the molecules. However, in some instances, when isomeric molecules are adsorbed the influence of their geometry becomes noticeable.

Thus, isoropylbenzene and *tert.*-butylbenzene, having alkyl substituents with branched chains, are retained by Silochrom more weakly than propyl- and *n*-butylbenzenes (Fig. 1). The retentions of isomeric xylenes differ insignificantly, but although its dipole moment is zero and the distribution of electronic density in the ring is most uniform, *p*-xylene emerges from the column after *m*-xylene in the entire temperature range investigated. On the GTCB surfaces, where the geometric factor plays the main role, the xylenes emerge in the sequence *m*-xylene followed by a mixture of *o*- and *p*-xylenes[8]. For the highly specific adsorbent barium sulphate, the emergence sequence is in accordance with the dipole moments and electronic density distributions: *p*-xylene emerges first, followed by *m*- and *o*-xylenes[9]. The effect of the geometric factor seems to predominate for adsorption on Silochrom when weaker specific interactions take place (the orientation of *p*-xylene on the adsorbent surface is more favourable than that of *m*-xylene and, hence, the interaction of *p*-xylene molecules with the surface is stronger).

It is interesting that in liquid chromatography on silica gel, when the contribution of dispersion interactions with the silica surface is considerably lower (because of the presence of a competitive solvent, *n*-alkane), the sequence of emergence of xylenes is determined by the electronic structures of these molecules and is $p$- < $m$- < $o$-[12].

Hence the differences in molecular geometry cause different extents of steric hindrance when a molecule choses the most favourable orientation on the adsorbent surface. This, in turn, results in different equilibrium distances of the molecules from the surface and strongly affects both the dispersion interaction energy and hydrogen bond energy, as the hydrogen bond strength is maximal when the proton donor group and the axis of an unshared electron pair orbital are colinear[13]. For trimethylbenzene isomers the retention corresponds to the electron density distribution, and the contribution of specific interactions becomes dominant. The first molecule to emerge is mesitylene, the electronic density distribution of which is symmetrical ($\mu$ = 0.1 D), followed by pseudocumene ($\mu$ = 0.3 D) and 1,2,3-trimethylbenzene ($\mu$ = 0.56 D).

Similar dependences of the retention of the molecules studied on their structure are also observed at other temperatures, the differences in retentions of molecules with different structures being more pronounced with decreasing temperature (for instance, at 80°C the differences are greater than at 150°C).

In Figs. 2–4 the dependences of log $V_{g,1}$ on $1/T$ for alkane and substituted benzene molecules, determined from the experimental data, are presented. In contrast to the alkanes, these dependences are curvilinear for substituted benzenes. One may assume that this non-linearity results from the temperature effect on the hydrogen bond energy, as neither the dispersion nor induction energy depends on temperature[14].

The calculation of the temperature dependences of differential heats of adsorption for low (zero) surface coverage, $\bar{q}_1$, performed in order to obtain quantitative estimates of the observed changes in heats of adsorption, showed that on increasing the temperature from 80 to 170°C the $\bar{q}_1$ values for substituted benzenes decrease by about 20–30 kJ/mol (Figs. 5 and 6) and at 170°C they become close to the $\bar{q}_1$ values for alkanes having the same number of carbon atoms in the molecule.

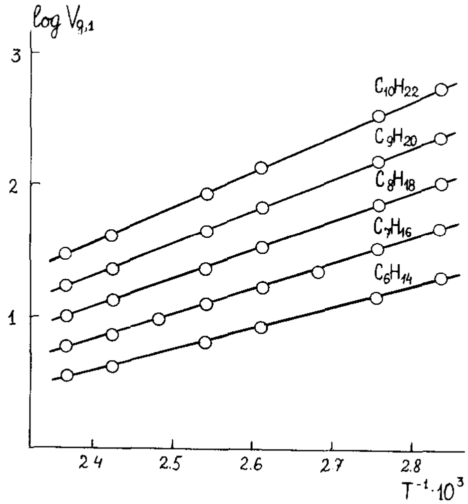
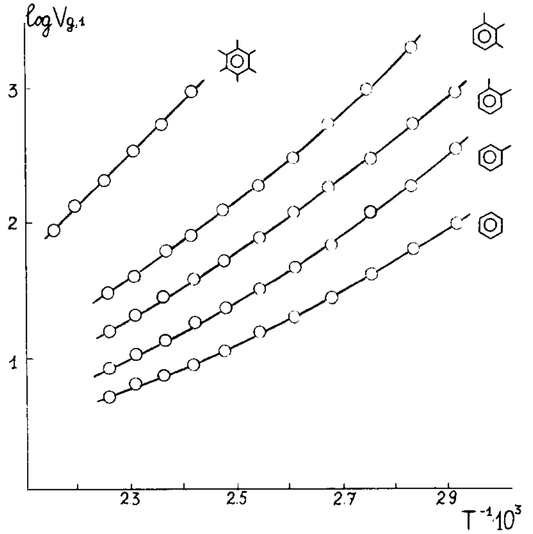


Fig. 2. Dependence of log $V_{g,1}$ on the reciprocal of the absolute temperature for *n*-alkanes on a Silochrom C-120 surface.



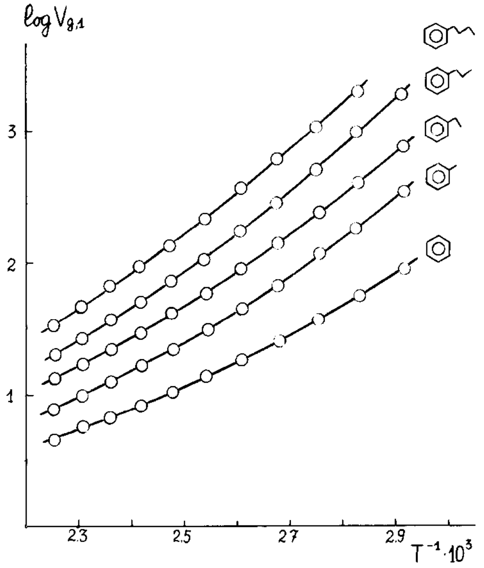


Fig. 3. Dependence of log $V_{g,1}$ on the reciprocal of the absolute temperature for polymethylbenzenes on a Silochrom C-120 surface.

Fig. 4. Dependence of log $V_{g,1}$ on the reciprocal of the absolute temperature for alkylbenzenes on a Silochrom C-120 surface.

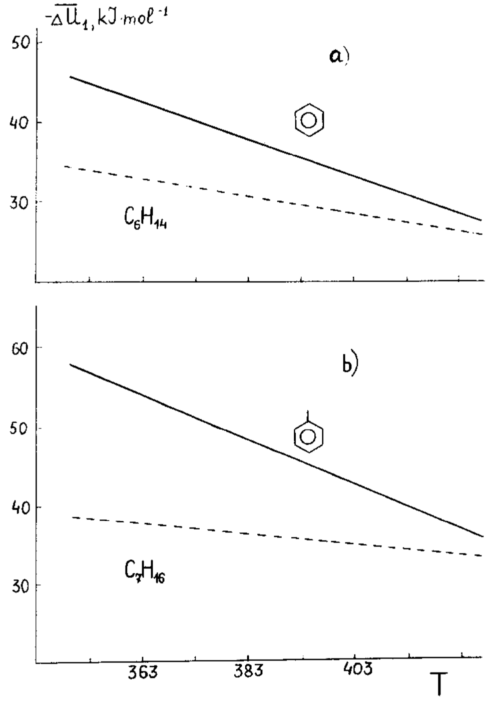


Fig. 5. Dependence of calculated $\bar{q}_1$ values on the absolute temperature for (a) benzene and *n*-hexane and (b) toluene and *n*-heptane.

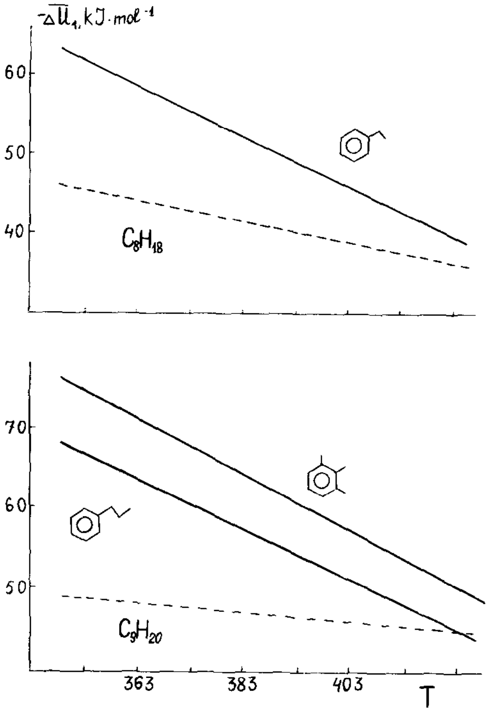


Fig. 6. Dependence of calculated $\bar{q}_1$ values on the absolute temperature for: (a) *n*-octane and ethylbenzene and (b) *n*-nonane, *n*-propylbenzene and 1,2,3-trimethylbenzene.

The data in Table I show the influence of temperature on the heats of adsorption and specific interaction contributions (*i.e.*, the hydrogen bond energies) of some substituted benzenes. Here, the differential heats of adsorption of substituted benzenes are given at low (zero) surface coverage and at two temperatures (80 and 170°C). Further, Table I also illustrates the differences between these values and specific interaction contributions, $\Delta q_{\mathrm{sp}} = (\bar{q}_1)_{\mathrm{Ar}} - (\bar{q}_1)_{n\text{-alk.}}$ at $t = 80°\mathrm{C}$, determined as the differences in the heats of adsorption of aromatic and saturated hydrocarbons (*n*-alkanes) having the same number of carbon atoms. Comparison of the $\bar{q}_1$ values obtained at 80°C shows that the heats of adsorption in the alkylbenzenes series increase more slowely than those of polymethylbenzenes. For ethylbenzenes and their isomeric xylene analogues the heats of adsorption are similar. However, the heats of adsorption of 1,2,3-trimethyl- and propylbenzenes differ by about 9 kJ/mol, this difference being related to the dissimilarities in their electronic structures.

The differences in the heats of adsorption at 80 and 170°C for the alkylbenzene series are virtually the same, the average being 25 kJ/mol. For polymethylbenzene this difference varies with increasing number of methyl groups; it is more than 20 kJ/mol for xylene and about 30 kJ/mol for trimethylbenzene. The contribution of specific interactions, found as the difference between the heats of adsorption of substituted benzenes and alkanes having the same number of carbon atoms in the molecule, changes in the same manner. For alkylbenzenes, $(\Delta q_{\mathrm{sp}})_{80°\mathrm{C}}$ is the same for all molecules in the series (about 21–23 kJ/mol). For polymethylbenzenes, the value

TABLE I

DIFFERENTIAL HEATS OF ADSORPTION AT LOW (ZERO) SURFACE COVERAGE, $\bar{q}_1$, FOR MOLECULES OF *n*-ALKANES AND SUBSTITUTED BENZENES ADSORBED ON SILOCHROM

| *Adsorbate* | *Number of carbon atoms in molecule,* $n_C$ | $\bar{q}_1$ *(kJ/mol)* | | | $\Delta\bar{q}_{sp}$ *(kJ/mol)* | | $\bar{q}_1$*, alkane (kJ/mol)* |
|---|---|---|---|---|---|---|---|
| | | *80°C* | *170°C* | *80 – 170°C* | *80°C* | *170°C* | |
| Benzene | 6 | 46 (45)* | 25 (24)* | 21 | 16 | –5 | 30 |
| Toluene | 7 | 58 (56)* | 33 (32)* | 25 | 22 | –3 | 36 |
| Ethylbenzene | 8 | 60 | 36 | 24 | 19 | –5 | 41 |
| Propylbenzene | 9 | 67 | 41 | 26 | 20 | –6 | 47 |
| Isopropylbenzene | 9 | 64 | 43 | 21 | 17 | –4 | 47 |
| *n*-Butylbenzene | 10 | 75 | 46 | 29 | 23 | –6 | 52 |
| *tert.*-Butylbenzene | 10 | 70 | 44 | 26 | 18 | –8 | 52 |
| *o*-Xylene | 8 | 59 | 42 | 17 | 18 | +1 | 41 |
| *p*-Xylene | 8 | 61 | 41 | 20 | 20 | 0 | 41 |
| *m*-Xylene | 8 | 59 | 43 | 16 | 18 | +2 | 41 |
| 1,2,3-Trimethylbenzene | 9 | 76 | 45 | 31 | 29 | –2 | 47 |
| 1,3,5-Trimethylbenzene | 9 | 74 | 46 | 28 | 27 | –1 | 47 |
| 1,2,4-Trimethylbenzene | 9 | 71 (67)* | 49 (49)* | 22 | 24 | +2 | 47 |

* These values were calculated by the thermodynamic relationship given in the footnote at the end of the Experimental section.

ranges from 18 to 20 kJ/mol for xylenes and from 27 to 29 kJ/mol for trimethylbenzenes. The heats of adsorption vary with temperature so that the specific interaction contributions become almost zero at 170°C.

The results show that the hydrogen bond energy in the alkylbenzene series is approximately the same for all the molecules in the series, and this corresponds to an almost equal distribution of electron density in the benzene rings of the molecules. For polymethylbenzenes, where the addition of every extra methyl group increases the ring electron density, a noticeable increase in hydrogen bond energy is observed on passing from xylenes to trimethylbenzenes.

Further, one can see that, although an increase in temperature leads to an almost complete disappearance of contributions from specific interactions for both alkyl- and polymethylbenzenes, the total energy of adsorption of the latter compounds in the high-temperature range remains 5 kJ/mol higher than that of the corresponding alkylbenzenes. This difference can be related both to the dissimilarities in the geometric structures of the molecules and to the stronger hydrogen bonds formed by polymethylbenzene molecules with the Silochrom surface hydroxyl groups, owing to some peculiarities of the electronic structure of polymetylbenzenes.

## REFERENCES

1 N. N. Avgul, A. V. Kiselev and D. P. Poshkus, *Adsorptsiya gazov i parov na odnorodnykh poverkhnostyakh (Adsorption of Gases and Vapours on Homogeneous Surfaces)*, Khimiya, Moscow, 1975.
2 A. V. Kiselev and Ya. I. Yashin, *Gas-Adsorption Chromatograph*, Plenum, New York, 1969.
3 N. K Bebris, A. V. Kiselev, V. Ya. Mokeev, Yu. S. Nikitin, Ya. I. Yashin and G. E. Zaitseva, *Chromatographia*, 1 (1971) 93.
4 N. K. Bebris, T. E. Zaitseva, A. V. Kiselev, Yu. S. Nikitin and Ya. I. Yashin, *Nephtekhimiya*, 8 (1968) 481.
5 N. K. Bebris, E. Ya. Ischenko, G. E. Zaitseva, A. V. Kiselev, G. L. Kustova, B. A. Lipkind, Yu. S. Nikitin and Ya. I. Yashin, *Nephtekhimiya*, 10 (1970) 776.
6 A. V. Kiselev and I. Ligin, *Infrakrasnye spectry poverkhnostnykh soedineniy i adsorbirovannykh veshchestv (Infrared spectra of Surface Compounds and Adsorbates)*, Nauka, Moscow, 1972.
7 A. Derkaui, A. V. Kiselev and B. V. Kuznetsov, *Zh. Fiz. Khim.*, 59 (1985) 159.
8 E. V. Kalashnikova, A. V. Kiselev and K. D. Scherbakova, *Chromatographia*, 7 (1974) 22.
9 L D. Belyakova, A. V. Kiselev and G. A. Soloyan, *Chromatographia*, 3 (1970) 254.
10 T. N. Gvozdovich, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 2 (1969) 234.
11 T. N. Gvozdovich, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 6 (1973) 179.
12 A. N. Ageev, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 13 (1980) 669.
13 R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York.
14 B. M. Yabvorsky and A. L. Detlar, *Spravochnik po fizike (Handbook on Physics)*, Nauka, Moscow, 1968, p. 246.