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Ultra-short open capillary columns in gas–liquid chromatography

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Abstract

New area in capillary gas chromatography (GC) was investigated. Many important analytical tasks can be solved only use very short capillary columns. Variation of chromatographic characteristics of ultra-short capillary columns with column length was originally studied at the conditions of gas–liquid chromatography. The column length varied from 500 to 10 cm. Dependencies of height equivalent to one theoretical plate (HETP) and separation number (SN) on carrier gas velocity were considered for columns of various length. Field of ultra-short open capillary columns in gas–liquid chromatography has the following peculiarities: (1) more shorter retention times of sorbates, (2) more low temperatures of short column, that has as final result (a) high selectivities of used column and (b) the possibilities to separation more thermal lability compounds. It was shown that short capillary columns can be successfully used at both isothermal and temperature programming conditions for express-analysis at lower oven temperatures. Examples of express-analysis (high speed), analysis of high boiling and thermolabile compounds are listed, which demonstrate some radically new applications of capillary gas chromatography.

Keywords: Capillary gas chromatography; Short and ultra-short open capillary columns; Analysis of thermolabile compounds; Analysis of high-boiling compounds; Carrier gas velocity; Efficiency

1. Introduction

Capillary chromatography, Golay [1] suggested about 50 years ago, is currently the main variant of analytical gas chromatography (GC). Theoretical and practical aspects of capillary gas chromatography are considered in the excellent monographs (see, for example [2–6]). However, researchers concentrated their attention on study and practical application of long capillary columns (10–150 m) since such columns allow realisation of high efficiency. But not all time very high efficiency is main goal in the solution of many analytical problems. By the way, a typical example of important chromatographic variant, which has a limitation in efficiency, but use very widely in practice, is TLC.

Plenty of investigators have focused their attention on the short columns as important method of approach for the chromatographic express separation. For example, Desty et al. [7] were first who showed rapid separation of 15 components mixture in 2 s on the short capillary column with length only 1.2 m. Now progress in express analysis (or high speed analysis) on the short capillary column is well-known conception, it was represented in detail in their monographs by van Es [3] and Poole [5].

Note that length of capillary columns, which are available from various manufacturers is not less than 10 m length. Not long ago the main parameters of capillary gas chromatography techniques were considered in paper [8] on the basis of recent publications in the *Journal at High Resolution Chromatography*. According to this data, capillary columns of 10–30 m length were used in most publications (75%), shorter columns were not in common use.

Early the short capillary columns were used by some investigators for practical applications (see, for example [9,10]). In our book [11] it was noted that optimization of chromatographic experiment is the complex task: “the data indicate a complex relationship between the various parameters and criteria of the chromatographic method. It is

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recommended that the relationship are used in the compilation of the programme for the optimization of a chromatographic separation". It must be noted that in this book the column length L was indicated as one of the most important parameters. However, high duration of the chromatographic separation is not sole reason for decreasing of column length (see, for example [11]). Second important goal in reducing of column length is possibility to decrease column temperature during chromatographic separation. As a result of decreased column temperature new opportunity in expand of practical application of GC is appeared due to using of the short capillary column to separation of thermally unstable or extremely high boiling compounds. Further, the short capillary column can be used for increasing of stationary phase selectivity with decreasing of temperature. Also it is possible to use of more selective but less thermally stable stationary phases. It must be noted that the mentioned above advantage in selectivity increasing due to decreasing of column length and column temperature consequently was not described in famous monographs [3,5]. For example, only the lessen of analysis time on short columns was studied in excellent book by Poole [5], it being interesting that the listed in this book examples is limit oneself to length 1.0 m.

At last years Amirav with co-workers [12–15] did a major step towards development gas chromatography on very short columns. They showed expediency of use of the short capillary columns with length 50, 100, 300, 400 and 600 cm in ultra-fast GC–mass-spectrometry (MS).

In one of the last paper by Fialkov [15] "extending the range of compounds amenable for gas chromatography–mass-spectrometric analysis" in the abstract the following important conclusion were be done: "GC–MC suffer from a major limitation in that an expanding number of thermally labile or low volatility compounds of interest are not amenable for analysis. We found that the elution temperatures of compound from GC can be significantly lowered by reducing the column length, increasing the carrier gas flow rate, reducing the capillary column film thickness and lowering the temperature programming rate. Pyrene is eluted at 287 °C in standard GC–MS with a 30 m × 0.25 mm i.d. column with 1 μm DB5ms film and 1 ml/min He column flow rate. In contrast, pyrene is eluted at 79 °C in our supersonic GC–MS system using 1 m × 0.25 mm i.d. column with 0.1 μm DBms film and 100 ml/min He column flow rate" [15].

We should like also to note, that using of MS as quantitative and qualitative instrument for chemical analysis is especially expedient for ultra-short columns, because MS increases the real resolution of short column.

The goals of our work were: firstly, systematical investigation of height equivalent to a theoretical plate (HETP) dependence on carrier gas linear velocity and on length of the open tubular capillary columns (in range of several meters down to 10 cm); secondly, to do attempts to see the field of application of short open tubular columns in practical GC; thirdly, to make different experimental examples of using of short columns for different types of analytical solutions with standard chromatographic instrumentation and standard flame ionization detection.

However, we assume that it is advisable to investigate the properties of short (ultra-short) columns by the way on the following reasons: (1) it is important to study all types of columns due to formation of full conception of GC columns; (2) ultra-short columns have interesting application characteristics for some types of analytical tasks (for example, for analysis of thermolabile and high-boiling compounds); (3) this investigation can be interesting from point of view of miniaturization of analytical equipment.

In the present study a new type of ultra-short capillary columns (0.1–5 m) was firstly systematic studied and application prospects for the columns application were considered. We think that ultra-short columns in gas chromatography are a new field in chromatography, because it must have special aspects in theory and instrumentation and already has new special field of applications.

2. Some aspects of chromatography on short capillary columns

It is very important to estimate the minimum possible length of capillary column, which is sufficient for separation of a critical pair of components, and also to estimate the minimum time of separation. For this goal it is possible to use equations, which are used in the monograph by van Es [3]. The following equation is recommended [3] for thin film columns and for very low pressure drop ($P_0/P_a \approx 1$):

$$t_R = (1 + k)N_{req}F(k)d_c^2/D_g \quad (1)$$

where k is the retention factor, d_c is the column diameter, D_g is the diffusion coefficient of the solute in the mobile gas phase at the column outlet pressure.

$$F(k) = \frac{1 + 6k + 11k^2}{96(1 + k)^2} \quad (2)$$

$$N_{req} = 16R_S^2\left[\frac{1 + k_2}{k_2}\right]^2\left[\frac{\alpha}{\alpha - 1}\right]^2 \quad (3)$$

where N_{req} is the number of theoretical plates required to obtain a certain resolution,

$$\alpha = \frac{k_2}{k_1} \quad (4)$$

$$R_S \approx \frac{(t_{R2} - t_{R1})}{w_{b2}} \quad (5)$$

where R_S is the necessary resolution of a critical pair of two components, t_{R1} and t_{R2} are retention times of two peaks, w_{b2} is the width of the second peak.

As a rule, we know HETP (H_c) = $f(u)$, where u is the linear velocity of mobile phase. Therefore, we can estimate mini-

mum of H_c using the following equation:

$$L_{min} = N_{req} H_c \quad (6)$$

Eq. (1) can be used for the estimation of minimum retention time.

Use of ultra-short columns allow us to realize minimum of two new (compare to long column) analytical effects as: (1) analysis of compounds with high boiling points, which earlier could not be chromatographed on the long columns due to their considerable retention; (2) express-analysis of the compounds, which retained a long time at the long columns.

Using very short capillary columns allow elution of thermolabile compounds, which is of great practical interest and extends gas chromatography application. Note also another effect, known earlier: as column temperature decreases the selectivity of column improves (see, for example [16]).

The known approximate expression can be applied for variation in retention factor with decrease in column temperature [17]:

$$\frac{k(T_1)}{k(T_2)} \approx \frac{P_0(T_2)}{P_0(T_1)} \cdot \frac{T_1}{T_2} \quad (7)$$

where $P_0(T_1)$ and $P_0(T_2)$ are the pressures of saturated vapours of the solute at temperatures T_1 and T_2 (K), respectively. To our estimation, the variation in retention factor with column temperature decrease for 50 °C is pronounced:

$$\frac{k(T_1)}{k(T_2)} \approx 4.0 - 7.0(T_1 = T_2 + 50^{\circ}C) \quad (8)$$

Hence, the expected retention of solutes should increase in five to six times approximately at the given conditions of low temperatures. However, comparison of separation on the columns of 30 and 0.5 m length (at temperatures T_1 and T_2, respectively) with Eqs. (7) and (8) shows that separation on the ultra-short column takes much less time (in eight to ten times) even at temperature decreased for 50 °C.

Of course, shorter column will have lower resolution. But for many samples we must have only limit information about a few components, which have good resolution from other.

Note that the above mention advantages of short capillary columns can be realised at temperature programming. It is of great importance for separation of compounds with wide range of boiling points.

The difficulties, which deal with column over-loading by samples, can be compensated with application of short columns with thick layers of stationary liquid phase (SLP), i.e. columns of higher capacity. But we think the best way is the using of packed (capillary or diameter to 2 mm) columns, which packed with solid support (for example, of fused silica) with small diameter of particles 0.100–0.003 mm (see for capillary packed columns, for example [18,19]).

3. Experimental

Chromatographic measurements were made using an HP 5890 (II) gas chromatograph (Hewlett–Packard, USA) equipped with an electronic pressure control, and autosampler, a flame ionization detection (FID) system and an integrator.

Chromatographic columns of the following lengths (m) were studied: 5.00, 3.00, 2.00, 1.00, 0.50, 0.35 and 0.10. As known, the minimum column length for the 5890 (II) gas chromatograph is 0.35 m. Hence, the column of 0.10 m length was connected with the injector and the detector through hollow capillary. All columns were obtained by cutting the 25 m × 0.15 mm i.d., 2.0 μm CP-Sil 5CB column (Chrompack, The Netherlands) into pieces of necessary

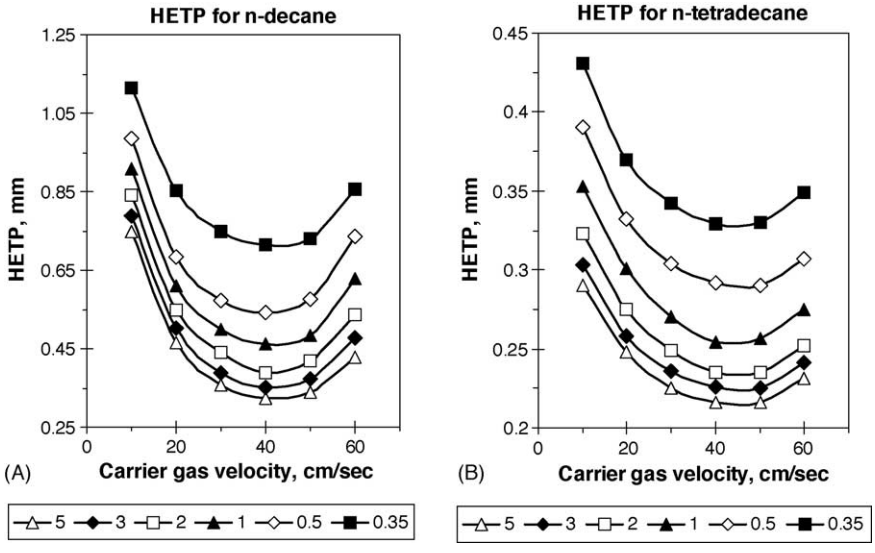

Fig. 1. Dependence of HETP on carrier gas velocity (helium) for *n*-decane (A) and *n*-tetradecane (B) on the columns of various length (0.35, 0.5, 1, 2, 3, 5 m). Experimental conditions: HP 5890 (II) gas chromatograph, oven temperature 170 °C, detector temperature 280 °C, injector temperature 250 °C, split ratio 1:100, sample size 1 μl.

length. *n*-Alkanes C_9–C_{20} were used as test compounds (Hewlett–Packard). Specific column efficiency HETP and separation number (SN) at isothermal conditions and SN at temperature programming were measured for the compounds. Methane was used as hold-up time determination. The split ratio was 100.

4. Results and discussion

4.1. Some general chromatographic characteristics of short columns

Dependencies of HETP and SN on carrier gas velocity on short and ultra-short capillary columns are shown in Figs. 1–4. The regularities obtained experimentally for short columns are in agreement with generally known HETP dependence on carrier gas velocity. But the HETP values for the short columns are noticeably greater than those for columns of standard length of 10–30 m.

Real HETP values for *n*-decane and *n*-tridecane obtained on the short columns of various length (0.35, 2.0 and 5.0 m) are listed in Table 1. As follows, efficiency of the short column (0.35 m) for *n*-decane decreases in two times approximately (in comparison with capillary column of 5 m length), but for *n*-tridecane that does for 50%. Most likely, that pronounced decrease in efficiency for the shortest column deals with some by-effects, for example, an increase in column temperature at the initial part of column, located right after injector. Note that the observed decrease in column efficiency is not the

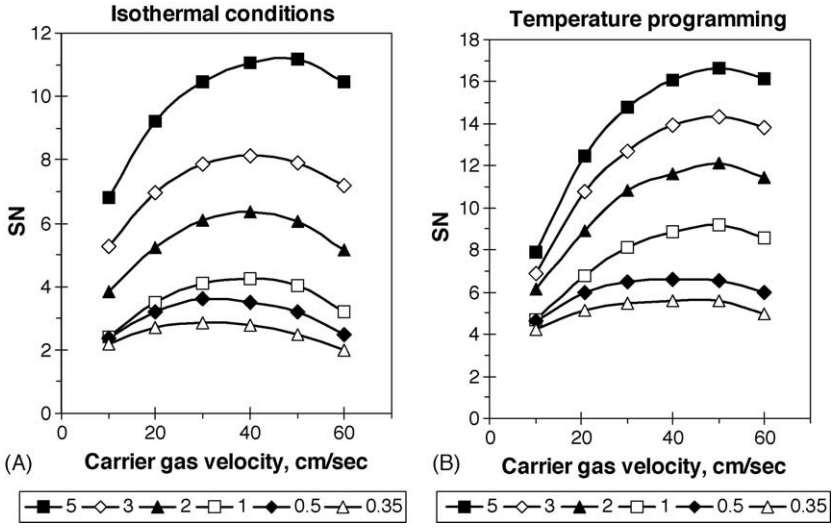

Fig. 2. Dependence of separation number (SN) on carrier gas velocity (helium) for pair *n*-dodecane/*n*-undecane at isothermal conditions (A) and at temperature programming (B) on the columns of various length (0.35, 0.5, 1, 2, 3, 5 m). Experimental conditions: HP 5890 (II) gas chromatograph, oven temperature 170 °C (isothermal), temperature programmed from 30 to 150 °C at 10 °C/min, detector temperature 280 °C, injector temperature 250 °C, split ratio 1:100, sample size 1 μl.

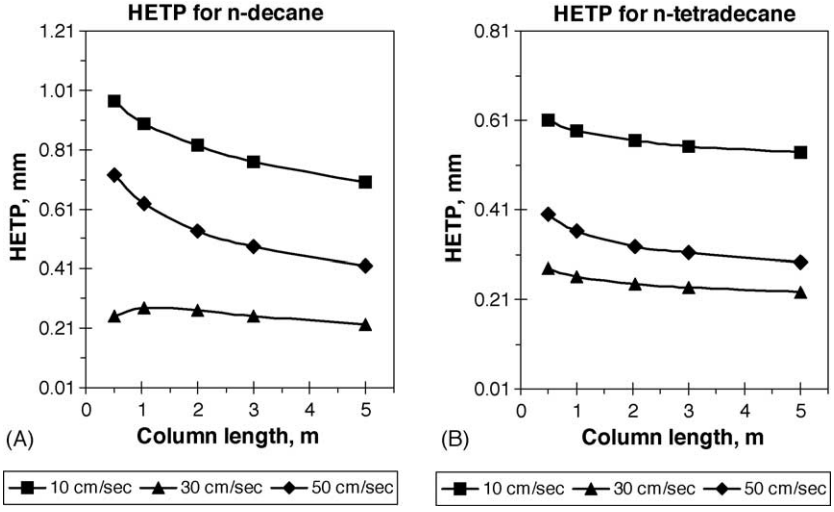

Fig. 3. Dependence of HETP on column length for various carrier gas velocities (10, 30, 50 cm/s) for *n*-decane (A) and *n*-tetradecane (B). Experimental conditions: HP 5890 (II) gas chromatograph, oven temperature 170 °C, detector temperature 280 °C, injector temperature 250 °C, split ratio 1:100, carrier gas helium, sample size 1 μl.

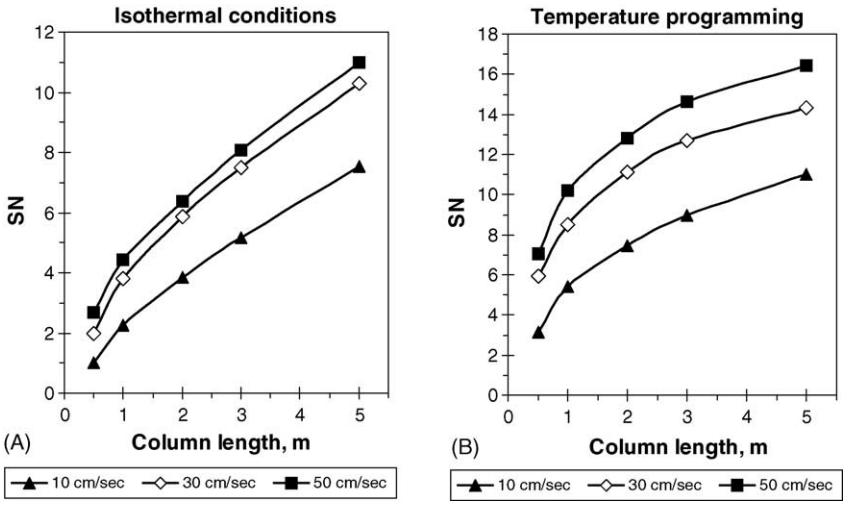

Fig. 4. Dependence of separation number (SN) on column length at various carrier gas velocities (10, 30, 50 cm/s) for pair *n*-dodecane/*n*-undecane at isothermal conditions (A) and at temperature programming (B). Experimental conditions: HP 5890 (II) gas chromatograph, carrier gas helium, oven temperature 170 °C (isothermal), temperature programmed from 30 to 150 °C at 10 °C/min, detector temperature 280 °C, injector temperature 250 °C, split ratio 1:100, sample size 1 μl.

principal obstacle for its successful analytical application (see below).

Variation of SN with carrier gas velocity at isothermal conditions and temperature programming is shown in Fig. 2. As seen, SN values are much greater at temperature programming than those at isothermal mode. This peculiarity of temperature programming should be taken into account for development of specific analytical techniques.

Note that surface of solid support (capillary walls) in capillary columns is more inert than in packed columns. It allows separation of polar compounds without losses due to irreversible adsorption of solutes by solid support and without formation of asymmetric zones, which can be observed for solutes with non-linear adsorption isotherm. The total amount of SLP in capillary column is much less than in packed one. This leads to considerable reduction in analysis duration.

Hence, short and ultra-short columns seem reasonable to be used in analytical purposes like express-analysis, analysis of thermolabile and high-boiling compounds at the expense of decrease in column temperature and reduction of retention of the solutes.

4.2. Some examples of separation on short columns

Let us list some applications of short columns. Chromatogram of ten common medicinal compounds on the column of 2 m length is shown in Fig. 5. Total duration of analysis is 3.5 min. Most solutes (seven compounds) elute for less than 1.5 min. Thus, the efficiency of the column is good enough to perform express-analysis of a great number of medicines, comprising these components. In Russia the column is in use in the lab which deals with certification of medicines.

Fig. 6 demonstrates the separation of mixture of *n*-C_9–*n*-C_{20} alkanes on the column of 0.5 m length at temperature programming. Such mixtures are used for estimation of boiling points of compounds to be chromatographed in various fields, especially in petrochemistry. With short capillary columns the analysis takes much less time (especially at temperature programming). It allows analysis of heavy compounds at low temperatures and reduction of analysis duration.

Analysis of analgin is shown in Fig. 7. Analgin is thermolabile and unstable compound, which can be hardly analysed even by HPLC. Column of 10 cm length used for the analy-

Table 1
Dependence of minimum HETP value (mm) on the length of short open capillary column for *n*-decane and *n*-tridecane

Solute	Column length (m)		
	0.35	2.0	5.0
n-Decane	0.72	0.46	0.33
n-Tridecane	0.33	0.26	0.22

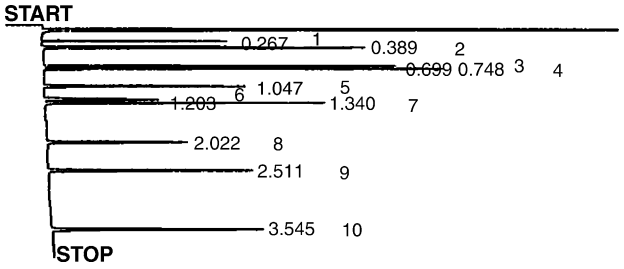

Fig. 5. Chromatogram of medicines. Solutes: 1—urotropin, 2—ephedrine, 3—paracetamol, 4—phenacetin, 5—caffeine, 6—theophlylline, 7—phenobarbital, 8—atrophin, 9—codeine, 10—papaverine. Experimental conditions: HP 5890 (II) gas chromatograph, capillary column 2 m × 0.15 mm, 0.2 μm CP-Sil 5CB, carrier gas helium, 80 cm/s, temperature programmed from 210 to 320 °C at 30 °C/min, detector temperature 250 °C, injector temperature 230 °C, split ratio 1:100, sample size 1 μl. Test mixture was used as a 1 mg/ml solution.

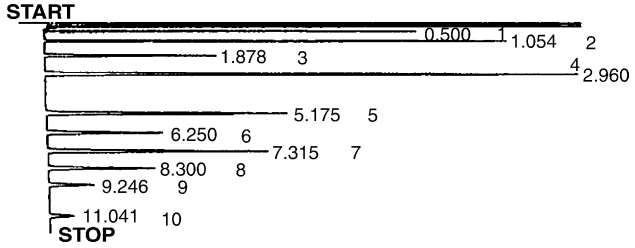

Fig. 6. Chromatogram of n-C_9–C_{20} alkanes. Solutes: 1—*n*-nonane, 2—*n*-decane, 3—*n*-undecane, 4—*n*-dodecane, 5—*n*-tetradecane, 6—*n*-pentadecane, 7—*n*-hexadecane, 8—*n*-heptadecane, 9—*n*-octadecane, 10—eicosane. Experimental conditions: HP 5890 (II) gas chromatograph, capillary column 0.5 m × 0.15 mm, 0.2 μm CP-Sil 5CB, carrier gas helium, 50 cm/s, temperature programmed from 40 to 150 °C at 10 °C/min, detector temperature 280 °C, injector temperature 230 °C, split ratio 1:100, sample size 1 μl.

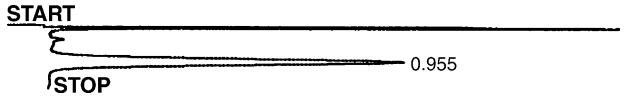

Fig. 7. Analysis of analgin by GLC. Experimental conditions: HP 5890 (II) gas chromatograph, capillary column 0.1 m × 0.15 mm, 0.2 μm CP-Sil 5CB, carrier gas helium, 60 cm/s, oven temperature 160 °C, detector temperature 220 °C, injector temperature 200 °C, split ratio 1:50, sample size 1 μl. Test compound was used as 25 μg/ml solution in chloroform.

sis. It was connected with injector and detector through capillaries. Peak areas for analgin were reproduced quite well. Therefore, quantitative analysis of analgin can be performed by GLC.

Chromatographic separation of 15 chlorinated organic pesticides is shown in Fig. 8. Temperature programming and splitless injection allows improvement of quantitative analysis. As seen, short columns (5 m) are appropriate for separation of complex mixtures. Column with low phase ratio β (i.e. with thick layer of SLP and therefore, with high capacity) was used.

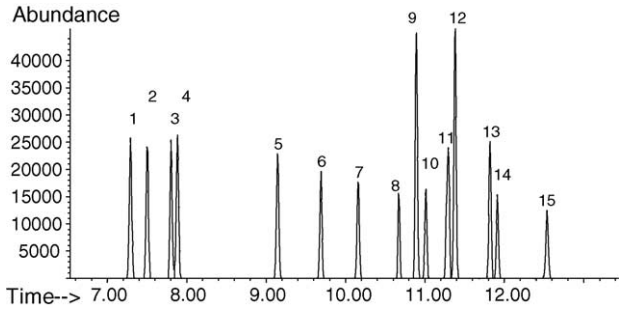

Fig. 8. Separation of 15-components organochlorine pesticides mixture by GLC–mass spectrometry. Solutes: 1—α-hexachlorcyclohexane, 2—β-hexachlorcyclohexane, 3—γ-hexachlorocyclohexane, 4—δ-hexachlorcyclohexane, 5—heptachlor, 6—aldrin, 7—heptachlor epoxide, 8—α-endosulfan, 9—*p*,*p*′-DDE, 10—dieldrin, 11—β-endosulfan, 12—*p*,*p*′-DDD, 13—endosulfan sulfate, 14—*p*,*p*′-DDT, 15—methoxychlor. Experimental conditions: HP 5890 (II) gas chromatograph equipped with an electronic pressure control, a mass-selective detection system HP 5972, capillary column 5 m × 0.15 mm, 0.2 μm CP-Sil 5CB, carrier gas helium, 76.3 cm/s, temperature programmed from 110 °C (2.5 min) to 190 °C at 30 °C/min, then to 290 °C at 15 °C/min, detector temperature 280 °C (detection by selected ions), injector temperature 250 °C, splitless injection, sample size 1 μl. Test compounds were used as 1 μg/ml solution in hexane (Hewlett–Packard, USA).

In our opinion, short columns with thick layers of SLP should be used for splitless injection.

The above results of investigation into short gas–liquid capillary columns can be extrapolate also to gas–solid capillary columns [20], because last columns have in generally the same properties as gas–liquid columns, but usually gas–solid columns has more large sorption capacity (compare to columns with liquid sorbents). Therefore, their using in gas chromatography is very promising.

5. Conclusion

Ultra-short capillary columns are new field in capillary chromatography. Many important analytical tasks can be solved only use very short capillary columns.

Main chromatographic characteristics of ultra-short capillary columns (10–500 cm) were studied. The studied regularities of the columns of this type and some typical applications allow extension of analytical resources of capillary gas chromatography. Listed practical application show expediency of ultra-short capillary columns in some practical tasks. We assume that development of this direction in capillary chromatography is advisable.

In our opinion, short an ultra-short gas-adsorption (gas–solid) capillary columns are also perspective for practical using as capillary gas–liquid columns.

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