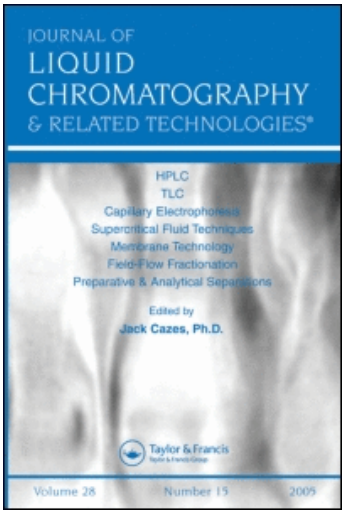

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HIGH-EFFICIENCY FUSED-SILICA CAPILLARY MICRO-PACKED COLUMNS IN GAS CHROMATOGRAPHY

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ABSTRACT

Due to convenience in operation, high efficiency, simplicity to prepare and wide range of problems solved, it is expedient to employ capillary micro-packed columns suggested several years ago.

The sorption capacity of such columns is sufficient for analyzing light compounds and for detecting admixtures. The high mass-exchange velocity facilitates the performance of rapid analysis. The above-suggested columns can be readily adapted to standard gas chromatographs, chromatographs designed for open-tubular columns, and chromatograph-mass spectrometers.

By analogy with liquid chromatography, it is reasonable to develop high-efficincy gas chromatograph of elevated pressure for broad application of capillary micro-packed columns.

INTRODUCTION

The column is the heart of the chromatographic device, because the process of chromatographic

separation is realized in the column. The development of chromatography is mainly determined by the development of chromatographic columns.

At present, open-tubular and packed columns of different types are used in analytical and physicochemical measurements. Packed columns have the following advantages over open-tubular columns: 1) they can be employed in gas-liquid chromatography (GLC) and in gas-solid chromatography (GSC) with any kind of sorbent, and 2) they have a high sorption capacity which facilitates the separation of relatively large sample. However, these columns are generally inferior to the open-tubular columns in terms efficiency. Thus, the development of investigations aimed at increasing of the efficiency of the packed columns is very promising.

The hierarchy of the packed columns is schematically shown in Fig.1. The figure illustrates the two known directions of increasing the separation efficiency in gas chromatography: 1) decreasing the column diameter, and 2) decreasing the particle diameter of the sorbent used. Therefore the symbiosis of the two above factors, i.e. the application of capillary micropacked columns is very perspective.

Discussing the scheme shown in Fig.1, it is also necessary to mention the following: firstly, in our opinion, columns of diameter of less than 2 mm can be related to capillary packed columns. According to data derived earlier (6,7), for columns approximately in the range of diameters up to 2 mm, the height equivalent to a theoretical plate (HETP) and the mass-transfer coefficient are substantially less than in the case of 3 mm diameter columns.

Secondly, columns of larger diameters packed with microparticles and described for example by Lu and

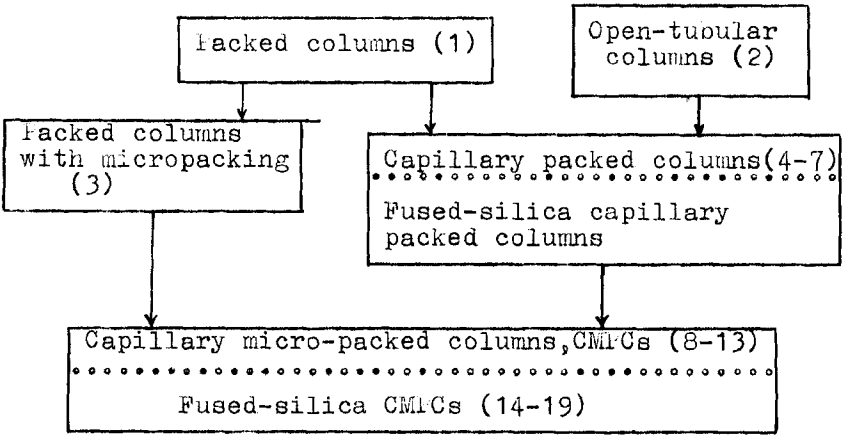

Fig.1. Scheme of genesis of fused-silica capillary packed columns.

coworkers (3) are characterized by high efficiency, but require using relatively larger quantities of narrow fractions of small-size sorbent which are much more expensive than coarse sorbent.

On the basis of the literature data available(15) we may conclude that the investigation of columns with a diameter less than 0.5 mm packed with sorbents which particle diameter is less than 30 μm, is of scientific and practical interest. Undoubtedly, it is expedient to use capillary columns also with sorbent particles of ordinary diameters alongside with columns of this type (6,7).

Several years ago we suggested and in 1983 began to investigate actively fused-silica capillary micro-packed columns (CMPC) (14-19), particularly polymer-coated flexible fused-silica capillaries 0.15-0.53 mm I.D. packed with sorbent particles diameter varying from 5 to 63-100 μm. The application of fused-silica

capillary packed columns as compared with columns of other materials (steel, glass) provides the following advantages: 1) flexibility, strength, convenience in operation, 2) catalytic and adsorption inertness, and 3) wall smoothness which is important when packing the column. The application of fused-silica packed columns affords additional advantages in comparison with capillary packed columns which were described in earlier publications (6,7).

Fused-silica packed columns are being successfully used by other investigators. For example, Al-Thamir presented a paper (20) devoted to the application of 0.42 mm I.D. column packed with Chromosorb 102 , 30-40 μm for separation of natural gas. Unfortunately such columns are relatively seldom used in chromatographic practice.

In this review the authors are discussed a systematic study of chromatographic characteristics, preparation techniques and area of application of capillary packed columns. Comprehensive chracteristics of such columns involving their comparison with classical packed and open-tubular columns facilitate their practical application and stimulate futher investigaticns in this area.

In this paper we emphasized the application of fused-silica CMPCs which proved to be most efficient in work. However, we do not hold the opinion that the use of columns of this type is universal. We still believe that in analytical chromatography it is expedient to use widely capillary packed columns loaded with sorbent of the average particle diameter 0.05-0.16 mm. This kind of columns is less efficient than CMPCs, however they are characterized by the low resistance of the carrier gas flow.

COMPARISON OF GAS-CHROMATOGRAPHIC CHARACTERISTICS OF FUSED-SILICA CMPC AND OTHER TYPES OF COLUMNS

From the data given in Tables 1, 2 and 3, it follows that the specific efficiency (number of efficient theoretical plates per metre of column, N_{eff}/L) of the fused-silica CMPCs is higher than that of other types of columns. In particular, for an 0.38 mm I.D. fused-silica column packed with 7.5 um silica gel, the HETP value is 0.03 mm, which corresponds to N_{eff}/L = 30,000theoretical plates per metre. This characteristics is greater than that of ordinary packed column (the diameter being more than 2 mm) and of open-tubular columns of about 10-30 and 5-10 times respectively. It means, for example, that the 10 cm fused-silica CMPC can be in some cases replaced by 3 m ordinary packed column.

The total efficiency (N_{eff}) varies from 3,000 to 35,000 theoretical plates for the investigated fused-silica CMPCs and prevails over the total efficiency of packed columns (Table 1), but falls short of the characteristics of open-tubular columns (Tables 2 and 3). However, it should be noted that the length of the the investigated fused-silica CMPCs does not exceed 6.5 m.

The resolution of the widely-used traditional packed columns in chromatography is insufficient for solving numerous complicated physico-chemical and analytical problems. In comparison with them, the fused-silica CMPCs allow one to make a more complete separation of the sample mixture, thus facilitating the solution of the above-cited problems. Small-size CMPCs have rendered it possible to decrease the amount of sorbent being used and to reduce the follow-up in temperature programming. The procedure for preparing

Table 1

Comparison of characteristics of fused-silica CMPCs and ordinary packed columns

Characteristics	Ordinary packed columns, I.D > 2 mm	Fused-silica CMPCs, I.D.=0.15-0.4 mm	CMPC advantages and drawbacks
N_{eff}/L, theoretical plates per metre	500-1000 (21)	3,000-20,000	CMPC length of 10-50 cm is equivalent to packed column length 1 m; sorbent economy
N_{eff}, theoretical plates	500-5,000	3,000-35,000	Higher separation capacity
Coefficient C, sec.	10^{-2}	10^{-3}-10^{-4}	Rapid analysis
Inlet pressure, atm.	up to 5	2-25	Drawback: elevated pressure. Inspite of this fact, standard devices can be used

Table 2

Comparison of characteristics of fused-silica CMPCs and open-tubular columns

Parameter	Open-tubular columns, I.D.= 0.2-0.4 mm	Fused-silica CMPCs, I.D.= 0.15-0.4 mm	CMPC advantages and drawbacks
N_{eff}/L, theoretical plates per metre	1,300-3,000 (22-24)	3,000-20,000	Small column size
N_{eff}, theoretical plates	20,000-100,000 (22-24)	3,000-35,000	If $L > 6$ m and $P > 25$ atm., total efficiency can be increased
Coefficient C, sec.	10^{-3}	10^{-3}-10^{-4}	Rapid analysis
W_{max}, μg	0.2 (25)	2	Analysis of admixture(without enriching of the sample)
Stationary phase	liquid phases for GLC	sorbents for GLC and GSC	Separation selectivity, i.e. for light compounds
Inlet pressure, atm.	up to 2-5	2-25	Drawback: elevated pressure

Table 3

Comparison of characteristics of fused-silica CMPCs and wide-bore, thick-film capillary columns (WTCC)

Characteristics	WTCC, I.D.=0.53 mm	Fused-silica CMPCs, I.D.=0.15-0.4 mm	CMPC advantages and drawback
N_{eff}/L, theoretical plates per metre	1,700 (26)	3,000-20,000	Small length
N_{eff}, theoretical plates	up to 52,000 (26)	3,000-35,000	If $L > 6$ m and $P > 25$ atm., total efficiency can be increased
Sample volume	medium	large	Admixture analysis
Stationary phase	Bonded silicon and polyethylene glycol	sorbents for GSC and GLC	Universality
Inlet pressure, atm.	1.2 (26)	2-25	Drowback: elevated pressure

the efficient fused-silica CMPCs is not more complicated than that for ordinary packed columns.

Open-tubular columns are characterized by a high total efficiency, however their potentiality is realized largely in GLC (Tables 2 and 3), whereas in fused-silica CMPCs, all kinds of sorbents are used, including adsorbents.

It was interesting to evaluate to what extent CMPC and open-tubular columns are optimal for light and heavy compounds using not only the value of N_{eff} but also the retention time of the compounds being analyzed, t_R.

Plots of $lg(N_{eff}/t_R)$ vs. the nubmer of C atoms for non-selectively retained alkanes are shown in Fig.2. From these data it follows that at Z up to 5-6, the fused-silica CMPC has a better ability than that of the open-tubular column. In the case of selective separation, CMPCs can provide a better separation of substances at higher boiling point, for example, p- and m-xylenes.

Fig.3 illustrates the advantage of CMPC in separation light substances because they provide a more rapid analysis; the principal part of the chromatogram shows up prior to the onset of elution from the open-tubular column, as well as in the selective separation of butene-1 and isobutylene.

Viewing Tables 1, 2 and 3 again, we may state that the fused-silica CMPCs are characterized by small values of mass-transfer coefficient determined as coefficient C in the van Deemter equation. For example, for an 0.38 mm I.D. column packed with 7.5 μm silica gel, the coefficient C is about $4 \cdot 10^{-5}$ sec., while for ordinary packed column $C \approx 10^{-2}$ sec., and for open-tubular columns it equals about 10^{-3} sec.

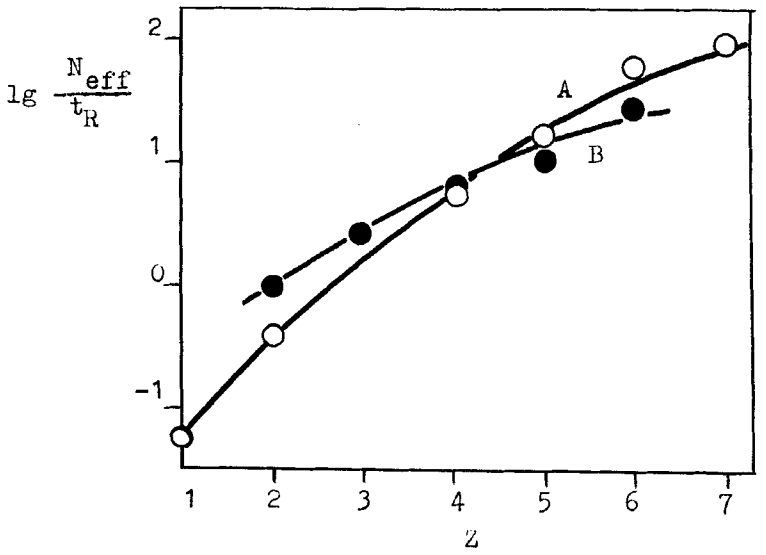

Fig.2. Logarithm of the number of efficient theoretical plates related to the retention time, $lg(N_{eff}/t_R)$, vs. the number carbon atoms, Z, for open-tubular column (A) and fused-silica CMPC (B); chromatographed compounds: n-alkanes;
A) 40 m x 0.21 mm; stationary liquid phase: bonded SE-30; 50°C;
B) 1m x 0.32 mm; sorbent: Pellosil HC, 30-40 μm; 50°C.

Due to the high specific efficiency and low coefficient C, comparatively short fused-silica CMPCs can be used and the separation can be carried out at a higher linear carrier gas velocity without any significant deterioration of the column efficiency. Therefore, fused-silica CMPCs are recommended for performing rapid analysis.

The maximum size of the sample of an individual component, W_{max}, for CMPC s is roughly of one order higher than that for open-tubular columns of 0.2-0.4m

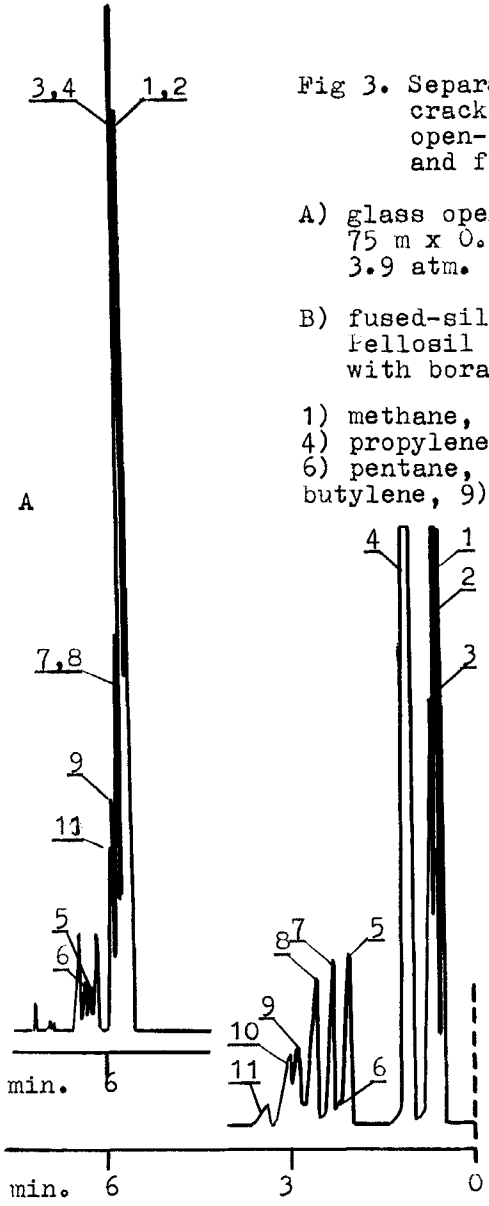

Fig 3. Separation of methanol cracking products on an open-tubular column (A) and fused-silica CMPC (B);

A) glass open tubular column, 75 m x 0.25 mm, squalane, 52°C, 3.9 atm.

B) fused-silica CMPC, 1 m x 0.32 mm Bellosil HC, 30-40 μm, modified with borax (1%), 50°C, 2.8 atm.

1) methane, 2) ethylene, 3) propane, 4) propylene, 5) isopentane, 6) pentane, 7) butene-1, 8) isobutylene, 9) trans-butene-2, 10) unidentified component, 11) cis-butene-2.

mm I.D. (Table 2) and about 2-4 times higher than that for wide-bore, thick-film capillary column. This fact makes CMPCs perspective use in determination of admixtures.

The application of sorbent microparticles is responsible for the elevated resistance of the carrier gas flow. Tables 1,2 and 3 show the pressure at the CMPC inlet up to 25 atm., which is the ultimate level of the gas pressure regulators used. However, this is not a principal hindrance for using CMPCs; standard gas chromatograph and accessories were used in our experiments. It should be also noted that for practical separation one can use fused-silica CMPCs with a inlet pressure of about 3-5 atm.; or maximum 10 atm. at the utmost.

The our data (15) support the known regularity: the less the sorbent particle size, the higher is the efficiency (for similar column diameters). A decrease in the column diameter leads to an increase in the efficiency, but it is less noticeable.

The highest efficiency obtained with a fused-silica CMPC in experiments packed with silica gel fraction of 7.5 μm in a column with an inner diameter equals 0.2 mm, the number of theoretical plates being 30,000 per metre.

When columns with I.D. = 0.15 mm were used, the efficiency was lower than that for I.D.=0.2 mm; for sorbent of 5 μm it was lower than for 7.5 μm. Probably, this is due to the insufficient iniformity of the sorbent particles packing in these cases.

The elevated hydrodynamic resistance is particular not only of the fused-silica CMPCs. For example, Myers and Giddings (10) described a 1 m x 0.5 mm I.D. steel column packed with alumina, 13 μm. The inlet pressure of this column was 140 atm., the total

efficiency was 13,000 theoretical plates. Relatively short micro-packed columns were used by Huber and co-workers (12) and Lu and co-workers (3). They achieved a high specific efficiency, but the total efficiency did not exceed 15,000 theoretical plates.

When a long fused-silica CMPCs packed with pellicular sorbent produced for high-velocity liquid chromatography (Pellosil HC, 30-40 μm) are used, a high N_{eff} value can be attained, as high as 35,000 theoretical plates. Long columns packed with such a sorbent may be employed due to the elevated permeability of this sorbent. Both in the gas-solid and in the gas-liquid variants the inlet pressure is 2 to 6 times less than with other sorbents used (with similar column length). Pellicular aorbents are expensive, but thanks to the small CMPC size, this circumstance is not decisive importance.

Apparently, a higher total efficiency can be reached by lengthening the column, and increasing the inlet pressure. The development of gas chromatography of elevated pressure could, in prospect, make wider use of not only micro-packed columns but also of columns of other types.

MATERIALS AND PREPARATION OF FUSED-SILICA CMPC

We used polymer-coated fused-silica capillaries designed for gas chromatography on open-tubular columns, in particular, these manufactured in the USSR (31), and by Scientific Glass Engineering (Australia), Nordion Instruments (Finland) and Quartz et silice (France). The length of the columns varied from 30 cm to 6.5 m, the inner diameter being from 0.2 to 0.53 mm. The capillaries were packed with different sorbent, the particle size being from 7.5 μm to 63-100 μm.

The packings were the following:

- sorbents produced for liquid chromatography, namely Silasorb 600(LC) and Silasorb C_{18} (Lachema, CSSR), Pellosil HC (Reeve Angel, USA), Zipax RF and Permaphase ETH (du Pont de Nemour, USA), silica gel S-3 (USSR), etc.

- sorbents produced for gas chromatography, for example, activated coal SKT (USSR), molecular sieve 5A (USSR), etc.

Pellosil HC and Zipax RF for use in GLC were coated with squalane, Carbowax 20M, liquid crystalline phases, etc.

One of the variants of the fused-silica CMPC preparation was the following (32).

An 0.5-1 mm gas-permeable partition was prepared at the capillary end, made of granular material whose particles were bonded together as well as with the capillary walls by a binder, e.c. polyvinylpirrolidone. The granular material was chosen in such a way that the size of its particles should not exceed the diameter of the sorbent particles by a factor of 3. In this manner, the width of the partition pores did not exceed the diameter of the sorbent particles and the partition did not show any essential resistance to the carrier gas flow. The sorbent in the packed capillary was fixed in the other end of the capillary by a second gas-permeable partition.

The method developed is characterized by a high reproducibility and allows to obtain high-efficiency micro-packed columns with a good packed sorbent layer. The relative standard deviation of the minimum height of equivalent theoretical plate of the columns prepared is around 7%; the quality of the packing shows little dependence with the column length. The

columns are reliably resistant to the pressure up to 25-40 atm.

Hence, the preparation of fused-silica CMPCs is not a complicated problem.

APPLICATION OF FUSED-SILICA CMPCs

The numerous possibilities of applying fused-silica CMPCs were examplified by the solutions of different practical analytical problems dealt with at the A.V.Topchiev Institute of Petrochemical Synthesis of the USSR Academy of Sciences (Moscow, USSR).

1.

To separate light hydrocarbons, two fused-silica CMPCs were coupled parallel to a capillary chromatograph Micromat 412 (Nordion Instruments, Finland) designed specially for open-tubular fused-silica columns. The carrier gas flow pressure was 3 atm. The products of methanol cracking (Fig.3B) and polypropylene pyrolysis were satisfactorily separated. Thus, if there are any separation problems when using open-tubular columns, they can be solved by replacing them for a fused-silica CMPC or by coupling one in parallel position.

2.

Fused-silica CMPCs were used in a gas chromatograph-mass spectrometer for identification of components of various nature with boiling point up to 115°C: hydrocarbons, oxygen-, chloro- and nitrogen-containing compounds. Due to the small carrier gas flow, these columns were connected directly to the ion source. This investigation was carried out jointly with the All-Soviet Scientific Research and Designing Institute of Chromatography (Moscow, USSR).

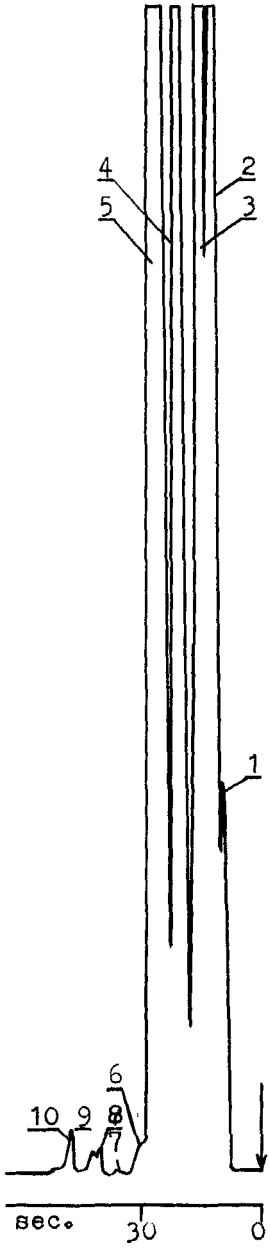

Fig.4. Determination of xylenes and ethylbenzene admixtures in hydrocarbon mixture.

Fused-silica CMPC, 49 cm x 0.37 mm, Zipax RF coated with p,p'-azoxyanisole and p,p'-azoxyphenetole (3:2); 98°C; 8.6 atm.

1) pentane, 2) hexane,
3) heptane, 4) octane,
5) toluene, 6) nonane,
7) ethylbenzene, 0.007% w/w,
8) m-xylene, 0.023%,
9) p-xylene, 0.019%,
10) o-xylene, 0.035%

On the basis of the equations for viscous flow through the column containing microparticles, it was theoretically shown that the H_{min} values both at the outlet atmospheric pressure and evacuation should be similar. This assumption was confirmed experimentally for the CMPC installed in standard gas chromatograph and chromatograph-mass spectrometer.

3.

The rapid determination of admixtures of three xylene isomers and ethylbenzene (at hundreds or thousands parts of percentage) was carried out on a fused-silica CMPC with a high-selective liquid crystalline phase (Fig.4). In this and in following examples, the fused-silica CMPC was connected to a gas chromatograph LKhM-8MD (Khromatograf Plant, Moscow, USSR) supplied with a flow splitter. Rubber sealings were used for reliable tighting.

The high mass-exchange rate in the CMPC renders it possible to conduct rapid analysis, which is especially important in investigating the quick reaction process.

4.

Components which are the constinuents of the water-gas (O_2, N_2, CO) were separated on active carbon. A flow of helium was added to the outlet carrier gas flow in order to increase the rate from 3-5 ml/min. to 10-30 ml/min., required for analysis on a standard termal conductivity detector.

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