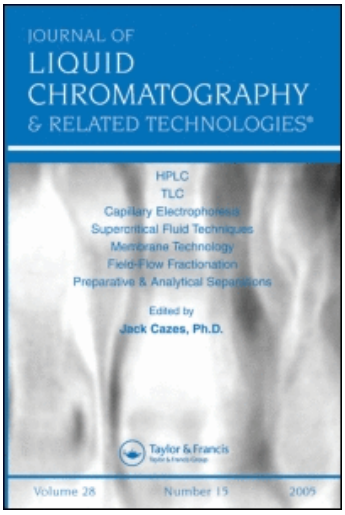

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Gel Chromatography With Silica Gels I. Column Systems for Conventional Polymer Separations Extended Towards Lower Molar Masses

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GEL CHROMATOGRAPHY WITH SILICA GELS
I. COLUMN SYSTEMS FOR CONVENTIONAL POLYMER SEPARATIONS EXTENDED TOWARDS LOWER MOLAR MASSES [+]

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ABSTRACT

Three procedures for preparation of silica gels with small pore diameters suitable for gel chromatography were tested. The materials with optimum properties were not obtained, however, it was shown that the column set with the separation range extended towards lower molar masses can be built using appropriately chosen silica gels.

INTRODUCTION

Since recently, SiO_2 based column filling materials have been rather frequently used in both conventional and high performance gel chromatography (size exclusion chromatography).

Silica based gels posses several advantages:

1. Their structure and, consequently, their both external and pore geometry is essentially independent of pressure, temperature and eluent.

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2. They are compatible with mobile phases of different polarities.
3. They allow to prepare column packings with
   - open pore structure exhibiting high separation efficiency due to fairly high velocity of the mass transfer
   - large pore volumes allowing to increase separation selectivity
   - desired pore sizes from about six nanometers up to few hundreds of nanometers
   - matched pore size distribution to obtain possibly highest separation selectivity
   - strictly spherical particle shape with diameters ranging from few micrometers up to hundreds of /um.
4. It is possible to modify their surface by simple chemical reactions.

High mechanical and thermal stability, universality as to the eluent and versatility in physico-chemical properties make SiO_2 aero-gels a welcome completion to the organic polymers based column fillings for gel chromatography (GPC).

On the other hand, the silica gels and porous glasses exhibit some drawbacks:

1. Free silanol groups cause the surface activity of the packing and, consequently, unwanted interactions with both electroneutral and charged samples.
2. Both SiO_2 matrix and its bonds with organic groups of the surface modifier are unstable in eluents with pH 7 - 8 and, generally, in aqueous mobile phases.
3. So far silica gels are not available with sufficiently large pore volume and narrow pore

size distribution with the large pores above 400 nm and with the small pores between about 2 and 6 nm in diameter. The column fillings with very large pore sizes are needed for fractionations of extremely large synthetic and biological macromolecules and for separations of particles of dispersions. On the other hand, gels with small pore dimensions would be used:

i. For both analytical and preparative selective GPC fractionation of oligomers or at least for their quantitative separation from high polymers

ii. For construction of GPC column sets with calibration dependences: log molar mass versus elution volume linear down to few hundreds g mol^{-1} molar mass values

iii. For separation of peaks of polymers from various ghost peaks caused by gases, water and other low molecular impurities and polymer additives often present in the injected solutions.

The linearity of the calibration curve simplifies substantially the GPC data processing while the quantitative separation of oligomeric and low molecular substances from the analysed polymer is a necessary condition for obtaining reliable data on mean molar masses and molar mass distribution: It is known that the disturbances of GPC traces in the region of high elution volumes decrease the precision of the values of number average molar mass of the macromolecular substance measured by gel chromatography.

In present paper, we describe our results concerning experimental work devoted to the solving the latter problem. The obtained results are presented in the form of calibration curves.

EXPERIMENTAL

The GPC calibration dependences were measured by means of a simple device assembled in this Laboratory. The eluent was transported by means of a single piston reciprocating membrane pump, Model VMC 300 (Workshops of Czechoslovak Academy of Sciences, Prague, Czechoslovakia) that was provided with a pulse damper according to (1). The three-way six-port injection valve was equipped with the loops 0.5 - 3 mL depending on the column set. The column dimensions were 1,220 or 610 or 500 mm in length and 8 or 4 mm in diameter. The detector was a differential refractometer, Model 2025/50 (Knauer K. G., Bad Homburg, FRG). The elution volumes were measured either by means of an automatic siphon system that was provided with a device diminishing the loss of eluent by evaporation (2) or with a drop counter Model DC 1002 (Laboratory Instruments Works, Prague, Czechoslovakia). Both siphon system and drop counter were calibrated by weighing.

Tetrahydrofuran (THF) was used as eluent after purification described in (3). Narrow polystyrenes with molar masses in the range from 6×10^2 up to 10^7 g mol^{-1} were products of Pressure Chemicals, Pittsburgh, PA, USA,or Toyo Soda MfG. Co., Ltd., Tokyo, Japan.

The column packings were products of Electro Nucleonics, Fairfield, NJ, USA (various types of porous glass CPG - 10); Merck, Darmstadt, FRG (set of Fractosils); Waters Inc., Milford, MA, USA (set of Porasils) and Glassworks Kavalier, Votice, Czechoslovakia (Silpearl). Silpearl sorbent was originally intended for TLC. Its surface area was about 600 m^2 g^{-1}, pore volume approx. 0.5 mL g^{-1}. In our experiments the particle fraction 30 - 60 μm was selected. All columns were dry packed by the classical tap-and-fill procedure.

RESULTS AND DISCUSSION

Figs. 1 - 3 show the GPC calibration curves for various commercial SiO_2 based column packings. Evidently, the selectivity of the separation is rather poor in the molar mass range below about 4×10^3 g mol^{-1} for all gels studied.

In an effort to change pore sizes of silica gels to make them more suitable for separation in lower molar mass region, three different procedures were used:

a. Diminishing the pore sizes by depositing various materials into wide-pore packings. The easiest way seemed to be the polymerization of different monomers on the pore walls of silica gels. Various epoxy resins were formed within the pores. The amount of resin varied from 10 to 60 mass % calculated on the starting silica gel. The results were not promising: While the smallest pores had been already completely blocked by the resin the large pores have still remained too large. If the amount of deposited resin was further increased, both the pore diameters and pore volumes decreased simultaneously so that the resulting material with desired pore size had too small pore volume.

b. Controlling the polymerization of silicic acid so that presumably small pores were formed in resulting silica gels. Various conditions for fine pore formation were tested: Concentration of starting sol of silicic acid, time and temperature of polymerization as well as postpolymerization treatment. The results obtained were again not satisfactory (cf. Fig. 4). The silica gels so far prepared had either too large mean pore diameters or too small pore volumes.

c. Increasing the pore diameters of the silica gel with very small pores. In our experiments, we have chosen

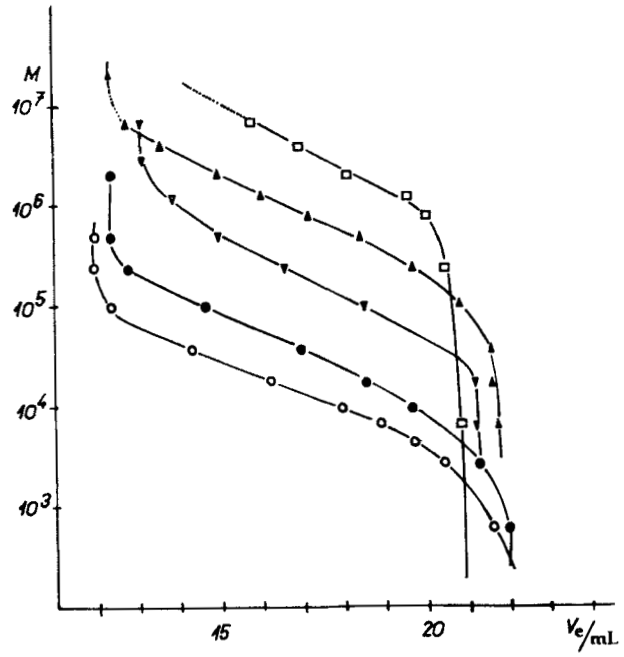

FIGURE 1. GPC calibration curves for Fractosils. □ - Fractosil 500 nm; ▲ - Fractosil 250 nm; ▽ - Fractosil 100 nm; ● - Fractosil 50 nm; ○ -Fractosil 15 nm. The numbers represent the mean pore diameters of the gels given by the producer.

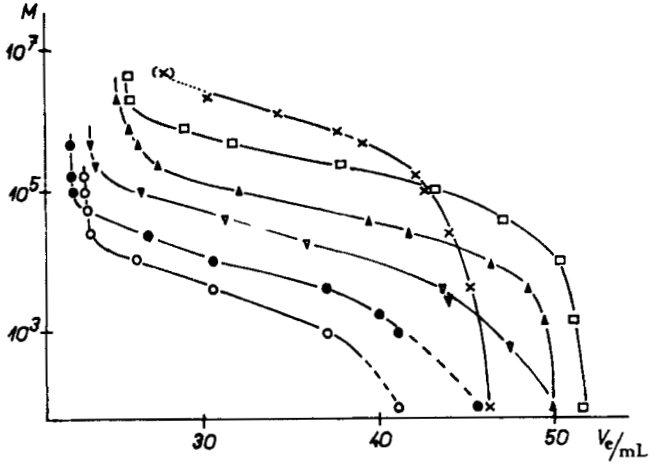

FIGURE 2. GPC calibration curves for Porasils. ○ - Porasil A; ● - Porasil B; ▽ - Porasil C; △ - Porasil D; □ - Porasil E; × - Porasil F. Column dimensions 610 x 8 mm.

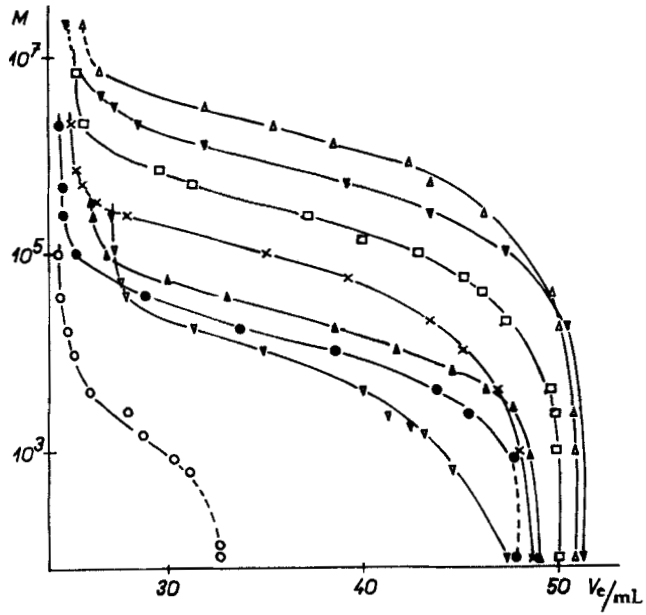

FIGURE 3. GPC calibration curves for CPG - 10 Porous Glasses. △ - 204.5 nm; ▼ - 142.2 nm; □ - 72 nm; × - 36.8 nm; ▲ - 15.6 nm; ● - 11.8 nm; ▽ - 7.5 nm; ○ - 4 nm. Column dimensions 1220 x 8 mm.

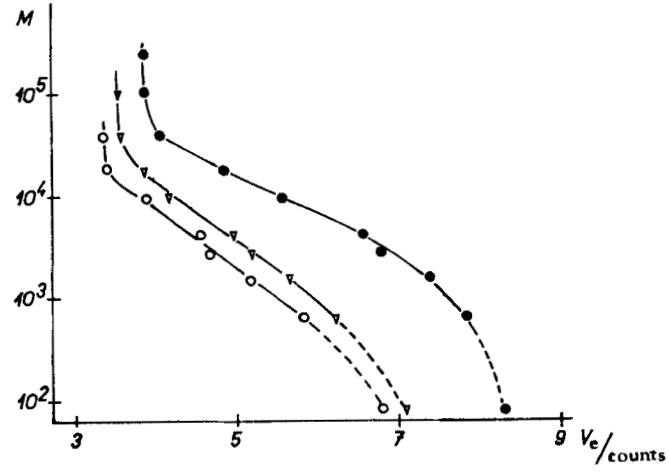

FIGURE 4. GPC calibration curves for experimental irregular silica gels. ● - SG-3N; ▽ - SG-15N; ○ - SG-10N. Column dimensions 500 x 6 mm. 1 count represents 0.7 mL.

silica gel Silpearl despite of its rather small pore volume. We used various leaching techniques applying solutions of alkaline (NaOH, KOH) or acidic (HF) leaching agents at different concentrations, temperatures and reaction times. Here again, we have found that probably due to the interface tension between leaching agent and silica gel, as well as due to the restricted diffusion rate of the leaching agent into small pores, the dissolution of gel matrix started preferably in larger pores. In other words, leaching resulted again in materials with too large pore diameters. The calibration curves for some materials obtained by leaching of Silpearl silica gel are shown Fig. 5.

Finally, we have decided to use the columns packed with original and leached Silpearl in combination with the above mentioned commercial wide-pore silica gels in order to prepare column sets with the separation ranges extended towards lower molar masses.

The examples of the calibration dependences for some column sets are shown in Fig. 6. The experimental points are compared with the courses of the calibration dependences obtained by simple addition of the elution volumes for particular single columns. The agreement is surprisingly good.

From the presented results it can be concluded that special types of narrow pore silica gels can be used for extending the separation range of the conventional wide pore SiO_2 based GPC packings towards lower molar masses. However, due to generally smaller pore volume of these materials, several columns packed with narrow pore silica gels must be added to the column systems in order to obtain linear calibration curves down to 10^3 g mol^{-1} and lower molar masses or, at least,

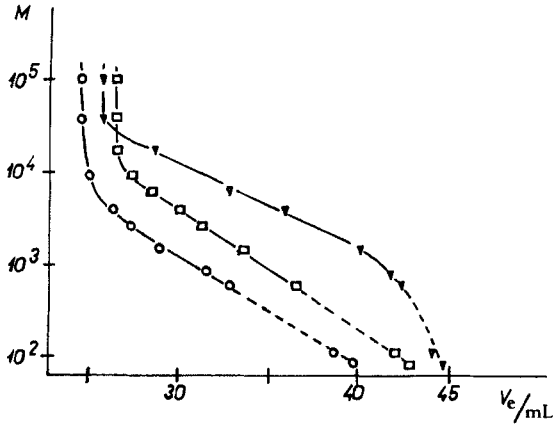

FIGURE 5. GPC calibration curves on Silpearl. ○ - starting sample; □ - sample leached by HF (0.5 hour in 3 % aqueous HF solution at 25 °C) ▽ - sample leached by NaOH (1 hour in boiling 2 % NaOH solution). Columns dimensions 1220 x 8 mm.

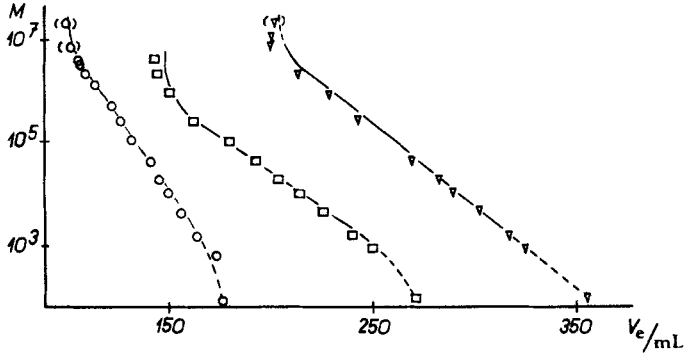

FIGURE 6. Combined calibration curves. ○ - Fractosils: 1 x 500 nm, 2 x 250 nm, 1 x 100 nm, 2 x 15 nm, plus 1 x Silpearl modified by NaOH, 1 x Silpearl modified by HF, columns 8 x 610 mm; □ - Porasils: C, D, E, 1 x original Silpearl, 1 x Silpearl modified by NaOH, 1 x Silpearl modified by HF, columns 8 x 1220 mm; ▽ - 1.5 x Fractosil 500 nm, 1 x CPG Porous Glass 142.2 nm, 1 x CPG Porous Glass 36.8 nm, 1 x CPG Porous Glass 15.6 nm, 1 x original Silpearl, 1 x Silpearl modified by NaOH, 1 x Silpearl modified by HF, columns 8 x 1220 mm; solid line - calculated curve, points - experimental.

column systems that resolve the peaks of polymers from the peaks of oligomeric or low molecular accompanying substances. Consequently, both the dead volume of the system and the time of analysis increase and the overall separation efficiency is partially sacrificed.

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