CHROM. 17 748

QUALITY CRITERIA AND STRUCTURE OF SILICA GEL COLUMN PACKING MATERIAL

M. VERZELE* and C. DEWAELE

Laboratory of Organic Chemistry, State University of Ghent, Krijgslaan 281 (S.4), B-9000 Ghent (Belgium)

and

D. DUQUET

R.S.L., Begoniastraat 5, B-9731 Eke (Belgium)

(First received February 8th, 1985; revised manuscript received March 21st, 1985)

SUMMARY

Silica gel and derivatised forms of silica gel are by far the most commonly used column packing materials in high-performance liquid chromatography. Quality criteria of silica gel for chromatography therefore merit attention. Most of them are discussed, and it is suggested that the apparent density is an important one.

INTRODUCTION

Most present-day columns for high-performance liquid chromatography (HPLC) have an internal diameter of *ca.* 4 mm and are packed with silica gel-based particles with a mean diameter of 5 or 10 μm[1]. Even in the trend towards miniaturization silica gel remains important[2,3]. This paper discusses a number of the quality criteria for chromatographic silica gel, and these are listed in Table I.

Table I lists values most generally used in HPLC, and also the values for an "ideal" chromatographic silica gel. Points 1–4 are usually mentioned when quality criteria for silica gel are considered. It might therefore be expected that these are the only, or at least the most important, quality aspects. It is the purpose of the present

TABLE I

QUALITY CRITERIA FOR SILICA GEL

Criterion	Most usual values	Ideal values
1. Specific surface area (m²/g)	150–400	200
2. Mean pore diameter (nm)	6–10 or 30	8
3. Specific pore volume (ml/g)	*ca.* 0.2–1	0.7
4. Mean particle size (μm)	3, 5 or 10	–
5. Ratio dp 90/dp 10	≪1.5	≪1.5
6. Trace metal content (ppm)	≪1000	≪1000
7. Apparent density	0.4–0.6	0.45
8. Particle smoothness		smooth
9. Surface pH		neutral

paper to show that this is *not* so, and that the other factors mentioned in the table are also important. Points 1–6, 8 and 9 have been discussed fully in the literature, and they are mentioned only briefly now. Some new ideas on the structure of silica gel and experiments on point 7 (apparent density) are discussed more extensively later in this paper.

Point 1 of the table determines the capacity ratio of chromatographed compounds. For the same eluent a silica gel of high surface area will give a higher capacity ratio. This can usually be controlled easily by a change in solvent composition. There is a tendency, though, towards using packing materials with lower surface area. The mean pore diameter (point 2) is also not that important for usual molecules. Size-exclusion effects for molecules with MW 100–500 become apparent when the average pore size is less than 4 nm, so this should be avoided. Good chromatography is possible, however, on both 6–10 nm and 30 nm pore size material. We find more difficulty with the latter; perhaps because we are not so used to handling it. For size-exclusion chromatography the pore size is also important of course. Point 3, the specific pore volume, is not a good criterion for evaluating silica gel as will be shown when point 7 is discussed later. The mean particle size (point 4) is of course important. When the range of particle sizes is large, it becomes very difficult to establish a mean value. The value derived from chromatographic data (column back-pressure or permeability) can then differ greatly from the value estimated by other means. The next factor is related to this: point 5, the ratio dp 90/dp 10 (dp 90 and dp 10 are the particle diameter values above and below which 10% of the total weight is found), has been studied by us previously[4], and our conclusion was that this factor has surprisingly little influence on column efficiency. The column back-pressure, however, is very much influenced. A value of *ca.* 1.5 for this factor is more than adequate and is indeed met by most commercial packing materials.

Point 6, the trace metal content, has also been discussed previously[5–7], because we are often involved in the analysis of hops and beer bitter acids, which are extremely sensitive to trace metal activity. We believe that the last word has not been said about the importance of trace metal content. Some strange effects seem to be linked to this factor and we hope to report on this in the future.

Point 8, the particle smoothness, is probably an underestimated quality factor for column packing materials. Some commercial materials have a shiny, obviously smooth surface when observed under a microscope, whereas others have a rough aspect, like orange peel. For a tight, stable packing, we believe that the particles should be smooth on the surface for optimum results. Smooth particles, just like a smooth column wall, will favour tighter packing, which is beneficial. This is especially important for very small spherical particles. Anderson has shown[8] that column-wall smoothness is not that important for 5-μm particles, but in our experience this is not always so clearcut, especially not with even smaller particles.

Point 9, the apparent pH of the silica gel, is an important characteristic as demonstrated recently by Engelhardt and Müller[9].

EXPERIMENTAL

Materials and apparatus

The HPLC system consisted of a Varian 5020 LC pump and a Varichrom

UV-50 detector. Samples were injected with a Valco 7000 p.s.i. sample loop (10 μl).

Polystyrene standards were from Polymer Laboratories (U.K.). Experimental batches of 5-μm spherical silica gel of different apparant densities were made in our laboratory. The materials were packed in stainless steel columns (150 × 4.1 mm I.D.).

Procedure

The interstitial and pore volumes were measured by size-exclusion experiments in tetrahydrofuran according to Nikolov *et al.*[10]. Polystyrene standards with MW 324, 540, 756, 2900, 20 000, 96 200 and 200 000 were used. Toluene was used as void volume marker. To determine the apparent density, *ca.* 2–5 g of dry silica gel is compacted by tapping in a graduated glass cylinder (1 cm I.D.) until the volume remains unchanged. From the known weight and the measured volume the apparent density is calculated.

RESULTS AND DISCUSSION

The structure of silica gel

Silica gel has been discussed extensively in the literature. A monograph by Unger on the subject is recommended[11]. A recent contribution from Berendsen and De Galan[12] discusses the structure of silica gel in terms of crystallographic parameters and analogues. Our approach, however, is to consider the structure in terms of a less obvious aspect. The enormous specific surface area of silica gel implies that the thickness of the membrane or wall between the pores is very thin. For chromatographic silica gel with a specific surface area of 250–400 m^2/g and with a specific gravity of the silica of 1.9[12,13], the average wall thickness can only be *ca.* 1–2 nm!

This means that most of the wall thickness contains only one or two silicon atoms. Some silicon atoms must even bear two silanol functions: one on each side of the silica gel skeleton wall. With the tetrahedral hybridization of silicon, a possible structure for this is shown in Fig. 1.
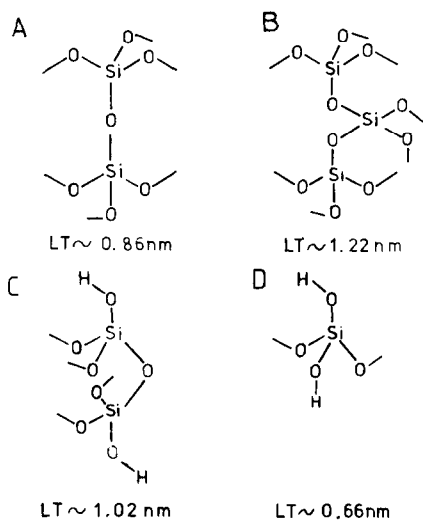

Fig. 1. Structures of silica gel, with different layer thicknesses (LT).

If every silicon atom had a silanol function, as in the structure shown in Fig. 1C, the stoichiometric formula of silica gel would be $SiO_{2.5}H$ and not SiO_2. The silanol content of such a silica gel would be 13.8 mmol OH/g. According to Berendsen and de Galan[5]. the most plausible figure for the number of hydroxy groups on the silica gel surface is $4.8/nm^2$. Recalculated, this is equal to 7.8 μmol/m^2, to 2.3 mmol/g for a 300 m^2/g silica gel and to *ca.* 4% hydroxy groups. Therefore only one in every six silicon atoms bears a silanol group in an average silica gel. Erard and Kováts[14] also mention 7.8 μmol hydroxy groups per m^2 for Cabosil with a specific surface area of 100 m^2/g. The structure of silica gel is then something in between A–B and C–D in Fig. 1. High-temperature treatment shifts the structure to A or B and aqueous treatments (alkaline or acidic) to C or D. These shifts do probably also occur, albeit slowly, in the HPLC columns, by reaction with reversed-phase aqueous solvent systems. This is probably accompanied by changes in pore structure and specific surface area. Such changes have been observed by Bidlingmeyer and Warren[15].

Silica gel is a reticulated foam: it has an open structure. This probably means that the skeleton made up of siloxane bonds has many defects with siloxane bridges opened to form silanol groups. The skeleton wall thickness of silica gel cannot be the same all over. A slight thickening at the base of the pores seems obvious. This also means that much of the surface area has only one silicon atom in the wall thickness, as shown in Fig. 1D with a layer thickness of only 0.66 nm. The structure closest to reality is probably that in Fig. 1A, although there is no apparent relationship between this structure and the chromatographic quality of a silica gel column packing material.

THE APPARENT DENSITY

The specific gravity of silica gel is 1.9, according to Strubert[13] and to Berendsen and De Galan[12]. This figure is probably slightly variable with the surface area of the silica gel. For an experimental silica gel of high specific surface area (*ca.* 450 m^2/g) we found a value of 1.8. The "apparent density", or the density of the silica gel packed as tightly as possible in the dry state, is much more variable. The method of determining this is described in the Experimental part: it sounds rather primitive but gives remarkably reproducible results.

We found apparent density values of 0.1–0.8 for various forms of laboratory-made and commercial silica gels.

All irregularly shaped silica gel particles and many spherical silica gels are made from silicate solutions. The concentration of the starting solution which is acidified is *ca.* 10%. The apparent density of a silica gel obtained from this could be expected to be 0.1. The gel as first obtained contains 90% water, and drying should indeed replace this water by air, leaving a three-dimensional polycondensate with 0.1 as the apparent density. Most silica gels obtained in this way, however, have, an apparent density of 0.2–0.5. Silica gel for chromatographic purposes usually has an apparent density of 0.4–0.5. Considerable contraction of the silica gel structure must therefore occur; the volume of the porous structure has to diminish about five fold on drying!

For a spherical particle it can be calculated that the radius is reduced to *ca.* 60% of the original value in this process (the cube root of 1/5 of original diameter).

This is important for the quality of silica gel-based packing material. Apparently, the reproducibility of the contraction process is not of the best and therefore the apparent density of silica gels can vary. Silica gels with low apparent density do not have the structural strength necessary to withstand HPLC packing pressure, and so do not pack as efficiently as silica gels with higher apparent density. The reason is probably that silica gel particles cannot only break (more pronounced for irregularly shaped silica gels) but also be deformed by the packing pressure (flattened): more pronounced with spherical silica gels).

Breaking of the particles leads to permeability problems and has a negative effect on column efficiency. Flattening of the particles under pressure also decreases permeability and must be avoided. This flattening or compression effect is revealed for some silica gels creeping out of a packed column when the top frits are removed or just after packing when the column is removed from the packing device. Silica gels should therefore have an apparent density of at least 0.40.

Apparent density is an often overlooked criterion of importance in assessing quality of silica gels. It is related to the specific pore volume: with an apparent density of 0.5 g/ml and a true density of the silica gel skeleton of 1.9, the true volume taken up by the silica gel per millilitre of material is only 0.26 ml. The total free volume is such a silica gel is therefore 0.74 ml/ml (1.48 ml/g). The same calculation for silica gel with an apparent density of 0.2 leads to a silica gel volume per millilitre of particles of *ca.* 0.1 ml and to a total free volume of 0.9 ml/ml (4.5 ml/g). The difference in total free volume between these two examples is very great.

For spheres packed regularly (cubic closed packed) the interstitial volume ($8r^3$ − $4/3\pi r^3$) and the sphere volume ($4/3\pi r^3$) are about the same size (the interstitial porosity is 0.476). For silica gel the sphere volume has to be reduced by the volume of the silica gel itself to obtain the pore volume. One gram of a silica gel with an apparent density of 0.5 would have a volume of 2 ml. About half of this (1.1 ml to be precise) would be the sphere volume; the pore volume would be *ca.* 0.6 ml/g. Titration of 3-, 5- and 10-μm silica gels (apparent density 0.47 g/ml) by the method described previously[16] gave figures of 0.75, 0.77 and 0.67 ml/g. This is not bad, but better could be expected. However, the titration measurements are much more difficult than the determination of the apparent density. The latter determination is therefore preferred. It is probably better to calculate pore volume from the apparent density as discussed than to rely on direct determination. Apparent density and pore volume are closely related, as shown above. The specific surface area and the mean pore size are also related to each other and to the other two parameters, although we have been unable to express these relationships in a formula, even by approximation.

The same calculation as above was done for four different silica gels (5-μm particle size) with an apparent density of 0.20, 0.40, 0.57 and 0.62, respectively. The calculated total volume is plotted in Fig. 2 (curve A). The experimental values for V_1 and V_P obtained by size-exclusion experiments (for experimental conditions see the caption to Fig. 2) for a 15 × 0.41 cm I.D. column filled with these silica gels are given in Fig. 2 (curves B and C).

The interstitial volume seems to be independent of the apparent density, which means that the columns were packed equally well. These values of V_1 and V_P can be corrected for the amount of silica gel in the column and give $V_{1cor.}$ (pore volume per
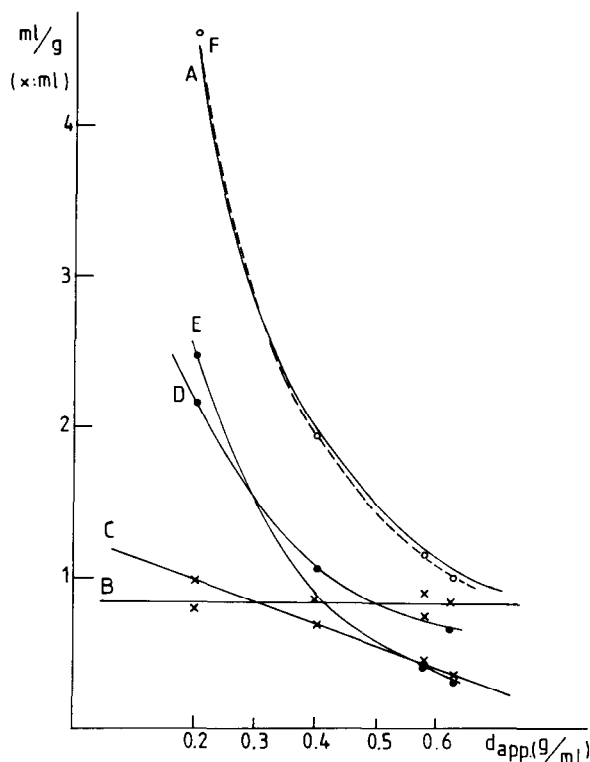
Fig. 2. Curve A: calculated total free volume following the procedures discussed in the text. Curves B and C: interstitial volume (V_I) and pore volume (V_P) for a 15 × 0.41 cm I.D. column. (V_I and V_P are measured by size-exclusion experiments in THF as eluent and with polystyrene standards as test mixture.) Curve D: $V_{Icor.}$, or interstitial volume per gram. Curve E: $V_{Pcor.}$, or pore volume per gram. Curve F: total volume per gram ($V_{Icor.}$ + $V_{Pcor.}$). d_{app} was measured by tapping a few grams of the various laboratory-made silica gels in a graduated tube until the volume did not change anymore.

gram). $V_{Icor.}$ and $V_{Pcor.}$ are also plotted in Fig. 2 (curves D and E). The total volume (experimental) is given in curve F. There is a good correlation between the calculated and experimental curves, which supports the theory discussed above.

CONCLUSION

An optimised silica gel column packing material would have the characteristics of the last column in Table I. With such a silica gel good chromatographic results are probable, but we readily admit that this cannot be guaranteed (especially with derivatised material). Therefore other aspects, still unknown, are also important for optimum chromatographic performance.

ACKNOWLEDGEMENTS

REFERENCES

1 R. Majors, H. Barth and C. Lochmüller, *Anal. Chem.*, 56 (1984) 300 R.
2 M. Verzele, *J. Chromatogr.*, 295 (1984) 81.
3 C. Dewaele and M. Verzele, *J. Chromatogr.*, 282 (1983) 341.
4 C. Dewaele and M. Verzele, *J. Chromatogr.*, 260 (1983) 13.
5 M. Verzele and C. Dewaele, *J. Chromatogr.*, 217 (1981) 399.
6 M. Verzele, *LC Magazine*, 1 (1983) 217.
7 M. Verzele and C. Dewaele, *Chromatographia*, 18 (1984) 84.
8 J. Anderson, *J. Chromatogr. Sci.*, 22 (1984) 332.
9 H. Engelhardt and H. Müller, *J. Chromatogr.*, 218 (1981) 395.
10 R. Nikolov, W. Werner and I. Halász, *J. Chromatogr. Sci.*, 18 (1980) 207.
11 K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979.
12 G. Berendsen and L. de Galan, *J. Liquid Chromatogr.*, 1(4) (1978) 403.
13 W. Strubert, *Chromatographia*, 6 (1973) 50.
14 J. Erard and E. Kováts, *Anal. Chem.*, 54 (1982) 193.
15 B. Bidlingmeyer and F. Warren, *8th International Symposium on Column Liquid Chromatography, New York, 1984.*
16 N. Fischer and A. Mottlau, *Anal. Chem.*, 34 (1962) 34.