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Study of the physico-chemical properties of some packing materials II. General properties of the particles

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Abstract

Scanning electron microscopy reveals the shape and illustrates the particle size distribution of four different brands of spherical silica particles used in preparative chromatography (C_{18}-bonded Kromasil, Vydac, YMC, and Zorbax). Pycnometry provides a direct estimate of the unaccessible volume fraction in a column. The retention volumes of benzene in dichloromethane and of uracil in methanol provide two independent estimates of the total column porosity which are in excellent agreement. Within 2 to 3%, the sum of these two fractional volumes is equal to unity, as expected, in spite of a possible disagreement between the two sets of measurements due to the fact that the C_{18} bonded chains are collapsed during the pycnometric measurements and are dissolved in the mobile phase during the chromatographic measurements. Finally, estimates of the volume fractions of the column occupied by the bonded layer and the silica skeleton for two of the packing materials suggest that the closed pore porosity is negligible (1 to 2% at most).

Keywords: Stationary phases, LC; Scanning electron microscopy; Preparative chromatography

1. Introduction

The reproducibility of packed columns for chromatography has always been a problem of serious concern for practitioners [1]. So far, the reproducibility of the thermodynamic properties has attracted most of the attention. Progress made over the years in the manufacturing processes used to prepare silica particles and to derivatize them when needed has resulted in the present situation. Batch-to-batch repeatability of chromatographic separations performed with a given brand of packing is quite reasonable for neat silica and alkyl-bonded silica materials. There are still some significant fluctuations of the retention factors, much smaller variations for the separation factors. The results are generally less satisfactory for some nonconventional bonded phases, in which case there may be considerable batch-to-batch variations in the yield of the bonding reactions. Hence, the repeatability of some otherwise difficult separations is not assured [2].

Until recently, the repeatability of the other col-

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umn characteristics was not a topic of great interest. Provided the needed separations could be obtained, the analysts were satisfied and paid little attention to possible fluctuations of the column porosity, its permeability or even, to some extent, its efficiency nor to the possible consequences of these variations. In most cases, pumps can deliver the mobile phase under pressures higher than needed, so changes in the column permeability are easily met with adjustments in the inlet pressure to keep the flow-rate at the required level.

Recently, however, two new types of problems have arisen, both related to preparative chromatography, both requiring a much better control of the various column characteristics. Their importance is going to change the situation described above and to confer great benefit to the ability of closely reproducing the values of all the column parameters. First and foremost is the rapid development of the interest of separation chemists for simulated moving bed separations (SMB). Second is the increasing economical importance of using physico-chemical parameters acquired with analytical columns for the scaling-up of industrial separations.

SMB is a continuous process of separation based on the ability of chromatographic columns to separate closely related components, e.g., enantiomers [3,4]. It operates at relatively high concentrations, thus applies the considerable enhancement of separations that nonlinear effects related to competitive adsorption behavior may provide [5]. The process uses 12 or 16 identical columns, three or four of which constituting each column section at any given time. The columns are switched cyclically, in order to simulate the counter-current migration of the liquid and the solid phase. The performance of the whole column must remain constant from period to period. Cyclical perturbations in the flow-rate or the retention pattern result from any difference between the packing density or the thermodynamic characteristics of the 12 or 16 individual columns. Such perturbations affect the stability of the steady-state operation of SMB and must be minimized. The production of batches of 16 nearly identical columns is not a simple problem, but must be achieved if the process is to become practical.

The selection of the design and operating parameters of an industrial-scale separation is still often done using empirical methods, some merely based on the gut feelings of the chemist in charge. This approach is costly and wasteful of feed, solvent and packing material, even in the implausible case when it converges toward the actual set of optimum conditions. A more sound procedure consists in determining the competitive isotherms of the components to be separated, and the correlation between the column efficiency and the mobile phase flow velocity on an analytical column, and calculating the optimum conditions of the separation, given the proper objective function [5,6]. The acquisition of competitive equilibrium isotherm, hydrodynamic, and efficiency data on analytical columns is rather straightforward as well as the calculation of optimum experimental conditions using simple models of chromatography [5]. However, the critical step is in the scaling-up of these data and results. Analytical and preparative columns are packed using quite different procedures and have significantly different packing density [7,8]. As long as the characteristics of both types are not highly reproducible, it will be difficult to scale-up experimental conditions calculated for analytical columns to the design and operation of preparative columns.

The aim of this work is the study of the parameters which control the reproducibility of column performance. In this paper, we report on the physico-chemical properties of four packing materials which are widely used in preparative chromatography. In a companion paper [9], we present and discuss data on the determination of the external porosity of columns packed with these materials.

2. Theory

We consider in this work the fractions of the column volumes occupied by different phases, or by phases having importantly different properties. They are listed in two groups as follows:

The inaccessible volume fraction, ϵ_U, from which the mobile phase and the solutes traveling along the column are completely excluded. It contains three different fractions: (1) The skeleton made of solid silica, which occupies a volume fraction ϵ_s. (2) The bonded layer composed of alkyl chains chemically bonded to the surface, which occupies a volume fraction ϵ_a. (3) The closed pores, pores which have been formed during the synthesis of the material and

have been closed at a later stage of particle growth. Their volume fraction, ϵ_c, is not accessible by chromatographic measurements.

The volume fraction occupied by the mobile phase in the column, ϵ_T, or total porosity. It includes: (1) The volume fraction occupied by the pores inside the particles also called internal pore volume, or internal porosity, ϵ_i. (2) The volume fraction of the voids between and around the particles, also called interparticle, interstitial or external pore volume. This is the external porosity, ϵ_e. While the external porosity is always reported to the geometrical column volume, the other porosities or volume fractions have been reported differently in chromatography and in chemical engineering. In the former area, the packing material is considered incompressible. So, these porosities have been conventionally reported to the geometrical column volume. In this case, the sum of all the porosities would be equal to 1. In chemical engineering, however, the internal porosity is conventionally reported to the actual volume of the particles. This has the advantage of giving a value of the internal porosity which remains constant in spite of any possible change in the packing density. We know now that the packing density may vary with the nature and intensity of the stress applied during column packing [7,8]. For this reason, the volumes fractions of the skeleton, bonded layer and closed pores should also be reported to the actual volume of the particles. Accordingly, the closure relationship is written:

$$\varepsilon_e + (1 - \varepsilon_e)(\varepsilon_i + \varepsilon_c + \varepsilon_s + \varepsilon_a) = 1 \quad (1)$$

This relationship will be helpful to assess the combined accuracy of the different methods used to determine the four volumes fractions listed above. The convention described above has been used in the calculation of the data reported in Table 3 and Table 4.

In the discussion of the methods of determination of the different volume fractions listed above, we must consider the definition of their boundaries. There are only three boundaries of importance, the column wall, the boundary between the external and internal pore volumes, and the interface between the internal pore volume and the inaccessible volume. The column wall is the only surface which we can safely assume to be flat with a clear geometrical definition. The inner column wall is most often polished stainless steel, with a surface area exceeding little its geometrical surface area and which is orders of magnitude smaller than the surface area of the packing material in the column. The definition of the other two boundaries is fuzzy.

The external pores are bound to be larger on the average and far less numerous than the internal pores. However, a classification based on pore size cannot avoid some ambiguities. In principle, the mobile phase flows through the external pores, but this definition is equivalent to the former one: the permeability of the pores increases as the square of their size. Perfusion would use flow across large internal pores. Hydrodynamic chromatography is based on the exclusion of particles from the small external pores. The surface at which the mobile phase velocity is 0 would be a good definition of the boundary if there were any method of measurement based on its consideration. We shall use later a definition based on the pore size, but we must recognize that this introduces a model error in the very definition, albeit this error seems to be small.

The last boundary to consider is the solid–liquid interface. With conventional adsorbents (e.g., silica, graphitized carbons), it is a surface which is not easy to define when liquid–solid adsorption is considered [10]. With chemically bonded phases, the problem may be theoretically the same, but the error increases considerably. Furthermore, we use in our work different methods to measure the various porosities. Some methods take place in a low-pressure gas phase where the bonded alkyl chains are most certainly collapsed, others in solution in organic solvents in which the alkyl bonded groups are well dispersed. This will introduce some discrepancies (see later). At any rate, since some of the methods used in this work are based on volume determinations and others on weight determination, we must handle separately the skeleton, with the density of silica, and the bonded alkyl chains, which will be assumed to have the density of liquid octadecane.

3. Experimental

3.1. Equipment

The chromatographic measurements were carried out using a Hewlett-Packard (Palo Alto, CA, USA)

HP1090M liquid chromatograph, equipped with a diode-array UV detector, an automatic sampling system, and a computerized data acquisition system. It has been reported previously [11] that the solvent delivery system of this equipment is highly stable and accurate. Accordingly, the reproducibility of retention volumes measurements was better than 0.1% and their accuracy between 0.1 and 0.2%.

3.2. Columns

Empty stainless-steel tubes (10 cm long, 0.46 cm I.D.) were purchased from Alltech (Deerfield, IL, USA). Samples of 10-μm spherical C_{18} ODS packing materials were obtained, Kromasil from Eka-Nobel (Stratford, CT, USA), Vydac from The Separation Group (Hesperia, CA, USA), YMC from YMC (Wilmington, NC, USA), and Zorbax from BTR (Wilmington, DE, USA). Each material was packed into five columns by conventional slurry packing [12], under the pressure recommended by the packing manufacturer. All the columns containing the same phase were packed on the same day, starting with column no. 1 and ending with column no. 5. The lot numbers of each material and the column packing conditions are listed in Table 1.

The weight of packing material in the column is reported and discussed separately, together with the porosity data (see Table 3). It was determined from the difference between the weight of the column tubing measured before packing it, and the weight of the dry column. After completion of a series of measurements by inverse size-exclusion chromatography [9], the columns were full of dichloromethane. They were emptied into a waste container, under slight nitrogen pressure, dried under a stream of nitrogen at 50°C for 8 h [13] and finally weighed.

3.3. Chemicals

Dichloromethane (J.T. Baker, Phillipsburg, NJ, USA) was used both as the mobile phase and the sample solvent. Benzene (M_r 78.11) was purchased from EM Science (Gibbstown, NJ, USA). Unless specified otherwise, all chromatographic measurements were carried out with UV detection at 254 nm, at a mobile phase flow-rate of 1.000 ml/min.

3.4. Measurement of the apparent density of the packing materials

The apparent density of the packing materials was determined by pycnometry, using an Accupyc 1330 (Micromeritics, Norcross, GA, USA). The test method is based on a determination of the porosity in which the accessible volume of a sample is determined by application of Boyle's law. The apparatus consists of two cylinders of known volume connected by a valve. One of the cylinders, the calibrated sample cell volume, has an accessible chamber for insertion of the test specimen and is connected to a source of dry gas, preferably helium as used in this work. The pressure in the sample cell volume is increased to a predetermined pressure and the exact value of the pressure, P_1, is noted. The valve between the two cylinders is then opened and

Table 1
Column packing conditions

Brand	Kromasil	Vydac	YMC	Zorbax
Lot. no.	DT0080	920714-28-1	EC16717	B32110
Pore size (Å)	100	90	120	150
Slurry solvent	CH_2Cl_2–isopropanol (30:70)	$CHCl_3$–acetone (60:40)	CH_2Cl_2	CH_2Cl_2–isopropanol (30:70)
Pushing solvent	Same as above	Isopropanol–methanol (33:67)	Methanol	Same as above
Pressure increase	Direct	Step	Direct	Direct
Maximum pressure (p.s.i.)	10 000	7000	4000	8000
Packing time (ca. min)	5	20	10	5
Settle time (ca. min)	5	30	5	5

Particle size: 10 μm. Column dimensions: 10 cm long×0.46 cm I.D. 1 p.s.i.≈$7 \cdot 10^3$ Pa.

Table 2
Density of the packing materials

Material	Density (g/cm^3)	R.S.D. (%)	Specific unaccessible volume (cm^3/g)
Kromasil	1.5674	0.02	0.638
Vydac	1.7589	0.02	0.568
YMC	1.6016	0.05	0.624
Zorbax	1.8039	0.03	0.554

the second, lower pressure, P_2, is again noted. The ratio of these pressures, P_1/P_2, is directly related to the volume of the calibrated sample cell volume displaced by the unaccessible volume of the sample. This procedure provides the volume of solid material (including the volume of non-connected pores) actually contained in the sample. The apparent density of the solid material of the particles and the specific unaccessible volume of the particles are given in Table 2. The unaccessible volume fraction, ϵ_U, of each column is given in Table 3, derived from these density data.

Table 3
Unaccessible and total porosities of the columns studied

Columns	W (g)	ϵ_U	$\epsilon_{T,b}$	$\epsilon_{T,u}$	$\epsilon_{T,b}+(1-\epsilon_e)\epsilon_U$
Kromasil					
1	1.1070	0.689	0.608	0.588	1.033
2	1.1287	0.688	0.597	0.580	1.030
3	1.1331	0.692	0.598	0.584	1.033
4	1.1374	0.689	0.595	0.581	1.032
5	1.1302	0.686	0.595	0.582	1.029
Vydac					
1	1.1269	0.614	0.637	0.634	1.022
2	1.1337	0.614	0.633	0.632	1.021
3	1.1132	0.603	0.635	0.638	1.016
4	1.1381	0.614	0.634	0.634	1.023
5	1.1277	0.608	0.635	0.641	1.021
YMC					
1	0.9037	0.560	0.707	0.698	1.046
2	0.8618	0.534	0.706	0.701	1.030
3	0.9557	0.591	0.703	0.697	1.062
4	0.8512	0.527	0.705	0.697	1.025
5	0.8641	0.537	0.706	0.700	1.031
Zorbax					
1	1.2513	0.694	0.603	0.593	1.020
2	1.2583	0.701	0.606	0.595	1.026
3	1.2651	0.697	0.599	0.590	1.021
4	1.2804	0.709	0.603	0.594	1.030
5	1.2539	0.695	0.600	0.590	1.018

Note that the definition used in this work for the porosities of particle parts (e.g., internal, skeleton) refers the corresponding void fractions to the actual volume occupied by the particles. See paragraph above Eq. 1.

3.5. Scanning electron micrography (SEM) of the packing materials

A small amount of each packing material was deposited onto an adhesive layer on an aluminum SEM stub and densely distributed across the stub. Each specimen was sputter-coated with Au/Pd alloy to impart electrical conductivity. These samples were examined with the secondary electron detector of a Hitachi S-800 SEM, looking at a fairly wide area of the sample surface. Regions which appeared to best typify the particles observed were photographed at 1000× magnification. A part of each region was selected to include details of anomalous particles and photographed at magnification 5000×. Two typical photographs were selected for each material. They are reproduced in Figs. 1–4.

4. Results and discussion

We present here a number of properties of the materials studied whose consideration will be useful later for the interpretations of other results. As explained above, the values of the particle internal porosity and other volume fractions (unaccessible pore volume, closed pore, silica or bonded group layer) should be referred to the total actual volume of the particles. This provides numbers which remain constant during consolidation of the particles, independently of the degree of consolidation of the packings [7,8]. However, it is necessary to know the value of the external porosity of the packing to derive these data from the measurements. The determination of the external porosity of chromatographic columns by inverse size-exclusion chromatography [14] is described in a companion paper [9] and will be validated by comparison with the results obtained using different other methods in a forthcoming publication [15]. To present here consistent data, we have used the values of the external porosity derived in Ref. [9] for their calculation.

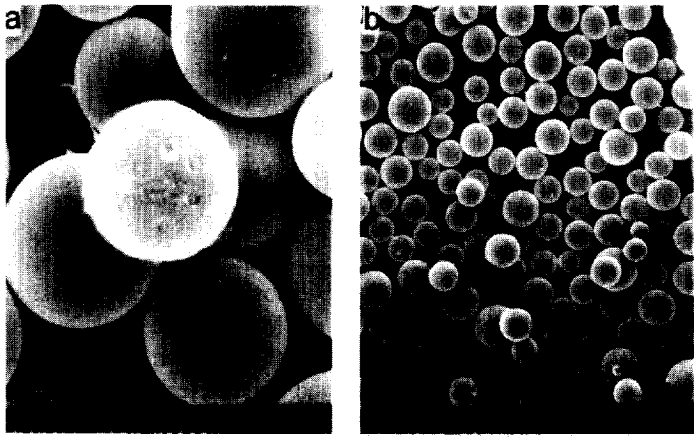

Fig. 1. Scanning electron microphotography of Kromasil particles. (a) ×5000; (b) ×1000.

4.1. Visual examination of the particles

The particles of Kromasil (Fig. 1) are most spherical. The most irregular particle seen in this lot is in the center of Fig. 1a. However, there are some very fine particles (Fig. 1a,b). The ratio of the largest to the smallest particle in the field of the microscope is close to 2 (Fig. 1b). Although the Vydac particles (Fig. 2) are generally spherical, there are a number of irregular-shaped particles, some in the shape of a wheat seed (Fig. 2a), others strongly chipped (Fig. 2b). There are few fine particles. The connections between closely placed particles (e.g., the line of four particles in the top left part of Fig. 2b) might be an artefact of sample preparation, although this phenomenon was not found in the other materials. The YMC particles (Fig. 3) are generally spherical (Fig. 3a), with a few irregular aggregates of very small spheres (Fig. 3b) and an occasional irregular particle (Fig. 3b). The Zorbax particles are also generally spherical, are often chipped (Fig. 4a), are some times agglomerated by pairs (Fig. 4b), with a few larger agglomerates (Fig. 4b) and include some particles which seem to originate from the breakage of these agglomerates.

All these particles are too irregular in shape and/or size to allow their packing as a regular hexagonal assembly of atoms, ions, or molecules in a crystal.

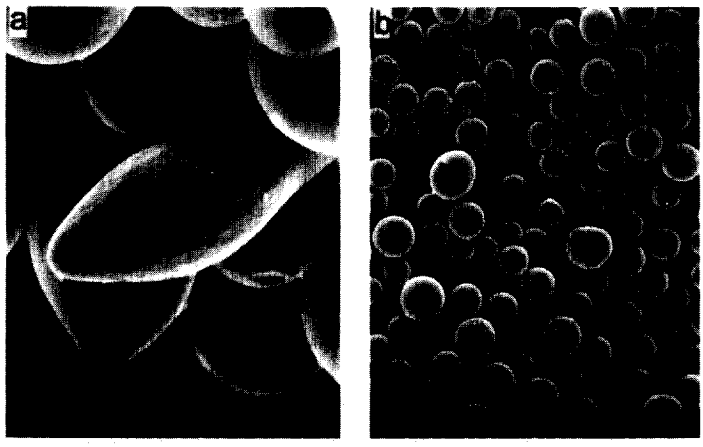

Fig. 2. Scanning electron microphotography of Vydac particles. (a) ×5000; (b) ×1000.

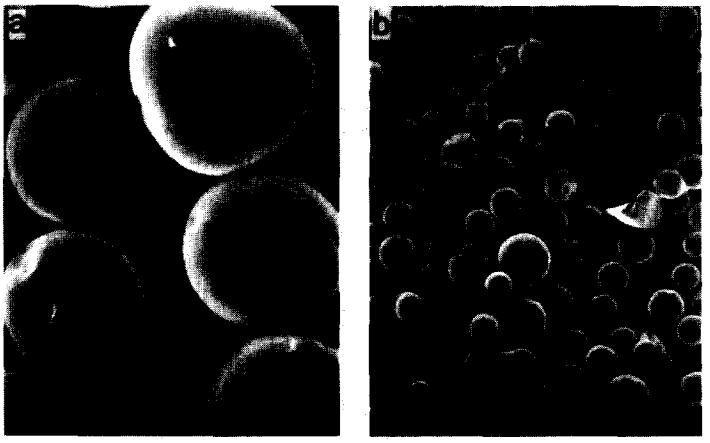

Fig. 3. Scanning electron microphotography of YMC particles. (a) ×5000; (b) ×1000.

The structure of the column packings must be irregular and, fortunately, the external porosity will be much larger than the minimum theoretically possible in a dense packing of regular spheres [9].

4.2. Unaccessible volume fraction

Pycnometry gives an accurate value of the volume nonaccessible to helium in a sample of known weight of the material. From this data, the apparent density or the specific volume of the material is easily calculated (Table 2). The only assumption made is that helium is not adsorbed by the solid at a temperature slightly above room temperature and this is certainly valid. However, it is highly probable too that the alkyl chains are collapsed on the surface, thus blocking access to some of the smallest internal pores and leading to a slight overestimate of the unaccessible pore volume.

The unaccessible volume fraction, ϵ_U, corresponds to the volume occupied by the solid silica skeleton, the C_{18} chains chemically bonded to the silica, and the non-connected or closed pores inside the skeleton, with[1]

$$\varepsilon_U = \varepsilon_s + \varepsilon_c + \varepsilon_a \quad (2)$$

[1]Note that the sum $\epsilon_U + \epsilon_T$ is not equal to 1 with our conventions. From Eq. 1, we have: $\epsilon_e + (1-\epsilon_e)(\epsilon_i + \epsilon_U) = 1$.

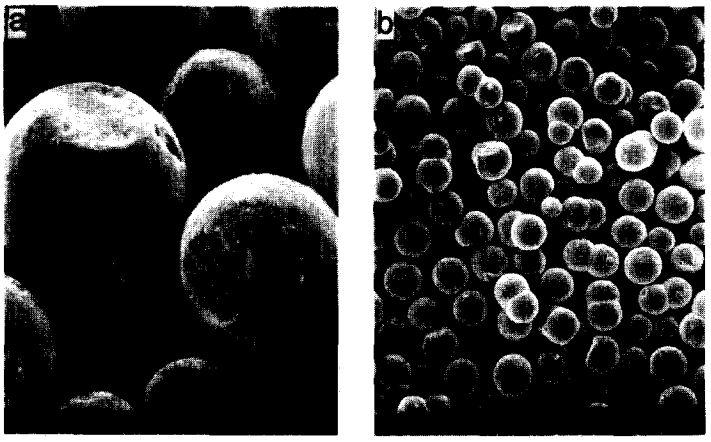

Fig. 4. Scanning electron microphotography of Zorbax particles. (a) ×5000; (b) ×1000.

With the restriction given above, this volume fraction is accurately known, irrespective of the density of the alkyl groups. It can be calculated for each column, from the weight of packing material, its specific unaccessible volume and the column geometrical volume. The result is given in Table 3. Note that the sum of the total porosity and the unaccessible volume fraction is not equal to 1. It is their combination following Eq. 1 which should be close to 1, as seen when comparing the data in the columns of Table 3.

An estimate of the three components of the unaccessible volume fraction, the volume fractions of the silica skeleton, of the alkyl group layer and of the closed pores can be made from the known proportion of organic bonded material in the packing material, assuming the skeleton to have the same density as silica (2.33 g/cm^3), the alkyl groups to have the same density as octadecane (0.777 g/cm^3) and the closed pores to be filled with gas (density 0), since the last operation of the silica material, prior to its bonding, is a high-temperature treatment. The corresponding fractions are reported in Table 4 for Kromasil and Zorbax, for which the percent carbon was available.

4.3. Solid volume fractions

Kromasil contains 19.40% carbon (data given by the manufacturer), hence approximately 3.35% hydrogen and 77.25% silica. For Zorbax these values are 11.04%, 1.98%, and 86.98%, respectively. From the weight of packing per column, the specific unaccessible volume, the column volume, and the weight fraction of silica in the packing material, it is possible to calculate the volume fraction of the particles which is occupied by the silica. Knowing the weight fraction of the bonded C_{18} chains allows the calculation of the volume fraction occupied by the bonded layer in each column. The difference with the total unaccessible volume gives the closed pore porosity. The results are reported in Table 4. Densities of 2.33 g/cm^3 for silica [13] and 0.777 g/cm^3 for the alkyl chains have been assumed.

There may be a slight, positive systematic error on both values. The mass of silica was obtained by drying and weighing the column after completion of the experiments and subtracting the weight of the empty column measured before packing. Although dry dichloromethane (b.p. 40°C) was used as the mobile phase and the column was purged with an excess of nitrogen at 50°C (until constant weight), the packing might not have been completely cleaned of adsorbed material. However, the column temperature cannot be raised above 50°C while it is purged with nitrogen, the bonded material becoming then too sensitive to oxidation.

The volume fraction occupied by the solid stationary phase is nearly the same for Kromasil and Zorbax (43 and 42%, respectively), it is about 25% smaller for YMC and 10% smaller for Vydac. For almost the same value of the external porosity as Zorbax, Kromasil has a 50% higher volume fraction of bonded layer.

Table 4
Volume fractions occupied by silica, the bonded chains and the closed pores

Columns	ϵ_U	ϵ_s^a	ϵ_a^b	$\epsilon_C = \epsilon_U - (\epsilon_s + \epsilon_a)$
Kromasil				
1	0.689	0.360	0.310	0.019
2	0.688	0.359	0.309	0.019
3	0.692	0.361	0.312	0.019
4	0.689	0.360	0.311	0.018
5	0.686	0.359	0.308	0.019
Zorbax				
1	0.694	0.467	0.210	0.017
2	0.701	0.472	0.212	0.016
3	0.697	0.469	0.212	0.016
4	0.709	0.472	0.214	0.017
5	0.695	0.468	0.209	0.017

[a] ρ_s: 2.33 g/cm^3.
[b] ρ_a: 0.78 g/cm^3.

4.4. Closed pores porosity

The closed pore porosity is very small, nearly negligible and could probably be neglected. It is of the order of 1% for Kromasil and Zorbax for which the relevant data were available. The significant value of the amount of bonded alkyl material is the cause for an apparent density of the solid material in the particles which is markedly lower than that of solid silica (Table 2).

Furthermore, the value of the closed porosity is indirectly and only weakly related to the column performance. It is just a wasted amount of space in

the column. It contributes neither to the retention nor to the particle mechanical strength but has, otherwise, no direct effect on column performance.

4.5. Column total porosity

The total column porosity is derived from the retention volume of either benzene in dichloromethane or uracil in methanol. Both methods give results which are in close agreement, albeit slightly different (see below, Table 2, and Ref. [9]).

It should be noted that the total porosity on the one hand, the inaccessible volume fraction on the other hand, are determined separately and independently. The former is derived from chromatographic data, the latter from pycnometric measurements. The combination of these two sets of data as indicated in Eq. 1 should be equal to 1. Deviation of this sum from unity reflects all the errors made in the determination processes. Except for two columns (YMC 1 and 3), the deviation is between +2 and +3%, which is small, considering the different conditions under which the measurements of density (hence, ϵ_U) and column hold-up volume (hence, ϵ_T) are carried out. This excess would be divided by approximately 2 if the retention volume of uracil instead of benzene was used. Note also that the difference between the numbers in the far right column of Table 3 and 1 is nearly constant for each stationary phase, suggesting the possibility of a systematic error of measurements which would be related to the nature of the material used.

The most important sources of error seem to be associated with the definition of the interface volume and the way it is accounted for. First, a fraction of the volume accessible to helium may be unaccessible to the mobile phase used in liquid chromatography, whose molecules are much larger than those of helium. Second, in the measurement of the inaccessible volume fraction, the packing material is dried under vacuum and the bonded alkyl chains are collapsed against the underlying silica surface. In the measurement of the total porosity, the packing material is impregnated with a solvent (dichloromethane) which wets well the solid and the alkyl chains swim in the mobile phase. The weight fraction of bonded organic material is of the order of 10–12% on the products used. An amount of liquid octadecane equal to the amount of bonded chain would account for approximately 6% of the column volume. Collapsed chains occupy a larger volume than independent ones; when collapsed they block the access of small pores, so it is possible that the volume accessible to helium is slightly lower than the volume accessible to dichloromethane in spite of the larger size of the latter molecules. Note that these two effects act in opposite directions and may compensate to some extent.

Finally, while the relative standard deviation (R.S.D.) on the inaccessible volume fraction is ca. 0.03%, the R.S.D. on the total porosity is 1%. The relative difference between the values of the total porosity derived from the retention volumes of benzene in dichloromethane (e.g., average $\epsilon_T = 0.599$, R.S.D. = 1% for Kromasil) and of uracil in methanol ($\epsilon_T = 0.582$, R.S.D. = 0.35%, also for Kromasil) is 2.8%, which is significant. This suggests that further interpretation of the porosity data reported here is not warranted until a better understanding of the behavior of the liquid–solid interface is reached. This question will be discussed again in a further publication [15].

5. Conclusion

Highly consistent data are obtained for all four packing materials. The relative standard deviations for the different volume fractions calculated are of the order of 0.5%. The agreement between the values of the unaccessible volume fraction derived from helium pycnometry and from the total porosity, itself obtained from the retention volumes of benzene in dichloromethane and uracil in methanol, is excellent. The next problem is the determination of the internal and external porosity and the study of the pore size and particle size determination. These issues are discussed in the companion paper [9] and will be revisited in further work [15].

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