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Porous zirconia and titania as packing materials for high-performance liquid chromatography

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ABSTRACT

Porous amorphous zirconia (ZrO_2) and titania (TiO_2) packings were synthesized as rigid micropar-ticulate beads by means of a sol–gel process. Sufficient rigidity and desired mesoporosity of the ZrO_2 and TiO_2 particles were achieved only by a gel hardening process, followed by heat treatment. The mean pore diameter, $\bar{p}_d$, the specific surface area, a_s, and the specific pore volume, v_p, were controlled by the heat treatment. Typical values were $\bar{p}_d = 8$ nm, $a_s = 80$ m^2/g and $v_p = 0.23$ ml/g. ZrO_2- and TiO_2-based revesed-phase packings were prepared by subjecting the native materials to a specific surface activation process and reaction with octadecyltrimethoxysilane. Native ZrO_2 and TiO_2 of graduated polarity, tested under normal-phase conditions, yielded a solvent strength series similar to those observed with silica and alumina. Retention of lipophilic analytes in *n*-heptane and dichloromethane was scarcely affected by the relative water content of the mobile phase. Native ZrO_2 and TiO_2 were found to be suitable for the separation of structural isomers. From calcined ZrO_2 and TiO_2 amines were eluted with totally sym-metrical peaks when water-modified dichloromethane was used as the mobile phase. The retention and selectivity of *n*-octadecyl-bonded ZrO_2 and TiO_2 packings were identical with those of silica-based materi-als, except for showing a pronounced pH stability up to pH 12 in aqueous–organic mobile phases.

INTRODUCTION

The development of high-performance liquid chromatography (HPLC) as an efficient separation technique was always dependent on the synthesis of suitable packing materials. Silica and its bonded derivatives still maintain a leading position as packings in HPLC. However, polymer packings have improved remarkably and are now being increasingly applied.

Many attempts have been undertaken to improve the quality of silica packings with regard to chemical stability and residual adsorptivity towards basic analytes. The limited chemical and pH stability of silica and its bonded derivatives in HPLC has led to extensive research activity to overcome these undesirable properties. Stabilized silicas have been prepared by drastically reducing inorganic impurities [1], by subjecting it to hydrothermal and acid treatment [2,3] or by coating it with alkali-resistant oxides [4]. These stabilized silicas were either made to react with protective silanes [5] or coated with polymeric phases [6] to yield stable reversed-phase

packings. In spite of all efforts to increase the pH stability, silica persists in being soluble in strong alkaline solution.

Porous aluminas are used as packing materials to a lesser extent. The potential of porous alumina has been re-investigated by De Galan and co-workers [7,8]. Recently, a polybutadiene-coated alumina has become commercially available [9].

A few attempts have been made to utilize titania and zirconia ceramics as packing materials, in HPLC [10,11]. A polybutadiene-coated microporous zirconia was prepared by Rigney et al. [12] which showed excellent chemical and thermal stability. Mesoporous crystalline zirconia beads have been studied by the same group, in particular their ion-exchange properties [13].

Both titania and zirconia are basic oxides and are therefore insoluble in alkaline media. Moreover, they are stable in acidic media, down to pH 1. Compared with conventional packing materials, titania and zirconia exhibit completely different chemical surfaces. As the interaction of analytes with the surface of the stationary phase determines the chromatographic selectivity, divergent selectivities could be expected when titania or zirconia is used as packing material.

We found all commercially available zirconia and titania products to be unsuitable for HPLC use. They were either highly crystalline and non-porous, with almost no chromatographic retentivity, or amorphous and microporous, showing poor chromatographic performance.

The objective of this work was to develop a method for preparing amorphous titania and zirconia particles, based on a sol–gel process, which permits the combination of oxide synthesis and control of their physical properties with the shaping of the final products [14]. The main problems were to obtain particles with a rigid texture, an adjustable particle size, a sufficient porosity and mesopores of mean pore diameter between 2 and 50 nm.

EXPERIMENTAL

Preparation of starting materials

Highly concentrated titania and zirconia sols were used as starting materials for oxide synthesis. They were obtained either by partial hydrolysis of the corresponding tetravalent metal chlorides [15] or, in the case of zirconia, by dissolving zirconyl chloride in water. Titania sol was prepared by hydrolysing 1 l of titanium tetrachloride (Merck, Darmstadt, F.R.G.) in portions of *ca.* 50 ml in 300 g of ice. Precautions were taken to collect the hydrogen chloride fumes evolved. The foam-like precipitates were dissolved in cold water.

Zirconia sol was supplied ready for use by Goldmann (Bielefeld, F.R.G.). The elemental analyses and physical properties of the sols are given in Table I.

Preparation of reactive sols and gelation reaction

To initiate the gel reaction, the acid-stabilized sols were made to react with an appropriate amount of a weak base, such as hexamethylenetetramine (HMTA) and urea [16]. Sufficient hydroxyl ions were released owing to hydrolysis (Fig. 1). It is essential to set the conditions of the gelation reaction properly in order to obtain homogeneous rigid titania and zirconia gels.

For the preparation of the titania sol reactive to gelling, 340 g of titania sol were

TABLE I

ELEMENTAL ANALYSIS AND PHYSICAL PROPERTIES OF TITANIA AND ZIRCONIA SOLS

Concentrations given in mol dm^{-3}.

Sol	$[M(IV)]^a$	$[H^+]^b$	$[Cl^-]^b$	$\delta/kg\ dm^{-3\,c}$	η/cSt^d
TiO$_2$	6.8–7.2^e	10.7–11.8^e	11.1–12.4^e	1.565–1.601^e	67–78^e
ZrO$_2$	2.35	4.80	4.86	1.385	3.5

^{a} Gravimetric analysis.
^{b} Titrimetric analysis.
^{c} Pycnometry.
^{d} Viscosimetry.
^{e} Tolerance range of different sol batches.

mixed with 380 g of HMTA (3.5 M) and 60 g of urea (8 M). For zirconia, 560 g of zirconia sol, 380 g of HMTA (3.5 M) and 65 g of urea (8 M) were used. The sols were converted to transparent monolithic hydrogels at elevated temperatures (40–45°C) within 8 min. The sol–gel transition occurred within a few seconds.

Emulsification

Prior to gelation, sols (so-called w phase) were emulsified in a water-immiscible liquid (so called o phase), containing various non-ionic surfactants to stabilize the liquid–liquid dispersion. Emulsion stability was optimized by utilizing the hydrophilic lipophilic balance (HLB) system with respect to a low coalescence rate to prevent the dispersion from breaking, creaming or sedimenting [17].

Finely divided w/o emulsions were achieved by making use of a high-shear rotor stator dispersion unit, generating small droplets within the organic phase [18]. The
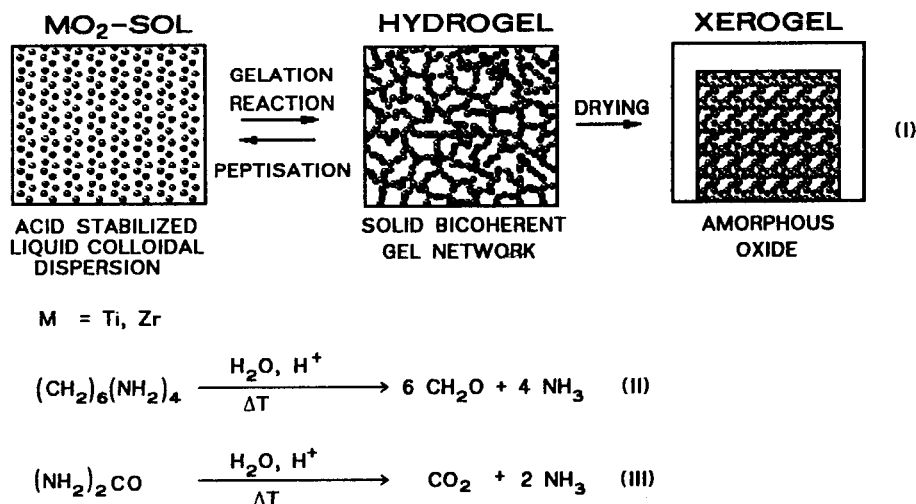

Fig. 1. Scheme for the sol–hydrogel–xerogel conversion (I) due to hydrolyis of hexamethylenetetramine (II) and urea (III).

organic phase was prepared by adding a multi-emulsifier complex ($HLB_{mixture}$ = 4.9), containing 49 g of Span 85, 15 g of Tween 85 and 11 g of Brij 30 (Serva, Heidelberg, F.R.G.), to 2.5 kg of light petroleum (b.p. 100–140°C) (Merck).

The sols were dispersed in the organic phase by means of an Ultra-Turrax T45/4G dispersion unit (Janke & Kunkel, Staufen, F.R.G.) at 6500 rpm for 30 s to prepare 2–25-μm particles and at 8500 rpm for 60 s to prepare 2–7-μm beads. After the gelation reaction had been accomplished, the former emulsified liquid sol droplets were converted to solid, transparent hydrogel particles.

Particle processing and characterization

To remove adherent light petroleum, surfactants and residual substances, such as hydrochloric acid, and unreacted base, the microparticulate, swollen hydrogel particles were subjected to a multi-stage washing procedure (Table II).

Drying was carried out either by conventional methods or by applying a gel-hardening process [19]. For gel hardening, 2 kg of hydrogel particles were suspended into 3.5 l of isoamyl acetate (Merck) in order to remove enclosed water by azeotropic distillation (b.p. 122–130°C).

Sizing of the xerogel spheres was achieved by means of a laboratory air classifier (Alpine, Augsburg, F.R.G.). The particle-size distribution was determined by laser diffraction (Mastersizer, Malvern, U.K.). Morphological studies of particles were performed by scanning electron microscopy (Philips PSEM 500).

Residual organic matter, enclosed in native products, was removed by controlled pyrolysis to obtain carbon-free calcined products. The calcination was carried out in a preheated oven (N3 R; Naber, Flörsheim, F.R.G.) with a constant height of the solid bed (15 mm) in flat-bottomed porcelain crucibles. As the thermal treatment diminished the number of surface hydroxyl groups, the calcined products were rehydroxylated at different pH values following a procedure described elsewhere [20].

The physical properties of the final products were determined by means of thermogravimetric and differential thermal analysis (Model 84; Linseis, Selb, F.R.G.), X-ray powder diffraction (Philips APD) and nitrogen adsorption measurements (4102 and 4433 microbalances; Sartorius, Göttingen, F.R.G.; Omicron 100; Omicron Techn., Berkeley Heights, NJ, U.S.A.). Particular emphasis was placed on the reproducibility and standardization of sample pretreatment. As is well known, the

TABLE II

HYDROGEL WASHING PROCEDURE

Chemicals: technical grade, Merck, Darmstadt, F.R.G.

Washing liquid	Amount (l)	Cycles	Washing time (h per cycle)
Light petroleum (b.p. 40–80°C)	1.5	1	0.5
Acetone	1.5	1	0.5
Ethanol	2	3	1
Water	2	3	0.5
Ammonia (2.5%)	1	1	12
Water	until neutral reaction of supernatant		

determination of the specific surface area and pore volume of metal oxides depends strongly on the sample history [21].

Preparation of reversed-phase packings, column filling procedures

Calcined titania and zirconia xerogels were activated and converted to reversed-phase packings by making the oxide spheres react with *n*-octadecyltrimethoxysilane (Wacker, Burghausen, F.R.G.), as described by Engelhardt and Orth [20]. The carbon content of modifying ligands was determined by elemental analysis. Stainless-steel columns (Hyperchrome, 125 × 4 mm I.D.; Bischoff, Leonberg, F.R.G.) were filled with the packing materials by conventional slurry packing techniques. Column filling was carried out with a home-made packing unit, provided with a 100-ml reservoir and a membrane pump (Model S 80; Orlita, Giessen, F.R.G.). For native zirconia and titania packings, ethanol served as the dispersant. Toluene–dioxane–cyclohexanol (4:4:1, v/v/v) was employed to suspend zirconia- and titania-bonded packings. The final filling pressure was kept below 45 MPa to avoid particle cracking.

Chromatographic tests

Chromatographic tests were carried out with standard HPLC equipment [pump, Kontron 420 (Kontron, Munich, F.R.G.); UV detector, LKB 2158 (wavelength 254 nm) (Pharmacia–LKB, Freiburg, F.R.G.); injection system (sample loop, 20 μl), Rheodyne 6125 (Bischoff); integrator, Shimadzu C-R3A (Shimadzu, Kyoto, Japan)].

Native and calcined titania and zirconia packings were tested under normal-phase conditions to assess the solvent strength sequence and the influence of water-containing eluents on retention. Capacity factors of solutes with different polarities were determined in order to evaluate the chromatographic selectivity of these packings, with chloroform as a t_0 marker.

N-Octadecyl-modified titania and zirconia packings were tested under reversed-phase conditions employing aqueous acetonitrile as the mobile phase.

The pH stability of reversed-phase packings based on titania and zirconia was monitored under dynamic conditions. The columns were flushed with buffers of increasing pH. The pH of the buffer was adjusted in steps of 0.5 unit. In each cycle the columns were operated for 24 h at a flow-rate of 1 ml/min before they were equilibrated to a 60% (v/v) aqueous acetonitrile eluent. A test mixture was then injected to monitor changes in capacity factors and peak width of test solutes due to a pH increase.

RESULTS AND DISCUSSION

Gel formation

The gelation reaction was found to be very sensitive to the reaction conditions with respect to the initial sol pH, the sol-to-base ratio, the concentration of urea and the reaction temperature. Among these the sol-to-base ratio turned out to be the most critical factor in gel synthesis. At a high ratio of sol to base, hydrous oxides precipitated owing to complete and rapid neutralization (Fig. 2a), whereas no gelation occurred at low sol-to-base ratios (Fig. 2c). However, rigid monolithic transparent hydrogels were exclusively obtained when the gel pH (Fig. 2d) was approached at the proper rate (Fig. 2b). Beyond that, urea was found to act as an additional factor controlling the rate of
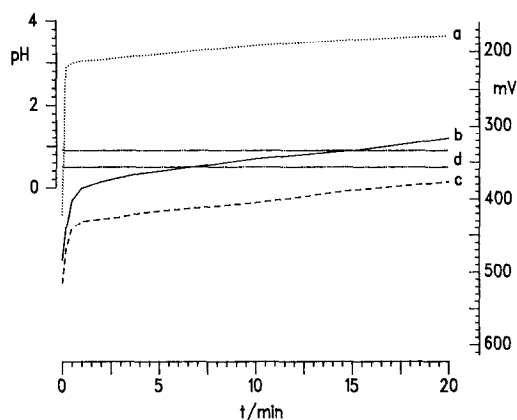
Fig. 2. Change in pH during titania sol–gel reaction at different sol-to-base ratios. (a) [Ti(IV)]/[HMTA] = 0.58, precipitation of hydrous oxides; (b) [Ti(IV)]/[HMTA] = 0.90, monolithic transparent gels; (c) [Ti(IV)]/[HMTA] = 1.25, viscous liquid sol (no gelation); (d) pH threshold of gel formation.

hydrolysis of the initial sols. This turned out to be useful for the preparation of large batches.

Physical properties of packings

Conventional drying procedures caused particle shrinkage, aggregation of particles, compaction of microstructure and hence a decrease in porosity, generation

TABLE III

COMPARISON OF PHYSICAL PROPERTIES OF CONVENTIONALLY AND AZEOTROPI-CALLY DRIED XEROGELS

a_s = Specific surface area; v_p = specific pore volume; $\bar{d}_p$ = mean pore diameter.

Conventional drying

	H_2O (%)[a]	a_s (m^2g^{-1})	v_p (ml g^{-1})	$\bar{d}_p$ (nm)	Pore size
TiO_2	31	470	0.105	<2	Microporous
ZrO_2	48	420	0.094	<2	Microporous

Azeotropic drying

	H_2O (%)[a]	a_s ($m^2 g^{-1}$)	v_p (ml g^{-1})	$\bar{d}_p$ (nm)	Pore size
TiO_2	31	343	0.251	2.9	Mesoporous
	65	309	0.337	4.2	Mesoporous
	85	327	0.472	5.8	Mesoporous
ZrO_2	48	335	0.152	1.4	Microporous
	65	319	0.161	2.2	Mesoporous
	85	327	0.274	3.3	Mesoporous

[a] Initial water content of sol.

of a large specific surface area and microporosity. These properties are very disadvantageous for the use of these packings in HPLC. A comparison of the physical characteristics of xerogels which had been subjected to different drying procedures is given in Table III. The physical data of conventionally dried gels indicated that microporous products were mainly formed. Azeotropically dried gels, however, exhibited larger pore volumes with a pronounced mesoporous structure. In addition, the porosity could be regulated by varying the initial water content of the sol.

Subjecing the hydrogels to azeotropic drying obviously prevented the pore structure from collapsing and led to mesoporous products, providing much faster mass transfer throughout the chromatographic process than conventionally dried products. In addition, azeotropic drying yielded free-flowing, fluffy powders, facilitating further particle processing. Scanning electron micrographs of the xerogels showed non-aggregated spherical partices without lumps, cracks or protrusions, and particle fragments (Fig. 3). By passing them through an air classifier, the starting polydisperse products were separated into narrow particle-size fractions (Fig. 4). This narrow particle-size distribution provided the necessary homogeneity of column packings at reasonable column back-pressures.

The xerogels contained up to 10% of residual organic matter, which had to be removed by pyrolysis to yield pure zirconia and titania materials. Therefore, the determination of the thermal properties of xerogels by means of thermogravimetric and differential thermal analyses was essential. The xerogels reached a constant weight
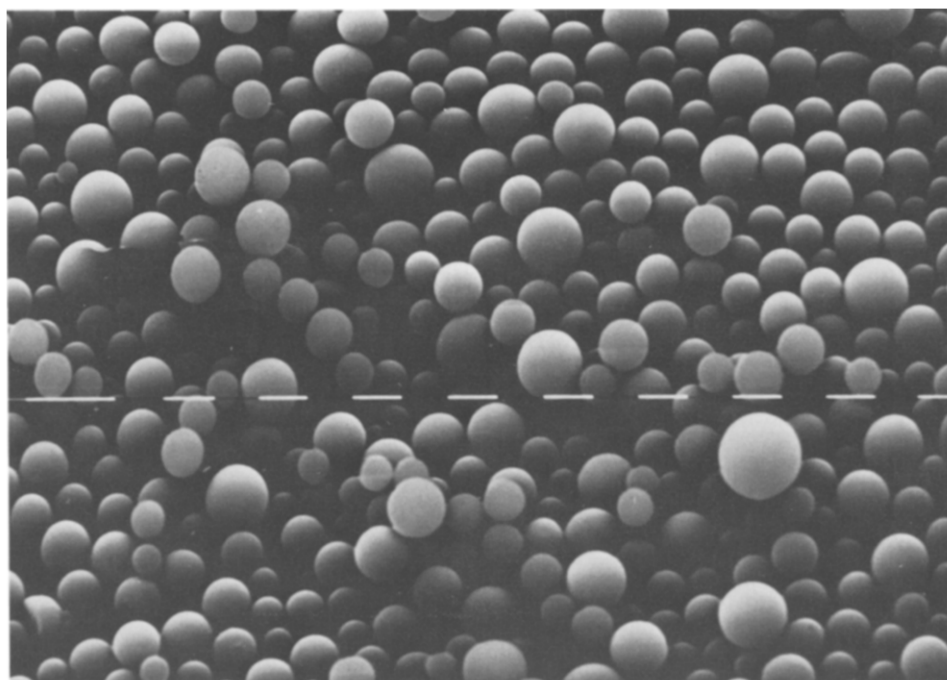

Fig. 3. Scanning electron micrograph of a zirconia xerogel, prepared according to the sol–gel process. White scale bars represent 10 μm.
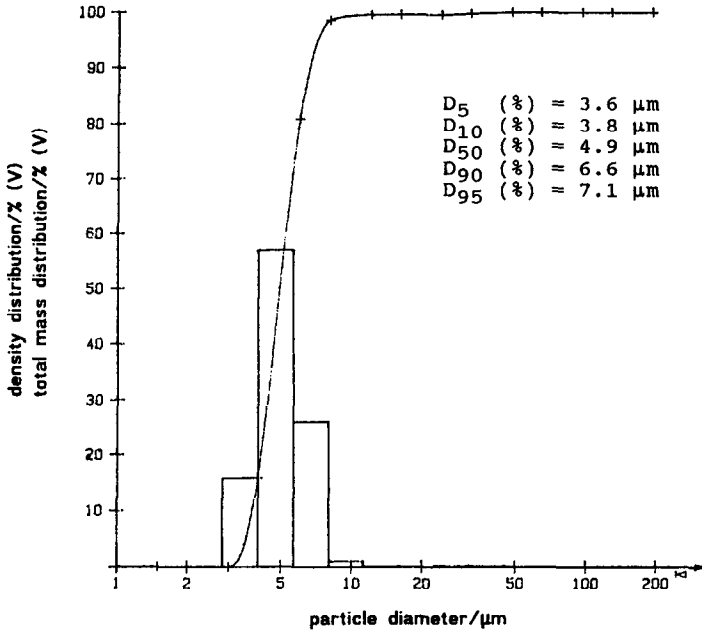
Fig. 4. Particle size distribution of a titania packing material ($\bar{p}_d$ = 5 μm).

at about 400°C, losing *ca.* 30–40% of their initial weight (Fig. 5). Up to 300°C a broad endothermic peak was observed, due to the release of water and coking of the organics. At about 400°C, a sharp exothermic peak indicated the beginning of the crystallization of amorphous oxides. This process is known as the glow phenomenon [22]. This behaviour indicated that the thermal properties of sol–gel-derived oxides were similar to those of precipitated products [23].

   As crystallization is always accompanied by a drastic decrease in specific surface area and porosity [24], the conditions of the heat treatment had to be carefully
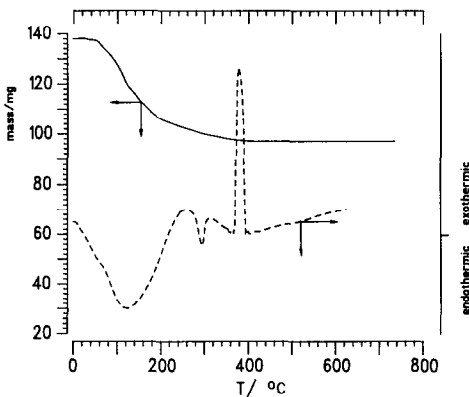
Fig. 5. Thermogravimetric (solid line) and differential thermal analysis (dashed line) of a titania xerogel.
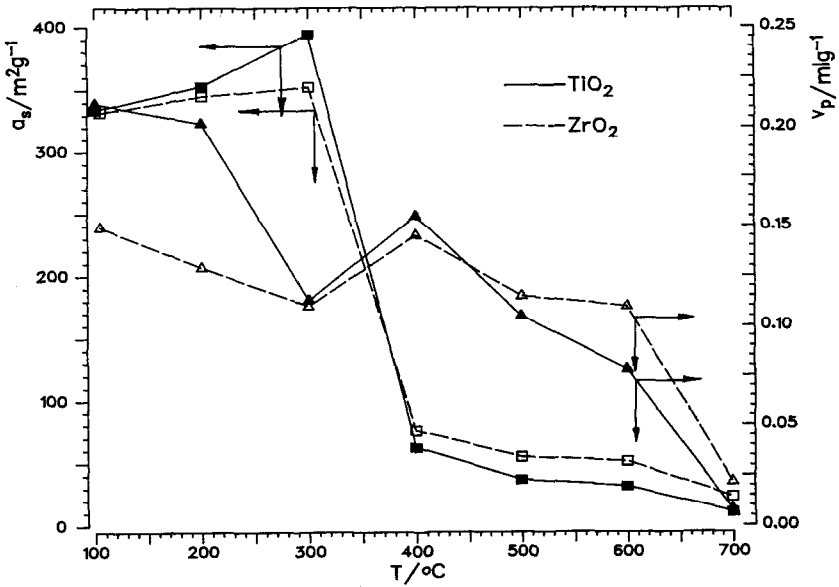
Fig. 6. Change in specific surface area (a_s) and specific pore volume (v_p) of titania (solid lines) and zirconia (dashed lines), xerogels as a function of calcination temperature (T).
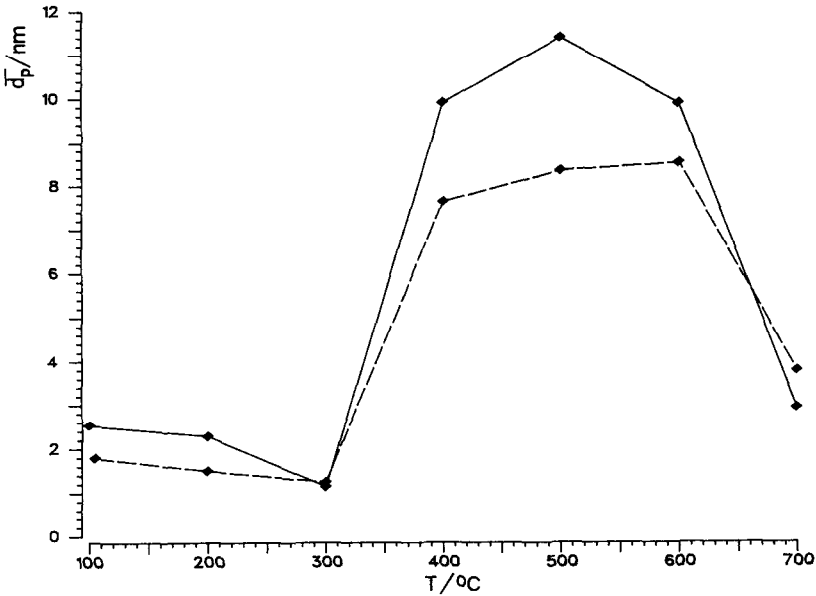

Fig. 7. Change in mean pore diameter ($\bar{d}_p$) of titania (solid line) and zirconia (dashed line) xerogels as a function of calcination temperature (T).

TABLE IV

PHYSICAL PROPERTIES OF TITANIA AND ZIRCONIA PACKING MATERIALS

a_s = Specific surface area; v_p = specific pore volume; $\bar{d}_p$ = mean pore diameter.

	a_s (m² g⁻¹)	v_p (ml g⁻¹)	$\bar{d}_p$ (nm)	Pore size
Native TiO₂	330	0.26	3	Micro-/mesoporous
Calcined TiO₂	78	0.23	8	Mesoporous
Native ZrO₂	308	0.18	2	Micro-/mesoporous
Calcined ZrO₂	104	0.15	6	Mesoporous

adjusted. Whereas the microporous structure of conventionally dried gels was insensitive to calcination, azeotropially dried gels showed a completely different behaviour (Fig. 6). On calcining these xerogels at different temperatures, a considerable decrease of ca. 70% in surface area was observed at about 400°C, whereas a_s remained almost constant on further temperature increase. The specific pore volume also decreased with increasing calcination temperature, but at a much slower rate.

Both a_s and v_p affected the development of pore size as a function of the calcination temperature. As Fig. 7 indicates, the mean pore diameter of products initially in the lower mesopore range could be enlarged to 10 nm by increasing the calcination temperature. The physical properties of titania and zirconia packings, subjected to chromatographic tests, are summarized in Table IV. X-Ray powder diffraction patterns indicated that neither native nor calcined xerogels were crystalline.
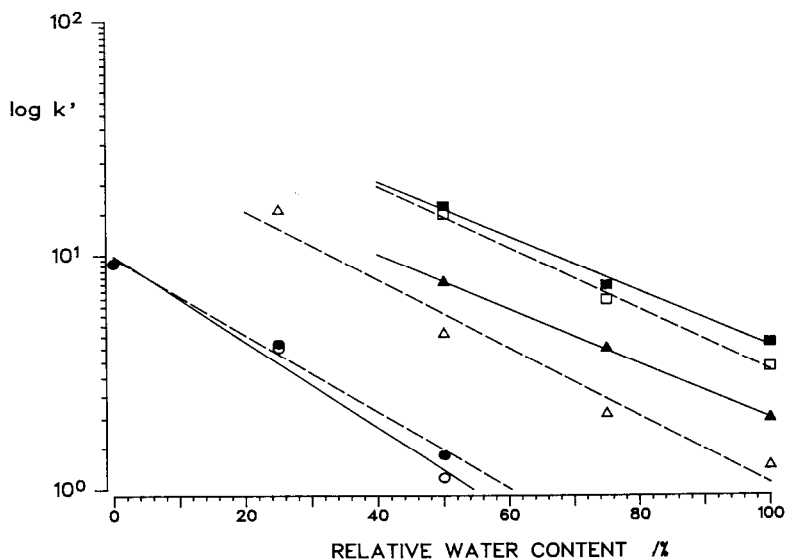

Fig. 8. Capacity factors of test solutes as a function of the relative water content of dichloromethane as the mobile phase, with calcined titania xerogel as packing material. $\bar{p}_d$ = 5 μm; injection volume, 20 μl; flow-rate, 1 ml/min. ■ = Diazepam; ▲ = pyridine; ● = o-toluidine; □ = p-toluidine; △ = aniline; ○ = N-methylaniline.

Normal-phase chromatography

The zirconia and titania particles prepared withstood a packing pressure up to 50 MPa without cracking.

Chromatographic tests under normal-phase conditions demonstrated that there was no major difference in the solvent strength sequence found for silica or alumina. Increasing the relative water content of the eluent affected the capacity factor of solutes, as shown for dichloromethane as eluent in Fig. 8. In normal-phase chromatography of silica and alumina packings, conditioning and reconditioning of columns has always been a time-consuming procedure [25]. Up to *ca.* 100 column volumes are required to equilibrate the silica and alumina with a non-polar mobile phase and water as modifier. In contrast, calcined zirconia and titania packings required only 5–10 column volumes for equilibration.

Native titania and zirconia exerted a strong retention towards hydrophobic solutes, such as polycyclic aromatic hydrocarbons. The latter were eluted only with
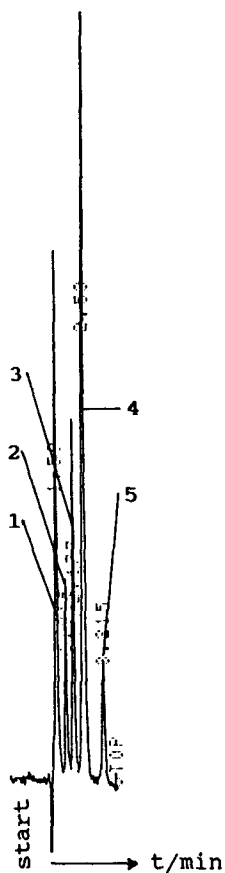
Fig. 9. Isocratic separation of lipophilic test solutes using native titania as packing material and a mobile phase of high solvent strength. $\bar{P}_d$, 10 μm; injection volume, 20 μl; eluent, dry methanol; flow-rate, 1 ml/min. Peaks: 1 = benzene (10.8 μg); 2 = naphthalene (3.2 μg); 3 = fluorene (2.5 μg); 4 = phenanthrene (4.3 μg); 5 = pyrene (2.2 μg).
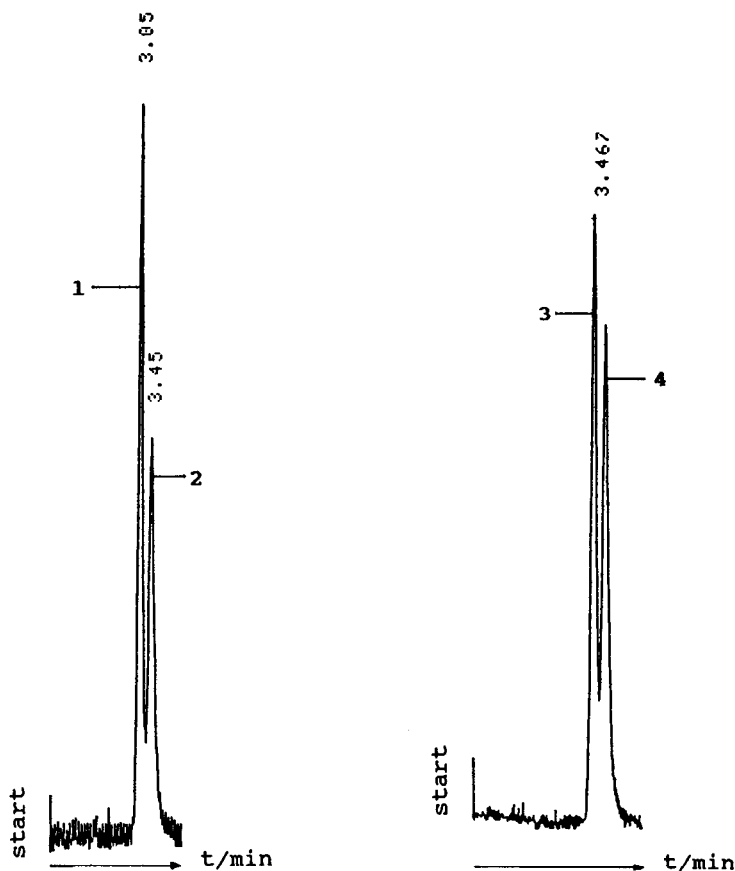
Fig. 10. Isocratic separation of isomers with native titania as packing material. $\bar{p}_d$, 10 μm; injection volume, 20 μl; eluent, n-heptane; flow-rate, 1 ml/min. Peaks: 1 = p-xylene (11.3 μg); 2 = o-xylene (6.2 μg); 3 = o-xylene (9.2 μg); 4 = m-xylene (7.7 μg).

eluents of high solvent strength, such as methanol, indicating a high solute surface interaction (Fig. 9). However, the same solutes were eluted from the calcined packings with n-heptane as mobile phase. These results demonstrate that the polarity of the adsorbents could be controlled by the conditions of heat treatment. As a result, the highly polar, native ZrO_2 and TiO_2 packings were well suited for the separation of isomers, as demonstrated in Fig. 10. However, on silica or alumina columns, this separation could not be performed under identical conditions.

It is well known that the acidic properties of silica are responsible for the strong retention of basic analytes, which is often accompanied by severe tailing. Basic compounds with pK_B values up to 11 were separated on calcined titania and zirconia packings with water-containing dichloromethane as eluent (Fig. 11). The basic analytes showed a high peak symmetry.

This chromatographic retention behaviour is due to the surface chemistry of titania and zirconia being different from that of silica and alumina. Amorphous
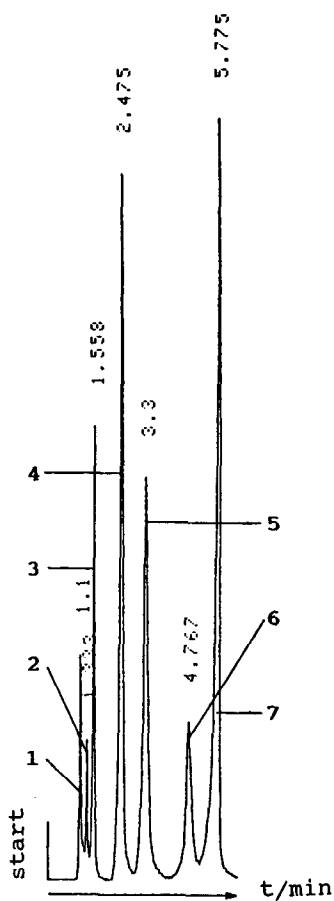
Fig. 11. Isocratic separation of basic analytes with calcined titania as packing material. $\bar{p}_d$, 5 μm; injection volume, 20 μl; eluent, dichloromethane (relative water content 100%); flow-rate, 1 ml/min. Peaks: 1 = N,N-dimethylaniline (10.8 μg); 2 = N-methylaniline (3.2 μg); 3 = o-toluidine (5.4 μg); 4 = aniline (15.4 μg); 5 = p-toluidine (5.4 μg); 6 = pyridine (3.4 μg); 7 = diazepam (1.9 μg).

titania, and also zirconia, represent more or less ionic compounds, carrying highly polar tetravalent metal cations. Hydroxyl groups attached to the surface metal ions neutralize the surface charge. It is known that titania and zirconia carry two different kinds of surface hydroxyl groups [26]. One type is singly bonded, acting as a base, whereas hydroxyl groups bridging two neighbouring metal ions are acidic in behaviour. The number and strength of these distinct hydroxyl groups are almost balanced. Therefore, the isoelectric point and the point of zero charge for pure tiania and zirconia are both at *ca.* pH 7.

Reversed-phase chromatography

The zirconia- and titania-based reversed-phase packings were C_{18}-modified with a surface concentration of 1.2–1.4 μmol/m^2. The packings exhibited typical
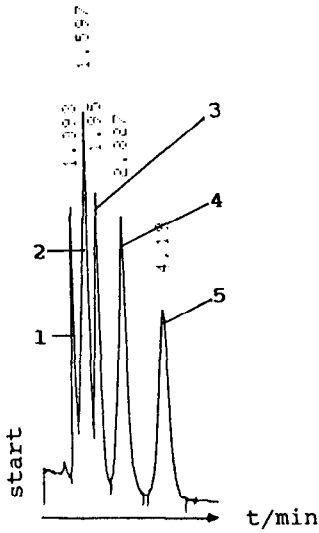
Fig. 12. Isocratic separation of polycyclic aromatic hydrocarbons with *n*-octadecyl-modified zirconia as packing material. $\bar{p}_d$, 10 μm; injection volume, 20 μl; eluent, 60% aqueous acetonitrile; flow-rate, 1 ml/min. Peaks: 1 = benzene (10.0 μg); 2 = naphthalene (4.2 μg); 3 = fluorene (2.9 μg); 4 = phenanthrene (4.6 μg); 5 = pyrene (2.2 μg).

features of reversed-phase packing such as lipophilic behaviour and an exponential increase in the capacity factors of solutes with increasing water content of the acetonitrile eluent. An example is the separation of a standard test mixture under reversed-phase conditions shown in Fig. 12.

The most useful feature of these reversed-phase packings is their pH stability. It was found that titania-based C_{18} packings are stable up to pH 11 and zirconia up to pH 12 without any noticeable effect on the capacity factor or peak width of test solutes. Even after a period of 500 h at pH 12, zirconia-based reversed-phase packings still maintained their performance level. From these results, we conclude that the porous oxide networks of titania and zirconia were neither altered nor attacked by strongly alkaline solutions. Even the heterogeneous metal siloxane binding system is, to a large extent, stable towards alkali. This reflects well that the sequence of hydrolytic stability of silanized oxides obeys the order given in Fig. 13, which has been established for binary siloxane compounds [27].
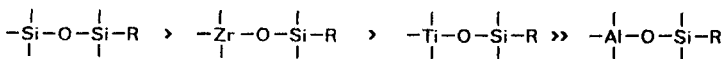

Fig. 13. Hydrolytic stability of binary siloxane compounds [27].

CONCLUSIONS

By means of a sol–gel process and special particle processing procedures, the synthesis of spherical mesoporous titania and zirconia particles was achieved. They satisfy the physical requirements for application as packing materials in HPLC. As the polarity of titania and zirconia packings can be varied to a large extent by heat treatment, their chromatographic retention and selectivity can be adapted to a range of separation problems. Thus, titania and zirconia xerogels appear to be well suited for normal-phase chromatographic separations of isomers in addition to basic analytes. Owing to the chemical nature of the amorphous oxide and the metal–siloxane bonds, stable reversed-phase titania and zirconia packings were obtained, which proved to be superior to other silanized inorganic oxides with respect to their hydrolytic stability towards alkaline eluents.

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