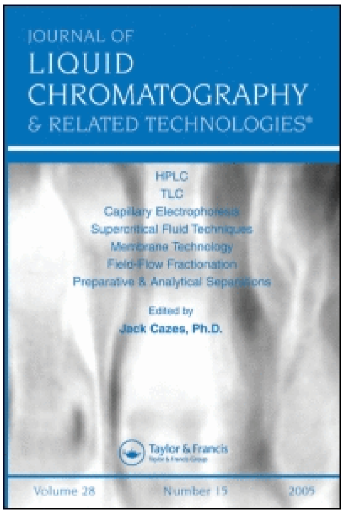

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CONTROLLING THE PORE STRUCTURE OF ZIRCONIA FOR CHROMATOGRAPHIC APPLICATIONS

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ABSTRACT

This paper describes the preparation of zirconia for chromatography. Size exclusion chromatography was used to evaluate the pore structure particularly as it applies to chromatographic applications. Using sodium chloride impregnation techniques during calcination, pore diameters, surface areas and pore volumes could be controlled to prepare zirconia stationary phases that had improved chromatographic characteristics. Without sodium chloride, poor quality pore structures were obtained.

INTRODUCTION

As a relatively new stationary phase material, zirconia has undergone development that has illustrated many of its potential applications. Studies have shown that complex elution mechanisms may be present but, because of the chemical stability of the support, a wide range of mobile phase modifiers may be added to control the chromatographic process. Studies by Blackwell and Carr illustrated the usefulness of the support in the analysis of Lewis bases[1,2] and compiled an extensive eluotropic series, illustrating the control of the separation process. The development of the eluotropic series served as an important step in analyzing proteins on zirconia supports.[3] Methods that control the highly heterogeneous surface of zirconia, and still maintain the novel selectivity afforded by the surface, have received considerable attention. Pre-adsorption of fluoride[4,5] or phosphate[6,7] are two processes involving surface modification that have allowed the controlled chromatographic use of these materials. In particular, these modified zirconias were shown to be useful for the separation of proteins. McNeff and coworkers[8] prepared anionic exchange zirconias with polyethyleneimine (PEI) surface modifications. Ghaemi and Wall[9] reported the first use of zirconia as a reversed phase material in LC using suitable surfactants in the mobile phase. Reversed phase zirconias have also been prepared by Rigney and coworkers[10] and Hanggi and Marks[11] using polybutadiene (PBD). Webber, Carr and Funkenbusch[12,13] described a technique for the preparation of carbon vapour deposited (CVD) zirconia supports where as much as 97% of the surface could be coated. Trudinger, Muller and Unger[14] reported the first successful derivatisation of zirconia with n-octadecylsilane. These phases exhibited similar behaviour to conventional silica C_{18} columns for polycyclic test solutes. Yu and El Rassi[15] also studied the behaviour of n-octadecyl derivatised reversed phase zirconia, comparing the stability of monomeric and polymeric coatings.

While these studies have been important in establishing the usefulness of zirconia as a chromatographic stationary phase, an important aspect of zirconia for chromatographic applications is, however, the optimization of specifically designed surfaces with suitable pore structures. The porous nature of the chromatographic support plays a very important role in the efficiency of the separation process and, ideally, the pores should allow rapid and unhindered equilibration of both solute and mobile phase molecules. Lorenzano-Porras and coworkers[16,17] studied the relationship between pore structure and diffusion tortuosity of zirconia colloidal aggregates and compared the differences in pore structure between two different colloidal aggregation processes. They found that classical methods of surface analysis were insufficient to evaluate the porous structure of zirconia and reported that NMR spin lattice relaxation and NMR self diffusion experiments were not compromised by pore restrictions, as are classical nitrogen sorption and mercury porosimetry. They concluded that in order to evaluate fully the pore structure of chromatographic packings, complimentary techniques of analysis are an invaluable asset.

Using nitrogen sorption experiments to investigate the pore structure of zirconia prepared by the polymerisation-induced colloid aggregation (PICA) method, the authors found that calcination at 700°C for three hours, followed by further calcination at 900°C for three hours, produced pore sizes in the range 35.0-55.0 nm. Nitrogen desorption measurements indicated that 70% of the pore volume lay behind throats that were only 10.0-25.0 nm in diameter. The authors found large differences in pore sizes depending on whether nitrogen sorption, Hg porosimetry or NMR spin lattice relaxation (NMR-SLR) was used for their determinations. They attributed these differences to pore constrictions on the zirconia and to the assumptions of cylindrical pore shapes. Lorenzano-Porras and co-workers have also shown that the pore size and porosity of zirconia was dependent upon the colloidal aggregation process used. In a recent publication by Dunlap et. al.,[18] a comparison was made between the pore structures of a PICA prepared zirconia and an oil emulsion prepared zirconia using a size exclusion method of analysis.

The chromatographic method of analysis offered the advantage of providing pore analysis results that directly reflected the actual chromatographically available surface for solute molecules during an elution process. They found that both methods of synthesis yielded zirconias with greatly varied pore structures. Mercera and coworkers[19] presented a study on zirconia as a support for catalysis with respect to the effect of calcination temperature on the pore structure. Zirconia was precipitated from zirconyl chloride in ammonia at pH 10.0. The particles were large and irregular, requiring grinding to a finer size of approximately 100 μm. Their results showed that this method of preparation produced zirconia with a surface area of 111 m^2/g when calcined at 450°C. As the temperature of calcination was increased, the surface area decreased by as much as 100 fold at 850°C. They attributed the decrease in surface area to crystallite growth accompanying phase transformations and inter-crystallite sintering, which in turn increased the pore size. Zirconia, that was thermally treated below 650°C, was reported to contain micropores, and this led to an over estimation of the BET surface area. Zirconias, calcined at temperatures above 750°C, were free from micropores. No maximum pore size was recorded for the uncalcined zirconia, indicating that the pores were less than 1.5 nm, whereas calcination at 850°C produced zirconia with a most frequent pore radius of 10.29 nm. Pore size distributions of all zirconia samples were unimodal. Recent studies in our laboratory also illustrate similar results for zirconias prepared for chromatography.[20]

Despite these recent studies on porous zirconia, few researchers have attempted to optimize the surface area, pore size and pore volume for specific separation problems. Krebs and Heinz[21] described a method of preparing macroporous silica using salt impregnation during calcination. Their technique primarily involved calcining narrow pore diameter silica in the presence of salts to enlarge the pores. Despite their success in preparing macroporous silica gel, few studies have since followed where pore structures could be optimized using their methods. Perhaps the bimodal pore size distributions of such silica gels as reported by Novák and Belek may have hindered its development.[22] In the current study we illustrate how the pore volume, surface area and pore diameter of zirconia can be optimized during the calcination process by the inclusion of sodium chloride. In particular, this study is important for applications in bio-molecule separations where larger pore diameters are required for the separation of high molecular weight proteins.

EXPERIMENTAL

The surfactants, Span 80, Brij 35, and Tween 85 were supplied by the Sigma Chemical Company Inc (St. Louis, MO. USA). Sodium metasilicate pentahydrate was obtained from BDH Chemicals Ltd (Poole, England). Zirconyl chloride (99%), urea and hexamethylenetetramine were supplied by the Aldrich Chemical Company Inc (Milwaukee Wis. USA). Polystyrene standards with molecular weights $1.8x10^6$, $8.5x10^5$, $4.5x10^5$, $1.85x10^5$, $8.7x10^4$, $4..4x10^4$, $28x10^4$, $1.02x10^4$, $3.355x10^3$,and $1.35x10^3$ were obtained from Shodex. HPLC grade methanol was obtained from BDH Chemicals (Poole, England) and AR grade dichloromethane was supplied by Ajax Chemicals (N.S.W., Australia). All chromatographic solvents were filtered through a 0.45 μm Millipore filter prior to use.

The preparation of zirconia was described in a previous publication.[20] The particle size of the amorphous zirconia prior to calcination measured using a Jeol 35JSM electron microscope was approximately 2 - 3 μm.

Sodium chloride impregnation of the zirconia microspheres was achieved by stirring a slurry of zirconia with the desired quantity of sodium chloride in water (4% w/v with respect to the zirconia). This slurry was stirred with heating (50°C-60°C) until all water evaporated (usually 36 hours). The resulting paste was dried overnight at 110°C and then mixed thoroughly using a mortar and pestle. The zirconia-sodium chloride mixture was then calcined in air using the appropriate calcination conditions. In all cases, the calcination temperatures involved a heating rate of 350°C h^{-1} to the temperature X-30°C, afterwhich, the heating rate was 60°C h^{-1} to the final temperature X°C. All zirconias were removed from the furnace immediately at the end of the calcination program and allowed to cool rapidly to room temperature. The sodium chloride was washed from the zirconia using copious quantities of water followed by washings in methanol and drying at 110°C.

Chromatographic columns were prepared in 5 cm x 0.46 cm stainless steel column blanks fitted with 0.5 μm stainless steel end frits. A Haskel air driven fluid pump (Haskel Engineering and Supply Co. Burbank, CA.USA.) was used as a packing pump and columns were packed in a downward slurry using a methanol packing solvent, a methanol slurry solvent, and a dichloromethane displacement solvent. Columns were packed until the flowrate became constant.

Surface areas, pore volumes and pore size distributions were measured using size exclusion chromatography according to the method of Halász and Martin.[23] Chromatographic analysis was achieved using a Varian 5000 chromatographic system fitted with a 10 μL Rheodyne injection port and a variable wavelength UV detector set at 254 nm. Size exclusion experiments were performed by injecting polystyrene standards of various molecular weights (0.5 mg/mL) into a dichloromethane mobile phase. For accuracy, flowrates were approximately 0.2 mL min^{-1}. The exact flowrate during the elution of each polystyrene standard was recorded during elution and elution volumes were corrected for actual flowrates. Column efficiencies were measured using benzene in 100% dichloromethane. All chromatographic experiments were carried out at 20°C ± 1°C and repeated in duplicate.

For ease of discussion, the stationary phases will be referred to using abbreviations such as Zr810NaCl(1:2), where Zr refers to a zirconia stationary phase, 810 refers to the temperature of calcination, and NaCl indicates that calcination was carried out in the presence of sodium chloride with a ratio of 1:2 zirconia:sodium chloride. Hence, Zr700, refers to a stationary phase of zirconia calcined at 700°C without salt, and Zr600NaCl(1:1) refers to zirconia calcined at 600°C in a 1:1 mixture of zirconia:sodium chloride.

RESULTS

The pore dimensions, determined in the present study, may be evaluated by comparing the results of two previous studies in which zirconias were extensively studied using both nitrogen-sorption experiments and size exclusion chromatograph.[20,24] The zirconia analyzed in previous studies will be referred to throughout this study. The largest difference in surface area measurements for four zirconias using the two techniques was 14% and the greatest difference in pore diameter was 30%, which was for a zirconia containing a high degree of micropores where the average pore size using nitrogen sorption BET measurements was 5.7 nm compared to 7.9 nm using the size exclusion method.[20,24]

Nitrogen adsorption/desorption isotherms for the reference zirconias may be obtained from reference[20] and size exclusion curves for each of these reference zirconias are presented in reference.[24]

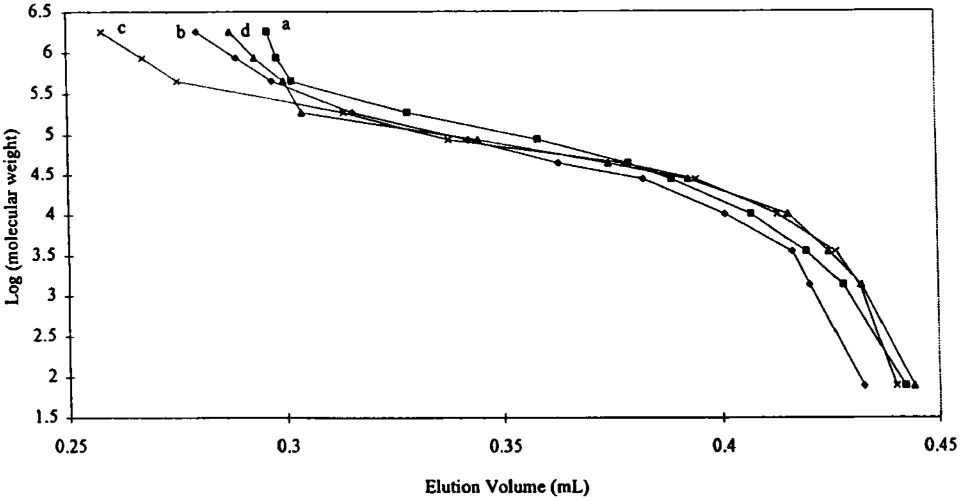

Figure 1. Size exclusion curves of polystyrene standards on the zirconias calcined with various concentrations of sodium chloride. (a) Zr810NaCl(4:1), (b) Zr810NaCl(2:1), (c) Zr810NaCl(1:1), (d) Zr810NaCl(1:2). Conditions, mobile phase was 100% dichloromethane at a flowrate of 0.2 mLmin^{-1}. Detection at 254 nm.

The Effect of Salt Concentration

The size exclusion elution behaviour of polystyrene standards with narrow molecular weight distributions was examined in a dichloromethane mobile phase on each of the zirconia stationary phases. The size exclusion curves for the zirconias calcined at 810°C with various salt concentrations are given in Figure 1. Pore size distributions were calculated from the size exclusion data for each of the stationary phases. The mean pore diameter (P_d) and the standard deviation (log σ) for each of the stationary phases was calculated by plotting the sum of residues versus the log of the pore diameter on probability paper.[23] The probability plots (not shown) for each of the zirconia samples resulted in a scatter of points along a straight line with some variation at the extremes, indicating the pore size distribution was approximately normal. The mean pore diameter determined from the probability plots are presented in Table 1, together with the standard deviation. Specific surface areas (S_a) were determined using the Guassian mean pore diameter according to the method of Halász and Martin[23] and these results are given in Table 1. The specific pore volumes (V_p) and column efficiencies are also included in Table 1.

Table 1

The Pore Dimensions of Zirconias Calcined with Various Concentrations of Sodium Chloride

Zirconia	P_d (nm)	Logσ	V_p (mL)	S_a (m^2g^{-1})	H(m)
Zr810NaCl (4:1)	34.0	0.423	0.1004	12.2	8.1×10^{-5}
Zr810NaCl (2:1)	42.0	0.396	0.310	12.4	8.1×10^{-5}
Zr810NaCl (1:1)	45.0	0.400	0.1324	11.8	7.5×10^{-5}
Zr810NaCl (1:2)	35.5	0.381	0.1136	12.8	8.5×10^{-5}

The size exclusion curves illustrated in Figure 1 indicate that all stationary phases produced classical size exclusion curves, as opposed to the exclusion curves previously observed for zirconia reference standards calcined without sodium chloride.[24] Each of the exclusion limits and inclusion limits of the zirconias in Figure 1 were similar, although slight differences were apparent as illustrated by the pore diameters in Table 1. Despite the constant calcination temperature, as the quantity of sodium chloride increased the mean pore diameter increased, except for the sample that had the highest quantity of sodium chloride (Zr810NaCl(1:2)), which showed a pore diameter similar to the zirconia prepared using the lowest concentration of sodium chloride (Zr810NaCl(4:1)). At this point, we cannot offer an explanation for the inconsistency, except to say that possibly, the high quantity of salt inhibited the salt diffusion into the pores. The surface areas of each sample remained approximately constant despite the differences in the pore diameters. However, a significant difference between each sample was the increase in pore volume as the concentration of sodium chloride increased up to a ratio of 1:1 zirconia:sodium chloride. The pore volume decreased for the highest salt concentration (1:2 zirconia:sodium chloride), which would be expected because of the smaller pore diameter. The most efficient stationary phase was the Zr810NaCl(1:1), which was consistent with the highest pore volume, indicating that mass transfer was less restricted by narrow necked pores.

The Effect of Calcination Temperature

A range of zirconia stationary phases, that each contained a 1:1 zirconia:sodium chloride mixture at calcination, were tested using size exclusion chromatography. Each zirconia was calcined at either 600°C, 700°C or 810°C. Size exclusion curves for each of these supports are illustrated in

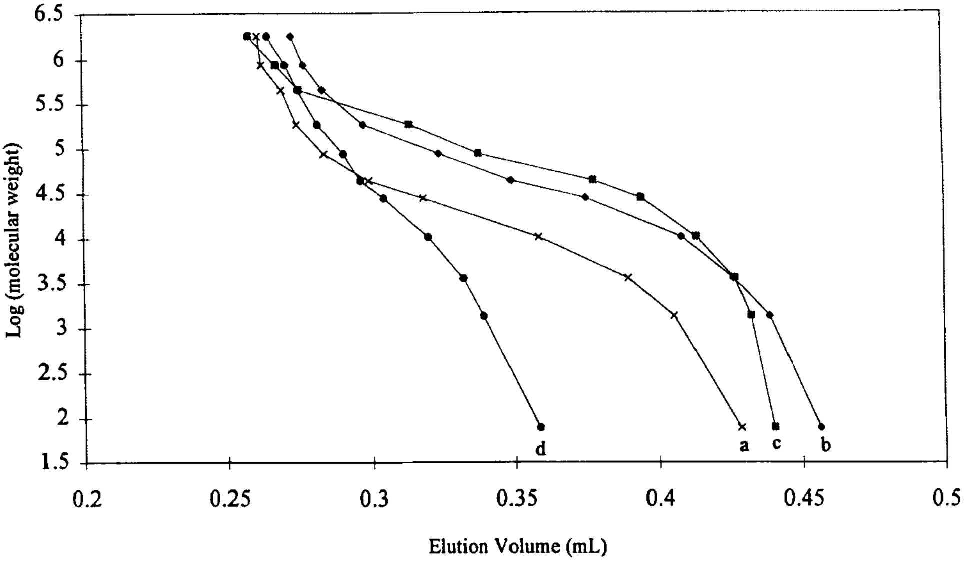

Figure 2. Size exclusion curves of polystyrene standards on the zirconias calcined at various temperatures with a 1:1 ratio of zirconia:sodium chloride. (a) Zr600NaCl(1:1), (b) Zr700NaCl(1:1), (c) Zr810NaCl(1:1), (d) Zr700. Conditions as in Figure 1.

Table 2

TheEffect of Calcination Temperature on the Pore Dimensions of Zirconia

Zirconia	P_d (nm)	Logσ	V_p (mL)	S_a (m^2g^{-1})	H(m)
Zr600NaCl (1:1)	19.0	0.387	0.1159	24.4	6.8×10^{-5}
Zr700NaCl (1:1)	28.1	0.378	0.1343	19.2	6.4×10^{-5}
Zr810NaCl (1:1)	45.0	0.400	0.1324	11.8	7.5×10^{-5}
Zr700	20.0	0.567	0.0511	10.2	1.0×10^{-4}

Figure 2. Pore size distributions were measured using the procedure outlined above. Pore diameters were calculated from the probability plots described above and are presented in Table 2. Table 2 also includes surface areas, pore volumes and column efficiencies calculated for each of the stationary phases. Cumulative pore size frequency plots are shown in Figure 3.

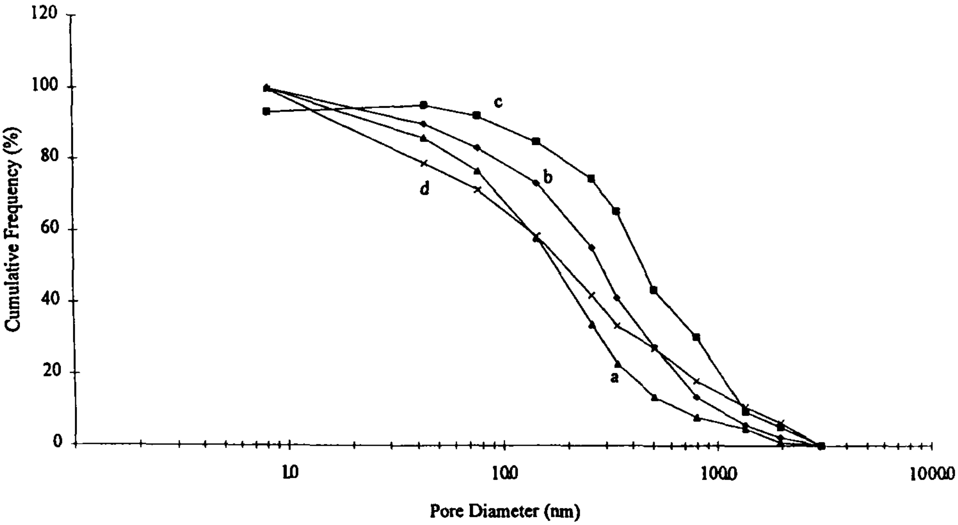

Figure 3. Cumulative frequency plots of zirconias calcined at various temperatures with a 1:1 ratio of zirconia:sodium chloride. (a) Zr600NaCl(1:1), (b) Zr700NaCl(1:1), (c) Zr810NaCl(1:1), (d) Zr700. Conditions as in Figure 1.

The size exclusion curves in Figure 2 show that the exclusion limit of each stationary phase increased as the temperature of calcination increased. Hence, the mean pore diameter increased as the calcination temperature increased and this can be observed by inspection of the cumulative frequency plots in Figure 3 and the results presented in Table 2. Such a result is not unexpected as the pore diameter has previously been shown to increase as calcination temperature increases.[19,20] The cumulative frequency plots in Figure 3 best illustrates the decrease in the percentage of smaller pores as the temperature of calcination increases.

Pore volume has been shown to decrease with increasing calcination temperature.[19,25] The pore volumes of our zirconia reference standards[20,24] calcined without the sodium chloride were consistent with these results. However, in the current study where sodium chloride was included during the calcination process, the pore volume increased between 600°C and 700°C, and decreased slightly at 810°C. However, the pore volume of the zirconia calcined at 810°C (0.1324 mL) was still much greater than the pore volume of the zirconia calcined at 600°C (0.1159 mL).

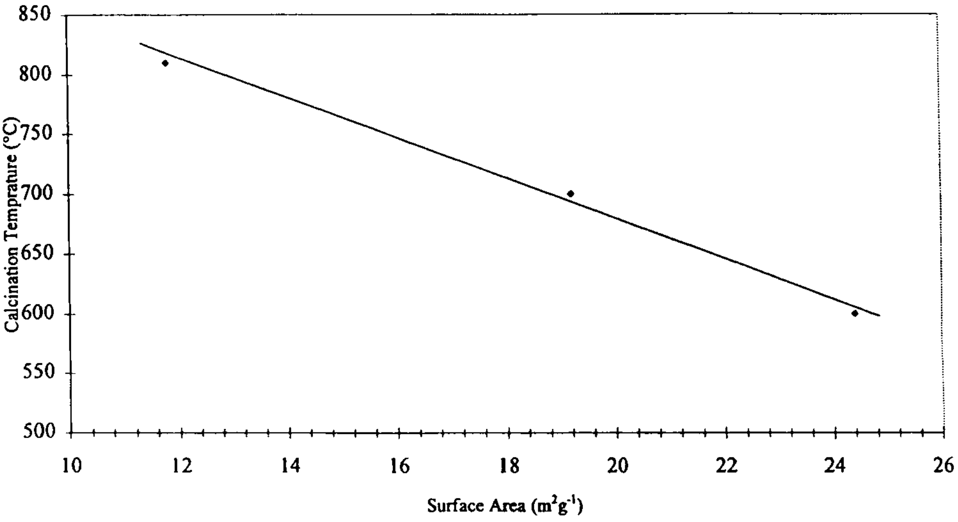

Figure 4. Plot of surface area versus calcination temperature for zirconias calcined in a 1:1 mixture of zirconia and sodium chloride.

The surface area of the zirconias decreased as the temperature of calcination increased, as illustrated in Table 2 and Figure 4. The linear relationship between surface area and temperature of calcination is somewhat fortuitous.

For comparison, a sample of zirconia was calcined at 700°C in the absence of sodium chloride. The size exclusion curve is illustrated in Figure 2 alongside the size exclusion curves of the salt impregnated zirconias. The pore dimensions of this zirconia are given in Table 2 and Figure 3 displays the cumulative frequency plot. These results clearly illustrate the significant part the sodium chloride plays during the calcination. Firstly, the salt-free zirconia yielded a size exclusion curve that had indistinct exclusion and inclusion limits with a very low pore volume [see Table 2 - less than half of that of the zirconia calcined with sodium chloride at the same temperature]. The mean pore diameter of the Zr700 was also smaller than the mean pore diameter of Zr700NaCl(1:1) and similar to the mean pore diameter of the Zr600NaCl(1:1). Significantly, the standard deviation of the mean pore diameter was higher than the standard deviations of the salt impregnated zirconias, indicating a greater distribution.

Table 3

The Effect of the Calcination Time of the Pore Dimensions of Zirconia

Zirconia	P_d (nm)	Logσ	V_p (mL)	S_a (m^2g^{-1})	H(m)
Zr700NaCl (1h)	28.1	0.378	0.1343	19.2	6.4×10^{-5}
Zr700NaCl (5 h)	31.6	0.468	0.1178	14.9	5.1×10^{-5}

The cumulative frequency plots in Figure 3 illustrate that the percentage of small pores is much greater when sodium chloride is not present during calcination for a given calcination temperature. Additionally the surface area of the Zr700 stationary phase was almost half that of the Zr700NaCl (1:1) stationary phase (Table 2).

Examination of the column efficiencies of each stationary phase provides some valuable information. The most efficient material was the Zr700NaCl(1:1) stationary phase, despite the higher surface area and smaller mean pore diameter of the Zr600NaCl(1:1) stationary phase. This is most likely due to a small yet discernible contribution from pores that may have partially closed necks not yet eliminated from the Zr600NaCl(1:1) stationary phase. The lower efficiency of the Zr810NaCl(1:1) stationary phase would be expected due to a much larger pore size and lower surface area. Clearly, calcination in the presence of sodium chloride greatly improved stationary phase mass transfer, as the least efficient column was the Zr700 stationary phase as shown in Table 2.

The Effect of Calcination Time

Two zirconia samples, each containing a 1:1 mixture of zirconia:sodium chloride were calcined at 700°C for a period of 1 hour and 5 hours respectively. The resulting size exclusion curves of these materials are illustrated in Figure 5. Pore size distribution plots for both materials are given in Figure 6. Pore volumes, surface areas, mean pore diameters and column efficiencies are given in Table 3.

Both materials produced almost identical size exclusion behaviour, with only a slight increase in pore diameter being observed with the increased calcination time. However, the pore volume and surface area decreased as the calcination duration increased.

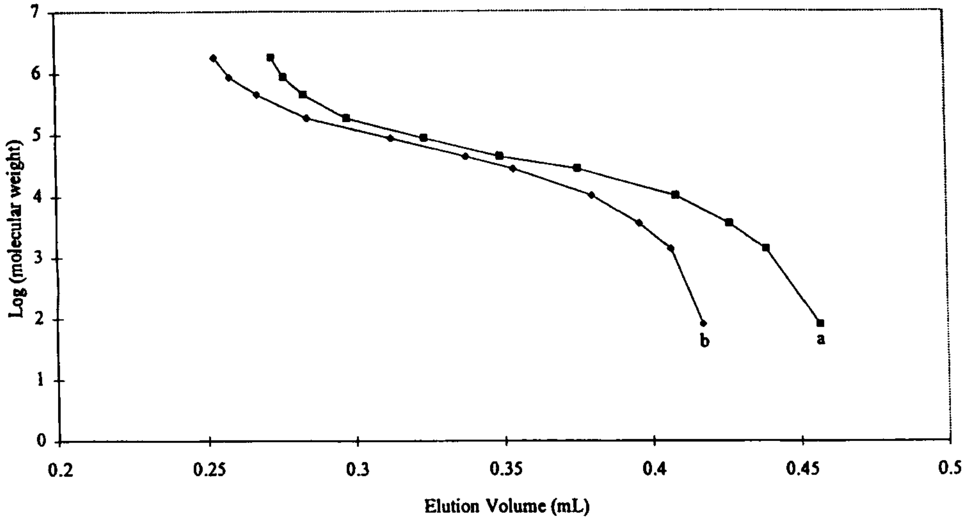

Figure 5. Size exclusion curves of polystyrene standards on the zirconias calcined for (a) 1 hour and (b) 5 hours at 700°C with a 1:1 ratio of zirconia:sodium chloride. Conditions as in Figure 1.

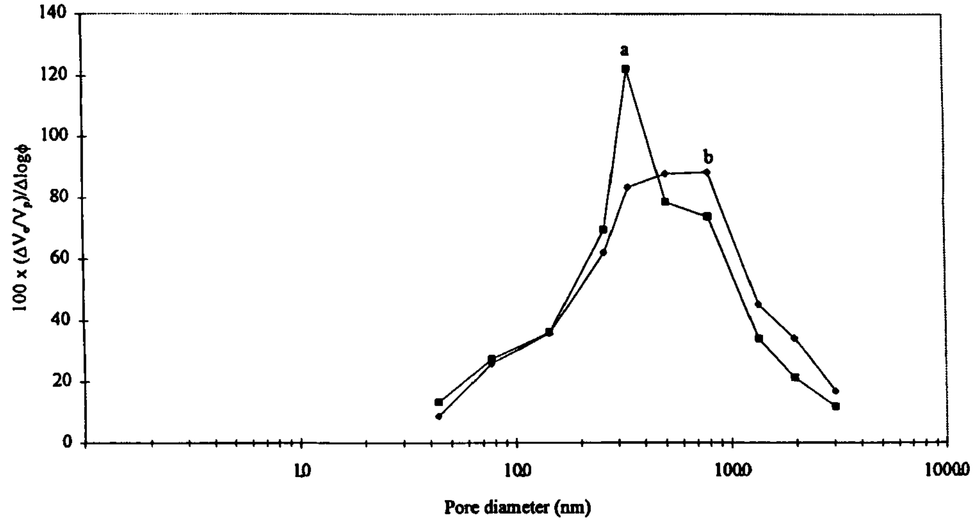

Figure 6. Pore size distribution plots of (a) Zr700NaCl(1h) and (b) Zr700NaCl(5h).

Comparison between plate heights on stationary phases with different calcination times, show that increasing the duration of the thermal treatment improves mass transfer, despite a reduction in the surface area and pore volume. This fact, together with the increase in pore diameter, would suggest that narrow pore openings are still being broken even after one hour of calcination.

Further studies would be required to optimise the duration of thermal treatment.

DISCUSSION

Zirconia chromatographic supports will become more widespread if the pore structure can be optimized to produce ideal chromatographic behaviour for a given separation problem. This means that the porous structure should be designed to maximize the surface area, pore volume and allow precise control over desired pore diameters.

In a previous publication,[20] we showed that the reference sol-gel zirconia, calcined without the sodium chloride, produced nitrogen sorption isotherms indicative of 'ink bottle' shaped pores (type H2 isotherms). Such surfaces offer inefficient chromatography due to the slow diffusion of solute and solvent molecules into and out from the pores.

Calcination of the same zirconia in the presence of sodium chloride produced type H1 isotherms indicating that the necks of the pores were broken leaving cylindrical pores. Such pores are more favorable chromatographic surfaces as diffusion becomes a more efficient process. In the present study, we have illustrated how complete control over the porous structure of the zirconia may be obtained by consideration of the factors outlined.

Column efficiency measurements support our data, which suggest that the inclusion of sodium chloride in various quantities and judicious selection of calcination conditions allows the pore structure of the zirconia to be controlled. Although nitrogen sorption experiments have not been undertaken on the current materials, when compared to our reference zirconias,[20,24] the results indicate that these materials would probably contain pores with type H1 hysteresis loops.

Certainly, the size exclusion curves have been significantly improved by the inclusion of the salt during calcination. The pore diameters, surface areas and pore volumes can be optimized in such a manner that zirconias could be prepared for a given separation problem and this could be particularly useful in the analysis of proteins and macromolecules where larger pore sizes are desirable.

CONCLUSION

Increasing the salt concentration increases the pore diameter and specific pore volume, to a limiting degree, while surfaces areas remain constant.

For a constant concentration of salt, increasing the calcination temperature increases the pore diameter, and decreases the surface area in a linear relationship.

Specific pore volumes of salt impregnated zirconias do not decrease rapidly in the same manner as for zirconias treated without sodium chloride.

Increasing the duration of the heat treatment, marginally increases the mean pore diameter and decreases the specific pore volume and surface areas, but increases the column efficiency.

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