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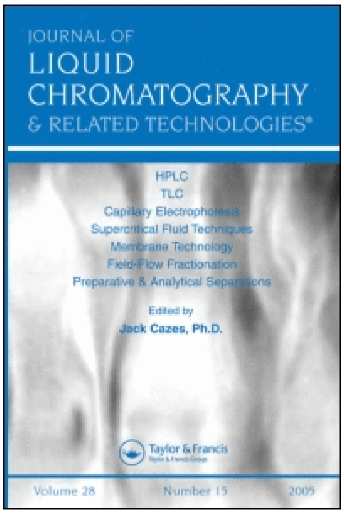

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
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The Measurement of Pore Size Distributions, Surface Areas, and Pore Volumes of Zirconia and Zirconiasilica Mixed Oxide Stationary Phases Using Size Exclusion Chromatography

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To cite this Article Shalliker, R. A. , Douglas, G. K. , Rintoul, L. , Comino, P. R. and Kavanagh, P. E.(1997) 'The Measurement of Pore Size Distributions, Surface Areas, and Pore Volumes of Zirconia and Zirconiasilica Mixed Oxide Stationary Phases Using Size Exclusion Chromatography', Journal of Liquid Chromatography & Related Technologies, 20: 10, 1471 — 1488

To link to this Article: DOI: 10.1080/10826079708010988

URL: http://dx.doi.org/10.1080/10826079708010988

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J. LIQ. CHROM. & REL. TECHNOL., 20(10), 1471–1488 (1997)

THE MEASUREMENT OF PORE SIZE DISTRIBUTIONS, SURFACE AREAS, AND PORE VOLUMES OF ZIRCONIA AND ZIRCONIA-SILICA MIXED OXIDE STATIONARY PHASES USING SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

Size exclusion chromatography was used to evaluate the surface areas, pore volumes, and pore size distributions of a variety of zirconias and silica-zirconia composites. In addition to the size exclusion results presented, the zirconias had been previously analysed using nitrogen sorption experiments making comparisons to established methods feasible. Agreement between the nitrogen sorption and size exclusion techniques was reasonably good with the size exclusion method serving to illustrate the chromatographic significance of the pore structure.

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Due to the stabilisation of the amorphous silica-zirconia composites the surface areas were shown to be much higher than the surface areas of the zirconias. However, after crystallisation the surface area decreased very rapidly. The results also illustrate that the inclusion of salts during calcination allows the widening of the pores for amorphous materials and increases the pore volume of both amorphous and crystalline materials.

INTRODUCTION

Recent studies on the development of zirconia as a new stationary phase support for liquid chromatography have yielded interesting results.[1-6] Zirconia has been shown to be a highly chemical resistant support that often exhibits, often complex, elution mechanisms due to the heterogeneous nature of the surface. However, because of the chemical stability of zirconia, a wide choice of eluent modifiers may be employed and this allows control of elution mechanisms and some excellent separations have been obtained. Nawrocki and coworkers[6] have recently reviewed the use of zirconia in chromatographic systems and described the changes in surface area, pore size, and pore volume obtained as a result of thermal treatment. Because of microcrystallite growth and intercrystallite sintering during thermal treatment, samples treated above 500°C generally have specific surface areas less than 100 m^2/g and the surface area further decreases as the calcination temperature increases. If the thermal treatment is less than 400°C the resulting zirconia is usually microporous. The crystalline phase of zirconia has also been shown to influence the surface area. Mercera and coworkers[7] for instance, have shown that the monoclinic phase has a higher thermal stability than the tetragonal phase and shows a slower decrease in surface area as the calcination temperature increases. Even so, because microporosity dominates, surface areas of tetragonal zirconia may remain as high as 90 m^2/g even after heat treatment at 800°C. The same authors showed that the doping of zirconia with either yttrium or lanthanum stabilises the tetragonal zirconia, and in particular, lanthanum-stabilised tetragonal zirconia was found to be more thermally stable than the corresponding monoclinic zirconia due to the inhibition of the processes of crystallite growth.

Recently Kaneko and coworkers[8] combined silica with each of zirconia, alumina, magnesia, and titania as stationary phase materials. The preparation of their composite supports involved the coprecipitation of silica with each of the corresponding oxides. The resulting particles were irregular and had broad size distributions that required milling followed by size separation to obtain a suitable particle size and distribution for chromatographic applications. The

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composite stationary phase materials were dried at 110°C and the zirconia-silica stationary phase was predominately microporous with an average pore size of 2.1 nm.

In a previous communication we described[9] the preparation of spherical zirconia-silica composites for chromatography. These composites crystallised into a tetragonal crystal structure after calcination at a temperature dependent on the concentration of silica. Thermal treatment of the composites at temperatures as high as 1300°C produced zircon ($ZrSiO_4$) when the atomic ratio of silicon to zirconium approached unity. The tetragonal phase was less stable when low concentrations of silica were present and this allowed the formation of a monoclinic phase at high temperatures. Such transitions in crystalline state with varying degrees of silica content may produce a stationary phase that has a variety of porous states, offering varying and possibly novel selectivities. However, to date, very little chromatographic behaviour has been studied on these supports.

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Studies on the porous structure of zirconia[10] have shown that the inclusion of sodium chloride during the calcination process changes the pore shapes from restricted 'ink bottle' shapes to more open cylindrical pores. Inclusion of sodium chloride during the calcination process was shown to increase the pore volume, surface area and pore diameter when compared to a zirconia calcined under the exact same conditions but without the sodium chloride. The method of salt inclusion for increasing pore sizes of narrow pore size silica gel was first introduced by Krebs *et al.*[11] Novák and Belek[12] showed that the inclusion of sodium chloride during calcination often caused bimodal pore size distributions or cracks to develop in the particles and suggested that improvements in the mixing of the salt and silica may improve the pore size homogeneity. Very little information regarding the nature of the effects of salt inclusion during calcination has been published since and no publications have been reported for zirconia or silica-doped zirconia composites.

The usual method of pore size determinations typically involves nitrogen sorption experiments, according to the theory of Brunauer, Emmet and Teller, or mercury porosimetry. However, Halász and Martin[13] described a method for determining pore size distributions of porous materials using size exclusion chromatography. The method relies solely on the elution of polystyrene standards when the chromatographic column is used in a size exclusion mode. Mobile phases must have a high solvent strength in order to avoid any adsorption of the polymer onto the stationary phase. The method assumes that, for a given column geometry, elution of the polystyrene is a function of the molecular size of the polymer. Hence, the stationary phase must be rigid so that the pore geometry does not undergo variations in size during elution.

Simply, the method is the reverse of classical size exclusion chromatography, where the porous structure of the chromatography column is known and the molecular weight of the polymer is unknown. Calibration of the molecular size of polystyrene standards was achieved by analysing the polystyrene standards on silica gel that had a narrow pore size distribution, which had been previously evaluated by classical methods.

The current work utilises size exclusion chromatography to study the changes in pore structure that occur for zirconia and a zirconia-silica composite, as the thermal treatment of the material is varied. In our laboratory, a large number of stationary phase supports are routinely prepared and size exclusion chromatography is an excellent method that allows a rapid identification of stationary phases suitable for more detailed investigations. An important advantage of the size exclusion method of pore analysis is that it allows the evaluation of the chromatographically available pore structure, hence, the results are directly applicable to chromatographic systems.

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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 8.50×10^5, 4.50×10^5, 1.85×10^5, 8.7×10^4, 2.8×10^4, 1.02×10^4, 3.55×10^3, and 1.35×10^3 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 Millipore 0.45 μm filter prior to use.

The preparation of zirconia and the zirconia-silica composites was described in previous publications.[9,10] In the present work a composite material was prepared containing a silica concentration that would allow a change in the crystal structure from the amorphous state to the tetragonal phase at a temperature corresponding approximately to the melting point of sodium chloride, namely 804°C. This specifically involved the hydrolysis of zirconyl chloride octahydrate (80 g) in water (60 mL) and the formation of zirconia microspheres with particle sizes of approximately 2 μm. Sodium metasilicate pentahydrate (52.7 g) was hydrolysed in water (80 mL), which was then added to the zirconia microspheres in a total volume of 500 mL. The reaction was allowed to proceed for 48 hours allowing the water to evaporate until a thick paste was obtained. The resulting composite was washed and calcined at either 500°C, 655°C or 810°C for two hours. Two samples of the zirconia-silica composite were calcined in the presence of either sodium iodide or sodium chloride. In both instances the amorphous zirconia-silica composite was stirred overnight in water containing one part composite to one part salt (%w/w). The total volume of water was such that the concentration was approximately 5% w/v with respect to the composite. The water was allowed to evaporate and the composite/salt mixture dried overnight at 110°C. The composite/salt mixture was then calcined for two hours at either 655°C (in the case of sodium iodide impregnation) or 810°C (for sodium chloride impregnation). The calcined composite materials were then washed in copious quantities of water to remove the salts. Previous studies have shown that the resulting zirconia-silica materials are in fact composites after calcination and not a mixture of silica and zirconia particles.[9]

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The zirconia stationary phases were calcined at 450°C, 600°C and 810°C as described previously.[10] Additionally, the zirconia was calcined in the presence of sodium chloride at 810°C. This involved stirring one part amorphous zirconia with one part sodium chloride in water (% w/w), the initial concentration of zirconia being 5% w/v. The mixture was stirred overnight, after which the water was slowly evaporated with heat and the solid dried overnight at 110°C. The zirconia was then calcined at 810°C for one hour. The remaining sodium chloride was removed by washing with copious quantities of water.

Particle sizes and particle size distributions were determined using a Jeol 35CF JSM scanning electron microscope (SEM)(Jeol Ltd., Tokyo, Japan). Particle size distributions were determined by measuring the diameters of at least 300 spheres. Xray elemental analysis was performed by firstly mounting the samples in resin and grinding the surface to a highly polished, flat finish. The sample plug was then coated lightly with carbon and analysed using the Tracor Xray facilities on the SEM at 25 KeV.

Differential thermal analysis (DTA) was used to determine the temperature of transformation from the amorphous state to a crystalline phase.[14] The zirconia and zirconia-silica composites were subjected to thermogravimetric analysis (TGA) and DTA using a Setaram TGA 92 at heating rates of 5°C/min (Setaram, Saint-Cloud, France).

Raman spectra were obtained using a Perkin Elmer System 2000 FT-Raman spectrometer (Perkin Elmer, Cal., USA). The FT-Raman spectrometer was equipped with a quartz beamsplitter and a continuous-wave Spectron Laser Systems SL301 Nd:YAG laser emitting at 1064 nm and an InGaAs detector operated at ambient temperature. The mirror velocity was 0.2 cm s^{-1}, and strong Beer-Norton apodisation was used. A notch type Rayleigh filter was installed to provide an extended scan range from 3600 - 100 cm^{-1}. Typically, 200 scans were recorded at a resolution of 4 cm^{-1} and laser power of 400 mW. All FT-Raman spectra were corrected for instrumental effects.

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 flow rate became constant.

Chromatographic analysis was achieved using a Varian 5000 chromatographic system fitted with a 10 μL Valco 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^{-1}) into a dichloromethane mobile phase. Flowrates were approximately 0.3 mL min^{-1} as indicated in the text. The exact flowrate during the elution of each polystyrene standard was recorded during elution and elution volumes were corrected for actual flowrates. All chromatographic experiments were carried out at 23°C ± 1°C and were replicated.

For ease of discussion, the stationary phases will be referred to using abbreviations such as Zr810NaCl, 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. Hence, Zr-Si655, refers to a composite stationary phase of zirconia and silica calcined at 655°C without salt, and Zr-Si655NaI refers to the same material calcined in the presence of sodium iodide.

RESULTS AND DISCUSSION

Using electron microscopy, it was determined that the particle sizes of each of the zirconia-silica composite stationary phases were within the range 2.0 μm ± 0.6 μm. No significant difference in particle size was apparent between composites calcined in the presence of salts compared to those calcined without salts. The zirconias used for stationary phases in this work were identical to the zirconia used in a previous publication that described the particle size as 1.3 μm ± 0.5 μm.

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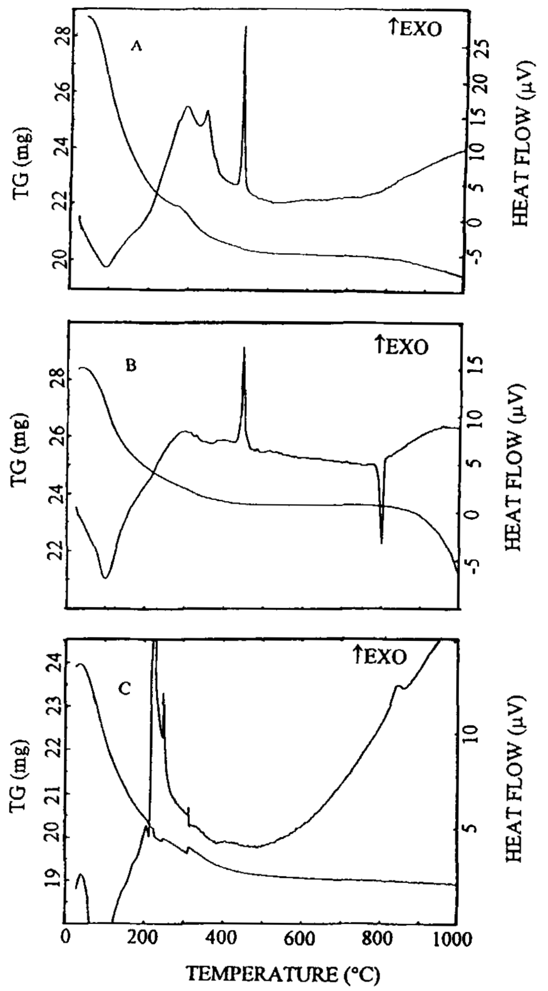

Figure 1. Differential thermal analysis and thermal gravimetric analysis of (A) zirconia and (B) sodium chloride impregnated zirconia at heating rates of 5°C min^{-1}, and (C) zirconia-silica composite at a heating rate of 2°C min^{-1}.

Differential thermal analysis (DTA) of the zirconia (Figure 1a) and the sodium chloride impregnated zirconia (Figure 1b) show the presence of a sharp exothermic 'glow' peak at 467°C and 450°C respectively. Previous workers have assigned this peak to a phase change from amorphous zirconia[14-18] to a metastable tetragonal phase, after which the zirconia undergoes a further phase change to a monoclinic form. Previously we reported Raman spectral results

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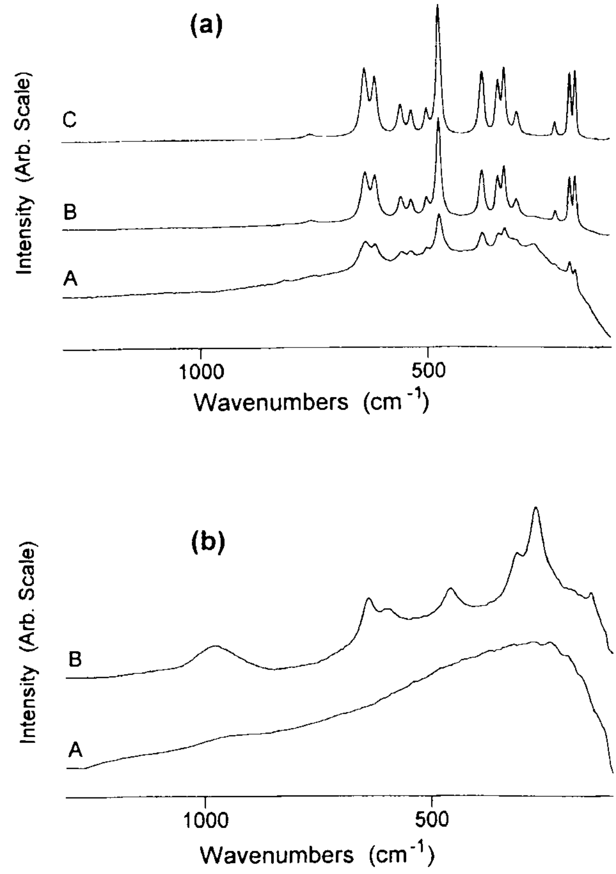

Figure 2. (a) Raman spectrum of the zirconia calcined at (A) 450°C, (B) 600°C, and (C) 810°C. (b) Raman spectrum of the zirconia-silica composites calcined at (A) 655°C and (B) 810°C.

that showed zirconia calcined at a temperature slightly above the crystallisation temperature according to DTA, transformed to a tetragonal phase, which when left at room temperature for two weeks further crystallised into the monoclinic phase[9]. Figure 1b also shows the presence of a large endothermic peak at 804°C corresponding to the melting of sodium chloride. Figure 1c illustrates the DTA and TGA of the zirconia-silica composite. A small exothermic 'glow' peak with a maximum at 844°C is apparent. This is associated with a phase change from the amorphous state to a tetragonal phase.[9] All DTA results showed a broad endothermic peak at around 100°C due to the loss of water, and

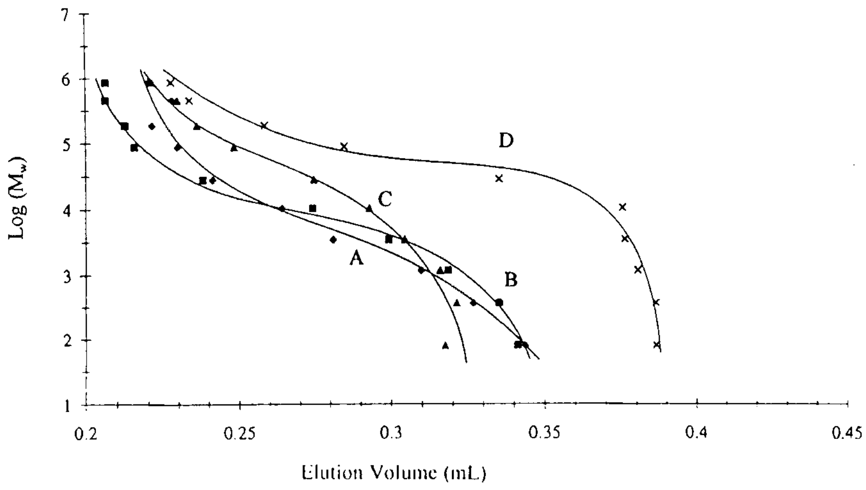

Figure 3. Size exclusion curves for the zirconia columns (A) Zr450, (B) Zr600, (C) Zr810 and (D) Zr810NaCl. Flow rate 0.4 mL min^{-1}, temperature 23°C ± 1°C.

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an exothermic region at approximately 300°C due to the combustion of residual organics. Previous workers[17] determined that no phase change occurred within this temperature range. TGA shows a large mass loss within this temperature range, supporting the loss of water and organics.

Raman spectroscopy has been shown to be a useful method for determining phase compositions of zirconia.[19] Raman spectral analysis of the zirconia stationary phases showed that each sample contained varying degrees of monoclinic zirconia. The sharpness and the peak intensity, indicative of the monoclinic crystalline phase, was much greater for the zirconias calcined at 810°C, and 600°C than that of the zirconia calcined at 450°C, which was mainly amorphous with slight monoclinic crystallinity (Figure 2a). The Raman spectrum of the zirconia-silica composite (Figure 2b) calcined at 810°C showed the sample contained some tetragonal zirconia, with much of the material remaining amorphous. All samples calcined below the crystallisation temperature according to the DTA remained amorphous (for example ZrSi655, Figure 2b).

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 each of the zirconia columns are illustrated in Figure 3. Pore size distributions

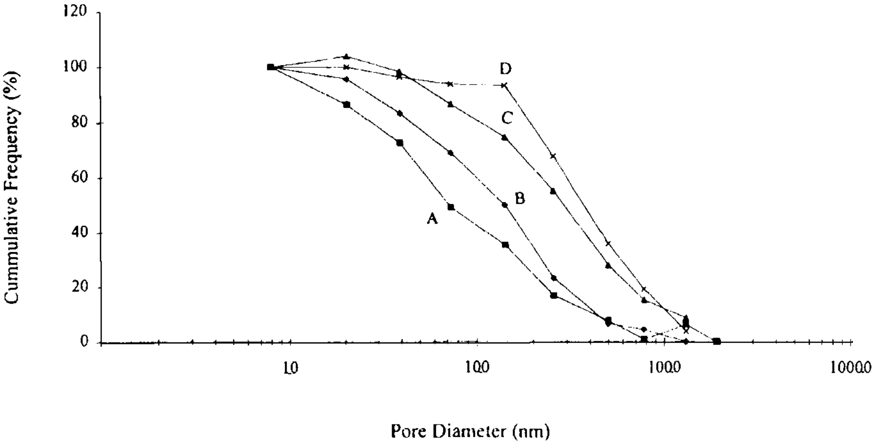

Figure 4. Cumulative pore size frequency distribution curves for the zirconia stationary phases (A) Zr450, (B) Zr600, (C) Zr810 and (D) Zr810NaCl columns.

were calculated from the size exclusion data for each of the stationary phases. Figure 4 illustrates the cumulative frequency of pores versus the pore size for each of the zirconia stationary phases and Figure 5 illustrates the pore size distribution curves for zirconia samples Zr 600 and Zr810NaCl as examples. The mean pore diameter and the standard deviation for each of the stationary phases were calculated by plotting the sum of residues versus the log of the pore diameter on probability paper.[13] 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 Gaussian. The mean pore diameter determined from these Gaussian curves are presented in Table 1, together with the standard deviation (log σ). Specific surface area estimates were determined using the Guassian mean pore diameter for each of the zirconia stationary phase supports and these results are given in Table 1. The specific pore volumes are also included in Table 1.

The size exclusion results illustrate that qualitatively two types of zirconia packing materials resulted after calcination. The first type is derived from the zirconia materials calcined at 450°C (curve A), 600°C (curve B) and 810°C (curve C). As the calcination temperature increased the exclusion limit and the inclusion limit of these stationary phases increased. Hence an increase in pore size occurred as illustrated by the pore size frequency distributions in Figure 4. This result is supported by nitrogen adsorption measurements previously

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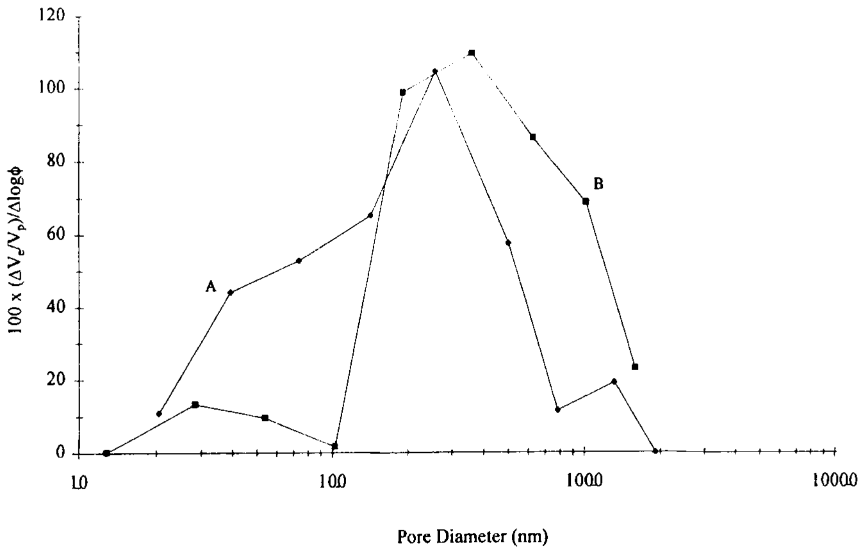

Figure 5. Pore size distribution curves for the zirconia stationary phases (A) Zr600, and (B) Zr810NaCl columns.

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Table 1

Pore Size, Surface Areas, and Pore Volumes of the Zirconia Stationary Phases Determined from Size Exclusion Chromatography

Stationary Phase	Pore Size [nm] (Gussian)	Pore Size Std. Dev. (logσ)	Specific Surface Area [m^2/g]	Specific Pore Volume [mL]
Zr450	7.9	0.54	46	0.0912
Zr600	13.5	0.51	27.5	0.0930
Zr810	28.2	0.50	8.5	0.0600
Zr810Na	35.5	0.49	14.9	0.1324

conducted[10] on these samples. The Zr450 sample produced a poor quality pore size distribution curve, which reflected the limit of the size exclusion method for determining pore sizes as the microporous region is approached, particularly if the size distribution is broad. Note that this sample had an average pore size of 7.9 nm determined by size exclusion and 5.7 nm

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determined by nitrogen adsorption measurements.[10] The size exclusion curve for Zr450 shows that the inclusion limit of the column was indistinct, illustrating the broad pore size distribution of smaller diameter pores. To a lesser extent, the size exclusion curve of the Zr600 stationary phase also showed that there was a broad size distribution of the smaller diameter pores as the inclusion region of the column was also not distinct. Less resolution is observed for the low molecular weights on the Zr810 stationary phase indicating fewer smaller mesopores and micropores. This is further illustrated by the pore size frequency plots in Figure 4 where the percentage of small pores decreased significantly as the temperature of calcination increased. For instance, examination of the Zr450 phase shows that 50% of the pores were less than 7.0 nm in diameter with approximately 14% of the pores being microporous. In comparison, for the Zr810 support, 50% of the pores were less than 30.0 nm and the microporosity was essentially zero percent.

The second type of zirconia packing material is illustrated by the size exclusion curve of the Zr810NaCl stationary phase (Figure 3, curve D), which was clearly different from the group of size exclusion curves obtained on the Zr450, Zr600, and Zr810 stationary phases. While the exclusion limit was similar to the exclusion limit of the Zr810 stationary phase, the inclusion region of the Zr810NaCl stationary phase was markedly different. Within the inclusion region, all polystyrenes with molecular weights up to 10 kdaltons co-eluted, and this indicated a significant change had occurred in the smaller mesoporous/microporous structure of the stationary phase compared to the zirconia calcined at the same temperature without the sodium chloride. The cumulative frequency plot for the sample Zr810NaCl in Figure 4 illustrates this effect, with only 7% of the pores being between 2.0 nm and 7.0 nm and 50% of the pores were greater than 40.0 nm and no microporosity was apparent. However, the most significant difference between the sodium chloride impregnated zirconia and the zirconias calcined without sodium chloride was the specific pore volumes. The Zr810NaCl material produced a specific pore volume that was slightly over twice the specific pore volume of the Zr810 stationary phase. This improved the linear region of the size exclusion curve (indicated by the slope of the linear portion of curve D). The specific pore volume of the Zr810NaCl stationary phase was a third greater than the specific pore volume of the Zr450 stationary phase, which contained a significant degree of microporosity. However, no microporosity was apparent on the Zr810NaCl stationary phase (see Figure 4).

Size exclusion curves for each of the zirconia-silica columns are illustrated in Figure 6. Pore size distributions were calculated from the size exclusion data for each of the stationary phases. Cumulative pore size frequencies are shown in Figure 7. Pore size distributions of the zirconia-silica

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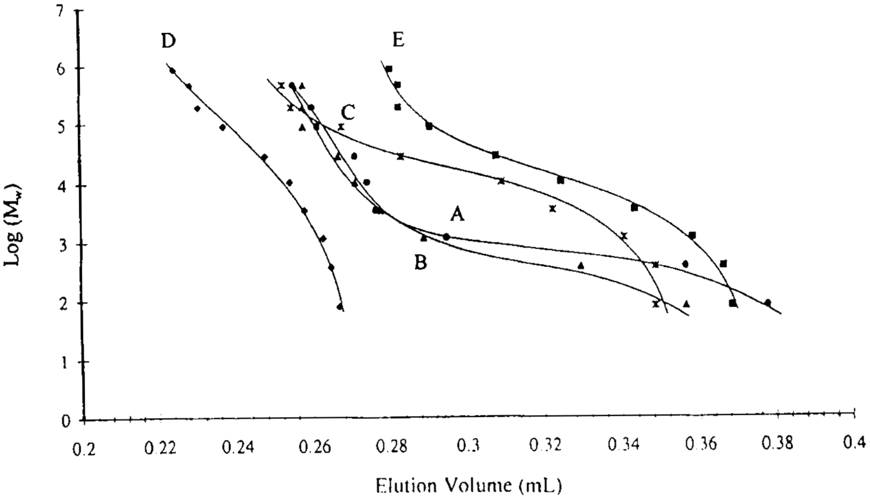

Figure 6. Size exclusion curves for the zirconia-silica columns (A) Zr-Si500, (B) Zr-Si655, (C) Zr-Si655NaI, (D) Zr-Si810 and (E) Zr-Si810NaCl. Flow rate 0.3 mL/min, temperature 23°C ± 1°C.

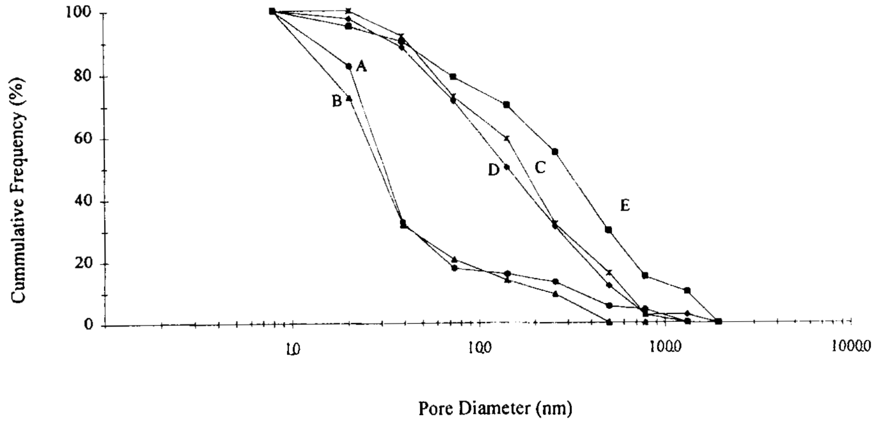

Figure 7. Cumulative pore size frequency distribution curves for the zirconia-silica stationary phases (A) Zr-Si500, (B) Zr-Si655, (C) Zr-Si655NaI, (D) Zr-Si810 and (E) Zr-Si810NaCl.

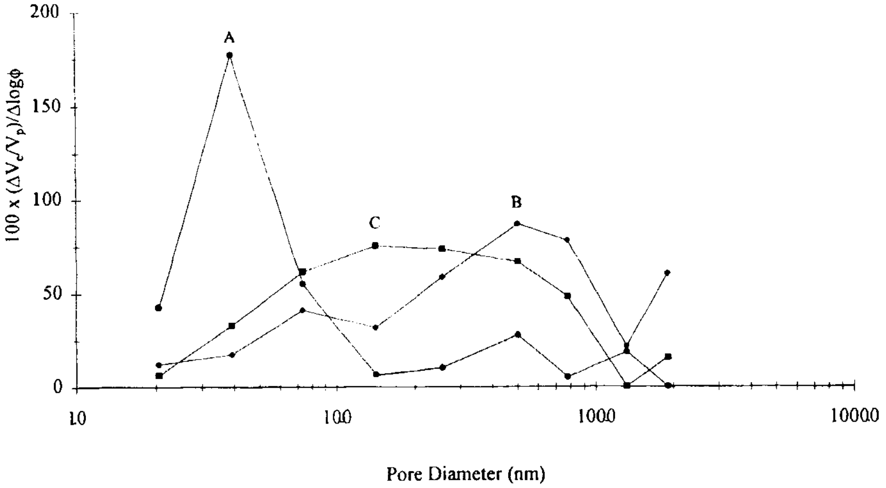

Figure 8. Pore size distribution curves for the zirconia-silica stationary phases (A) Zr-Si500, (B) Zr-Si810 and (C) Zr-Si810NaCl columns.

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composites Zr-Si500, Zr-Si810NaCl and Zr-Si810 are shown as examples in Figure 8. The mean pore diameter and the standard deviation for each of the zirconia-silica stationary phases were calculated by plotting the sum of residues versus the log of the pore diameter on probability paper.[3] These probability plots resulted in a scatter of points along a straight line for the Zr-Si810NaCl, Zr-Si810 and Zr-Si655NaI stationary phases indicating the pore size distribution was approximately Gaussian. The probability plots of the Zr-Si655 and the Zr-Si500 stationary phase indicated that the pore size distribution may be bimodal, but further experiments using nitrogen sorption will be required to confirm this. Nevertheless, because the support was dominated by micropores, an averaged unimodal pore size distribution was assumed. The mean pore diameter determined from the probability plots for each of the stationary phases are presented in Table 2, together with the standard deviation (log σ). Surface area estimates and specific pore volumes are also included in Table 2.

Increasing the calcination temperature of the composite materials in the absence of salt increased the exclusion molecular weight and increased the pore size, but only after the calcination temperature exceeded the crystallisation temperature of the support. Despite a difference in calcination temperature of 155°C, both the Zr-Si500 and Zr-Si655 stationary phases produced very similar size exclusion calibration curves that indicated a microporous support. Both of

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Table 2

Pore Size, Surface Areas, and Pore Volumes of the Zirconia-Silica Composites Determined from Size Exclusion Chromatography

Stationary Phase	Pore Size (Gussian) [nm]	Pore Size Std. Dev. [logσ]	Specific Surface Area [m^2/g]	Specific Pore Volume [mL]
Zr-Si500	2.0	0.80	368	0.1482
Zr-Si655	1.25	1.00	296	0.1198
Zr-Si655NaI	16.6	0.55	2.49	0.1035
Zr-Si810NaCl	15.8	0.50	2.27	0.0898

these phases remained amorphous at their respective calcination temperatures. A further increase in calcination temperature of 155°C to 810°C increased the exclusion limit of the stationary phase from 3.55×10^3 daltons (Zr-Si600 and Zr-Si500) to 1.85×10^5 daltons (Zr-Si810). The mean pore size of the Zr-Si810 stationary phase was 25.1 nm and the specific pore volume was less than 25% of the specific pore volume of the Zr-Si500 stationary phase. The Zr-Si810 stationary phase was essentially free of microporosity as shown by the pore size frequency plots in Figure 7.

Calcination of both the zirconia-silica composites and the zirconia in the presence of sodium salts significantly altered the pore structure of the support. The most significant effect was the increase in specific pore volume of the stationary phase as a result of the inclusion of the sodium salts. The specific pore volume of the Zr-Si810NaCl stationary phase was 2.8 times that of the Zr-Si810 stationary phase for which no salt was added and this resulted in an extension of the linear region of the size exclusion curve for the salt impregnated stationary phases as shown in Figure 6. Additionally the inclusion limit of the sodium chloride impregnated composite was more distinct and occurred at a slightly lower molecular weight. Previous studies on zirconia have shown that the inclusion of salt during calcination and the subsequent increase in specific pore volume leads to a more distinct pore structure where pores change from the 'ink bottle' shape to the more favourable cylindrical shape.[10]

The size exclusion curve of the zirconia-silica stationary phase calcined in the presence of sodium iodide at 655°C (curve C) is very different from the size exclusion curve of the same material without the salt. The exclusion region of the Zr-Si655NaI stationary phase was almost 1.85×10^5 daltons and the mean pore diameter was 16.6 nm compared to the microporous Zr-Si655 stationary phase that had an exclusion limit approximately 3.55×10^3 daltons. Both the Zr-Si655 and Zr-Si655NaI stationary phases had similar specific pore volumes, but this is clearly a result of microporosity in the Zr-Si655 material. The linear region of the size exclusion curve of the Zr-Si655NaI stationary phase is more defined. In fact, the size exclusion curve is almost the same as the size exclusion curve for Zr-Si810NaCl stationary phase, yet the Zr-Si655NaI stationary phase is totally amorphous and the Zr-Si810NaCl is at least partially tetragonal after calcination at a temperature 155°C higher. Hence, crystallisation of the composite inorganic oxide is not solely responsible for the increase in pore size. The pore size distribution curves and cumulative pore size frequency plots clearly indicate that the addition of the salt has almost eliminated the microporosity.

In the current study, the inclusion of salts has been shown to be beneficial in the preparation of materials that yield more uniform pore size distributions, having a narrow pore size range, larger pore volumes and higher surface areas than identical supports prepared without the salt. The increase in pore volume due to the inclusion of the salts during calcination is significant, as large pore volumes are particularly useful for size exclusion chromatography where separation is based on a molecular sieving mechanism carried out within the column pore volume. A large pore volume equates to better separations as illustrated by the improvement in the linear region of the size exclusion curves for material calcined in the presence of the salts. Additional benefits may also be sought in liquid-liquid partition chromatography and interactive liquid chromatography.[20]

These results show that significant differences in pore sizes exist between the zirconia and the zirconia-silica composites for similar temperatures of calcination. For instance, the zirconia-silica material remained microporous when calcined at 655°C compared to a zirconia stationary phase that had a mean pore size of 13.5 nm calcined at 600°C. Surface areas of the amorphous zirconia-silica composites were much higher than the monoclinic/amorphous zirconia. However, the rate of decrease in the surface area of the zirconia-silica composite as a result of thermal treatment was much more rapid than for the zirconia. For example, the specific surface area for the zirconia-silica composites decreased from approximately 300 m^2/g to 0.5 m^2/g with a change in calcination temperature from 500°C to 810°C. In comparison, the specific surface area of the zirconia decreased from approximately 40 m^2/g at 450°C to 8.5 m^2/g at 810°C. These results illustrate that the monoclinic zirconia is more thermally stable than the amorphous-tetragonal composites and this supports the study be Mercera *et. al.*[15] where they found the monoclinic zirconia to be more stable than the tetragonal form.

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The size exclusion method of analysis has proved a useful tool for a comparative study on pore structures of various supports. The results for the zirconia supports were very similar to those obtained by nitrogen adsorption measurements previously determined[10] and the method allows a large number of supports to be examined quickly to determine which stationary phases warrant further detailed examination. The largest difference in surface area was 14% and the greatest difference in pore size was 30%, which was for the Zr450 stationary phase where the average pore size using nitrogen adsorption BET measurements was 5.7 nm compared to 7.9 nm using the size exclusion method. Hence, a high degree of confidence may be placed in the size exclusion results, particularly when used as a comparative method to examine differences between mesoporous stationary phases.

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ACKNOWLEDGEMENTS

The authors express their gratitude for support from the Centre for Instrumental and Developmental Chemistry, Queensland University of Technology. One of the authors (RAS) would like to gratefully acknowledge the receipt of a Queensland University of Technology Postdoctoral Research Fellowship. We would like to thank Mr Shane Russell for his assistance in the thermal gravimetric analysis.

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Received August 15, 1996
Accepted September 30, 1996
Manuscript 4272

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