peaks observed matched favorably (Figures 6-8, Table III) to those in the corresponding synthetic mixtures in Figure 5. Note the similarity in the IMS spectra of Comtrex A-S and Sinutab II (Figure 6). Both preparations have virtually identical amounts (Table I) and hence the same ratio of the active acetaminophen and pseudoephedrine ingredients. A different ratio and lower amount of these two pharmaceuticals are found in Children's Cotylenol (Table I). This not only alters the intensity distribution of the 10.3- and 11.9-ms ion mobility peaks but also allows the 10.9-ms chlorpheniramine peak to be visible (Figure 7). Even though chlorpheniramine is present in the Comtrex A-S formulation, its ion mobility peak is essentially absent (Figure 6). This could be due to the different amounts and/or ratio of acetaminophen and pseudoephedrine as compared to the Cotylenol formulation (Table I and Figures 6 and 7). Thus, filler, binder, and coloring agents evidently had no significant debilitating effects on the presence of ion mobility peaks. However, significant differences in relative peak abundances between respective synthetic and commercial mixtures were apparent for the binary and ternary mixtures. This may have been caused by inhomogeneity in sampling the capsules or pills or by secondary ingredients that altered the ion-source chemistry without being ionized. Commercial formulations that were comprised of a single active ingredient exhibited mobility spectra with intense product ion peaks as expected and without serious interference from other components (compare Figures 1 and 2 and Table I with Figures 6-8). Note in particular the similarity of the IMS spectra of Tylenol and Regular Strength Anacin III (Figure 8) with that of acetaminophen (Figure 2). Certainly, issues of precision, quantitative predictability, sensitivity to variations in content, and mass-identified examination of ion-molecule chemistry for ternary mixtures must be thoroughly examined by IMS/MS if future applications of IMS in pharmaceutical facilities are considered. Mobility spectra would be simplified and memory effects would be improved if the IMS inlet and tube could be operated at temperatures from 80 to 125 °C.

**Registry No.** Acetaminophen, 103-90-2; chlorpheniramine maleate, 113-92-8; brompheninamine maleate, 980-71-2; acetylsalicyclic acid, 50-78-2; pseudoephedrine hydrochloride, 345-78-8; phenylpropanolamine hydrochloride, 4345-16-8; caffeine, 58-08-2.

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# Simultaneous Deactivation and Coating of Porous Silica Particles for Microcolumn Supercritical Fluid Chromatography

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**A new method for the simultaneous deactivation and coating of porous silica particles for supercritical fluid chromatography (SFC) has been developed. This method is based on a dehydrocondensation reaction between polymeric silicon hydride reagents and the silanol groups on the surface of the particles. The procedure produces a less active surface than conventional silica packings, which results in less adsorption and improved peak shapes for polar analytes. In SFC, more polar analytes can be chromatographed without the need for mobile phase modifiers. Furthermore, the sensitive and universal flame ionization detector (FID) can be used, since modifiers are not necessary. To avoid splitting of the column effluent before FID detection, packed capillary columns were utilized in this study. The ability to use packed capillary columns for the analysis of polar compounds, while at the same time allowing the use of a wide range of detection methods, serves to expand the number of useful applications for packed column SFC.**

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## INTRODUCTION

Packed columns typically exhibit higher than acceptable surface activity when mobile phases of low polarity are used in SFC. The high surface area silica-packing materials adsorb polar solutes, resulting in poor chromatographic peak shape and less sensitivity for trace analysis. Therefore, polar mobile-phase modifiers are frequently used to passively deactivate these active sites by competitive adsorption. Unfortunately, these modifier/stationary phase interactions can modify the retention mechanisms and can lead to irreproducible solute retention. Furthermore, modifiers often reduce overall detector sensitivity and limit the use of universal detection methods such as the flame ionization detector (FID). The use of modifiers also limits the effectiveness of mass spectrometric (MS) detection. UV absorption is often selected when organic modifiers are used; elimination of interferences from the modifier can often be done by careful selection of the wavelength monitored. However, a mobile phase with either no modifier or a low percentage of modifier may allow UV detection for a wider range of wavelengths, increasing the applicability of the detector.

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Various methods have been used for the deactivation of silica particles. According to a recent review of bonded phases for LC (*1*), most, if not all, commercial alkyl phases are monomeric in nature (i.e., a monolayer coverage of the solid support as a result of chemically bonded monomeric reagents). Monofunctional reagents, such as chloro- or alkoxysilanes, react with silanol groups on the silica material to produce monomeric stationary phases. This is usually accomplished by refluxing the reagent with the particles in an organic solvent, such as toluene. Di- and trichlorosilanes are more chemically reactive than their monofunctional counterparts. However, surface attachment occurs with only one or two siloxane bonds from the same reagent molecule, due to steric constraints. The unreacted functional groups can be hydrolyzed to silanols in the presence of trace amounts of water. Subsequently, polymerization of the polyfunctional reagent can be induced. To ensure monomeric coverage by the phase, care must be taken to exclude water from the reaction. Studies (*2*) have shown that residual silanol concentrations increase with the number of reactive functional groups on the reagent molecule. Therefore, even though the typical polyfunctional reagents may be more reactive and may modify a greater number of the active surface sites, they actually produce new silanol groups as a result of the hydrolysis of unreacted functionalities.

Due to differences in the reactivities of the individual silanol groups and the possible steric hindrances associated with the reagent molecules themselves, chemical modification of all of the silanol groups is unlikely. In an attempt to provide a more complete coverage, several research groups (*3–5*) have taken advantage of the ready polymerization of the chlorosilane reagents in the presence of water. By the introduction of controlled amounts of water, thicker polymeric phases result, possessing greater sample capacities and unique shape selectivities. However, because additional silanols are created during the polymerization, further endcapping is required to remove these equally reactive silanol sites.

Another approach to preparing polymeric phases in LC was introduced by Schomburg et al. (*6*) and was based on free-radical-initiated cross-linking procedures used to immobilize polymeric stationary phases in capillary GC. This type of polymeric phase is bonded to the surface only by cross-linking to the deactivation layer. Silanols can be end-capped prior to coating of the phase, which improves deactivation. This cross-linked phase only partially shields the residual surface silanols from interacting with polar solutes. These polymer coatings are claimed to be more uniformly distributed than conventional monomeric bonded phases.

In this study, silica particles were deactivated by dehydrocondensation of hydrosiloxane polymers with the silica surface, a reaction widely used for surface deactivation in open tubular (capillary) columns (*7, 8*). In packed columns, this reaction produces a thin stationary phase film as well as a deactivated surface. Experiments were conducted to optimize the reaction by studying the influence of preconditioning, reaction temperature, percent hydride content of the polymer, and variations in particles from different manufacturers.

## EXPERIMENTAL SECTION

**Materials.** Unreacted Nucleosil particles (300-Å pores, 5-μm diameter) were obtained from Machery-Nagel, Duren, West Germany. The same support material, modified with a bonded $C_8$ stationary phase, was also acquired as a reference. Unreacted Vydac silica particles (300-Å pores, 5-μm diameter, The Separations Group, Hesperia, CA) were also purchased and used to evaluate the applicability of this deactivation procedure to particles from different manufacturers. Fused silica tubing, used for columns and connections, was obtained from Polymicro Technologies, Phoenix, AZ. Column connections were made using Valco ZU1T zero dead volume unions (Valco Instruments Co., Houston, TX). Micro-frits ($^1/_{16}$-in. diameter × 0.2-μm mesh, Mectron Industries, City of Industry, CA) were used to support the packed bed. Capillaries were packed using a Varian 8500 syringe pump (Varian, Walnut Creek, CA). An acetone slurry was sonicated and then placed in the packing reservoir. The reservoir was sealed, and the line to the pump (already at pressure) was opened. The pump was stopped after 30 min, and the system was allowed to depressurize. Column testing was performed using a modified Isco Model 314 syringe pump (Isco, Lincoln, NE) controlled through a pressure feedback system and an Apple IIe microcomputer or through an Isco μLC-500 syringe pump. All chemicals were purchased from Aldrich Chemical Co. unless otherwise specified.

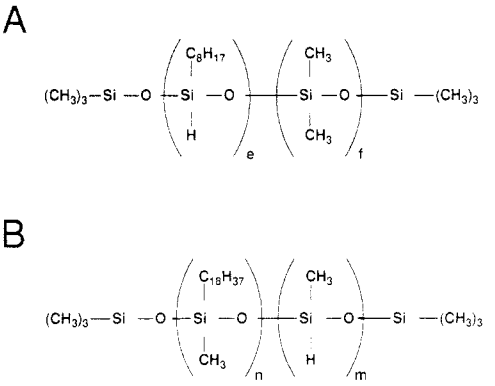


**Figure 1.** Molecular structures for the hydrosiloxane polymers: (A) polyoctylhydrosiloxanes; (B) polyoctadecylhydrosiloxanes.

**Synthesis of Poly(octyl- and Poly(octadecylhydrosiloxanes) (Figure 1).** The starting material for the poly(octylhydrosiloxanes), dimethoxyoctylsilane, was obtained by first preparing dichlorooctylsilane by using a Grignard reaction between 1-chlorooctane and trichlorosilane followed by methoxylation in trimethyl orthoformate. The Grignard reagent was formed by the slow addition of 25 g (170 mmol) of 1-chlorooctane into 500 mL of anhydrous refluxing ether containing 4.5 g of magnesium. A nitrogen atmosphere was maintained above the reaction medium throughout the entire procedure. After the magnesium was consumed, the ether containing the Grignard reagent was added slowly to a large excess of trichlorosilane that had been freshly distilled from quinoline. The mixture was refluxed for 1 h, and the solvents were removed under reduced pressure. The remaining solid was vigorously mixed with *n*-hexane and then filtered to remove the magnesium salts. The *n*-hexane was removed, and the product was isolated by distillation to give 18 g (50%) of a clear liquid (bp 60 °C/0.1 mmHg). This monomer was converted to the corresponding dimethoxy material by heating it in an excess of trimethyl orthoformate to give dimethoxyoctylsilane, bp 71 °C/0.1 mmHg. The polymeric octyl material was prepared by the slow addition of water to a Teflon vial containing a mixture of benzene–acetonitrile (1:1), 6.0 g (29 mmol) of dimethoxyoctylsilane, and 0.2 g of dry Amberlyst 15 resin. After the water was added, the mixture was allowed to react for 3 days. By performing the polymerization in this fashion, the polymeric chains were kept to a minimum length. End-capping was accomplished by adding 0.5 g of hexamethyldisilazane and stirring for 3 h. The resulting polymeric polyoctylhydrosiloxane was washed 3 times with distilled water and dried in vacuo overnight at 65 °C to give 70% yield of the 50% hydride product (poly-50-$C_8$, Figure 1A, $e = 100\%, f = 0\%$). Other polymeric compositions were prepared by mixing the appropriate monomers together, hydrolyzing, and end-capping. For example, a 15% hydride material (poly-15-$C_8$, Figure 1A, $e = 30\%, f = 70\%$) was prepared by mixing dimethoxyoctylsilane and octamethylcyclotetrasiloxane in the appropriate molar ratios.

The polymeric octadecyl material was prepared by the slow addition of water to a Teflon vial containing a mixture of acetone–toluene (1:1), 16 g (44 mmol) of octadecylmethyldichlorosilane, and 15 g of bicarbonate. After the water was added, the mixture was allowed to react for 7 days. The solvents and water were then removed. A small amount of dichloromethane was added to redissolve the solid octadecyl hydrolyzate, to which 2.6

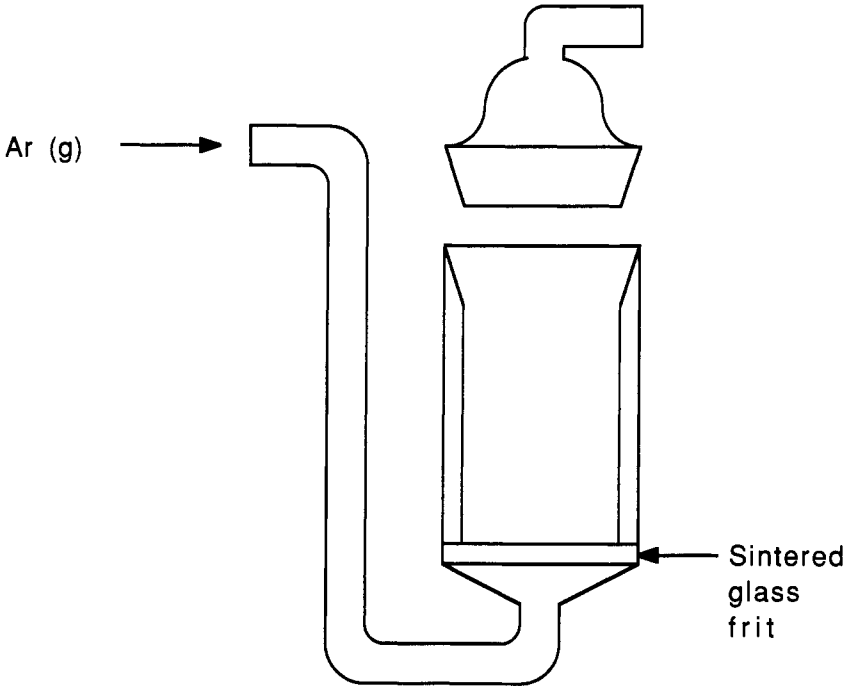


**Figure 2.** Schematic diagram of the reaction vessel.

**Table I. Comparison of Chromatographic Properties of Nucleosil-$C_8$, Poly-50-$C_8$, and Poly-25-$C_{18}$ Packing Materials**

| | | $k$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $n$,[a] plates $m^{-1}$ | $n$-$C_{18}$ | acetophenone | naphthol | benzo[$f$]quinoline | cholesterol | SN[b] | %C | $k_D/k_{Ac}$ |
| Nucleosil-$C_8$ | 30 800 | 5.9 | 5.3 | 9.3 | 15.9 | 16.9 | 2.3 | 4.5 | 1.05 |
| poly-50-$C_8$ | 27 800 | 12.5 | 4.9 | 8.9 | 11.9 | 14.4 | 4.0 | 8.7 | 0.63 |
| poly-25-$C_{18}$ | 39 600 | 14.9 | 3.7 | 6.2 | 11.3 | 13.3 | 6.8 | 3.6 | |

[a] Measured at $k = 6$. [b] Separation number (*11*). [c] SiOH index number: see text.

g (11 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane (Petrarch Inc. Bristol, PA; to give 25% Si–H groups), 0.56 g (3 mmol) of hexamethyldisiloxane, and 0.02 g of trifluoromethanesulfonic acid were added. This mixture was then stirred for another 7 days. The resulting polymeric material was washed with distilled water and dried overnight at 65 °C to give 60% yield of the poly(octadecylmethylhydrosiloxane) (Poly-25-$C_{18}$, Figure 1B, $n = 50\%$, $m = 50\%$).

**Deactivation.** A reaction vessel was constructed (Figure 2) that allowed both the coating and reaction steps to be performed in the same container. This apparatus also provided an inert atmosphere in which the reaction could take place. Purified and acid-pretreated silica particles were weighed, washed with HPLC grade water until a neutral pH was reached, and transferred into the reaction vessel. The vessel was connected to an argon line and placed in a chromatographic oven. Argon gas was introduced through the inlet, and the particles were dried at the desired temperature for 20 h. After cooling, the deactivation reagent (2-fold excess, assuming $6 \times 10^{18}$ silanols $m^{-2}$) was taken up in 50 mL of HPLC grade $n$-hexane and introduced into the reaction vessel. At this point, the reaction vessel was loosely covered with foil to allow the evaporation of the solvent. The argon gas, bubbling up through the porous frit into the slurry, created a boiling action that aided in the uniform coating of the oligomer onto the particles. As the solvent evaporated from the slurry, the walls of the vessel were washed with small quantities of solvent. When the particles had dried, the glass cap was positioned in place, and the device was allowed to purge for at least 1 h to ensure the elimination of air. The vessel was again placed in the chromatographic oven, still under Ar(g) purge, taken from 50 °C to a reaction temperature of 270 °C at 4 °C $min^{-1}$, and held for 20 h.

The packing was removed from the vessel, placed in a sintered glass funnel, washed with 50 mL each of HPLC grade $n$-pentane, carbon tetrachloride, methylene chloride, and ethanol, and then allowed to air dry. The percent loading was determined by elemental analysis, shown as %C in Table I (M-H-W Laboratories, Phoenix, AZ). Test solutions were prepared to provide ≈200 ng/component injected on-column.

## RESULTS AND DISCUSSION

The dehydrocondensation reaction bonds the silicon hydride polymers to the solid support with the concomitant generation of hydrogen gas (*7, 8*). The reaction occurs at relatively high temperatures (above 200 °C), well above the boiling point of any useful organic solvent. In addition, the reaction is very sensitive to oxygen and water.

To optimize the dehydrocondensation reaction, the particles must first be adequately dried, evenly coated, and then reacted under an inert atmosphere. Therefore, a reaction vessel was constructed according to the design in Figure 2, which allowed continuous Ar(g) purge throughout the drying, coating, and reaction steps.

The drying of the packing material prior to deactivation was of crucial importance to maximize reaction with the silica surface before cross-linking of the polymer. Water reacts readily with silicon hydrides to form silanols, which can promote cross-linking of the oligomeric chains. To remove water trapped in the pores of the particles, temperatures above 200 °C were necessary (*9*).

In this study, various drying temperatures were tested, both with and without vacuum. Preliminary studies showed that the use of a vacuum was cumbersome and provided no advantage over the use of an inert gas purge. The use of an Ar(g) purge through the packing efficiently swept away the water vapor as it emerged.

Three pretreatment (drying) temperatures (250, 300, and 350 °C) were evaluated for two different hydrosiloxane

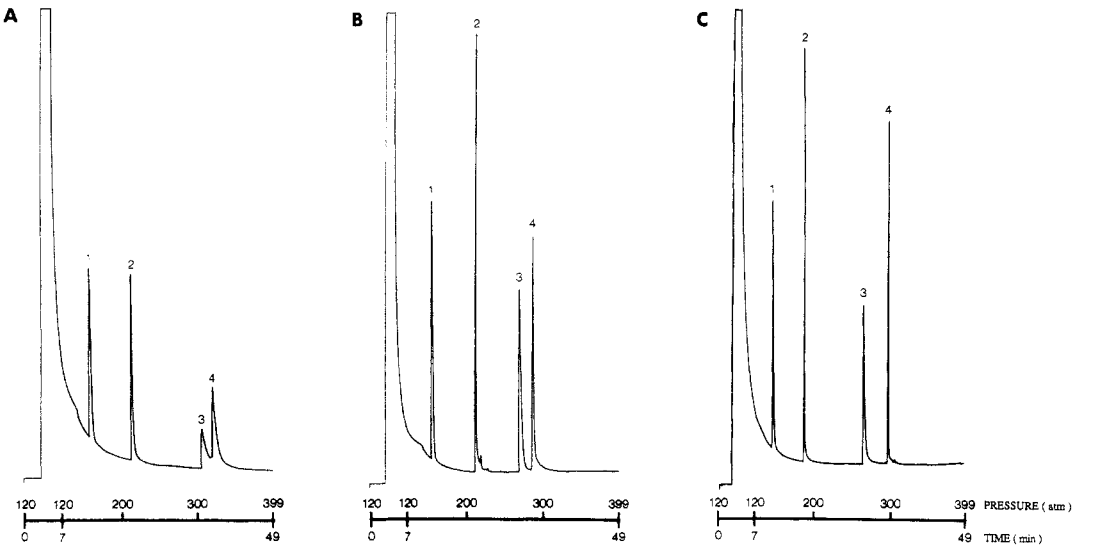


**Figure 3.** SFC chromatograms of a polarity test mixture separated on 30-cm × 250-μm i.d. packed fused silica columns, packed with (A) Nucleosil-$C_8$, (B) poly-50-$C_8$ modified Nucleosil packing material, and (C) poly-25-$C_{18}$ modified Vydac packing material. Conditions: 100 °C; pressure program from 120 to 400 atm at 7 atm $min^{-1}$ after an initial 7-min isobaric period. Peak identifications: (1) acetophenone, (2) naphthol, (3) benzo[*f*]quinoline, (4) cholesterol.

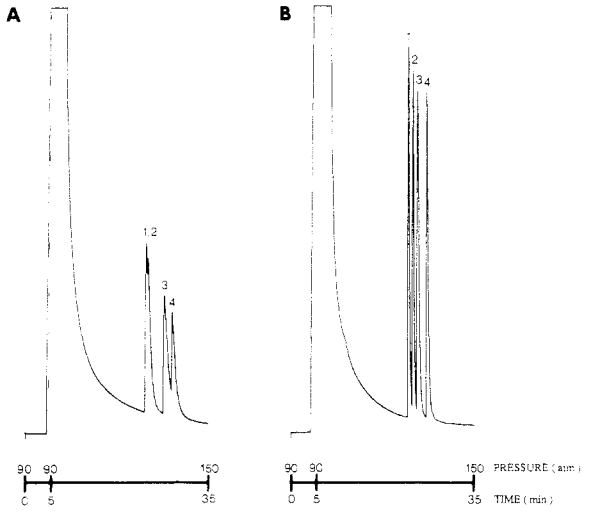


**Figure 4.** SFC chromatograms of trimethylphenol isomers separated on 30-cm × 250-μm i.d. packed fused silica columns, packed with (A) Nucleosil-$C_8$ and (B) poly-50-$C_8$ modified Nucleosil packing material. Conditions: 75 °C; pressure program from 90 to 150 atm at 2 atm $min^{-1}$ after an initial 5-min isobaric period. Peak identifications: (1) 2,3,6-, (2) 2,4,6-, (3) 2,3,5-, (4) 2,3,4-trimethylphenol.

polymers (poly-50-$C_8$ and poly-25-$C_{18}$) to determine the optimum pretreatment temperature for the subsequent dehydrocondensation reaction. The deactivated packings that had been dried at 250 °C showed improved peak shapes for all of the polar analytes tested in comparison to the corresponding commercial packing material (Figures 3 and 4). The packing materials dried at 300 °C also gave good peak shapes. The use of 350 °C produced materials that were inferior to the commercial material in terms of deactivation. Therefore, the temperature range 250–300 °C was found to be acceptable for pretreating the silica particles.

Two procedures for coating the silicon hydride polymers on the silica particles (supercritical fluid coating and evaporative precipitation coating) were evaluated. The use of a supercritical fluid in the coating process was considered due to an assumption that a supercritical solvent should be able to provide greater penetration into the particle pores. Two attempts were made, either using supercritical *n*-pentane or $CO_2$. Unfortunately, neither of these produced packings of as high quality (measured by chromatographic peak shape) as the evaporative precipitation method discussed below.

Evaporative precipitation was performed by adding the polymer reagent (dissolved in HPLC grade *n*-hexane) to the previously dried particles still in the reaction vessel (Figure 2). The reaction vessel was sonicated for 5 min under an Ar(g) purge which eliminated any agglomeration of the particles. The Ar(g) purge provided a homogeneous slurry, due to the boiling action it created, which allowed the reagent to have greater access to the particles. As a result of the superior quality deactivated packings produced, evaporative precipitation was the method of choice for coating.

The influence of the percent hydride content of the polymeric reagent was also studied. Reagents containing 15, 25, and 50% hydride substitution were synthesized. Both of 25 and 50% hydride reagents performed well in chromatography, with the 25% yielding the best peak shapes. The 15% hydride reagent did not perform as well, indicating that there were too few hydride moieties to effectively deactivate the surface. Reagents were reacted with unmodified Nucleosil and Vydac silica packing materials and were found to give equally good results for both.

Differential scanning calorimetry was used to determine the temperature at which decomposition of the polymer began. This was found to be 280 °C for the octyldecyl reagent; therefore, a reaction temperature of 270 °C was chosen for the deactivation/immobilization reaction.

Packed fused silica columns (250-μm i.d.) were selected for evaluating the new packing materials in this study. The dimensions of typical packed columns used in LC and SFC are 10–25 cm long and 1–4.6 mm i.d. The optimum flow rate for all packed columns is much greater than for open tubular columns. To use the FID at or above the optimum flow rate, the flow from a typical packed column normally must be split before introduction into the detector. Not only are there discrimination problems associated with flow splitting, but the increased sample capacity obtained by using a packed column becomes of little value when most of the sample is split away. Packed capillary columns of 100–400 μm i.d., such as were used in this study, are a good compromise because of their reduced mobile-phase flow rates when compared to larger packed columns and their greater sample capacities when compared to open tubular columns.

Several procedures were used to test the various packing materials. A procedure was developed by Walters (*10*) to

determine the free silanol content on support material surfaces under reversed-phase LC conditions using the ratio of average capacity factor values of *N,N*-dimethyl-*m*-toluamide ($k_D$) and anthracene ($k_A$) to give an SiOH index number ($k_D/k_A$). The lower the value of the SiOH index, the lower the corresponding relative free silanol concentration. When this test was applied in this study, the volumetric flow rate for the columns was held at 0.2 $\mu$L min$^{-1}$. The Nucleosil-$C_8$ and the poly-50-$C_8$ materials were packed and evaluated in this manner. The $k_D/k_A$ values listed in Table I indicate a relatively less active surface for the poly-50-$C_8$ material than for the commercial Nucleosil-$C_8$ material.

The columns were further tested under SFC conditions with polar analytes to compare activities as determined by peak shapes. Figure 3 shows chromatograms of a mixture containing acetophenone, naphthol, benzo[*f*]quinoline, and cholesterol. Peak shapes for each of the components were consistently better on the columns packed with poly-50-$C_8$ and poly-25-$C_{18}$ materials as compared to the Nucleosil-$C_8$ material. The retention order was the same on all three packing materials; however, $k$ values were lower for the poly-50-$C_8$ and poly-25-$C_{18}$ materials in comparison to the Nucleosil-$C_8$ column for these polar solutes. Even though the $k$ value for an *n*-alkane (*n*-$C_{18}$) was higher on the poly-50-$C_8$ and poly-25-$C_{18}$ packings, the analysis times for the polar analytes were shorter because of the lower surface activity (Table I).

Figure 4 gives an example of the superior resolving capabilities of the hydrosiloxane deactivated materials for a series of four phenolic isomers when using pure $CO_2$ as the mobile phase. The average measurements of efficiency, separation number (SN), and percent carbon content of three of the packing materials are given in Table I. The superior SN for the columns packed with the poly-50-$C_8$ and poly-25-$C_{18}$ materials, despite the fewer theoretical plates measured for the poly-50-$C_8$ columns, suggests that more stationary phase is accessible for interaction with the sample, thereby enhancing selectivity and providing greater resolution. The percent carbon content values show approximately twice the carbon loading for the poly-50-$C_8$ and poly-25-$C_{18}$ materials as for the Nucleosil-$C_8$ packing. These observations, along with the lower observed activity, imply that a more complete and even coverage was obtained.

A major advantage of SFC is the ability to chromatograph thermally labile compounds that are not amenable to GC analysis. Results from the analysis of two samples of this type were included to show the application of the hydrosiloxane-deactivated materials for the separation of polar analytes of current environmental interest. A chromatogram of a dichloromethane extract of a double-base propellant (MK90) is shown in Figure 5, and an analysis of a standard mixture of polycyclic aromatic hydrocarbons (PAH) and high explosives is shown in Figure 6.

The question of the potential for plugging of the pores in the porous material by the polymeric reagents was raised early in this work. If significant amounts of plugging were to occur, the available surface area would be decreased with a concomitant loss of sample capacity. To estimate the sample capacities for the different packing materials, relative reductions in efficiencies were compared. The introduction of 2 mg of sample onto the Nucleosil-$C_8$ column resulted in a 29% reduction in efficiency; the same quantity of sample caused only a 22% decrease for the poly-50-$C_8$ column. Since the loss in efficiency of the poly-50-$C_8$ column was less than that of the Nucleosil-$C_8$ column, the former possessed a larger sample capacity, which gives strength to the argument that no significant plugging of the pores occurred. Additionally, if pore plugging had occurred, retention values would have been expected to decrease; instead a large increase was observed for nonpolar molecules.

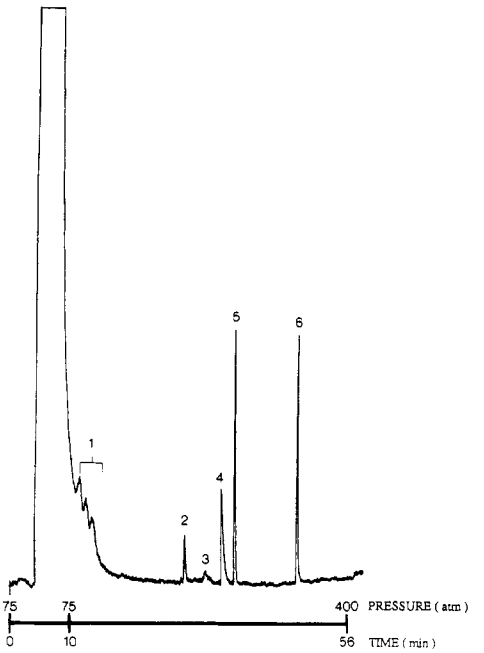


**Figure 5.** SFC chromatogram of a dichloromethane extract of a double-base propellant separated on a 25-cm × 250-$\mu$m i.d. packed fused silica column, packed with a poly-50-$C_8$ modified Nucleosil packing material. Conditions: 120 °C; pressure program from 75 to 400 atm at 7 atm min$^{-1}$ after an initial 10-min isobaric period. Peak identifications: (1) candellila wax, (2) 2-nitrodiphenylamine, (3) resorcinol, (4) nitroglycerine, (5) triacetin, (6) di-*n*-propyl adipate.

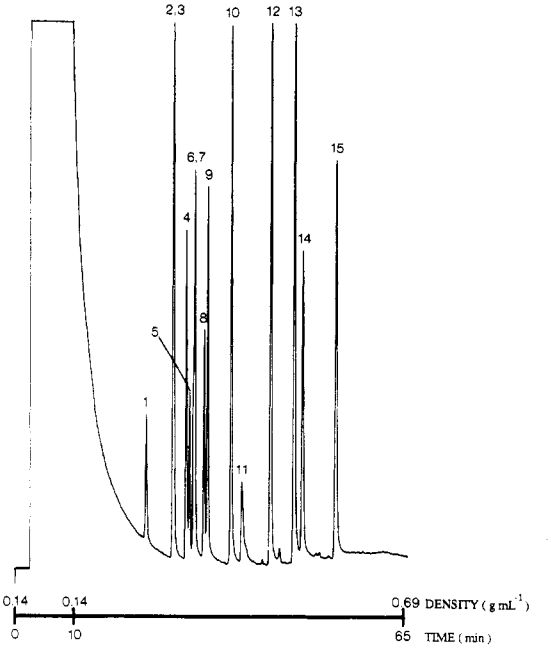


**Figure 6.** SFC chromatogram of a mixture of explosives and polynuclear aromatic hydrocarbons (PAH) separated on a 25-cm × 250-$\mu$m i.d. packed fused silica column, packed with a poly-50-$C_8$ modified Nucleosil packing material. Conditions: 100 °C; density program from 0.14 to 0.64 g mL$^{-1}$ at 0.01 g mL$^{-1}$ after an initial 10-min isobaric period. Peak identifications: (1) naphthalene, (2) 2,6-dinitrotoluene, (3) dibenzofuran, (4) 2,4-dinitrotoluene, (5) *n*-nitrosodiphenylamine, (6) 2,4,6-trinitrotoluene, (7) 1,3,5-trinitrobenzene, (8) biphenyl, (9) 2-nitronaphthalene, (10) phenanthrene, (11) 2-nitrophenol, (12) pyrene, (13) benz[*a*]anthracene, (14) 1-nitropyrene, (15) benzo[*a*]pyrene.

## CONCLUSION

The use of the dehydrocondensation reaction to bond short polymeric chains to silica particles is an effective means of

achieving a well-deactivated surface. The ability to attach a variety of pendant groups to the hydrosiloxane backbone to achieve a wide range of selective phases adds to the future importance of this method for preparing packed columns for chromatography.

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# Multidimensional Packed Capillary Coupled to Open Tubular Column Supercritical Fluid Chromatography Using a Valve-Switching Interface

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**An on-line two-dimensional supercritical fluid chromatographic system (SFC/SFC) was constructed by utilizing a rotary valve interface to provide independent flow control of the two dimensions. A cold trap was employed to refocus solutes from single or multiple fractional cuts, after being transferred to the second dimension. Improved performance, including time savings, was achieved with a packed capillary to open tubular column arrangement and two independently controlled pumps, compared to earlier reported single-pump open tubular column SFC/SFC and packed capillary column SFC/SFC systems. The packed capillary in the first dimension provided a rapid chemical class separation, while the open tubular column in the second dimension provided high resolution of closely related isomers.**

## INTRODUCTION

Samples for chemical analysis often contain so many components, that only a multidimensional chromatographic system can approach their complete separation (*1*, *2*). Furthermore, high molecular weight samples have exponentially increasing numbers of isomers, requiring even greater resolution than their low molecular weight counterparts. Numerous reports have been published describing multidimensional chromatography using GC (*3*), LC (*4*), SFC (*5*), and their combinations (*6-8*). Since SFC is a high-resolution technique and is suitable for separation of high molecular weight samples, it is a natural choice for combining in a multidimensional configuration.

An operational advantage of multidimensional SFC/SFC is that the transferred sample from the first dimension can be easily refocused. At atmospheric pressure in the focusing region, the mobile phase instantly loses its solvating power. This solubility loss is enhanced by the cooling effect of the expanding carrier, resulting in effective precipitation of the compounds of interest in a narrow band. The problems associated with elimination of the carrier from the first dimension is, therefore, much easier to solve in SFC than in LC.

Packed columns can provide faster analysis times and higher sample capacities than open tubular columns. A recent paper describing a multidimensional packed capillary SFC/SFC system (*9*) reported short analysis times but insufficient efficiency in the second dimension to separate many closely related isomers. The properties of packed capillary columns, however, make them an excellent choice for use in the first dimension.

Open tubular columns with their high resolving power are, on the other hand, the column type of choice for the second dimension. Multidimensional open tubular column SFC/SFC has been shown (*10*) to be a promising, but time consuming, technique for resolving complex mixtures.

It was already proposed (*9*) that a suitable compromise between speed and resolution could be reached by using a packed capillary column for a faster group type separation in the first dimension and an open tubular column in the second dimension to provide the final high-resolution separation of individual compounds. Due to the significant differences in the optimum volumetric flow rates of packed capillary and open tubular columns, earlier attempts to combine a packed capillary to an open tubular column for multidimensional SFC/SFC have failed because the flow rates could not be independently controlled.

In this paper, a two-dimensional packed capillary to open tubular column SFC/SFC system is reported that uses a valve-switching interface in line with a cryogenic trap for refocusing of analyte fraction cuts in the second dimension. This interface allowed independent flow-rate control of the two columns, providing a simple means for selective transfer of one or more solute fractions to the second dimension. The system was evaluated by using a certified coal tar that had been used previously for evaluating open tubular column SFC/SFC and packed capillary SFC/SFC (*9*, *10*).

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