**Investigation of a Novel, Sol-Gel Derived Stationary Phase for Gas Chromatography**

Raoul Cervini, Gary Day, Angus Hibberd, Gerard Sharp, SGE International Pty Ltd, Ringwood, Australia, and Angela Froud, SGE Europe Ltd, Milton Keynes, Buckinghamshire, UK.

A novel, organic–inorganic stationary phase for capillary gas chromatography (GC) has been developed using sol-gel technology. This sol-gel phase was specifically developed to closely match existing poly(ethylene glycol) or wax-based GC phases in the marketplace. Fused-silica capillary columns coated with this sol-gel based phase are inert, robust, thermally stable and exhibit good retentive characteristics for a wide range of substances.

**Introduction**

During the past 20 years, a variety of materials have been used as stationary phases for capillary gas chromatography (GC), many of which have been based on polyorganosiloxanes (1, 2). In fact, the majority of phases currently used in commercial GC columns are based on polysiloxanes. Over time, improvements leading to superior stationary phase technology have resulted in GC columns with enhanced inertness and thermal stability, allowing for a greater range of GC applications (3).

The use of sol-gel materials in many scientific areas has increased in recent times (4, 5). Their use as stationary phases for GC capillary columns is an attractive option because of their ease of preparation, highly porous nature and excellent thermal stability at relatively high temperatures. However, while sol-gel technology has been successfully exploited in the field of liquid chromatography (6), the use of sol-gel materials has been limited in other fields of chromatography (7–10).

Sol-gel is prepared using the sol-gel process (4). Generally speaking, sol-gel processing consists of hydrolysis and condensation of an alkoxide (e.g., tetraethoxysilane or TEOS) to form a glassy or ceramic-type material at room temperature. During this process, a colloidal suspension of particulates (a ‘sol’) is converted into a ‘gel’ via polymerization (polycondensation). In essence, the hydrolysed monomers of the metal alkoxide undergo polycondensation reactions promoting cross-linking to form a three-dimensional network. Upon drying, the material is transformed into a dehydrated gel. Although the hydrolysis step can be catalysed by either acid or base, at high pH the polycondensation step has been shown to proceed faster (4–7).

In this article, the effectiveness of using a novel, sol-gel material incorporating poly(ethylene glycol) (PEG) or wax as a capillary column stationary phase will be described. Chromatograms demonstrating inertness, partitioning capability and robustness for a range of applications will also be presented.

**Experimental**

The methods for preparing capillary columns using sol-gel stationary phases have been well documented (8–10). SolGel-WAX columns (SGE Int., Ringwood, Australia) were used for all analyses. Column specifications and run conditions for individual chromatograms are listed in the figures. General gas chromatographic analyses were performed using either an HP 5890 series II gas chromatograph with a flame ionization detector (FID), or an HP 6890 series GC system with a 5973 mass selective detector (MSD) (both Agilent Technologies, Wilmington, Delaware, USA). Data acquisition was controlled by HP Chemstation (Revision A) software (Agilent Technologies).

**Figure 1:** General chemistry involved in making the wax-based sol-gel phase.
Results and Discussion

The sol-gel process is a very common procedure used to produce silica glasses or ceramics, the properties of which are often determined by the nature of the precursor alkoxide used. Previous work concerning sol-gel GC stationary phases involved organically modifying sol-gel precursor materials, forming the sol-gel matrix in solution using an acid catalyst, then dynamically coating the fused-silica capillary columns with this solution to produce a thin film of the stationary phase material (8–10). Our approach is slightly different in that the column coating process produces thin films of sol-gel material on the fused silica, to which industry standard stationary phase material can be anchored. In essence, the capillary column surface is coated with a composite material consisting of the sol-gel and the phase. Using this methodology, the sol-gel columns can be prepared with a selectivity closely matching that of GC capillary columns currently available in the marketplace. The general chemistry involved in the preparation of the wax-type sol-gel phase is outlined in Figure 1. Wax (or PEG) GC columns are polar in nature and useful for separating substances such as alcohols, aromatics, solvents, fatty acid methyl esters (FAMEs) and essential oils. Figure 2(a) shows the separation of a selection of compounds using a capillary column coated with the wax-based sol-gel phase. After initial

![Figure 2](image-url)

Figure 2: Separation of a selection of compounds using a column coated with the sol-gel phase (30 m, 0.25 mm i.d., 0.25 µm film thickness). (a) before heating at 250 °C for 1 h with the carrier gas turned off and (b) after heating at 250 °C for 1 h with the carrier gas turned off. Conditions: carrier gas, helium; injection split (150:1, 250 °C); detector, FID 280 °C. Temperature programming: isothermal 155 °C, 12 min. Peaks: 1 = solvent, 2 = 2-octanone, 3 = tetradecane, 4 = 1-octanol, 5 = hexadecane, 6 = naphthalene, 7 = 2,4-dimethylanaline, 8 = 2,6-dimethylanaline.

![Figure 3](image-url)

Figure 3: Retention times of acetone in water over 300 injections using a wax-type sol-gel column (30 m, 0.25 mm i.d., 0.25 µm film thickness).

![Figure 4](image-url)

Figure 4: Separation of a range of common industrial solvents using a column coated with the sol-gel phase (30 m, 0.32 mm i.d., 0.5 µm film thickness). Conditions: carrier gas, helium; injection split (83:1, 240 °C); detector, FID 270 °C. Temperature programming: 35 °C to 230 °C at 15 °C/min, hold for 4 min. Peaks: 1 = acetone, 2 = ethyl acetate, 3 = isobutyl ketone, 4 = contaminant, 5 = iso-propanol, 6 = ethanol, 7 = methyl isobutyl ketone, 8 = toluene, 9 = butyl acetate, 10 = iso-butanol, 11 = propylene glycol monomethyl ether, 12 = n-butanol, 13 = ethylbenzene, 14 = p-xylene, 15 = m-xylene, 16 = o-xylene, 17 = butyl cellosolve acetate, 18 = cyclohexanone, 19 = butyl cellosolve, 20 = butyl glycol acetate, 21 = hexyl cellosolve, 22 = isophorone, 23 = butyl carbitol, 24 = benzyl alcohol.
testing, the thermal stability of the column was examined. The column was heated to 250 °C, left at that temperature for one hour with the carrier gas turned off, then re-tested using the same conditions as before. Figure 2(b) shows the re-testing of the column. It is evident from the shortened retention times in Figure 2(b) that there has been some phase loss. However, there was no evidence of peak broadening for the early eluting compounds indicating that the phase had not degraded appreciably, even though the conditions used to test this sol-gel phase on the column would begin to destroy most wax (PEG) phases. It is clear that in this instance, the sol-gel matrix significantly aided thermal stability of the stationary phase without having a detrimental effect on the partitioning capability of the column.

The impact of water on a wax-based sol-gel capillary column was tested by examining the retention time of acetone in water from repeated injections at low temperature (Figure 3). Examination of the retention times for acetone from 300 injections showed that the water in the testing sample had no effect on the partitioning performance of the column. The advantage of using the sol-gel phase in this instance was clearly demonstrated by the inertness of the column to water over time. One useful application of this water resistance would involve low-level detection of industrial solvents in wastewater. The chromatogram in Figure 4 shows the separation of a range of common industrial solvents using the sol-gel column.

Commercially available PEG or wax-type columns are commonly used to separate isomers of xylene, in particular, m- and p-xylene. The selectivity of a wax-based sol-gel column was examined using a range of aromatic compounds with similar chemical structures (BTEX) (Figure 5). It is evident that all compounds could be successfully partitioned with good peak shape and response, indicating that the selectivity of the column coated with the sol-gel phase closely matched other PEG or wax-type columns currently available.

Mixtures of organic acids and esters are routinely analysed by GC, sometimes with less than satisfactory results. Tailing of the acids is often seen with many column types. One potential problem using the sol-gel matrix as part of a stationary phase related to whether all hydroxy (active) sites on the sol-gel would be covered by the stationary phase. It was decided to analyse a series of acrylate monomers that have a tendency to tail on many phases, using one of the wax-based sol-gel columns (Figure 6).

In this instance all monomers were obtained with good response and peak shape, even though this is often difficult with compounds such as acrylic and methacrylic acid. This result suggests that all active sites on the sol-gel matrix were covered.

It was anticipated that the porous nature of the sol-gel matrix could be exploited for analysis of volatile compounds, which is usually performed using GC capillary columns with thick stationary phase coatings (> 1 µm). With a stationary phase that is highly porous in nature, it was probable that the volatile components of a mixture being separated would have a high degree of interaction with the phase, leading to good response. This was tested by analysing the US EPA 502.2 test mix on a thin-film (0.25 µm), wax-based, sol-gel column (Figure 7). Under normal circumstances, a thick film column (> 1 µm) is usually required to obtain good response for the volatiles in this test mix, regardless of the diameter of the column.

As is the situation for most analyses of this test mix, even when performed using different thick-film column types, the chromatogram in Figure 7 exhibited some coeluted peaks. However, the peak response was excellent for all compounds and the analysis time was short (~17 min). While it is clear that more work is required, this experiment has demonstrated that thin-film, highly porous, sol-gel columns can be used in place of certain thick-film columns for particular applications.
Conclusion
It has been clearly shown from these applications that the performance of the GC columns is enhanced when coated with this sol-gel phase. Capillary columns coated with the wax-type, sol-gel stationary phase are inert, thermally stable and can be successfully used to separate a range of compounds because the coating technology uses industry standard stationary phase material. It has also been demonstrated that the highly porous nature of the sol-gel material can be exploited to analyse volatile organic compounds using thin-film columns.

Figure 7: (a) Separation of US EPA 502.2 volatiles test mix using a wax-type sol-gel column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Conditions: carrier gas, helium; injection split (100:1, 250 °C); detector, MS. Temperature programming: 40 °C, 1 min, 40 °C to 210 °C at 6 °C/min, 210 °C to 260 °C at 15 °C/min, 260 °C for 5 min. (b) Expanded view of same separation from 1–4 min. Peaks: 1 = dichlorodifluoromethane, 2 = chloromethane, 3 = chloroethene, 4 = trichlorofluoromethane, 5 = chloroethane, 6 = bromomethane, 7 = 1,1-dichloroethene, 8 = 2,2-dichloropropane, 9 = 1,2-dichloroethene (cis), 10 = 1,1-dichloro-1-propene, 11 = 1,1,1-trichloroethane, 12 = carbon tetrachloride, 13 = 1,1-dichloroethane, 14 = dichloromethane, 15 = benzene, 16 = 1,2-dichloroethene (trans), 17 = trichloroethene, 18 = tetrachloroethene, 19 = chloroform, 20 = toluene, 21 = 1,2-dichloropropane, 22 = bromochloromethane, 23 = 1,2-dichloroethane, 24 = ethylbenzene, 25 = p-xylene, 26 = 1,3-dichloro-1-propene (cis), 27 = m-xylene, 28 = o-xylene, 29 = bromodichloromethane, 30 = dibromomethane, 31 = isopropyl benzene, 32 = 1,3-dichloropropane, 33 = n-propylbenzene, 34 = chlorobenzene, 35 = 1,3-dichloro-1-propene (trans), 36 = t-butylbenzene, 37 = 1,2,4-trimethylbenzene, 38 = sec-butylbenzene, 39 = 1,2-dibromoethane, 40 = styrene, 41 = 1,1,1,2-tetrachloroethane, 42 = 1,1,2-trichloroethane, 43 = 4-isopropyltoluene, 44 = 1,3,5-trimethylbenzene, 45 = dibromochloromethane, 46 = 2-chlorotoluene, 47 = n-butylbenzene, 48 = 4-chlorotoluene, 49 = bromobenzene, 50 = 1,4-dichlorobenzene, 51 = 1,3-dichlorobenzene, 52 = bromoform, 53 = 1,2,3-trichloropropane, 54 = 1,2-dichloroethene, 55 = hexachlorobutadiene, 56 = 1,1,2,2-tetrachloroethane, 57 = 1,2,4-trichlorobenzene, 58 = 1,2-dibromo-3-chloropropane, 59 = 1,2,3-trichlorobenzene, 60 = naphthalene.
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References

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Dr Gary Day has worked as a synthetic polymer chemist for eight years and is in charge of all phase synthesis for capillary columns.

Dr Raoul Cervini held a post doctoral position at Cambridge University, UK, working on polymer synthesis before joining SGE as the research and development chemist for phase synthesis.

Dr Angus Hibberd completed his PhD at Monash University, Australia before moving to the Commonwealth Scientific Industrial Research Organization (CSIRO). He joined SGE as the applications chemist and is now involved in the development of new and existing phases.

Dr Gerard Sharp has had a wide variety of experiences in the forensic, chemicals, paints and environmental fields. He has an intimate knowledge of gas chromatography techniques.