Sol-Gel Technology for Gas Chromatographic Columns

INTRODUCTION

Capillary gas chromatography (GC) is a separation technique that has existed for many years. Over time, a variety of materials have been used as capillary column stationary phases, most of which have been based on polyorganosiloxanes.[1,2] Superior stationary phase technology has led to enhanced thermal stability and improved inertness of many GC columns, allowing for a greater range of GC applications.[2]

The use of Sol-Gel materials as stationary phases for GC capillary columns is an attractive option due to the materials having good retentive characteristics, being inherently inert, easy to prepare and thermally stable at relatively high temperatures.

Sol-Gel processing consists of hydrolysis and condensation of a metal alkoxide (for example, tetraethoxysilane or TEOS) to form a glassy material at room temperature.[3,5,6] During this process, a colloidal suspension of particulates (a 'Sol') is converted into a 'Gel' via polymerization (polycondensation). In essence, the hydrolyzed monomers of the metal alkoxide undergo polycondensation reactions promoting crosslinking to form a three dimensional network. Upon drying the material is transformed into a dried gel. The hydrolysis can be either acid or base catalyzed, while the condensation has been shown to proceed faster at higher pH.[3,5,6]

This paper reviews the use of Sol-Gel capillary columns demonstrating inertnes, partitioning capabilities and robustness.

EXPERIMENTAL CONDITIONS

Chemicals

All general chemicals were purchased from Sigma-Aldrich (Australia). Polymeric and sol-gel based stationary phases used in this study were synthesized in-house.

Column Preparation

Polyimide coated fused silica capillary columns were manufactured in-house. The coating procedure followed the general method outlined previously,[6,8] the exact details of which are proprietary.

Chromatography Instrumentation

General gas chromatographic analyses were carried out using a Hewlett Packard 5890 series II gas chromatograph with a flame ionization detector. Bleed tests were carried out using a Hewlett Packard 6890 series GC system with a 5973 mass selective detector. Data acquisition was controlled by HP Chemstation (Revision A) software.

RESULTS

The chemistry involved in the preparation of the sol-gel phases is outlined in Figure 1. The SolGel-1ms™ material is non-polar, since commercially available poly(dimethylsiloxane) (PDMS) is part of the matrix. The SolGel-WAX™ material is more polar, since standard poly(ethylene glycol) (PEG) is part of the matrix, and is designed to be used in a similar manner to conventional wax-based stationary phases.

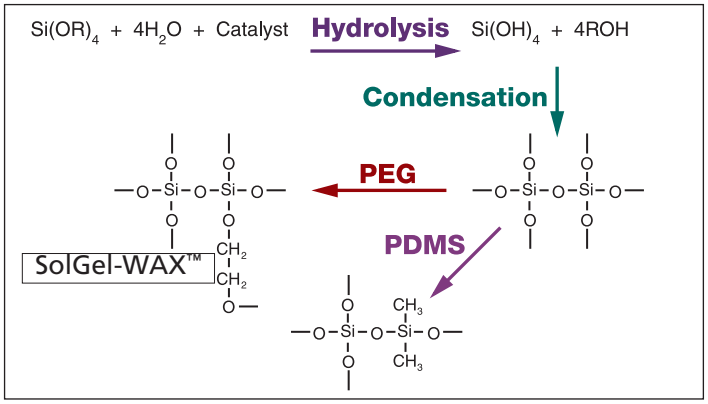

Figure 1. General chemistry involved in making SolGel-1ms and SolGel-WAX™ phases.

The non-polar SolGel-1ms™ column was tested using a stringent test mix containing a primary amine, an alcohol and an acidic phenol (Figure 2). The lack of activity towards the amine or phenol demonstrates the inertness of the sol-gel phase on the column. It also indicates that complete coverage of the active sites on the sol-gel is achieved. In order to test the partitioning properties of the SolGel-1ms™ column a Kovats Index comparison between the SolGel-1ms™ capillary column, the SGE BP1 100 % poly(dimethylsiloxane) column and a non-SGE 100 % poly(dimethylsiloxane) column was undertaken (Table 1). It is evident from Table 1 that all three columns are virtually identical in terms of partitioning capability. This result means that SolGel-1ms™ capillary columns can be used with existing chromatographic methods for analyses using standard 100 % poly(dimethylsiloxane) columns, with almost identical chromatographic results.

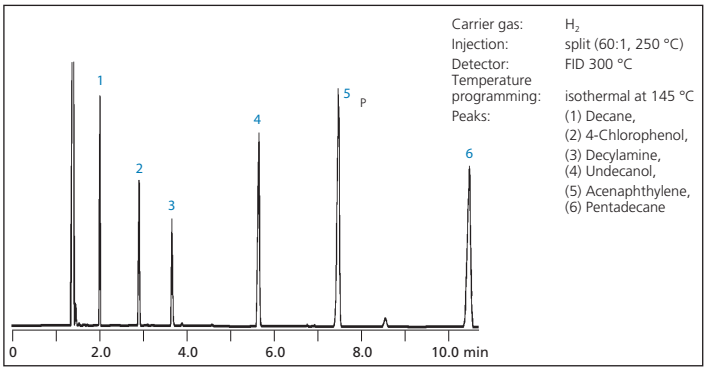

Figure 2. Standard test mix run on a SolGel-1ms™ column (30 m x 0.25 mm ID x 0.25 µm film thickness).

No.	Component	Kovats		
		SolGel-1ms™	BP1	Non-SGE 100 % Poly(dimethylsiloxane)
1	Decane	1000	1000	1000
2	4-Chlorophenol	1165	1167	1164
3	Decylamine	1240	1241	1239
4	Undecanol	1357	1358	1356
5	Acenaphthylene	1433	1434	1434
6	Pentadecane	1500	1500	1500
All columns 30 m, 0.25 mm ID, 0.25 µm film thickness; run conditions listed in Figure 2.				

Table 1. Kovats Index comparison of a SolGel-1ms column with BP1 and a non-SGE 100 % polydimethylsiloxane columns.

The chromatograms in Figure 3 show the separation of a selection of compounds taken from the US EPA 8270 semi-volatiles method using a SolGel-1ms™ column. Excellent response was achieved for all compounds, including 2,4-dinitrophenol (peak 5) and 4-nitrophenol (peak 7), for which it is often difficult to obtain a satisfactory peak response.

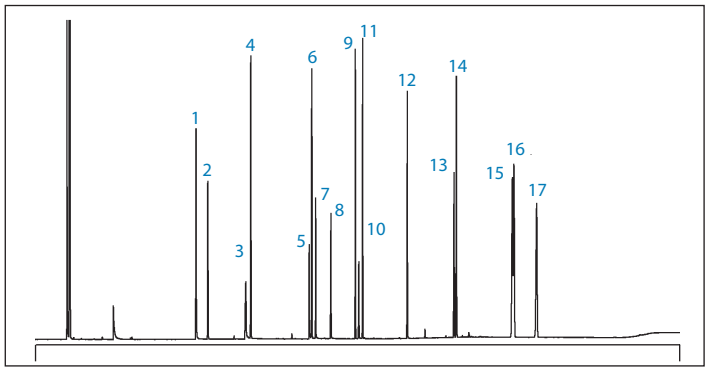

Figure 3a. The chromatogram shows separation of a selection of compounds from the US EPA 8270 semi-volatiles method using a SolGel-1ms™ column (30 m x 0.25 mm ID x 0.25 µm film thickness).

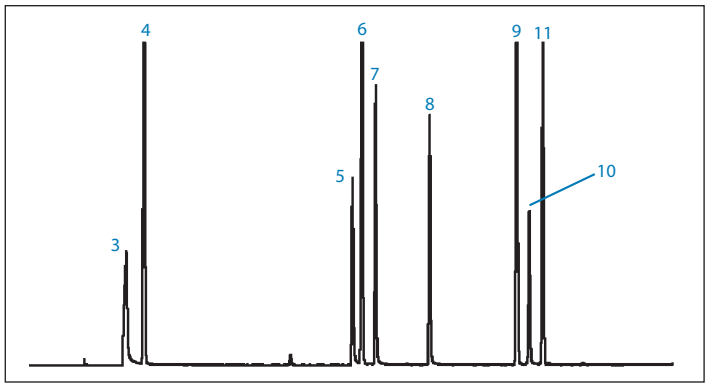

Figure 3b. Expansion of peaks 3-11.

Carrier gas:	He
Injection:	Split (80:1, 250 °C)
Detector:	FID 300 °C
Temperature programming:	40 °C to 270 °C at 10 °C min^{-1}, hold 12 min, 270 °C to 300 °C at 30 °C min^{-1}.
Peaks:	(1) Aniline, (2) 1,4-Dichlorobenzene-d4, (3) Benzoic acid, (4) Naphthalene-d8, (5) 2,4-Dinitrophenol, (6) Acenaphthylene-d10, (7) 4-Nitrophenol, (8) 2-Methyl-4,6-dinitrophenol, (9) 4-Aminobiphenyl, (10) Pentachlorophenol, (11) Phenanthrene-d10, (12) Benzidine, (13) 3,3'-Dichlorobenzidine, (14) Chrysene-d12, (15) Benzo[b]fluoranthene, (16) Benzo[k]fluoranthene, (17) Perylene-d12

Bleed comparisons were made between a commercially available, low bleed 100 % poly(dimethylsiloxane) column and a SolGel-1ms™ column using a mass selective detector (Figure 4). Conditioning of the commercially available column was performed according to the manufacturer's instructions. While the magnitude of the bleed for the non-polar SolGel-1ms™ column was lower at all temperatures tested, the bleed chromatogram also exhibited significantly lower noise, which is important for detection of compounds at very low concentrations.

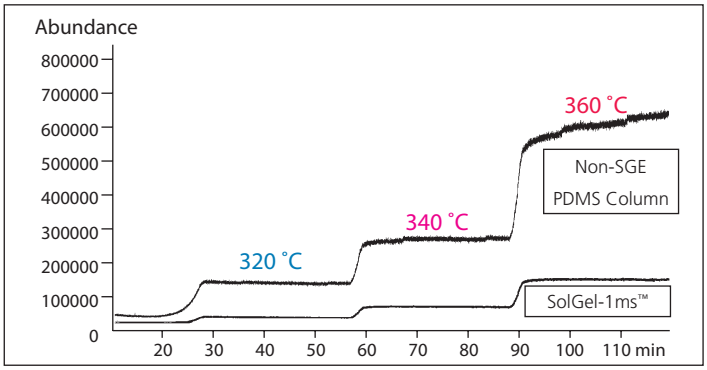

Figure 4. Bleed chromatograms generated from a commercially available poly(dimethylsiloxane) (PDMS) column (top) and a SolGel-1ms™ column (bottom) using a mass selective detector. Both columns were 30 m x 0.25 mm ID x 0.25 µm film thickness.).

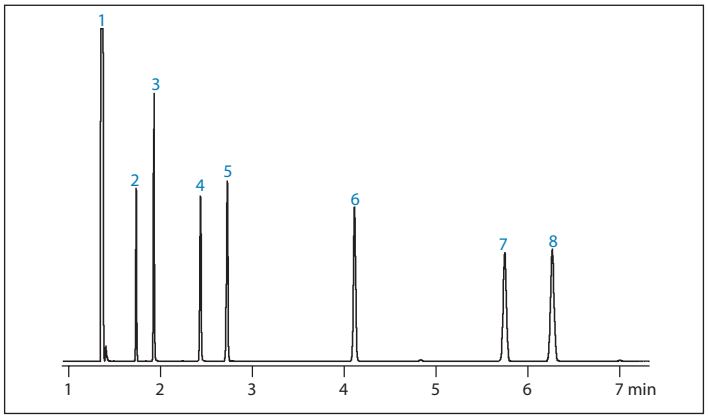

Figure 5a. Separation of a selection of compounds using a SolGel-WAX™ column (30 m x 0.25 mm ID x 0.25 µm film thickness), before heating at 250 °C for 1 hour with the carrier gas turned off.

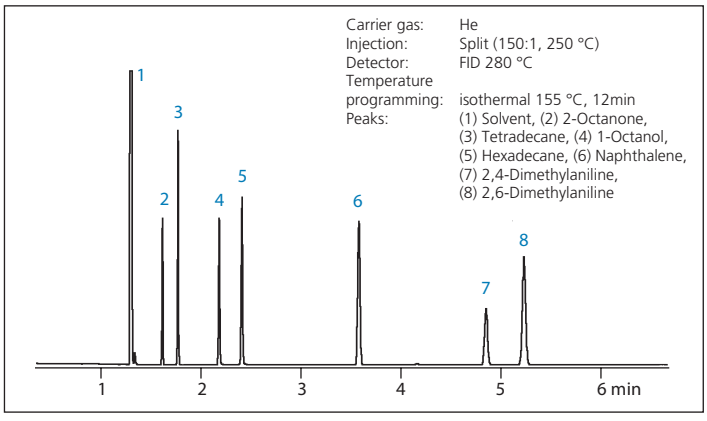

Figure 5b. SolGel-WAX™ column (30 m x 0.25 mm ID x 0.25 µm film thickness) after heating at 250 °C for 1 hour with the carrier gas turned off.

The chromatogram in Figure 5a shows the separation of various compounds using a SolGel-WAX™ column. This column was subsequently heated to 250°C and held at this temperature for one hour with the carrier gas turned off. The chromatogram in Figure 5b shows the re-testing of this column with identical conditions. It is evident from shortened retention times in the bottom chromatogram that there has been some phase loss. There was no evidence of peak broadening of the early eluting peaks which indicates that the phase has not been extensively degraded. The harsh conditions used to test the robustness of the SolGel-WAX™ column would begin to destroy most PEG (wax) phases, so the sol-gel matrix has significantly aided thermal stability of the stationary phase without having a detrimental effect on the partitioning capability.

The impact of water on a SolGel-WAX™ capillary column was tested by examining the retention time of acetone in water from repeated injections (Figure 6). Examination of the retention times for acetone from 300 injections showed that the water in the testing sample had no effect on the performance of the column. The advantage of using the sol-gel phase in this case was clearly demonstrated by maintenance of the inertness of the column to water. One useful application of this water resistance would involve low level detection of industrial solvents in waste water. To this end, the chromatogram in Figure 7 shows the separation of a range common industrial solvents using a SolGel-WAX™ column.

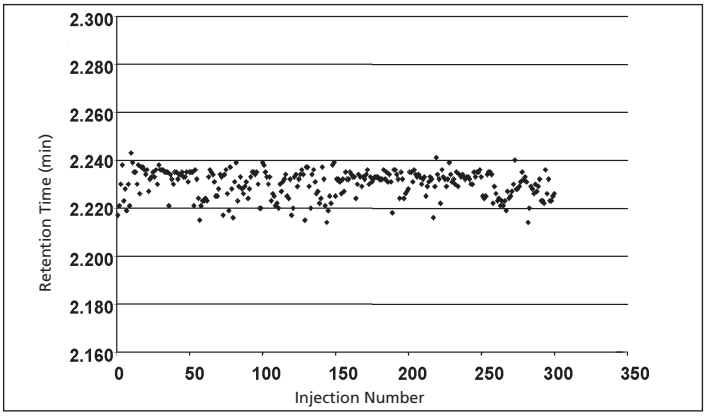

Figure 6. Graph showing the retention times of acetone in water over 300 injections using a SolGel-WAX™ column (30 m x 0.25 mm ID x 0.25 µm film thickness).

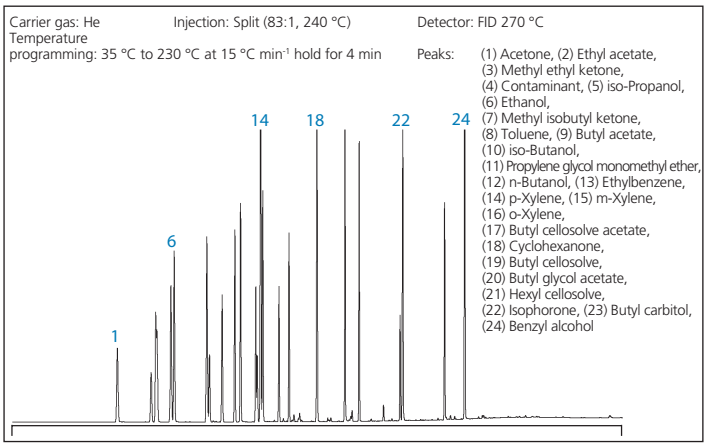

Figure 7. SolGel-WAX™ column (30 m x 0.25 mm ID x 0.25 µm film thickness) after heating at 250 °C for 1 hour with the carrier gas turned off.

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 SolGel-WAX™ column was examined using a range of aromatic compounds with similar chemical structures (BTEX) (Figure 8). From the chromatogram in Figure 8 it is evident that all compounds could be successfully partitioned with good peak shape and response being obtained.

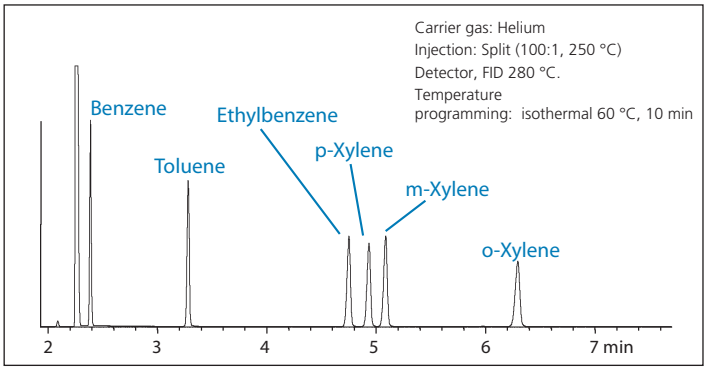

Figure 8. Chromatogram showing separation of a BTEX mixture using a SolGel-WAX™ column (30 m x 0.25 mm ID x 0.25µm film thickness).

CONCLUSION

GC capillary columns with stationary phases based on Sol-Gel materials are inherently inert, thermally stable and can be successfully used to separate a range of compounds as the coating technology uses standard stationary phase material.

ACKNOWLEDGEMENTS

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AUSTRALIA & PACIFIC REGION
SGE Analytical Science Pty Ltd
Toll Free: 1800 800 167
Tel: +61 (0) 3 9837 4200
Fax: +61 (0) 3 9874 5672
Email: support@sge.com

CHINA
SGE Shanghai Representative Office
Tel: +86 21 6407 9382
Fax: +86 21 6407 9386
Email: china@sge.com

MIDDLE EAST
SGE Gulf
Tel: +971 6 557 3341
Fax: +971 6 557 3541
Email: gulfsupport@sge.com

EUROPE
SGE Europe Ltd
European Head Office
Toll Free: 00800 2790 8999
Toll Free Fax: 00800 2626 2609
Tel: +44 1908 568 844
Fax: +44 1908 566 790
Tel France: +33 1 69 29 80 90
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Email: europe@sge.com

INDIA
SGE Laboratory Accessories Pvt Ltd
Tel: +91 22 24715896
Fax: +91 22 24716592
Email: sgeindia@vsnl.com

JAPAN
SGE Japan Inc
Tel: +81 45 222 2885
Fax: +81 45 222 2887
Email: japan@sge.com

UNITED STATES OF AMERICA
SGE Incorporated
Toll Free: (800) 945 6154
Tel: +1 512 837 7190
Fax: +1 512 836 9159
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