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NON-EXTRACTABLE STATIONARY PHASES FOR GAS CHROMATOGRAPHY CROSS-LINKED BY EXPOSURE TO LOW-TEMPERATURE PLASMAS

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SUMMARY

Non-polar and medium-polarity stationary phases, such as SE-30, SE-52 and SE-54, can be completely cross-linked by exposure to low-temperature plasmas. Plasma-exposed polymers on glass coverslips resist solvent dissolution and were judged fully cross-linked. SE-30 coated on glass beads was also rendered insoluble by plasma treatment. Columns packed with treated beads show no reduction in chromatographic performance. A simple method for generating plasmas within evacuated capillaries is presented. Tests made with *in situ* cross-linked capillary columns demonstrate plasma exposure does not affect retention characteristics. The advantages of plasmas are described, and additional applications are proposed.

INTRODUCTION

In recent years, chromatographers have cross-linked polymer stationary phases to improve the performance of capillary gas chromatography (GC) columns. Only a few cross-linkages on each polymer chain are required to greatly increase the average molecular weight and render the material insoluble, thus giving rise to the term "non-extractable phase".

For capillary GC applications, cross-linked stationary phases provide several benefits[1]. First, these phases withstand large solvent injections. A second benefit is the freedom to wash columns with solvent to remove non-volatile sample components. Resistance to dissolution has also facilitated the development of capillary supercritical fluid chromatography and open-tubular liquid chromatography with partition retention mechanisms. A third feature of cross-linking is enhanced film stability. This is particularly important for polar polysiloxane phases, which are often subject to film disruption at elevated temperatures due to reductions in phases viscosity[2].

A variety of cross-linking techniques have been reported in the chromatographic literature. Siloxane polymers have received the most attention, though other phase classes have also been cross-linked. Two distinctly different types of cross-linking may be considered: with linkages formed either through the linear backbone of the polymer or through substituent groups.

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Polysiloxane stationary phases are usually linear. *In situ* concatenation of a partially polymerized siloxane results in highly stable coatings[3]. Blomberg *et al.*[4] prepared cross-linked phases by adding tri- or tetrafunctional silanes during the polymerization step to form cross-linked phases. Both approaches invariably suffered from increased stationary phase activity due to the presence of uncapped functional sites.

The application of free radical induced cross-linking to GC stationary phases[1] was a major improvement over earlier techniques. This approach, directly adapted from basic silicone chemistry developed in the fifties, creates cross-linkages through substituent groups, leaving the polymer backbone intact. Because polymers that are not based on the siloxanes can have these same substituents, free radical cross-linking has been applied to a broad range of stationary phases including polyethylene glycols[5]. In addition, this method can be performed *in situ* after the phase has been deposited on the column wall.

Several different initiators have been successfully used to stimulate the cross-linking chain reaction. Initial experiments were with organic peroxides; however, active by-products were incorporated into the stationary phase layer. Another drawback involved the elevated temperatures required to cause free radical formation. When heated, those phases exhibiting only marginal physical stability may coalesce into droplets, thus drastically reducing column efficiency. Azo compounds seem to be preferred over peroxides due to their lower decomposition temperatures and relatively clean decomposition products[6]. Ozone has also been shown to cause *in situ* cross-linking of certain phases at room temperature[7].

With each of these chemical cross-linking agents, the incorporation of residual groups into the polymer structure can cause residual activity. A second drawback is that chemical initiators, except for ozone which reacts spontaneously at room temperature, must be heated before cross-linking occurs. Even though the temperatures used to stimulate cross-linking are usually well below those encountered during separations, it may be preferable to avoid heating some polar phases before their mechanical stability has been augmented by cross-linking.

Forming free radicals directly in the stationary phase by irradiation with gamma rays has also been reported[8], but columns prepared in this manner still exhibit undesirable adsorption of polar solutes. Other problems with irradiative cross-linking include damage to the outer polyimide coating and the general inaccessibility of irradiation facilities.

Cross-linking procedures can be judged on the following criteria: (1) cross-linking should not degrade column performance as measured by selectivity and efficiency; (2) adsorptive activity should not be increased by the cross-linking procedure; and (3) cross-linking procedures should be applicable across a broad spectrum of stationary phases. At present, the phases that can be cross-linked are somewhat limited. Commercial high-polarity polysiloxanes remain resistant to existing procedures. Although part of this problem is the unavailability of highly polar gum phases, the presence of functional groups certainly affects cross-linking[9,10].

In this work, a new agent for initiating cross-linking in GC stationary phases is described: the low-temperature plasma. The ability of low-temperature plasma to cross-link polymers is well documented[11]. Low-temperature plasmas are produced when a low-pressure gas (generally *ca.* 100 Pa) is excited by strong electric fields. The electrons in such plasmas are not in thermal equilibrium with the molecular and atomic species, with the gas temperature typically one or two orders of magnitude less than the electron temperature[12]. Energetic electrons can thus stimulate chemical reactions by transferring energy to gas molecules and forming ions, free radicals, metastable species, and atoms while the gas remains near ambient temperature. These active species then react with polymers in their vicinity.

For chromatographic purposes, plasma cross-linking presents several potential advantages. First, low-temperature plasmas are generated in a controlled, low-pressure atmosphere, therefore contamination from extraneous species should be minimal. Next, noble gases, the most common sustaining medium, are unlikely to become chemically attached to the polymer. The reactive noble-gas species serve only to initiate the free radical cross-linking chain reactions. Since the same noble gas atom can be repeatedly energized in the plasma, free radicals are created as long as external energy is supplied. Also, values for gas pressure, composition, plasma excitation energy, and exposure time can all be optimized, if necessary, for each stationary phase. Finally, plasma cross-linking should permit external energy to be selectively coupled to the gaseous plasma species, thus avoiding indiscriminate heating throughout the entire column.

The chromatographic applications of plasmas are by no means limited to cross-linking. At least three brief reports have described plasmas being used to prepare chromatographic columns. Masada *et al.*[13] not only showed scanning electron micrographs of glass capillaries etched with plasmas of organo-fluorine compounds, but also claimed to have plasma-polymerized dimethyldichlorosilane on the column wall, though no chromatograms were produced. Such films are probably inferior to conventional polysiloxanes for separating organic solutes, as studies of plasma-polymerized siloxane monomers have shown the resulting polymers to exhibit a marked inorganic character[14]. Two other groups[15,16] have treated column packing materials with plasmas to improve performance.

A preliminary demonstration of stationary-phase cross-linking by means of exposure to a low temperature plasma is reported here. Several other novel uses of plasmas will also be discussed as they apply to fused-silica capillary columns.

EXPERIMENTAL

The effectiveness of low-temperature plasmas for cross-linking GC stationary phases was initially evaluated using glass microscope coverslips coated with a thin film of stationary phase. The coverslips were first cleaned in a boiling solution of dilute hydrochloric acid. After thorough washing with deionized water, the plates were dried in air overnight at 110°C. Stationary phase was applied to tared microscope coverslips as a dilute solution that was allowed to dry. The amount of phase deposited was determined gravimetrically. This system resembles the thin film of stationary-phase polymer on the walls of a capillary GC column, though the layer was appreciably thicker.

Coverslips coated with polydimethylsiloxane (SE-30, GC grade, Alltech Assoc., Deerfield, IL, U.S.A.) were placed in a low-temperature argon plasma (PDC-23G Plasma Cleaner, Harrick Scientific, Ossining, NY, U.S.A.). Exposure times and argon pressures were varied systematically. Immediately following exposure, the coverslips were reweighed to determine if the plasma had removed any polymer. The extent of cross-linking was taken to be the fraction of the original polymer weight remaining after a 1-h immersion in a gently rocked bath of dichloromethane.

Tests were carried out at 130 Pa of argon to determine if other stationary phases (Alltech) could be cross-linked. A series of polysiloxanes consisting of SE-30 (100% methyl), SE-52 (5% phenyl), OV-61 (33% phenyl), OV-17 (50% phenyl), and OV-25 (75% phenyl) were exposed to plasmas. SE-54 (1% vinyl, 5% phenyl) was also tested.

Next, a stationary phase coated on diatomaceous earth was cross-linked. Gas-Chrom P, 80–100 mesh, coated with 10% polydimethylsiloxane (OV-101, Applied Science Labs., State College, PA, U.S.A.) was placed in a shallow boat and exposed to a 130-Pa argon plasma within the generator chamber. After each successive 1-min interval, the material was thoroughly stirred and a small portion removed for gravimetric evaluation of cross-linking following a 1-h solvent extraction with dichloromethane. A sample exposed for a total of 1 h was then evaluated chromatographically in a well-packed, 1.85 m × 0.216 cm stainless-steel column. Retention and efficiency for the plasma exposed material were compared with an identical column packed with unexposed material.

Based on the results with conventional packing material, similar tests were performed with coated glass beads (*ca.* 0.10–0.11 mm diameter, Sargent-Welch, Springfield, NJ, U.S.A.). These beads supported a loading of 0.5 w/w% SE-30. Assuming uniform coverage, this corresponds to a coating thickness of 0.2 μm. Plasma exposure with 130 Pa of argon consisted of two 5-min periods separated by stirring. Again, the same column tubing was used to compare the performance of untreated and plasma-treated glass beads, based on retention and efficiency measured under identical conditions. Following these tests, the plasma-exposed beads were removed from the column, extracted in dichloromethane for 1 h with stirring, and repacked to form the third column. This column was used to evaluate the effect of extraction on chromatographic performance.

Polysiloxane-phase capillary columns were prepared following the basic procedure of Woolley *et al.*[17]. Column lengths were generally 4–6 m with an I.D. of 250 μm. Untreated fused silica was obtained from Polymicro Technologies (Phoenix, AZ, U.S.A.). Capillaries were purged with helium for 2 h at 250°C before use. Columns to be coated with SE-30 were deactivated with polymethylhydrosilane (Petrarch Systems, Bristol, PA, U.S.A.) before coating. An OV-215 column was first deactivated with mixed cyclics of trifluoropropylmethylsiloxanes (Petrarch) at 420°C based on the procedure of Blomberg *et al.*[18]. A column coated with SuperOx 0.1 (Alltech) was not deactivated. Columns were statically coated with a 0.4 w/v% (0.6 w/v% for OV-215) solution of the stationary phase dissolved in an appropriate solvent. After coating, columns were briefly conditioned before testing.

The ends of coated capillary columns which were to be cross-linked were first sealed into 0.636 cm O.D. glass tubing. The glass tubing was then connected by means of a simple vacuum fitting to a vacuum system with a liquid-nitrogen trapped diffusion pump capable of pressures less than 10^{-6} Pa. Before evacuation, columns were purged extensively with argon (minimum purity 99.998%, MG Industries, Valley Forge, PA, U.S.A.). Due to the inherently high flow impedance of capillaries, pumping times on the order of 1–2 h were used for these columns. Following evacuation, the columns were gently back-filled with the desired pressure of argon (130 Pa) as measured at the column head by a thermocouple pressure gauge. Columns were then sealed by melting the glass tubing. Sealing in this manner provides a low-pressure reservoir at the column end.

Several *in situ* methods of producing plasmas in capillary columns were explored. An ordinary Tesla-coil leak detector (Fisher Scientific, Pittsburgh, PA, U.S.A.) generates a glow discharge in low-pressure glass chambers by delivering an electrical arc of 50 kV and *ca.* 0.5 MHz. Several "electrodeless" systems were surveyed for suitability. In these cases, the column was first removed from its metal cage. Microwave (Little Litton, Model 1146, Litton Systems, Minneapolis, MN, U.S.A.), radiofrequency (Rf generator from a Low Temperature Dry Asher, Tracerlab, Richmond, CA, U.S.A.), and audio-frequency (Leco Induction Furnace No. 537, Laboratory Equipment, Saint Joseph, MI, U.S.A.) electrical fields were applied to the low-pressure argon within columns. In the case of radio frequency excitation at 13.56 MHz, both capacitive and inductive coupling were examined. Finally, attempts were made to strike a plasma by means of a 7500-V neon sign transformer connected to tungsten electrodes sealed into the column ends.

The ability to cross-link stationary phases for chromatographic separations was assessed for both packed and capillary columns. Chromatographic evaluation was done using a Varian VISTA 4600 GC (Varian Instruments, Walnut Creek, CA, U.S.A.) equipped with an on-column injector for packed columns and a split injector for capillaries. Detection was by flame ionization detector. Volumetric flow-rates through the packed columns were maintained at 10 ml/min (t_0 = 16 s), as measured by a soap bubble flowmeter, and were not optimized. Linear flow-rates of helium carrier gas through the capillary columns were between 20 and 30 cm/s and were not optimized. When comparing columns before and after plasma treatment, the flow-rate was kept constant. All columns were evaluated based on efficiency and retention. Capillaries were also assessed by the selectivity and activity shown for a mixture of polar solutes separated at 100°C based on the method of Grob[19]. Column activity refers to undesirable secondary retention mechanisms that cause polar compounds to elute as skewed peaks and can also negatively affect minimum detection limits. Column performance parameters were measured from the statistical moments of solutes separated isothermally at 100°C.

Chromatograms were digitally recorded using a CHROM-1 A-to-D board (Metrabyte, Taunton, MA, U.S.A.) operating within a PC's Limited 286 microcomputer (PC's Limited, Austin, TX, U.S.A.). The software controlling the data acquisition was LABTECH NOTEBOOK (Laboratory Technologies Corporation, Wilmington, MA, U.S.A.). For packed column separations, the sample size was *ca.* 500 ng. For capillary work, detector sensitivity was set so less than 1 ng of an alkane produced a full-scale response ($8 \cdot 10^{-12}$ A.f.s.). Detector output was captured at 10 points-per-second with a height resolution of *ca.* 2000 points for a full-scale response. Moment analysis of the digital data was accomplished with software written in Pascal (Borland International, Scotts Valley, CA, U.S.A.).

Chromatographic evaluation of capillaries was done both before and after *in situ* plasma exposure. A third evaluation was performed after the column had been rinsed with *ca.* 10–20 column volumes of dichloromethane [or ethyl acetate–diethyl ether (1:4) in the case of OV-215]. As with the packed columns, the extent of cross-linking in a capillary column was considered to be the adjusted retention time of an alkane (dodecane for SE-30, pentadecane for OV-215 and SuperOx 0.1) on an extracted column divided by the retention of that compound on the same column prior to extraction.

RESULTS AND DISCUSSION

In Fig. 1, the average fraction of stationary phase remaining on its coverslip after extraction is plotted *versus* time of plasma exposure for three different argon pressures. After 3-min exposure at any of the three pressures, the polymer is insoluble and is considered to be completely cross-linked. Except for a small number of cov-

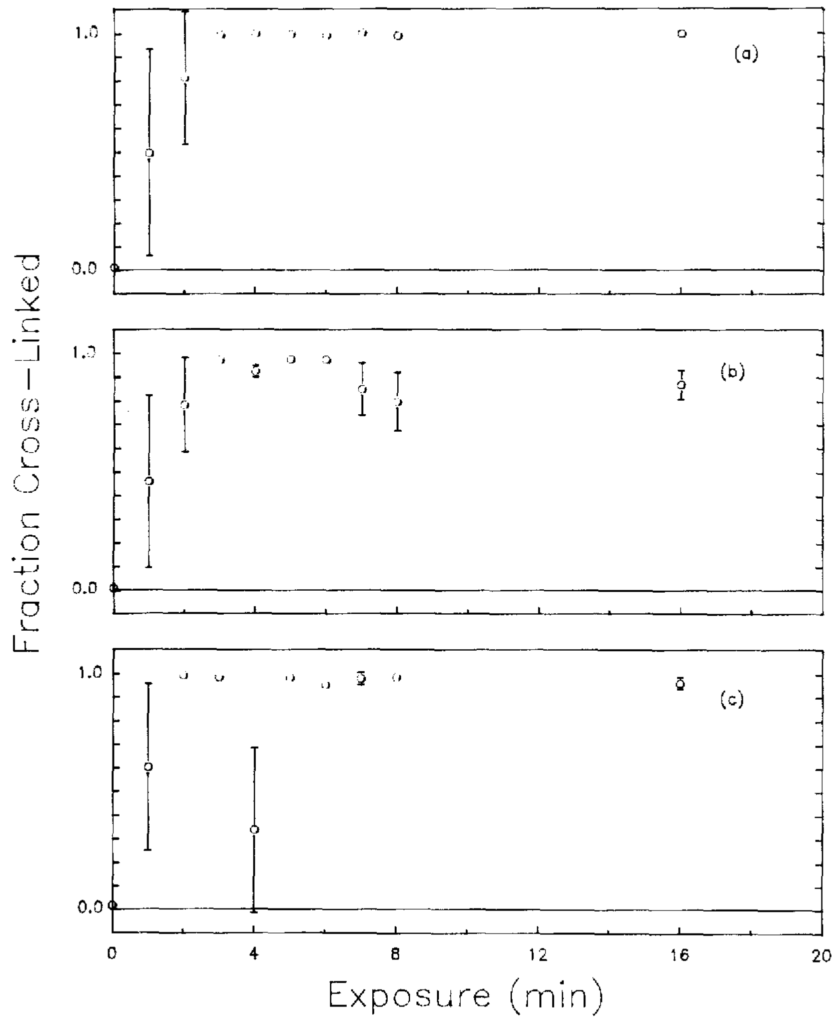

Fig. 1. Plot of polymer fraction cross-linked (mean ± S.D., $n = 3$) *vs.* plasma exposure time at three different pressures for SE-30 deposited on coverslips. Phase loss determined gravimetrically after 1-h agitation in dichloromethane. (a) 13-Pa Ar; (b) 130-Pa Ar; (c) 670-Pa Ar.

erslips, well over 95% of the polymer remained on the coverslip, even after extensive extraction. In a few cases, pieces of highly cross-linked material were dislodged from the glass and were noted in the extraction vessel. These plots confirm that a polysiloxane stationary phase can be converted into a non-extractable form by relatively brief exposure to a low-temperature plasma. These data also indicate plasma pressure only marginally affects the cross-linking process.

Considerable differences were observed between the stationary phases tested. In general, the degree of cross-linking decreases with increasing phenyl substitution. SE-30, SE-52, and SE-54 all show complete cross-linking after 240 s of plasma exposure (more than 98% of the phase resisted extraction). The more polar polysiloxanes remain partially soluble even after 16-min contact, but display evidence of some cross-linking. A 16-min treatment resulted in 20% cross-linking for OV-61 and *ca.* 10% for OV-17 and OV-25. All phases tested could be quantitatively extracted if not subjected to plasma exposure.

Phenyl substitution has been reported to hinder chemically induced cross-linking[9,10]. A similar trend shown by plasma cross-linking is consistent with the hypothesis that free radicals formed in the plasma initiate stationary-phase cross-linking. In these experiments, other factors, such as polymer chain length, polymer purity, and surface wettability, are likely to contribute to the observed differences in cross-linking for different phases and may obscure important distinctions between the two techniques. Further investigations are required to adequately determine the range of stationary phases that plasmas can cross-link.

Both packed and capillary chromatographic columns were prepared with plasma cross-linked stationary phases to determine if the plasma corrupts the inert nature of the phase. The two different geometries presented different obstacles for successful plasma treatment. Diatomaceous earth column packings were subjected to plasma exposure in the same chamber as the coverslips to allow similar treatment conditions. One concern was that the plasma would not penetrate the material evenly. Fig. 2

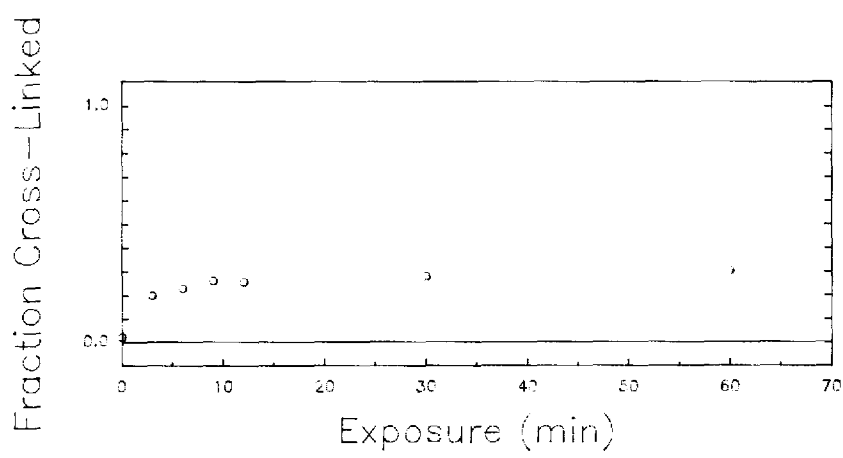

Fig. 2. Plot of polymer fraction cross-linked *vs.* plasma exposure time at 130-Pa Ar for 10% OV-101 on Gas-Chrom P, 80–100 mesh. Material was thoroughly stirred after each exposure interval. Phase loss determined after 1-h agitation by weighing polymer extracted in 10 ml of dichloromethane.

shows the fraction of stationary phase remaining on extracted packing material as a function of exposure time. The weight of polymer phase isolated from the extraction solvent and the weight loss measured for the packing material were equivalent in all cases.

After exposure for 360 s, the material was 23% cross-linked. This value did not increase significantly even after repeated extended exposures interspersed with mixing. From these data, it was concluded reactive plasma components penetrate the interparticulate spaces. If penetration had not occurred, the fraction cross-linked should increase markedly at each exposure interval after the material was thoroughly stirred, presumably exposing particles coated with virgin polymer. However, though the plasma apparently penetrates between particles, the phase was not completely cross-linked even after prolonged treatment. The porous nature of diatomaceous earth supports is suspected as the cause of this failure. These pores form highly tortuous paths which reactive plasma species do not seem to penetrate, and thus a fraction of polymer that remains soluble is shielded from the plasma.

Both the cross-linked and non-cross-linked columns displayed similar performance for separating alkanes. At 100°C, the control column generated 2400 effective plates for decane at $k' = 22.5$. Under identical conditions, a column packed with plasma-treated material produced 2200 effective plates at $k' = 22.2$. Sample retention is unchanged, confirming that the plasma does not significantly alter solute solubility. Because of the large amount of surface activity present on the packing material, polar solutes eluted with distorted peak shapes on both columns.

The inability to completely cross-link the stationary phase on ordinary packings prompted experiments with glass beads. With no internal pores available, the stationary phase is confined to the surface. Low liquid phase loadings and reduced surface area allow the film thickness of capillary columns to be approximated. A third advantage of glass bead solid supports is their mechanical strength. Unlike Gas-Chrom P, coated beads can be removed from the column, extracted with solvent, and repacked without damage. This property allows the fraction of polymer cross-linked to be assessed chromatographically as well as gravimetrically.

Coated glass beads proved more amenable to cross-linking than diatomaceous earth, but still less than expected from the coverslip experiments. After two 300-s exposures at 130 Pa, samples were 60% cross-linked based on gravimetric analysis of the extracted phase. As shown in Table I, column performance was virtually unaffected by plasma treatment.

From the measured decrease in chromatographic retention following extraction, 55% of the phase withstood extraction, in agreement with the gravimetric measurement. This value, though higher than for the diatomaceous earth support, was significantly below the fraction cross-linked during the coverslip studies. This loss may arise from abrasive action during the stirred extraction removing fully cross-linked polymer from the exposed bead surface. Phase pooling at contact points between glass beads is well documented[20] and may also account for incomplete cross-linking of SE-30 on glass beads.

Several schemes designed to strike a plasma in a capillary were tried using low-pressure argon in various diameter tubing. Experiments were first performed with 4-mm I.D. glass tubing, then the bore was reduced to 1 mm. The next step was to attempt striking a plasma in a 250-μm capillary. In every case, decreasing the volume

TABLE I

CHARACTERISTICS OF PACKED COLUMNS TREATED WITH PLASMAS

Column dimensions, 1.85 m × 0.216 cm I.D.; 0.10–0.11 mm glass beads. Height equivalent to an effective plate (HEEP) and capacity ratio for dodecane at 100°C.

Glass-bead column No.	*Stationary phase and treatment*	*Capacity ratio*	*HEEP (mm)*
1	0.5% (w/v) SE-30, no treatment	20.3	0.85
2	0.5% (w/v) SE-30, 2 × 5 min 130-Pa Ar plasma	19.6	0.95
3	Beads from column 2, extracted 60 min	11.1	0.72

to surface area ratio made it progressively more difficult to generate and sustain the plasma.

The neon-sign transformer successfully lit only the larger glass tubes and contamination was observed from the internal electrodes. The discharge tubes quickly became hot. The induction furnace easily ignited plasmas at 20 kHz in the glass tubing without significant warming over a 1-h excitation. Capillaries resisted plasma excitation. Brief flashes occurred only when a short section of column was held near the induction coil. Radio frequency excitation was applied with two reactor designs. Using a capacitive reactor as described by Masada *et al.*[13], no plasmas could be ignited in capillaries after repeated attempts. An induction-coil reactor sustained a plasma in the glass tubes, but not in a capillary. Heating was more pronounced with this system than with the 20-kHz furnace. Microwave excitation sustained plasmas only in the glass tubing and the tubes rapidly became too hot to touch.

Of the plasma generation methods tested to date, the Tesla coil provides the most reliable plasma generation. Energy can be coupled from the coil to the capillary using two approaches. In the first, a column containing argon at 130 Pa is unwrapped from it metal cage. A column section is held centered in a 2-cm I.D. glass tube wrapped with ten turns of bare copper wire. By touching the wire with the Tesla coil, a plasma is ignited over a 20-cm length within the straight capillary. This discharge is quite bright. By pulling the column through the outer tube at *ca.* 20 cm/s, the entire column is briefly exposed to the plasma. Columns cross-linked by this process displayed poor chromatographic performance although they were completely resistant to solvent extraction. The intense plasma appears to damage the polymeric stationary phase.

The second Tesla coil excitation method is even simpler and produces a less vigorous plasma over the entire column. The coil is brought close to a metal cage holding a column containing argon at 130 Pa. As the tip approaches the cage, a faint discharge is visible throughout the entire column. This discharge flickers somewhat and appears a pale greenish orange when viewed through the outer polyimide layer.

The small cross-sectional area of capillaries, coupled with their extreme length, leads to slow evacuation. When an entire column is simultaneously excited, plasma inhomogeneities due to atmospheric contamination are easily observed as color variations across the column length. To minimize contamination by air, capillaries were extensively purged with argon prior to evacuation. Severe pressure gradients cause dramatic changes in plasma intensity over the column length. Data from coverslip experiments indicate pressure gradients within a more moderate range should not interfere with *in situ* cross-linking of capillary columns. Successful cross-linking of a polydimethylsiloxane stationary phase within a capillary column is illustrated in Table II. Utilization of theoretical efficiency (U.T.E.) is reported relative to an ideal column of the same diameter providing identical solute retention at optimal flow velocity. The U.T.E. values reported here are conservative. Both detector and injector volume contribute slightly to band broadening as evidenced by a 5–10% increase in U.T.E. for 10-m columns. Using statistical moments to calculate column performance is more sensitive to instrumental distortions than traditional measures of peak-width at half-height. The ability to measure U.T.E. values consistently between 80 and 90% [height equivalent to an effective plate (HEEP) = 0.31 mm at capacity ratio = 7.5] for untreated SE-30 capillaries confirms proper system operation.

Capillary column 1 is an untreated control. The dramatic loss in retention following extraction confirms the phase is largely soluble. A second solvent wash of 10 ml removed an additional 3% of the original phase. The decrease in U.T.E. upon extraction is largely due to the decrease in retention. At greatly reduced capacity ratios, ordinarily minimal bandbroadening contributions from dead volume, injection plug width, and detector time constant significantly degrade the relative efficiency for weakly retained solutes on short capillaries. (Similar U.T.E. values were measured for decane prior to extraction, where decane eluted with the same capacity ratio as dodecane following extraction.)

TABLE II
CHARACTERISTICS OF CAPILLARY COLUMNS TREATED WITH PLASMAS

Column dimensions, *ca.* 5 m × 0.25 mm I.D. Utilization of theoretical efficiency (U.T.E.) measured for dodecane on columns 1 and 2. Pentadecane used for columns 3 and 4. (a) Before plasma treatment; (b) after plasma treatment; (c) after solvent extraction.

Capillary column No.		*Stationary phase*	*U.T.E. (%)*	*Fraction cross-linked (%)*
1	a	0.4% (w/v) SE-30	82	–
	c		39	23
2[a]	a	0.4% (w/v) SE-30	87 ± 4	–
	b		37 ± 3	–
	c		40 ± 1	96 ± 3
3	a	0.6% (w/v) OV-215	72	–
	b		67	–
	c		31	36
4	a	0.4% (w/v) SuperOx 0.1	68	–
	b		38	–
	c		32	12

[a] Average of three columns ± S.D.

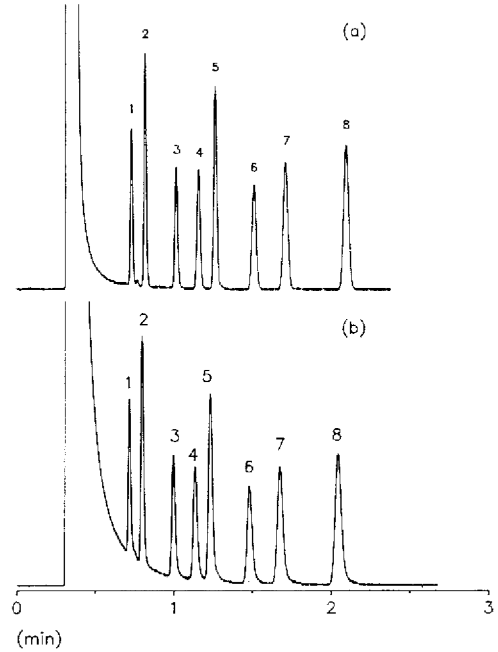

Fig. 3. Typical gas chromatogram of a test mixture at 100°C for capillary column 2. Peaks: 1 = 2-octanone; 2 = decane; 3 = octanol; 4 = dimethylphenol; 5 = undecane; 6 = dimethylaniline; 7 = naphthalene; 8 = dodecane. (a) Before plasma exposure, column length = 5.2 m; (b) after 4-s plasma exposure at 130-Pa Ar and extensive extraction, column length = 4.7 m.

The data for capillary column 2 are averages from three columns. Solute retention diminished only slightly after cross-linking. This minor reduction probably arose from conditioning before testing rather than the plasma itself. Solute retention was completely maintained after solvent extraction. A second solvent wash of 10 ml did not measurably alter retention. These data confirm such columns are effectively cross-linked.

Unfortunately, the present plasma generation method markedly reduces column efficiency. As shown in chromatogram b of Fig. 3, the test solute peaks all tail appreciably, with pronounced tailing in the solvent peak. The second statistical moment, used here to measure column efficiency, is highly sensitive to tailing peaks. This sensitivity is reflected in the low U.T.E. values for the cross-linked capillaries.

Interestingly, alkanes tail to the same extent as polar solutes. Plasma exposure does not change the peak areas for polar compounds relative to the alkanes. For properly deactivated columns, even the highly polar test solutes described by Lee *et al.*[17] elute with the proper peak area relative to the alkanes. Furthermore, peak shape does not change significantly when the sample size is increased by a factor of ten to 10 ng per compound on column. These observations are inconsistent with the usual cause of tailing, exposed active sites.

If present, active sites affect polar solutes much more than alkanes, therefore we suggest the loss in efficiency is not due to chemical changes in the polymer, but to physical disruption of the stationary phase during plasma generation. Normally, low-temperature plasmas do not disturb delicate structures. Inductively generated plasmas did not diminish column efficiency when either column packing or glass beads were treated. Even exposure times well in excess of those needed for cross-linking showed no deleterious effects on packed columns. The present method of exciting plasmas in capillaries, however, involves coupling an energetic electrical arc from a Tesla coil through the column to the plasma. Multiple tiny arcs, where the metal cage contacts the column, penetrate the fused-silica tubing and the thin polymer layer before reaching the plasma in the column interior. It is suspected that the inner film is damaged only at these localized areas.

Capillary column 3, coated with a trifluoropropyl-substituted polysiloxane, was partially cross-linked *in situ*. Unlike the polydimethylsiloxane column, plasma exposure by itself did not greatly affect column efficiency. Extraction with the coating solvent removed 64% of the phase. Tests with the extracted column show reduced efficiency, although the peak shape remained symmetrical in this instance. The reasons why OV-215 behaved differently than SE-30 are not clear.

The polyethylene glycol phase, SuperOx 0.1 (capillary column 4), exhibited the least propensity for cross-linking. Chemically induced cross-linking at elevated temperatures has been effective for these polymers[5]. The problem with plasma induced cross-linking of SuperOx is suspected to be the polymer's physical state. At room temperature, this phase is a solid. Methylene radicals created on the polymer chain may not exist long enough to come into proximity with an adjacent chain. At the cross-linking temperature, all of the other phases tested in this work were either liquids or gums where molecular motion is greater than in the solid state. Other factors may also contribute to the failure with SuperOx.

Efforts are being made to cross-link columns without reducing their efficiency. High-frequency electromagnetic fields are commonly used to create plasmas. Matsuzawa and Yasuda[21] described a capacitively-coupled plasma polymerization apparatus for coating the inside of plastic tubing as small as 1.5-mm I.D. A slightly modified version of their device has been constructed and initial trials on 0.25-mm I.D. fused-silica capillaries have been promising.

In addition to initiating cross-linking in capillaries, low-temperature plasmas may be uniquely applicable for other column preparation steps. Oxidizing plasmas produced within glow discharges have long been used for cleaning glass and other surfaces[22]. Similar treatments should be equally useful for fused-silica capillaries. The principal advantage over aqueous and non-aqueous cleaning solutions is the reduced opportunity for contamination by trace impurities.

In the past, the surface of glass capillaries was often chemically roughened to improve the wettability of polar stationary phases. Most of these techniques are not applicable to fused silica. The introduction of organo-fluorine compounds into a plasma forms reactive fluorine species which etch fused silica[23]. Although roughening invariably increases surface activity, there may be applications where etched surfaces are desirable. It may be possible to create highly deactivated, fused-silica surfaces which remain wettable for polar films by plasma deposition of appropriate materials. The doping of plasmas with certain polar compounds may also greatly increase the polarity of previously coated stationary phases. As these films are already mechanically stable due to cross-linking, the *in situ* addition of polar moieties should not disrupt the film's structure. In this manner it is may be feasible to prepare highly polar phases which normally could not be coated on low-energy, deactivated surfaces. The enhanced retention of polar compounds relative to the alkanes has already been observed when air inadvertently contaminated the plasma during cross-linking. A final possibility is the preparation of porous-layer open-tubular (PLOT) columns through plasma deposition of aluminum oxide or other adsorbent layers. Plasma deposition of these materials at low temperatures has been reported within the semiconductor industry[24].

At this early stage, capillary plasma applications other than cross-linking are speculative extrapolations based on existing processes. These potential uses do serve, however, to illustrate the broad utility of low-temperature plasmas. Investigations into these areas are being conducted.

CONCLUSIONS

Low-temperature plasmas cause cross-linking of GC stationary phases in a variety of geometries. Exposing the stationary phase to plasmas in a large chamber does not seem to affect chromatographic performance. Plasmas can also be generated within coated capillary columns with relatively simple equipment. These columns exhibit cross-linked behavior, but show diminished efficiency. Chromatographic tests reveal no gross chemical transformations have occurred to alter retention patterns. It is suggested that the polymer layer is physically disrupted by the discharge as it passes through the capillary wall. A suitable method of generating plasmas without disturbing the interior coating is essential for further developments.

The fundamental properties of low-temperature plasmas make them attractive for a variety of column fabrication steps. Many of the potential applications, including cleaning, deactivation, chemical modification, and material deposition, are predicated on the widespread use of such plasmas in a variety of technological areas.

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