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GLASS SURFACE ANALYTICAL STUDIES IN THE PREPARATION OF OPEN TUBULAR COLUMNS FOR GAS CHROMATOGRAPHY

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SUMMARY

Modern surface analytical techniques, Auger electron spectroscopy and X-ray photoelectron spectroscopy, have been used to study the chemical compositions of glass surfaces which have been treated according to various procedures used in the preparation of glass capillary columns. Auger electron spectroscopy was found to be particularly valuable because the electron beam could be focused on the interior wall of the capillary column.

It was found that leaching Pyrex glass with 20% HCl solution at 110°C for 48 h produced a nearly pure silica surface which retained its integrity after heat treatments at 400°C. Leaching of soft glass was not complete.

Chromatographic performance evaluations showed that Pyrex columns that were leached with aqueous acid solutions and subsequently silylated at 400°C were extremely well deactivated and produced excellent non-polar phase columns.

INTRODUCTION

Even with the many successes of capillary column gas chromatography, many workers are still reluctant to take full advantage of the technique. This may be attributed in part to the discrepancies, irreproducibilities, and disappointments in column preparation which are often experienced. In fact, column preparation has often been accused of being a poorly understood art rather than a science. Improvements in column technology have most often been empirical and developed mainly by trial and error. Certainly, an understanding of the chemical composition of the surface would be an important factor in the preparation and chromatographic performance of capillary columns. Until recently, surface compositions were only inferred from indirect evidences and were not directly obtainable. Fortunately, however, sophisticated surface analytical instrumentation utilizing electron spectroscopy [*e.g.* Auger

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electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS or ESCA)] and ion spectroscopy [*e.g.* secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS)] have been developed in the last few years, which permit analysis of the surface from the top monolayer into the bulk material.

In a recent report by Lee *et al.*¹ it was shown that AES is particularly valuable in the analysis of glass capillary columns because the electron beam can be focused on the interior wall of the column. It was reported that columns which were treated with HCl gas and washed with formic acid² exhibited better deactivation and a higher degree of inertness toward sensitive compounds than columns in which the "acid leaching" was omitted. Analysis showed that the formic acid removed most of the sodium and calcium from the glass surface.

In this paper the results of a comprehensive study of the chemistry occurring on the glass surface during column preparation is presented. Starting with the drawing procedure and continuing throughout the entire preparation sequence, the compositions of glass capillary column surfaces were examined by AES. Various leaching procedures were studied with particular emphasis being placed on the purity of the silica surface formed, the depth of the silica layer, and the stability of the silica layer towards back-diffusion of ions at elevated temperatures. When columns are properly acid-leached and further deactivated by high-temperature silylation, highly efficient, well deactivated, and thermally stable columns are obtained.

In addition to AES, ESCA was also employed to obtain complementary and more sensitive surface data. In addition to providing information about the chemical state of atoms on surfaces, it also provides a "softer" method of analysis since X-rays rather than high-intensity electrons are used to irradiate the sample. This is particularly important in the analysis of insulating materials such as glasses because the danger of damaging the surface or accidentally sputtering away the top monolayer is completely eliminated. The chemical composition of the glass as a function of depth (or distance from the surface) can be obtained by ion milling which gradually erodes away the upper surface layers and exposes new material for analysis. However, due to sample size requirements, glass slides instead of actual capillary columns were studied using ESCA techniques.

EXPERIMENTAL

Column preparation

Glass capillary columns were drawn from two types of glass; Kimble R6 Flint (soda-lime) (Kimble Glass Products, Toledo, OH, U.S.A.) and Corning 7740 Pyrex (Corning Glass Works, Corning, NY, U.S.A.). During the drawing process several columns were purged with pure dry oxygen.

Capillary columns were dynamically leached by forcing 20% HCl at *ca.* 110°C (the boiling point) through the column. This was done by placing the column in an oven such that both ends were extended to the outside. One end of the column was connected with heat-shrinkable PTFE tubing to a 50-ml reagent reservoir, while the other end was left free to allow purge liquids to drip into a collection vessel. Generally, long lengths (*i.e.* 90 m) of capillary were leached with 50 ml of acid for approximately 48 h. After all the acid solution had passed through the column, the oven was heated to 400°C and held for 12 h. After cooling to 110°C, an additional 50 ml of 20% HCl

were added to the reagent reservoir and the leaching procedure was repeated. After all of the acid had passed through the column, the reagent reservoir was rinsed and filled with deionized water which was then forced rapidly through the column to remove any acid residues. The column was dried and dehydrated by increasing the oven temperature to 150°C while continuing to purge the column with nitrogen for about 12 h. Static hydrochloric acid leaching was done according to the methods outlined by Grob *et al.*³⁻⁵.

Columns were dynamically silylated in the following manner: A column was broken into the desired finished length and placed in the oven so that both ends were extended outside the oven. One end was connected to a bubbler with heat-shrinkable PTFE. While the oven was heated to the appropriate temperature (usually 400°C), a few milliliters of the silylating reagent(s) were placed in the bubbler. Dry nitrogen was used to carry the silylation vapors through the column for a period of approximately 48 h. A 5:1 mixture of hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) (Applied Science Labs., State College, PA, U.S.A.)^{6,7} was generally used, while in some instances HMDS was used alone. For columns longer than 15 m, the bubbler was disconnected after 24 h and reconnected to the other end of the column and silylation continued for an additional 24 h. After silylation, the oven was cooled to 200°C, the bubbler removed, and dry nitrogen passed directly through the column for about 30 min to flush out any non-reacted silylation vapors. Static silylation was done according to the procedures outlined by Grob *et al.*^{4,8}.

Columns were coated statically with SE-52 as described by Bouche and Verzele⁹. To facilitate coating, pentane was used as the solvent¹⁰ and the column ends were sealed with Apiezon N. The stationary phase solution was of such concentration that a 0.25- μ m thick film was deposited. Fresh coating solutions were prepared weekly to avoid possible problems of stationary phase decomposition^{11,12}.

Gas chromatography

A Varian 1400 gas chromatograph was used with a home-built injection port and a modified flame-ionization detector (FID) inlet. Helium at a linear velocity of 50 cm/sec was used as the carrier gas. Injections were made at room temperature, and after elution of the solvent peak, the oven was temperature programmed at a pre-selected rate. In order to prevent saturation of column active sites and a resultant decrease in the sensitivity of column performance indicators (peak shape and efficiency), small quantities of various test compounds were injected. The sensitivity of the instrument was adjusted to give full-scale response for approximately 20 ng.

Glass slide preparation

Glass slides were made from Kimble EXAX soft glass and Corning 7740 Pyrex glass. The Pyrex slides were of the same bulk composition as were the Pyrex capillary columns, however, the soft glass slides were of a slightly different bulk composition (see Tables I and II). The slides were cut to a size suitable for ESCA analysis (*ca.* 1 cm²) and cleaned with deionized water.

The glass slides were leached in a 20% HCl solution by mounting in preleached fluorocarbon holders and placing in the boiling (*ca.* 110°C) leaching solution for various lengths of time. The volume of the acid in the reaction vessel (800 ml) was sufficiently large that a minimal increase in ion concentration occurred during leach-

ing. After removal from the acid bath, the slides were rinsed three times in deionized water and allowed to dry in room air.

The glass slides were heated in a muffle furnace at a temperature of $400 \pm 10^\circ\text{C}$ under a flowing inert gas atmosphere for various lengths of time.

Surface analysis

AES analyses of the inner capillary surfaces were accomplished with a Physical Electronics Industries Model 545 scanning Auger microprobe. The capillaries were cracked lengthwise to expose the inner surface, mounted on the sample carousel and evacuated in the instrument vacuum chamber. The inner bore of each capillary was located with the absorbed current image and the Auger beam focussed on the interior. The Auger beam was reduced to minimum beam current ($< 1 \text{ nA}$), slightly defocused with the electron gun objective lens, rastered over a $70 \times 70 \mu\text{m}$ area, and accelerated at 3 keV. The vacuum in the instrument during analysis was below $5 \cdot 10^{-8}$ torr.

The spectra were recorded on an x - y plotter and the peak heights manually measured. The observed peak heights were normalized (using relative sensitivity factors for the appropriate Auger lines) to relative atomic concentrations¹³. The total of the atomic concentrations was set to unity and the relative percentages of each element present were then calculated. A typical Auger spectrum obtained from the interior of a glass capillary column is shown in Fig. 1.

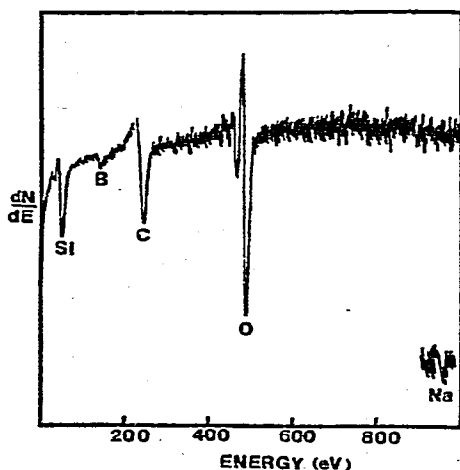


Fig. 1. A typical Auger electron spectrum of the interior surface of an untreated Pyrex glass capillary column.

Due to the geometry and small size of the glass capillary column samples, depth profiling by argon ion milling caused excessive charging and meaningful data were unobtainable.

XPS analyses of the glass slide surfaces were done using a Leybold-Heraeus LHS-10 XPS/AES/SIMS spectrometer with multichannel averaging. All samples were irradiated with magnesium K_{α} X-rays at 240 w power. Each analysis consisted of adding sixteen 1-min scans from 300 to 1300 eV with 4096 data points. The analyzer

was operated in a constant transmission mode with a lens retarding ratio of 3. Sputtering was done using a differentially pumped ion gun producing 3 keV argon ions at a beam current of approximately $3 \mu\text{A}$ rastered across a square $10 \times 10 \text{ mm}$. Depth compositional profiling obtained by ion milling was calibrated by direct measurements on the sample using a stylus measuring technique.

Peak heights for the most intense lines of each element observed were measured in arbitrary units from the recorder output. The peak height was measured as the peak maximum less the background level directly under the peak. This background level was determined by drawing a straight line between the signal levels on either side of the peak. The peak heights measured in this manner were then corrected for elemental sensitivities by dividing by the appropriate relative sensitivity factors. These factors were taken from the work of Berthou and Jorgensen^{14,15} for peak heights with magnesium K_{α} radiation. The value for boron was taken uncorrected from Wagner's data¹⁶ for aluminum K_{α} radiation. The elemental concentrations thus obtained for all elements observed were summed and the total normalized to unity. The percentage of each element was then calculated as a fraction of the total.

A typical XPS spectrum of a glass slide is shown in Fig. 2.

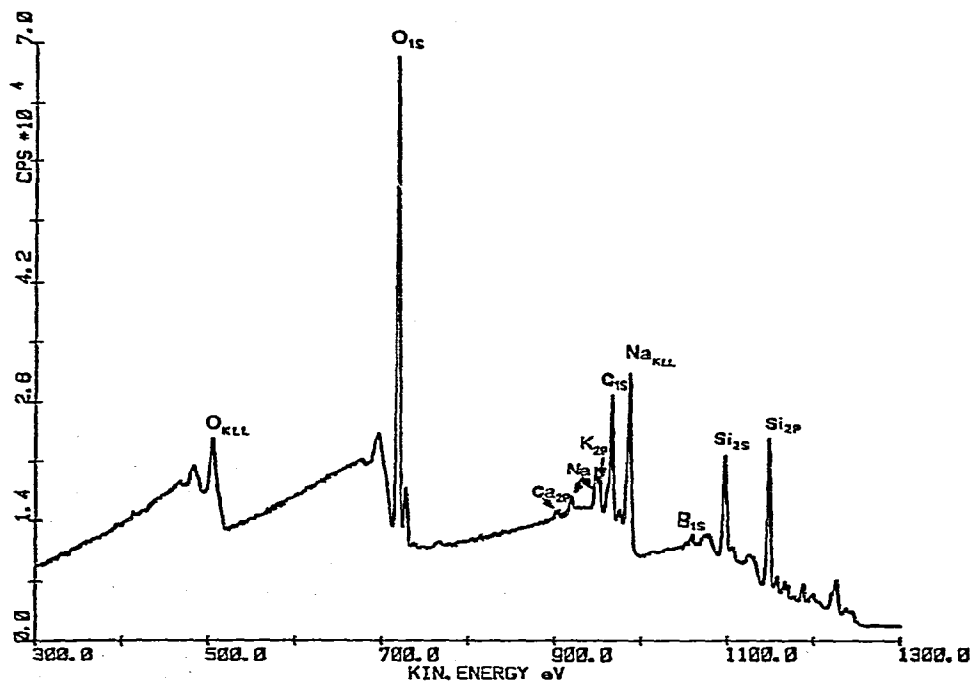


Fig. 2. A typical ESCA spectrum of an untreated soft glass slide.

RESULTS AND DISCUSSION

Glass surface composition

Through the use of modern surface analytical techniques it is now known that the composition of the glass surface is usually significantly different from the bulk

composition^{17,18}. In addition to bulk composition, factors such as environment, fabrication variables, and thermal history all affect the formation and stability of surface layers developed on glasses¹⁹.

The bulk compositions given by the manufacturers for the Pyrex and soft glasses used in the preparation of the capillary columns are given in Table I. The major differences between these two glasses is the higher boron content (present as B₂O₃) of the Pyrex and the higher alkali content (present as Na₂O and CaO) of the soft glass. It is these compositional characteristics that give Pyrex its distinctive acidic character and soft glass its basic character. Also shown in Table I are the surface compositions obtained by AES of untreated capillary columns that were drawn from these glasses. The surface composition of the Pyrex columns is very similar to the bulk composition, while the surface of the soft glass columns shows an enrichment of sodium and calcium.

TABLE I
COMPOSITION OF GLASS CAPILLARIES

Element	Kimble R6 Flint		Pyrex 7740	
	Bulk* (atomic %)	Surface** (atomic %)	Bulk* (atomic %)	Surface** (atomic %)
Si	23.4	11.4	25.5	24.0
O	59.4	57.8	64.0	69.0
Na	10.4	16.0	2.4	—
Ca	2.1	12.0	—	—
B	1.0	1.6	7.1	7.0
K	0.3	1.2	0.2	—
Mg	2.0	—	—	—
Ba	0.2	—	—	—
Al	1.2	—	0.8	—

* Calculated from the weight percent bulk oxide given by the manufacturer.

** Obtained from Auger electron spectroscopic analysis.

The bulk compositions of the Pyrex and soft glass slides used for ESCA analysis are shown in Table II. Although the composition of the soft glass slides is somewhat different from that of the glass used for the capillary columns, they are similar enough that comparisons can readily be made. Basically, the glass slides have slightly more calcium and slightly less aluminum and sodium than the capillary columns. Also included in Table II are the surface compositions obtained by ESCA for the untreated glass slides. As is immediately observable, ESCA analysis is more sensitive to trace element concentrations. For the Pyrex slides, the surface shows a slight enrichment of aluminum and potassium and a depletion of boron. The soft glass slides also show a slight enrichment of aluminum and sodium on the surface and a depletion of calcium.

Comparing the surface compositions of the untreated glass slides with those of the drawn capillaries (Tables I and II), it appears that the heat treatment involved in drawing the glass capillaries enriches the surface in boron for the Pyrex columns and in sodium and calcium for the soft glass columns. It is possible that at the high temperatures used in capillary drawing, some of the metal oxides (*e.g.* Na₂O, B₂O₃, etc.) are volatilized and then redeposited on the glass surface²⁰.

TABLE II
COMPOSITION OF GLASS SLIDES

Element	Kimble EXAX		Pyrex 7740	
	Bulk* (atomic %)	Surface** (atomic %)	Bulk* (atomic %)	Surface** (atomic %)
Si	25.5	18.0	25.5	26.0
O	60.7	67.6	64.0	65.5
Na	8.5	13.0	2.4	2.1
Ca	3.2	0.2	—	—
B	—	—	7.1	4.0
K	0.1	—	0.2	1.3
Mg	1.5	—	—	—
Al	0.5	1.2	0.8	1.1

* Calculated from the weight percent bulk oxide given by the manufacturer.

** Obtained from ESCA analysis.

Probably the most noticeable feature of the glass surface composition is the high concentration of carbon. In nearly every sample analyzed, concentrations of over 25% were observed. In Tables I and II the surface compositions were normalized without the carbon signal so that direct comparisons between the surface and bulk compositions could be made. To better understand the relative distributions of contaminant carbon with respect to other surface elemental concentrations, a homogeneity study was made in which a Pyrex column was sequentially broken into lengths of one meter each and analyzed. For the most part the elemental composition (excluding carbon) was constant (within the limits of the method). However, the carbon concentration varied from less than 15% to over 50% of the total surface composition. Since AES is sensitive to the top 2 or 3 monolayers, it is possible that in some instances a complete monolayer of carbon covered the glass surface. Essentially the same situation was observed with soft glass columns. The glass slides analyzed by ESCA also showed significant coverages of carbon. The binding energy of the carbon line observed at 285 eV indicates that the species is organic in nature and is not an inorganic carbonate. This erratic carbon contamination is probably responsible for many of the problems of irreproducibility observed in column preparation.

Columns which were purged with oxygen while being drawn and carefully handled afterwards showed remarkably less surface carbon. In a similar homogeneity study as previously described, the carbon concentration varied from less than 10% to actually no observable carbon. Samples which were exposed to laboratory air without having the ends sealed showed increased carbon concentrations when analyzed again, indicating that much of the carbon found on the surface of the columns probably arises from environmental contamination.

Acid leaching

Glass contains metallic cations which function as Lewis acid sites and give glass undesirable chemical activity. A complete discussion of the structure, properties, and reactivity of glass surfaces and their relationship to chromatographic performance is contained elsewhere²¹. Controlled acidic leaching removes these sites to form a

silica-rich surface. The formation of such a surface layer greatly minimizes the effects of glass variety on subsequent treatments and lends a higher degree of reproducibility to column preparation.

Below a pH of about 7, glass is hydrolytically decomposed. The Si-O-R bonds rather than the Si-O-Si bonds are cleaved. R, an alkali or alkaline earth ion, can form a water-soluble salt that passes into solution and is replaced by an H⁺. The original Si-O-R bond is converted to an Si-OH bond and a surface gel is formed. This process is generally thought to be diffusion controlled with the amount of alkali extracted proportional to the square root of time²².

The boric oxide phase, being amphoteric in nature, is also extractable by acidic leaching²⁰. To a lesser extent, the alumina phase is also extractable. Alkaline solutions (e.g. NaOH) break the Si-O-Si bonds and form Si-O-Na and Si-OH, thus bringing about the actual dissolution of the silica surface. Rather than an enriched surface layer of silica, a porous surface structure is formed.

In this study, various leaching solutions were evaluated. These included mildly basic solutions, basic solutions followed by acidic solutions, various acidic solutions, and solutions involving complexing agents. Early results indicated that 20% HCl was as effective as any other reagent or combinations of reagents. Also, less structural surface damage was observed when using HCl than other reagents (*i.e.* NaOH or H₃PO₄). In fact, HCl leaching did no discernible surface roughening as detectable by SEM, although some roughening may have occurred on a molecular level. This is important since smoother surfaces facilitate more efficient coating. Since the rate of extraction of material from the glass surface is proportional to the square root of time, longer leach times produce a silica surface of greater depth and purity. However, the conditions must remain mild enough (*i.e.* no steam formation) so that longer reaction times do not cause surface roughening.

The results of ESCA analyses of Pyrex glass slides leached in 20% HCl are shown in Table III. For unleached glass, the carbon overlayer is decreased from over 25% coverage to less than 7% by sputtering for 1 min which removes the surface material to a depth of approximately 2 Å. However, as the slides were leached for longer periods, the carbon concentration increased, indicating that carbon is picked up from the leaching solution. Of particular interest is the very low initial concentrations of sodium, potassium, and calcium. Prior to analysis these slides had been rinsed with distilled water which effectively formed a depletion layer of these elements. More importantly the boron and the aluminum were depleted as the length of leach increased.

Depth profiling data obtained by ion milling (sputtering) gives an indication of the depth of the purified silica layer (see Table III). It is only the uppermost monolayers in which significant chromatographic interactions occur. When Pyrex glass is leached for 48 h the surface of the glass is essentially free from impurities. The aluminum concentration, present as a trace, is near the detection limits and it is difficult to verify its existence. Significant quantities of boron do not appear for several monolayers into the glass. In fact, the boron concentration at about 100 Å into the bulk glass is less for glass leached for 48 h than the level of boron just a few angstroms beneath the surface of glass leached for 1 h. As expected, both the aluminum and boron concentrations increase with depth while the carbon contamination decreases.

The surface compositions of soft glass slides leached with 20% HCl are listed

TABLE III
DEPTH PROFILING ANALYSIS OF LEACHED GLASS SLIDES

Glass type	Leach time (h)	Sputter depth (Å)	Atomic composition (%)								
			Al	Si	B	Na	C	K	Ca	Mg	O
Pyrex	48	0	0.4	8.5	—	—	26.3	—	—	—	64.8
		0.5	0.5	13.0	0.7	—	22.1	—	—	—	63.7
		2	0.5	14.6	0.7	—	13.5	0.1	—	—	70.6
		6	0.5	15.8	1.1	—	8.5	0.2	—	—	73.9
		12	0.5	16.6	1.5	—	6.9	0.3	0.1	—	74.1
		20	0.5	18.7	1.9	—	6.1	0.3	0.1	—	72.4
		40	0.7	17.9	2.1	—	3.9	0.3	0.1	—	75.0
		80	0.8	19.3	2.5	—	3.6	0.3	0.1	—	73.4
Pyrex	14.5	0	0.4	7.2	0.6	—	40.5	—	—	—	51.3
		2	0.6	14.6	1.0	—	19.8	0.2	0.1	—	63.7
		14	1.0	17.4	1.6	—	4.5	0.2	0.1	—	75.2
Pyrex	5	0	0.5	11.5	1.1	—	36.0	—	0.1	—	50.8
		2	0.7	15.2	1.0	—	15.1	0.2	0.1	—	67.7
		14	0.9	17.1	1.7	—	4.2	0.3	0.1	—	75.7
Pyrex	1	0	0.4	14.6	1.9	0.3	12.6	0.2	—	—	70.0
		2	0.6	17.1	2.5	0.1	2.4	0.3	0.1	—	76.9
		14	1.0	17.4	3.1	—	0.5	0.2	0.1	—	77.7
Pyrex	0	0	0.6	6.6	0.9	0.3	25.4	—	0.1	—	66.1
		2	1.0	15.8	3.0	0.3	6.7	0.1	0.1	—	73.0
		6	1.3	16.4	3.9	0.3	3.0	0.2	0.1	—	74.8
Soft	14.5	0	0.7	17.0	—	0.8	36.4	0.2	0.2	—	44.7
		2	1.5	24.0	—	0.4	5.8	0.4	0.4	—	67.5
		16	3.0	25.6	—	0.2	0.8	0.3	1.7	0.5	67.9
		40	4.2	25.3	—	0.3	—	0.2	2.8	1.3	65.9
		120	4.8	24.6	—	0.3	—	0.1	3.3	1.7	65.2
Soft	4	0	2.4	17.5	—	1.1	31.1	0.2	0.3	—	47.4
		2	1.7	24.9	—	0.6	1.9	0.5	0.8	0.5	69.1
		10	3.2	24.8	—	0.5	—	0.1	1.9	0.8	68.7
		40	3.4	25.3	—	0.4	—	0.2	2.6	0.9	67.2

in Table III. The levels of sodium, potassium, calcium, and aluminum all decrease with leach time. However, the carbon and the magnesium increase with longer leach times. These elements are probably picked up from the leach solution. The aluminum, magnesium, and calcium concentrations increase with depth into the bulk glass while the sodium and potassium actually decrease. The surface of soft glass does not form as pure or deep of depletion layer as does the Pyrex glass.

The stability of the leached surface layers were tested by heating leached slides at 400°C for various lengths of time. Although this temperature is much higher than that normally used in gas chromatography, it was chosen to reduce the time-frame required to perform these experiments at lower temperatures. Using normal chromatographic temperature conditions, it was found in a previous study¹ that no observable migration to the surface occurred. The data obtained are found in Table IV. After heating for 32.5 h, traces of aluminum, boron, and potassium begin to reappear on the surface. However, since the total leach time was only 14.5 h, a relatively thin depletion layer was originally produced.

TABLE IV
SURFACE COMPOSITION OF GLASS LEACHED FOR 14.5 h AND THEN HEATED AT 400°C

Glass type	Heating time (h)	Atomic composition (%)								
		Al	Si	B	Na	C	K	Ca	Mg	O
Pyrex	0	—	25.8	—	—	35.2	—	—	—	39.0
Pyrex	1.75	—	33.6	—	0.5	3.9	0.4	—	—	61.6
Pyrex	32.5	1.0	34.2	2.5	0.4	4.2	0.1	—	—	57.6
Soft	0	1.5	24.0	—	0.4	5.8	0.4	0.4	—	67.5
Soft	1.75	1.4	25.2	—	1.0	0.6	0.2	0.3	—	71.3
Soft	32.5	1.0	25.0	—	2.1	0.9	0.3	0.6	0.6	69.5

The surface compositions of soft glass slides that were leached for 14.5 h and heated at 400°C for various lengths of time are listed in Table IV. Slight increases in calcium, sodium, and magnesium are observed on the surface after extended heating. It appears that the aluminum concentration decreases with heating, and as expected, the carbon contamination is partially removed with heating.

Even though a large leaching volume as compared to the amount of glass leached was used in the ESCA experiments just described, the conditions were still static. That is, a fresh leaching solution was not being supplied continually to the glass surface. Hence the surface concentrations of carbon, and in some instances, magnesium increased with longer leaching times. Pyrex columns dynamically leached by continuous passage of fresh acid have surfaces free of carbon even when the original surfaces were carbon coated. In other words, dynamic leaching not only removes the boron and other detectable impurities, but also the carbon contamination. In fact, silicon-to-oxygen ratios are close to 1:2 as would be expected for SiO₂. For soft glass columns the carbon levels are low and do not increase with longer leach times. Homogeneity studies of leached columns of up to 90 m in length show that essentially the same surface is obtained throughout the entire length of the column.

During column preparation, a 400°C heat treatment is applied after columns have been dynamically leached. AES surface data show that usually a carbon layer is formed (deposited from the carrier gas) and some migration of sodium to the surface occurs. A second dynamic leach removes these impurities and forms a thicker silica surface layer (see Table V). For soft glass columns the dynamic leach does not completely remove the carbon contamination nor does it totally remove the calcium. A 400°C heat treatment tends to increase the calcium surface layer and the carbon contamination. Columns leached statically have a higher concentration of surface carbon than dynamically leached columns. They also tend to show some sodium and traces of boron on the surface (see Table V).

The surface compositions of Pyrex glass capillary columns obtained from various other surface modification methods are also listed in Table V. An HF etch, applied only lightly (350°C for 3 h) effectively removes the carbon contamination from the surface and leaves a silica surface somewhat enriched in boron. The higher boron concentration is feasible considering the volatile nature of B₂O₃. It is also consistent with experimental observations that "whisker" surfaces are extremely active²³. The amount of barium deposited by the non-polar column preparation procedure using dilute Ba(OH)₂ (ref. 24) is below the detection limits of AES. ESCA

TABLE V
SURFACE COMPOSITION OF VARIOUS CAPILLARY COLUMNS

Glass type	Treatment	Atomic composition (%)						
		Si	O	C	B	Na	Ca	Ba
Pyrex	Dynamic leach	30.3	69.7	—	—	—	—	—
Pyrex	Dynamic leach, 400°C heat treatment	11.4	35.8	46.9	—	5.9	—	—
Pyrex	Dynamic leach, 400°C heat treatment, Dynamic leach	26.0	74.0	—	—	—	—	—
Soft	Dynamic leach	23.1	68.7	5.0	—	—	3.2	—
Soft	Dynamic leach, 400°C heat treatment	24.2	55.2	16.3	—	—	4.3	—
Pyrex	Static leach	14.3	48.8	27.9	0.6	8.4	—	—
Pyrex	HF etch	27.0	64.0	—	9.0	—	—	—
Pyrex	BaCO ₃ (non-polar)	19.3	37.7	35.5	7.5	—	—	—
Pyrex	BaCO ₃ (polar)	18.5	58.9	12.1	—	—	—	10.5
Pyrex	Carbowax	16.6	30.9	52.5	—	—	—	—

analysis of a glass slide treated similarly gave a barium level of less than 0.5%. Columns prepared for polar coatings employing the more concentrated Ba(OH)₂ solution, however, exhibited concentrations of approximately 10% barium on the surface. Columns deactivated by the Carbowax method in which a thin layer of Carbowax is heat-treated and exhaustively extracted with solvent²⁵ produced over 50% carbon coverage. Columns analyzed before they were extracted with solvent showed nearly 100% carbon coverage.

Silylation

Obviously, acidic leaching of a glass surface increases the density of the surface hydroxyl groups. Consequently, acidic leaching must be followed by some treatment that effectively blocks the surface silanol groups, or the net effect is an increase in surface activity. Fortunately, silanol groups can be adequately deactivated by silylation. In silylation, the active hydroxyl groups are replaced by inert silyl-ether groups. The most commonly used silylation reagents are the methylchlorosilanes, particularly TMCS, and HMDS or combinations of the two. Grob *et al.*⁴ have advocated the use of diphenyltetramethyldisilazane and the authors have recently found that dichlorooctamethyltetrasiloxane produces a stable, hydrophobic surface suitable for coating with non-polar stationary phases.

For successful silylation the proper temperature must be chosen so that the number of free hydroxyl groups are at a maximum, thus giving a maximum density of grafted silyl groups which form a homogeneous and hydrophobic surface. It would appear from theoretical considerations which are discussed in detail elsewhere²¹ that temperatures around 400°C are necessary. However, it was not until 1977²⁶ that high-temperature silylations were attempted. The low temperatures used in earlier studies probably account for the general disappointments experienced by many. To verify that high temperatures are needed in silylation, several columns were prepared and silylated at various temperatures. In addition, to illustrate the effects of acid leaching

on chromatographic performance, several columns were prepared without leaching. A dynamic method of silylation was used. That is, fresh silylation vapors were continually purged through the column which was maintained at a suitable silylation temperature. Although this procedure provided an assured excess of silylation reagent, the problem of excess silylation as discussed by Grob *et al.*⁴ was eliminated. The concentrations of liberated reaction products of the silylation reactions such as NH_3 (from HMDS) could not build up and react with the glass since the column was constantly purged.

Shown in Fig. 3 is a chromatogram of a test mixture obtained on a Pyrex column that was dynamically silylated with the vapors of a 5:1 mixture of HMDS and TMCS at 200°C. No other treatments prior to coating with SE-52 were applied. The

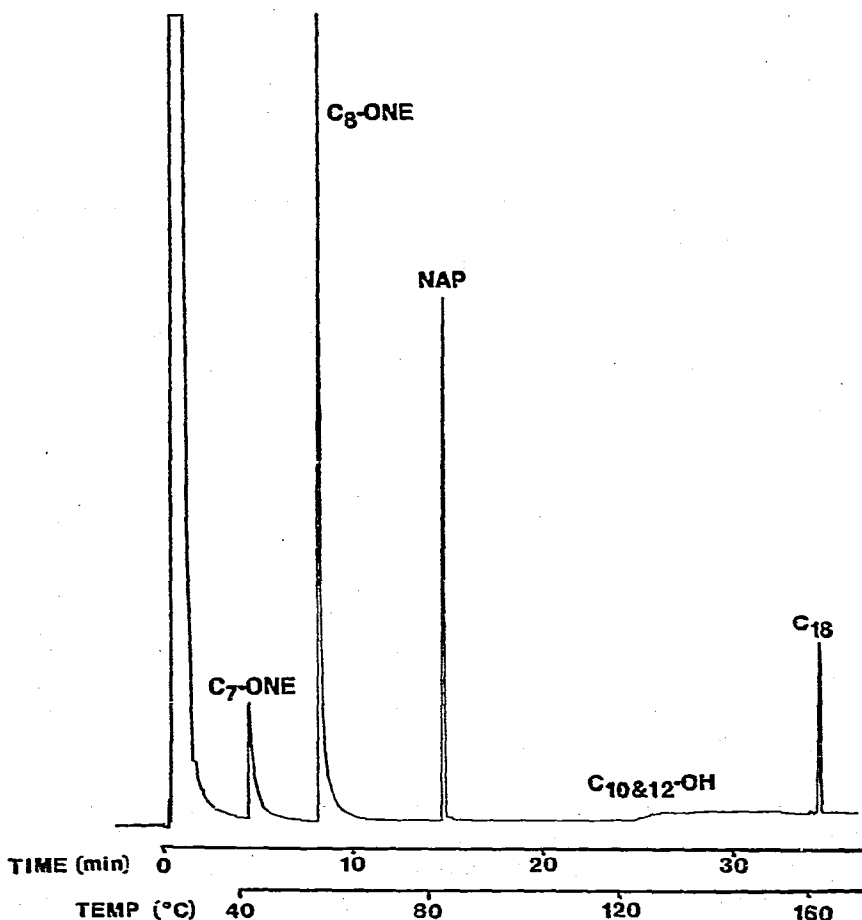


Fig. 3. Test chromatogram of a polarity mixture on an unleached Pyrex glass capillary column. Chromatographic conditions: 15 m × 0.30 mm I.D. column coated with 0.25- μm SE-52. Oven held isothermal at 40°C during elution of the solvent and then programmed at 4°C/min. Helium carrier gas velocity 50 cm/sec. Peaks: C₇-one = 2-heptanone; C₈-one = 2-octanone; NAP = naphthalene; C₁₀-OH = *n*-decanol; C₁₂-OH = *n*-dodecanol; C₁₈ = *n*-octadecane.

most noticeable aspect of the column performance is the nearly total adsorption of the alcohols and significant peak-tailing of the ketones. At least two factors are responsible for this. The metallic impurities in the glass and the incomplete blockage of the surface hydroxyl groups insure a nearly maximum surface activity. A vast improvement in column performance is immediately noticeable when Pyrex glass columns are leached prior to silylation. Shown in Fig. 4 is a chromatogram of the same test mixture obtained on a column that was dynamically leached prior to dynamic silylation at 200°C. Even when less than the optimum temperature was used in the silylation procedure, the improvement in column performance is remarkable. Although tailing, the alcohols are now eluted as distinctive peaks rather than being totally adsorbed. The peak shapes for the ketones are also improved. However, the naphthalene peak shape is slightly worse. This can be attributed to the increased concentration of surface hydroxyl groups as a result of the leach which were subsequently incompletely silylated. A chromatogram of the same test mixture obtained on a column that had

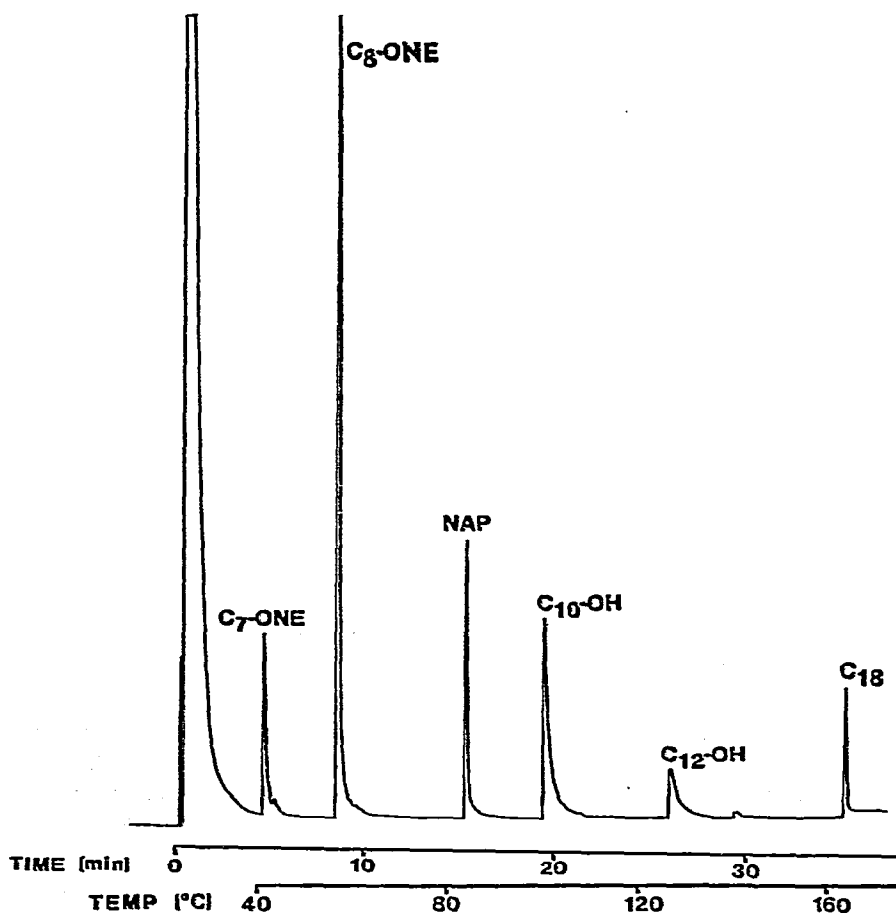


Fig. 4. Test chromatogram of a polarity mixture on a leached but improperly silylated Pyrex glass capillary column. Conditions as in Fig. 3.

been dynamically leached and then dynamically silylated at 400°C is shown in Fig. 5. The alcohols show minimal tailing as do the ketones and the naphthalene. What appears to be a tailing octanone peak can now be discerned as a contaminant eluting on the shoulder.

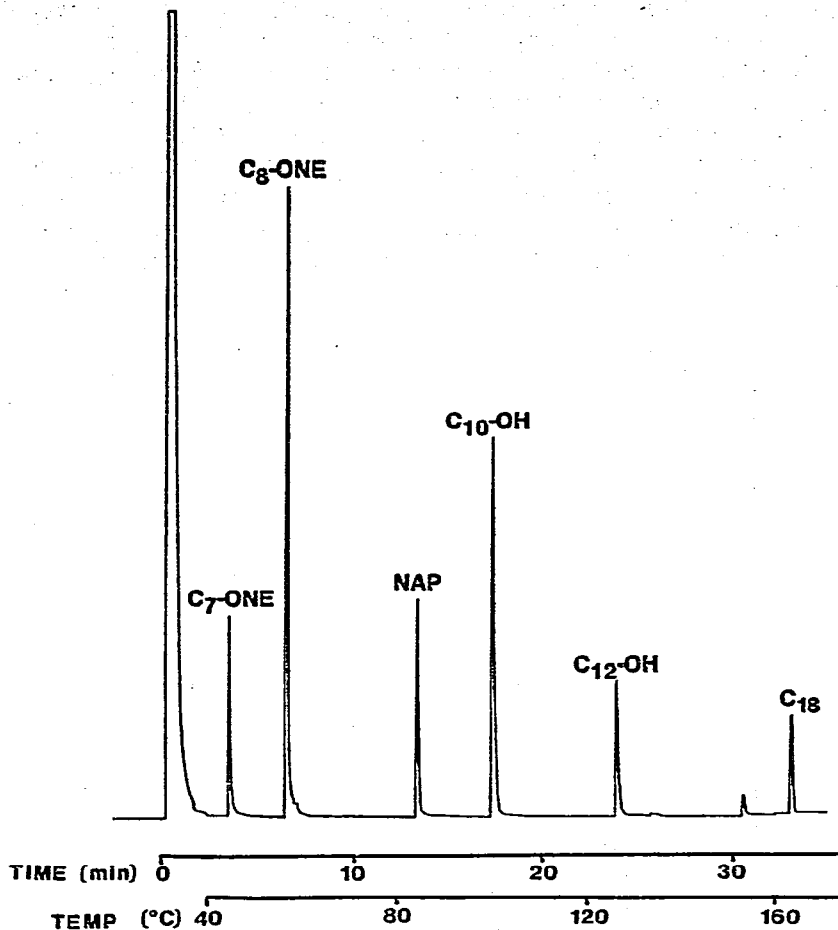


Fig. 5. Test chromatogram of a polarity mixture on a leached and properly silylated Pyrex glass capillary column. Conditions as in Fig. 3.

With the use of modern surface analytical methods, a greater understanding of the glass surface and its behavior toward a variety of treatments can now be obtained. Application of these methods has led to further improvements in column technology.

REFERENCES

- 1 M. L. Lee, D. L. Vassilaros, L. V. Phillips, D. M. Hercules, H. Azumaya, J. W. Jorgenson, M. P. Maskarinec and M. Novotny, *Anal. Lett.*, 12 (1979) 191.
- 2 M. L. Lee, *Doctoral Thesis*, Indiana University, Bloomington, IN, 1975.

- 3 K. Grob, G. Grob and K. Grob, Jr., *Chromatographia*, 10 (1977) 181.
- 4 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 31.
- 5 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 527.
- 6 M. Novotny and K. Tesarik, *Chromatographia*, 1 (1968) 332.
- 7 M. Novotny, L. Blomberg and K. D. Bartle, *J. Chromatogr. Sci.*, 8 (1970) 390.
- 8 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 677.
- 9 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
- 10 K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 93.
- 11 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 221.
- 12 A. Venema, L. G. J. v.d. Ven and H. v.d. Steege, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 69.
- 13 *Handbook of Auger Electron Spectroscopy*, Physical Electronics Industries, Eden Prairie, MN, 2nd ed., 1976.
- 14 C. K. Jorgensen and H. Berthou, *Faraday Discuss. Chem. Soc.*, 54 (1973) 269.
- 15 H. Berthou and C. K. Jorgensen, *Anal. Chem.*, 47 (1975) 482.
- 16 C. D. Wagner, *Anal. Chem.*, 44 (1972) 1050.
- 17 S. M. Budd, in D. E. Day (Editor), *Glass Surfaces*, North-Holland, Amsterdam, 1975, p. 55.
- 18 D. M. Sanders and L. L. Hench, *J. Amer. Ceram. Soc.*, 52 (1973) 666.
- 19 L. L. Hench and D. E. Clark, *J. Non-Cryst. Solids*, 28 (1978) 83.
- 20 A. M. Filbert and M. L. Hair, *Advan. Corros. Sci. Technol.*, 5 (1976) 1.
- 21 M. L. Lee and B. W. Wright, *J. Chromatogr.*, 184 (1980) 235.
- 22 T. M. El-Shamy, J. Lewis and R. W. Douglas, *Glass Tech.*, 13 (1972) 81.
- 23 G. Schomburg, H. Husmann and F. Weeke, *Chromatographia*, 10 (1977) 580.
- 24 K. Grob, Jr., G. Grob and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 149.
- 25 D. A. Cronin, *J. Chromatogr.*, 97 (1974) 263.
- 26 Th. Welsch, W. Engewald and Ch. Klaucke, *Chromatographia*, 10 (1977) 22.