

Development of fluorinated low temperature glassy carbon films for solid-phase microextraction

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Abstract

Solid-phase microextraction (SPME) fibers with supported fluorinated glassy carbon are demonstrated for the first time. Oligo[1,3-dibutadienylene-1,3-(tetrafluoro)phenylene] was synthesized and heated to temperatures that varied from 200 to 1000 °C to produce the fluorinated glassy carbon. The extent of graphitization of the glassy carbon increased as the processing temperature increased. The fluorinated glassy carbon selectively extracted monohalogenated benzenes from an aqueous solution when compared to the extraction of toluene. The selectivity increased in the order of φ -F < φ -Cl < φ -Br < φ -I. The selectivity for the halogenated compounds was greatest for the fluorinated glassy carbon phase processed at temperature below approximately 400 °C. Preliminary studies on the retention mechanism of the LTGC phase show that dispersive interactions are very important to the retention of halocarbons on the fluorinated LTGC. Finally, the selectivity of the fluorinated LTGC for halogenated compounds was compared to that of commercially available SPME fibers, such as poly(dimethylsiloxane), poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB), and poly(dimethylsiloxane)/Carboxen (PDMS/Carboxen) fibers. As expected the fluorinated LTGC was more selectivity for the halogenated compounds. Interestingly the order of the increase in selectivity is opposite when comparing the fluorinated-LTGC and the three commercial fibers. A decrease in selectivity was observed going from fluorobenzene to iodobenzene using PDMS/DVB and PDMS/Carboxen fibers. While for the pure PDMS phase, there is a slight increase in selectivity from fluorobenzene to chlorobenzene but the remaining trend shows little change for bromobenzene and iodobenzene.

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1. Introduction

Fluorinated and perfluorinated stationary phases encompass a unique niche in the realm of chromatography. This is a direct result of introducing the highly electronegative fluorine heteroatom into the carbon-based stationary phase structure. The strong electron withdrawing power of the fluorine atom produces a very strong bond with carbon that results in stationary phases that are highly hydrophobic and inert [1,2]. In certain cases, these deactivated phases can be utilized in separating reactive chemical species, such as hydrogen, sulfur and phosphorus as well as metal fluorides [3,4]. These caustic compounds would destroy conventional columns and packings.

Another benefit of fluorinated phases is the weak molecular interactions exhibited between the stationary phase

and solute. In most instances, this is due to a reduction of the stationary phase's ability to engage in dispersive interactions with solute molecules compared to their unfluorinated analogs [5]. This can be beneficial for separating thermally-labile compounds in gas chromatography by reducing the temperature needed for elution [4]. In liquid chromatography, this enables the separation of proteins using mobile phases with low organic modifier content, allowing the recovery proteins with minimal denaturing [6]. Fluorinated stationary phases are also highly selectivity for compounds containing lone electron pairs such as alcohols, ketones, nitro-compounds and chlorofluoro-compounds [7]. This selectivity has also been extended to the separation of fluorine isomers in liquid and gas chromatography [7,8].

The same unique attributes that make fluorine phases attractive for chromatographic applications also make them difficult to implement. Support coatings with perfluorinated liquid polymers are difficult to prepare due to poor wetting characteristics. Also, these phases show

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poor thermal stability due to a high temperature coefficient of viscous flow resulting in the disruption of continuous films at high temperatures [1,4]. To ameliorate this effect, support silanization has demonstrated some successes as well as preparing coatings on polytetrafluoroethylene and polychlorotrifluoroethylene supports [1,3]. Another approach to improving film stability is the inclusion of polar groups into the fluorocarbon backbone as is the case with poly(perfluoroalkyl) ether Fomblin oils and fluorinated alkyl esters [4]. Polysiloxanes containing fluorine have also been prepared, however severe weakening of the silicon–carbon bond can occur if the fluorine group is in the α or β position (relative to the silicon atom) leading to low thermal stability [3]. Generally, stable polysiloxane phases can be produced by placing the fluorine functionality in the γ position as in the trifluoropropyl polysiloxane stationary phase.

Herein, the application of a fluorinated carbon phase is demonstrated for solid-phase microextraction (SPME) by preparing films with a fluorinated low temperature glassy carbon (F-LTGC). The F-LTGC SPME fibers are used to extract a series of halogenated benzene molecules from headspace samples and compared to extractions performed with the silicon-containing low temperature glassy carbon oligomer (Si-LTGC). The extraction data are correlated with a free energy adsorption model developed for perfluorobenzenesulfonate and benzenesulfonate phases [9]. These results combined with information from mass-loss analysis and X-ray photoelectron spectroscopy (XPS) are used to elucidate the nature of the solute-stationary phase interaction as well as to clarify structural changes occurring in the glassy carbon oligomer as a function of thermal processing. To date, there are no existing fluorinated phases commercially available for SPME nor has there been any demonstration of fluorine phases for SPME applications in the chemical literature.

2. Experimental

2.1. Synthesis of precursor polymers for Si-LTGC and F-LTGC

2.1.1. Chemicals

1,3-Diethynyl-2,4,5,6-tetrafluorobenzene, the Si-LTGC oligomer-oligo[1,3-dibutadiynylene-1,3-(5-trimethylsilyl)phenylene], were prepared using a previously documented procedure [10]. Ethynylpentafluorobenzene and the F-LTGC oligomer-oligo[1,3-dibutadiynylene-1,3-(tetrafluoro)phenylene] were synthesized in modified procedures as below.

2.1.2. Preparation of ethynylpentafluorobenzene

A mixture of diisopropylamine (340 ml), bis(triphenylphosphine)palladium(II) chloride (0.48 g, 0.68 mmol) and copper(I) iodide (0.13 g, 0.68 mmol) was stirred and degassed via rapid stream of argon. To the mixture, a solution of (trimethylsilyl)acetylene (3.67 g, 37.4 mmol) and

pentafluoroiodobenzene (10 g, 34 mmol) was added at room temperature. The mixture was stirred at room temperature for 30 min and then gradually heated to reflux. Heating and stirring continued until thin layer chromatography indicated that the reaction was completed (2 h). The solution was filtered and washed with dichloromethane. The filtrate was concentrated under reduced pressure to give a dark oil product. The product was applied to a silica gel column packed in hexane. Elution with hexane yielded the desired product pentafluoro[(trimethylsilyl)ethynyl]benzene (6.1 g, 68%) as a colorless liquid. To a solution of the pentafluoro[(trimethylsilyl)ethynyl]benzene (3 g, 11.4 mmol, in methanol, 120 ml) was added potassium hydroxide (77 mg, 1.38 mmol, in water, 2.5 ml). The solution was stirred at room temperature until gas chromatographic analysis showed that the reaction was completed (2 h). The reaction solution was diluted with water (120 ml) and extracted with pentane (5×120 ml). The combined organic layers were dried over MgSO_4 , and the solvent was removed under reduced pressure to yield a yellow liquid (3.2 g). The liquid was purified via vacuum distillation to give a colorless liquid (2.8 g). ^1H NMR measurement indicated that the solution contained 70% (by weight) of the desired product ethynylpentafluorobenzene in pentane. The solution was directly used in the preparation of oligo[1,3-dibutadiynylene-1,3-(tetrafluoro)phenylene]. ^1H NMR (200 MHz, CDCl_3) δ 3.55 ppm.

2.1.3. Preparation of oligo[1,3-dibutadiynylene-1,3-(tetrafluoro)phenylene]

A solution of *o*-dichlorobenzene (250 ml), TMEDA (0.5 g, 4.30 mmol), copper(I) iodide (0.15 g, 1.52 mmol) and pyridine (10 ml) was stirred under oxygen at 65 °C. A solution of 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (10 g, 40.3 mmol) and ethynylpentafluorobenzene solution in pentane (1.2 g, 6.25 mmol) was added to the reaction mixture. Heating and stirring under oxygen were continued for 2 h. The heating bath was removed and the reaction mixture was stirred for an additional 3 h. The mixture was poured into acidic methanol (2% HCl) and the precipitation was formed. The precipitation was collected by filtration. The solid product was re-dissolved in *o*-dichlorobenzene and treated with TMEDA to remove any residual copper. The solution was poured into acidic methanol (2% HCl), the precipitate was collected by filtration and rinsed with methanol. A yellow solid product (7.80 g, 85%) was obtained after drying at room temperature: ^{13}C NMR (67.7 MHz, 1,2-dichlorobenzene- d_4) 167.1, 155.2, 150.1, 137.7, 132.6, 97.1, 83.2, 68.0 ppm; ^{19}F NMR (67.7 MHz, 1,2-dichlorobenzene- d_4) 160, 147, 133, 121, 102 ppm. Elemental analysis: calcd. for: C 51.76, F 48.23. Found: C 57.07, F 41.83.

2.2. LTGC-SPME fiber preparation

The Si-LTGC and F-LTGC SPME fibers were prepared using a three-step process [11]. First, porous silica

beads were coated with the LTGC oligomer precursors and then thermally treated to form the glassy carbon thin film, encapsulating the silica particle. Next, the porous LTGC-encapsulated silica was immobilized on stainless steel fibers 1.0 cm in length with a diameter of 200 μm (Small Parts, Miami, Lakes, FL) using a sol-gel process. Finally, the fibers were mounted into commercial SPME fiber assemblies (Supelco, Bellefonte, PA) by retrofitting the devices with the LTGC fibers.

For the Si-LTGC oligomer, approximately 1.5 g of encapsulated porous silica was prepared using a method previously published [11]. For the F-LTGC oligomer, an alternative coating strategy had to be used due to the difference in solubility between the silicon and fluorine oligomers. In this case, 1.5 g of porous silica with a mean particle diameter of 5 μm and a surface area of 401 m^2/g (Phenomenex, Torrance, CA) and 0.12 g of the F-LTGC oligomer were measure out into a 25 ml round bottom flask. This amount of oligomer was chosen to produce an 8% coating. To the flask, 25 ml of toluene was added and the solution was sonicated to dissolve the oligomer and disperse the silica. The flask was then immersed in a mineral oil bath and the solution was gradually heated while stirring vigorously until the toluene began to evaporate. Portions of neat dodecane (a non-solvent for the oligomer) were added to the flask replacing the volume of toluene lost. Heating was carried out until a temperature of approximately 200 $^{\circ}\text{C}$ was reached and 25 ml of neat dodecane was added. The liquid was allowed to cool and the particles to settle. The supernatant dodecane was decanted leaving the coated silica in the flask. The particles were dried for a minimum of 24 h at 100 $^{\circ}\text{C}$ under nitrogen flow to remove the remaining solvents.

To form the silylated (Si-LTGC) and fluorinated (F-LTGC) low temperature glassy carbon, the oligomer-encapsulated particles were divided into 10 equal batches of 0.3 g each, consisting of five samples of the Si-LTGC and five samples of the F-LTGC coated silica. The five batches were thermally processed in pairs using a quartz tube furnace with a linear temperature ramp of 1 $^{\circ}\text{C}/\text{min}$, starting at room temperature and ending at a series of final temperatures of 310, 400, 600, 800 and 1000 $^{\circ}\text{C}$. The final processing temperatures were held for a minimum of 10 h. All thermal processing was carried out in an atmosphere of 5% hydrogen/95% nitrogen.

2.3. Instrumentation

A Hewlett-Packard 5890 Series II Plus gas chromatograph equipped with an electronic pressure-controlled split/splitless injector port and a 5972 mass selective detector (MSD) was used for the analysis of all the compounds. The instrument was calibrated daily by injecting replicate samples of a 100 ppb standard solution diluted in dichloromethane. A small-volume injection sleeve with an inner diameter of 0.75 mm was used in conjunction with an SPB-5 capillary column (1.0 μm film thickness, 30 m long, 0.25 mm inner diameter), both pur-

chased from Supelco (Bellefonte, PA). For comparative extractions, 100 μm polydimethylsiloxane (PDMS), 65 μm poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB), and 75 μm poly(dimethylsiloxane)/Carboxen (PDMS/Carboxen) fibers were used and also purchased from Supelco.

For analysis, the injection port and mass spectrometer transfer line temperatures were set at a constant 250 $^{\circ}\text{C}$. The oven temperature was held at 50 $^{\circ}\text{C}$ for 1 min and then ramped 30 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$. The mass spectrometer was tuned using perfluorotributylamine (PFTBA) mass fragments 50, 100 and 219. The MSD was operated in scan mode monitoring masses between 45 and 220 m/z , however only selected ions (the base peaks) were used for quantification: toluene (91 m/z), fluorobenzene (96 m/z), chlorobenzene (112 m/z), bromobenzene (156 m/z) and iodobenzene (204 m/z).

2.4. Chemicals

All the extraction solutes: toluene, fluorobenzene, chlorobenzene, bromobenzene and iodobenzene were purchased from Sigma-Aldrich (St. Lewis, MO) with a purity of 99% or greater. The Si-LTGC oligomer, 1,3-diethynyl-(5-trimethylsilyl)benzene, and the F-LTGC oligomer, 1,3-diethynyl-2,4,5,6-tetrafluorobenzene, were prepared in-house using a previously documented procedure [10].

2.5. Extraction procedure

A series of 40 ml EPA vials capped with PTFE-laminated silicone septa (National Scientific Co., Lawrenceville, GA) were filled with 25 ml of purified water leaving a headspace volume of approximately 15 ml. The water samples were spiked with 2.5 μl of a 1000 $\mu\text{g}/\text{ml}$ stock solution of toluene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene in methanol. The vials were quickly capped and stirred vigorously for 15 min before performing 30 s headspace extractions with the SPME fibers. The fibers were analyzed immediately after extraction.

2.6. Spectroscopy and mass-loss analysis

For X-ray photoelectron microscopy and mass loss studies, the oligomer precursors were pressed into pellets. Approximately 120 mg of oligomer was loaded into a pellet die and pressed into disks approximately 1 cm in diameter and 1 mm thick. A series of 14 pellets were pressed (seven of the fluorine and seven of the silicon oligomer) and thermally processed in an analogous manner to the coated silica. Processing was carried out to final temperatures of 100, 200, 310, 400, 600, 800 and 1000 $^{\circ}\text{C}$. To measure the mass loss as a function of temperature, replicate measurements were made before and after thermal processing using an analytical balance.

XPS was performed using a Perkin-Elmer Model 550 ESCA-Auger spectrometer with a magnesium X-ray source.

Survey scans were performed over a range of 0–1000 eV for five scans and 1 eV step size. Regional scans were also performed over ranges of approximately 275–295 eV for the carbon 1s peak; 525–545 eV for the oxygen 1s peak; 95–115 eV for the silicon 2p peak; and 675–704 eV for the fluorine 1s peak. Five scans were performed for each region with a step size of 0.1 eV. The data was reduced and analyzed using GRAMS/3[®] Spectral Notebook[™] version 4.02 (Galactic Industries Corp, Salem, NH).

3. Results and discussion

3.1. Coating of Silica Particles with F-LTGC oligomer

Using a similar coating strategy as employed for the Si-LTGC oligomer, a coating technique was developed for the F-LTGC oligomer based on binary solvent system containing a *good solvent* and a *poor solvent*. Choosing adequate solvents for the F-LTGC was more difficult due to the general inertness of the fluorine containing oligomer. To find an appropriate good solvent for the F-LTGC, a number of common solvents were tried. Dichlorobenzene was the best solvent for the fluorine oligomer, however toluene was chosen as the good solvent because it displayed adequate solubility for the oligomer as well as being less toxic and noxious to work with. The solubility comparison also clearly illustrated that the dominant feature controlling solubility is the aromaticity of the solvent and not the presence of halogen substituents. This is apparent by comparing the solubilities of dichlorobenzene (miscible), trichloroethane (insoluble) and toluene (miscible). If the dominant interactions controlling oligomer solubility in the dichlorobenzene were due to the presence of the chlorine atoms, one would expect that the oligomer would be readily soluble in the trichloroethane, which was not the case. This result was somewhat surprising based upon existing data suggesting that the solubility of perfluorocarbons is highly dependent on the degree halogenation of the solvent phase [1]. Additionally, the oligomer shows adequate solubility in toluene indicating that the interactions of the aromatic groups are the key feature controlling solubility. It has been noted in the literature that perfluoroaromatic stationary phases show less of a reduction in dispersive interactions with respect to their perfluoroalkyl analogs [1]. This may be partially responsible for the observed behavior. It should be noted, however, that the presence of the chlorine atoms did have a beneficial effect on solubility as the demonstrated by the long-term miscibility of the oligomer in the dichlorobenzene compared to toluene.

Once the good solvent was chosen, it was necessary to find an adequate non-solvent for coating system. The essential properties for the non-solvent are that it must be miscible in the good solvent, it must have a higher boiling point than the good solvent and obviously it must be a poor solvent for the oligomer. In the case of the silicon oligomer, heptane was

used as a suitable non-solvent and methylene chloride was used as the good solvent. The boiling points of methylene chloride and heptane are 40 and 98 °C respectively, giving a differential boiling point of 58 °C. In the case of toluene chosen for F-LTGC, the boiling point is 111 °C, therefore heptane could not be used as an appropriate non-solvent. A longer straight chain hydrocarbon, dodecane, was chosen instead. Dodecane displayed good characteristics as a non-solvent, however due to the substantial increase in boiling point of the longer chain length (216 °C), the drying time of the coated silica phase was substantially longer.

3.2. Thermal processing and mass loss

After the establishment of a coating regimen, the fluorinated-oligomer coated silica was thermal processed following the same methods and apparatus used for Si-LTGC. It was apparent that the fluorine oligomer was behaving quite differently than the silicon oligomer upon thermal treatment. The quartz boats used to contain the coated silica during processing were obviously etched, indicating the formation of corrosive hydrogen fluoride by the volatilization of some of the fluorine oligomer components reacting with the hydrogen.

The release of the hydrogen fluoride was also accompanied by a loss in mass. Fig. 1 compares the mass loss of F-LTGC and the Si-LTGC as a function of processing temperature. For both polymers, the mass loss increases until 600 °C after which the mass loss remains constant, approximately 13.2% for Si-LTGC and 40.0% for the F-LTGC. These results are almost identical to previously reported data on the thermogravimetric analysis of the silicon and fluorine oligomers. Pocard et al. [12] reported mass losses of 13.5 and 45.9%; and Hutton et al. [13] of 13 and 38% for the silicon and fluorine containing oligomers at 1000 °C, respectively. The thermogravimetric analysis reported in these papers was carried out in a pure nitrogen atmosphere. For the data presented in Fig. 1, the processing gas included a 5% mixture of hydrogen in nitrogen. It can therefore be concluded that hydrogen in gas mixture does not necessarily have degradative effect on the oligomer and that the mass

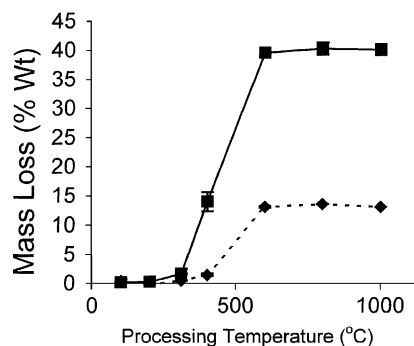


Fig. 1. Mass loss as a function of processing temperature for F-LTGC (■) and Si-LTGC (◆).

Table 1
Surface composition of Si-LTGC during processing

Processing temperature (°C)	Weight percent		
	Oxygen (1s)	Carbon (1s)	Silicon (2p)
Unprocessed oligomer	3.4	77.0	19.6
100	1.5	78.8	19.7
200	5.0	73.9	21.1
310	6.3	74.2	19.6
400	8.6	76.2	15.2
600	10.7	77.4	11.8
800	11.0	78.1	10.9
1000	9.2	81.2	9.6

loss can be attributed to the thermal treatment alone. In addition, even though the mass losses were noted in these early papers by Pocard and Hutton, there was no investigation into identifying the species lost.

XPS was used to further characterize the nature of the changes in the oligomers during thermal treatment. Tables 1 and 2 give the surface composition of the silicon and fluorine containing oligomers, respectively.

The initial composition of both oligomers is close to the theoretically predicted values. For the Si-LTGC oligomer, the theoretical composition is 80.8% carbon, 14.5% silicon and 4.7% hydrogen by weight. For the F-LTGC oligomer, the theoretical composition is 36.5% fluorine and 63.5% carbon by weight. The presence of chemisorbed oxygen and the inability of XPS to measure surface hydrogen are the likely cause of the larger deviation of the silicon oligomer from the theoretical prediction. As expected, the data indicate a loss of fluorine and silicon atoms as processing temperature increases (Fig. 2). The reduction in silicon for the Si-LTGC oligomer follows a similar trend as observed through elemental bulk and surface analysis of the oligomer as a function of temperature [14]. At the final processing temperature of 1000 °C, silicon atoms still persists at a concentration of 9.4%. Comparatively, the reduction of the fluorine atoms is much more dramatic and is below instrument detection for the oligomer processed at 1000 °C for five scans of the spectrometer (Table 2).

It was previously suggested that the persistence of the

Table 2
Surface composition of F-LTGC during processing

Processing temperature (°C)	Weight percent		
	Oxygen (1s)	Carbon (1s)	Fluorine (1s)
Unprocessed oligomer	1.0	63.0	36.0
100	2.0	63.6	34.4
200	3.8	62.2	34.0
310	3.3	66.3	30.4
400	5.9	78.1	16.0
600	8.0	88.0	6.9
1000	1.9	98.1	0.0

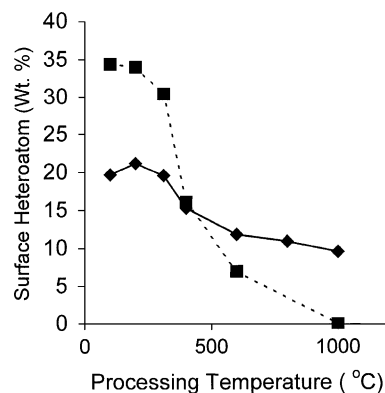


Fig. 2. Silicon or fluorine atom loss as a function of processing temperature for F-LTGC (■) and Si-LTGC (◆).

silicon species was an indication of incomplete graphitization of the carbon surface during processing [12,14]. Incomplete graphitization can lead to significant levels of chemisorbed oxygen resulting in poor chromatographic performance of stationary phases prepared with the material. Rittenhouse reported oxygen to carbon ratios (O/C) for the silicon oligomer that varied from 3 to 17% depending on processing conditions [14]. Chemisorption of oxygen occurred upon exposure to the atmosphere, post processing. Low levels of oxygen (<5%) could only be achieved by either sequestering the processed carbon stationary phases in oxygen deprived solvents or by thermally processing the oligomer at temperatures greater than 1000 °C for time periods in excess of 10 h. Still, the amount of surface carbon could not be reduced to levels measured for highly graphitized commercial glassy carbon of 0–2%.

By the same reasoning, a significant loss of fluorine and silicon during processing should be a positive indication of the degree of graphitization of the carbon surface. More complete graphitization of the carbon should lead to a reduction of chemisorbed oxygen due to the decrease in defect or edge plane sites. Indeed, this trend can be observed by comparing the amount of oxygen present as a function of processing temperature for the fluorine and silicon oligomers (Fig. 3). As the carbon surface is forming with thermal treatment, the amount of chemisorbed oxygen increases as the processing progresses until about 400 °C for the F-LTGC and 800 °C for the Si-LTGC. After these temperatures, the surface oxygen concentrations are shown to decrease indicating more complete graphitization. This turn-around effect is significant and was also noted by Rittenhouse [14] in processing the silicon oligomer. The temperature at which this effect occurs during processing is important because it is suggestive that the fluorine oligomer is reaching a more graphitic state at a lower temperature than the silicon-containing oligomer. This hypothesis is fundamentally supported by conductivity measurements performed by Callstrom et al. [10] demonstrating that the fluorine oligomer displays less resistance to current flow than the silicon at equivalent processing temperatures.

The surface oxygen concentration at the final processing temperature of 1000 °C is also a good indication of the degree of graphitization. In these experiments, no special effort was made to sequester the samples after processing and before XPS analysis. In the case of the oligomers processed to 1000 °C, the samples were exposed to the atmosphere for approximately 24 h after thermal treatment before they were loaded into the XPS. The final oxygen concentrations of the Si-LTGC and F-LTGC were 9.2 and 1.9%, respectively.

3.3. Extraction selectivity

Extractions were performed on a series of halogen substituted benzene molecule to elucidate the differences in selectivity between the Si-LTGC and F-LTGC SPME fibers. The selectivity was determined by plotting the peak area for each probe molecule divided by the peak area for toluene, which was used as an internal standard to compensate for differences in fiber loading.

Figs. 4 and 5 show the selectivity of the phases as a function of processing temperature. Several general trends are apparent when evaluating these plots. First, the fluorinated phase has a higher selectivity for the halogenated benzene rings compared to silicon-phase. Second, the trends indicate that the selectivity plots tend to converge as a function of processing temperature. For both Si-LTGC and F-LTGC, the variation of the peak selectivity versus temperature displayed the same general shape for all for compounds. However shape of the curves for the variation in peak area ratios with temperature was different for F-LTGC and Si-LTGC. Third, the general shape of the curves was controlled by the support material (i.e. in general, all molecules sorbed onto SiLTGC had a similar curves and all molecules sorbed onto F-LTGC had similar curves).

The finding that the F-LTGC phases are more selective toward the halogenated benzenes is not surprising. In most cases, halogenated stationary phases have higher selectivities for halogenated solutes [4]. However, the convergence of the lines for each plot (with the exception of the 1000 °C F-LTGC for chlorobenzene) indicates that the selectivity of

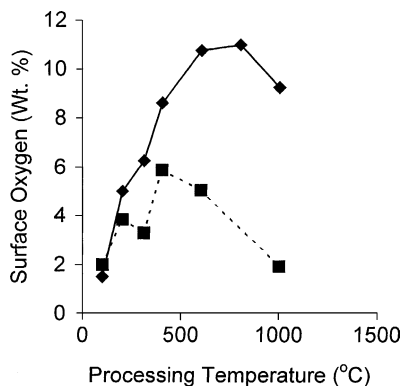


Fig. 3. Oxygen surface concentration as a function of temperature processing for F-LTGC (■) and Si-LTGC (◆).

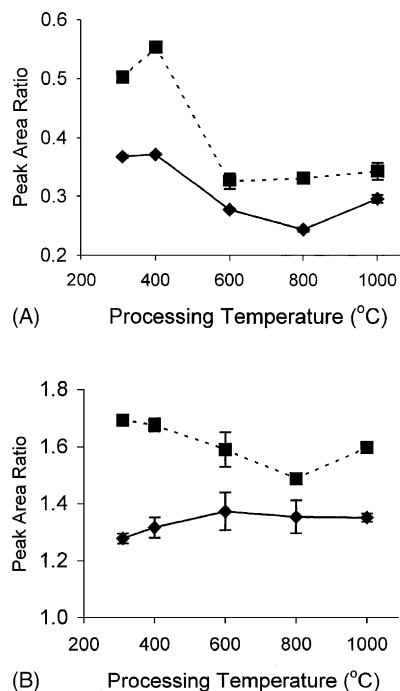


Fig. 4. Selectivity plots for extractions of with the fluorobenzene (A) and chlorobenzene (B) with respect to toluene for F-LTGC (■) and Si-LTGC (◆).

the fluorinated phase is approaching that of the Si-LTGC phase. This trend is likely due to the loss of fluorine and silicon atoms as processing temperatures increase (Fig. 2). Consequently, the phases are becoming more similar with

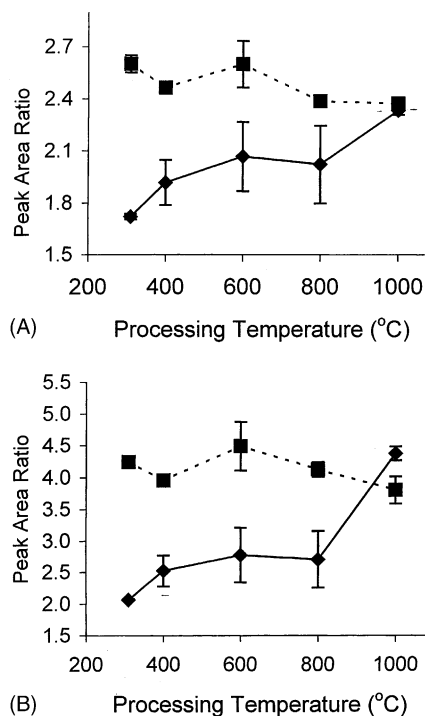


Fig. 5. Selectivity plots for extractions of bromobenzene (A) and iodobenzene (B) with respect to toluene for F-LTGC (■) and Si-LTGC (◆).

Table 3
Size of substituents and the polarizability of solute molecules

Compound	Van der Waal's radii (ppm) ^a	Polarizability (10 ⁻²⁴ cm ³) ^b
Fluorobenzene	147	10.3 ^b
Chlorobenzene	175	13.2
Bromobenzene	185	14.4
Iodobenzene	198	15.5

^a Values taken from reference [15].

^b Values taken from reference [16,17].

processing resulting in similar selectivity. Indeed, the greatest selectivity difference between the phases occurs at lower temperature indicating favorable interaction between the halogen groups. Interestingly, the selectivity of even the F-LTGC processed to 1000 °C (with the exception of the iodobenzene extraction) is greater than the Si-LTGC at the same temperature. This could either be caused by the persistence of low levels fluorine in the phase that could not be detected with the XPS at instrument conditions or due to the fact that the carbon surface at this temperature is more graphitized than the silicon-containing phase.

The greatest predictors of selectivity for the carbon are the cross-sectional area and the polarizability of the solute molecule. This trend can also be discerned in the selectivity plots of the halogenated benzenes. If one considers the size (van der Waal's radii of substituent) and polarizability changes in the solute molecules as substitution progresses down the halogen group, it can be seen that the changes in selectivity as a function of processing temperature are greatly influenced. When the selectivities for the 310 °C (Figs. 4 and 5) processing temperature are compared among the halobenzenes, the greatest selectivity occurs for the compounds with the largest size and the largest polarizability as shown in Table 3 (i.e. in the order φ -F < φ -Cl, < φ -Br < φ -I). The second column in table gives the van der Waal's radii of the substituents of the solute molecules [15] The third column is the polarizability of each solute molecule [16].

3.4. Extraction mechanism

Kollie and Poole developed a thermodynamic model to account for the transfer of solutes from the gas phase to a stationary phase in gas-liquid chromatography [9]. They used this model to compare solute retention characteristics for a series of perfluoroalkanesulfonate and alkanesulfonate stationary phases. They considered three main solute-solvent interactions occurring in the solvation process: (1) the creation of a cavity in the liquid stationary phase large enough to accommodate the solute molecule; (2) the reorganizational energy associated with the solvent rearrangement around the cavity; and (3) the selective interaction occurring between the solute and solvent molecules. They assumed that the free energy associated with step two was close to zero and was ignored in their further development. The equation derived for this model is given by:

$$\Delta G_S^{\text{SOLN}}(X) = \Delta G_S^{\text{CAV+NP}}(X) + \Delta G_{\text{SQ}}^{\text{P}}(X) + \Delta G_S^{\text{INT}}(X) \quad (1)$$

where $\Delta G_S^{\text{SOLN}}(X)$ is the partial Gibbs free energy of transfer of the solute (X) from gas phase to the stationary phase. The $\Delta G_S^{\text{CAV+NP}}(X)$ term is a composite term encompassing the free energy of cavity formation and nonpolar solute-solvent interactions. The $\Delta G_{\text{SQ}}^{\text{P}}(X)$ term accounts for polar interactions and certain nonpolar effects. The $\Delta G_S^{\text{INT}}(X)$ term accounts for polar orientation interactions. To encompass all nonpolar effects, the $\Delta G_S^{\text{CAV+NP}}(X) + \Delta G_{\text{SQ}}^{\text{P}}(X)$ terms must be taken together. Based on chromatographic retention data, Kollie and Poole generated values for the $\Delta G_S^{\text{CAV+NP}}(X) + \Delta G_{\text{SQ}}^{\text{P}}(X)$ and $\Delta G_S^{\text{INT}}(X)$ terms for a number of test solutes, including the solutes in this work. Comparing the values calculated by Kollie and Poole to the glassy carbon extractions, a more refined model of solute retention on the glassy carbon is achieved.

A few issues should be considered before applying this model to extractions performed with the glassy carbon. First, this model was designed to describe solute-liquid interaction, which in some cases can be quite different from solute-surface interactions. Nonetheless, it has been successfully applied to describing solute retention on stationary phases in which interfacial adsorption plays a significant role such as perfluorobenzenesulfonate and benzenesulfonate [2]. Another issue is that this model was developed for describing the behavior of organic salt stationary phases, therefore the polar orientation effects given by the $\Delta G_S^{\text{INT}}(X)$ term is dominated by hydrogen-bond base and dipolar interactions. To distinguish between these two contributing effects, Kollie and Poole used multiple least square regression analysis (MLSR) on a model proposed by Abraham and co-workers [18]. As expected, they found a significant reduction in the hydrogen-bond base activity of the perfluoro compared to benzene sulfonate due to the electron withdrawing effects of the fluorine groups. In comparison, the change in the dipolar contribution between the stationary phases was minimal. This evidence is also supported by the retention properties of phenyl and perfluorophenyl bonded phases in reversed-phase liquid chromatography. In a study by Reta et al., a linear solvation free energy relationship (LSER) model was used to determine the individual contributions to solute retention [19]. Interestingly, they found that for the unfluorinated and fluorinated aromatic stationary phases the dipolar contribution to solute retention was zero for all mobile phase compositions studied (45–65% methanol in water). They suggested this was caused by a canceling effect of the mobile phase. In all the models studied (free energy, MLSR, LSER), the cavity formation (nonspecific interaction) and hydrogen-bond base interaction terms are the most important predictors of retention. Since the data collected from Kollie and Poole were measured on organic salt phases, the polar orientation term cannot be applied

Table 4
Free energy and selectivity trends for F-LTGC and Si-LTGC

Compound	$-\Delta G^\circ$ (cal/mol) perfluoroaryl ^a	$-\Delta G^\circ$ (cal/mol) aryl ^a	F-LTGC ^b (nmol ext \times MW ^{1/2})	Si-LTGC ^b (nmol ext \times MW ^{1/2})
Toluene	1904	1896	2.06 (2.53)	3.10 (2.69)
Chlorobenzene	2256	2250	2.25 (2.69)	3.16 (2.77)
Bromobenzene	2634	2611	2.36 (2.79)	3.22 (2.94)
Iodobenzene	3014	2979	2.52 (2.94)	3.24 (3.16)

^a Values from reference [9].

^b Values outside of parentheses processed at 310 °C and inside parentheses 1000 °C.

to model the glassy carbon because it is dominated by the hydrogen-bond base interactions of the ionic salt. However, the consideration of the dispersion free energy terms alone for the glassy carbon, $\Delta G_S^{\text{CAV}+\text{NP}}(X) + \Delta G_{\text{SQ}}^{\text{P}}(X)$, is useful. In this way, a description of solute retention can be achieved based upon nonspecific interactions, independent of any specific effects caused by stationary phase heteroatoms (silicon and fluorine). In other words, the model allows the evaluation of changes occurring at the carbon surface and the degree of graphitization as a function of processing where dispersion is the predominant force.

The free energy dispersion terms for perfluoroaryl and aryl phases with respect to the substituted benzene solute molecules are given in Table 4. Included in the table are the nanomoles of each analyte extracted with the F-LTGC and Si-LTGC for the phases processed at 310 and 1000 °C, which are shown outside and inside parentheses, respectively. To compensate for difference in mass transfer, the nanomoles of analyte extracted were multiplied by the square root of the molecular weight because the rate of diffusion is inversely proportional to the square root of molecular weight [20]. Now, this term should be roughly proportional to a distribution or selectivity coefficient.

The values in Table 4 are plotted in Fig. 6A and B for extractions performed with the carbon phases processed at 310 and 1000 °C. The $-\Delta G^0$ values for aryl were plotted against the quantities extracted by the Si-LTGC phase and the ΔG^0 values for perfluoroaryl were plotted against the quantities extracted by the F-LTGC phase. (It should be noted that no direct comparison should be drawn between the absolute amounts of solute extracted for fibers processed at different temperatures due to differences in carbon loading.) The linear curves indicate the extraction of these compounds is highly dependent on dispersive interactions. The slopes of the curves for the Si-LTGC processed at 310 and 1000 °C indicates that as the extent of the dispersive interactions gradually increased as a function of processing temperature. The highly ordered surface of the carbon processed at 1000 °C shows a greater sensitivity for the solute molecules as a function of ΔG° compared to lower processing temperatures.

Interestingly, the slope of the curves for the F-LTGC (Fig. 6A) oligomer processed at 310 and 1000 °C do not show as great of a change as the silicon oligomer. This implies that the predominant extraction mechanism is es-

tablished at a lower temperature and remains invariant to a greater degree than the silicon oligomer as shown in Fig. 7. It is somewhat surprising that the substantial loss of the fluorine from 310 to 1000 °C (approximately 30%) does not seem to affect the selectivity of the extractions. However, this situation is quite analogous to data reported by Pomaville and Poole studying the partial molar free energy as a function of methyl group calculated for a homologous series of *n*-alkanes, 2-alkanones, 1-bromoalkanes and saturated fatty acid methyl esters [1]. When comparing

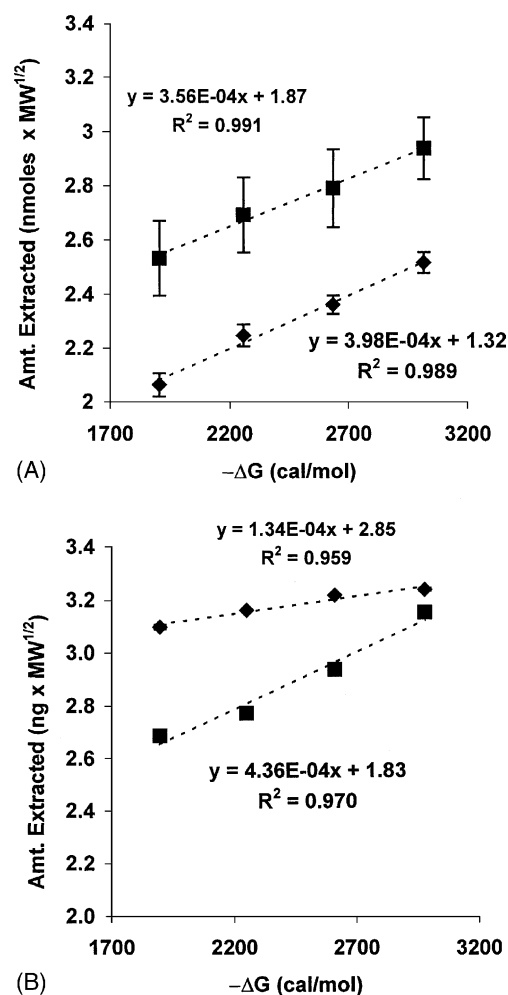


Fig. 6. Amount extracted for extractions with the F-LTGC (A) and Si-LTGC (B) for coatings processed to 310 °C (■) and 1000 °C (◆).

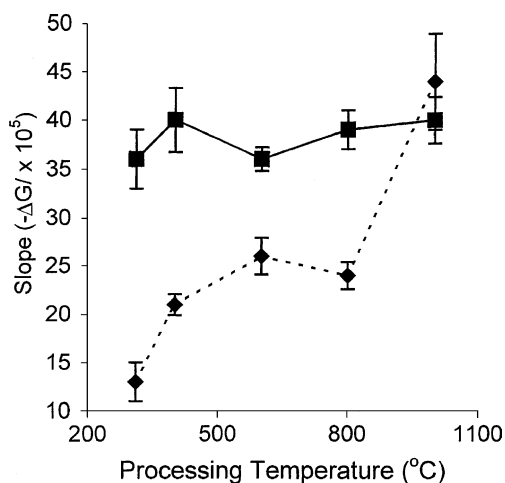


Fig. 7. Change in free energy of adsorption as a function of processing temperature for F-LTGC (■) and Si-LTGC (◆).

the free energies associated with separations of these compounds performed on a perfluoroaromatic phase (PPF-20, poly(perfluorophenylene) ether), they showed minimal lowering of dispersive interactions compared to perfluoroalkyl phases. They suggested that this is either caused by charge-transfer interactions or by the increased dispersive interactions attributed to the greater polarizability of perfluorinated aromatic compounds compared to perfluoroalkanes. Therefore, it appears that the level of fluorine present has a negligible effect on the dispersive component influencing the extraction of these compounds. This is also supported by the conclusions reached by Hutton et al. [13] concerning a chlorinated glassy carbon. Based on spectroscopic evidence, he concluded that presence of the halide does not affect the formation of the sp^2 -hybridized lattice and that the halide is bonded to the carbon structure at the graphitic edge planes. This suggests that the adsorption of these compounds is occurring to a large extent at the basal plane with minor contributions of the fluorine.

In summary, it appears that the ability of the F-LTGC to engage in dispersive interactions is established to a greater extent at lower temperatures and remains fairly constant as thermal-processing progresses compared to the Si-LTGC. Closely tied to this is the fact that the level of fluorine present in the oligomer has very little bearing on the degree to which it interacts dispersively with the solutes.

3.5. Comparative selectivity

The selectivity of several commercial phases was measured and compared to the glassy carbon phases. Fig. 8A shows the selectivity of 100 μm PDMS, 75 μm PDMS/Carboxen and 65 μm PDMS/DVB fibers for the extraction of the halogenated benzenes with respect to toluene. The general trend indicates a decrease in selectivity going from the fluorobenzene to iodobenzene in the composite PDMS/DVB and PDMS/Carboxen fibers. For the pure

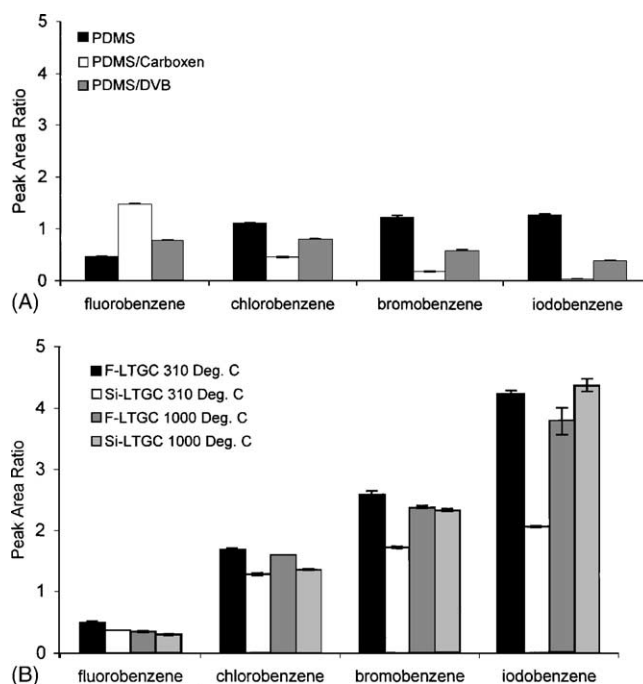


Fig. 8. Selectivity comparison for commercial phases (A) and glassy carbon phases (B). Peak area ratios are the peak area of the analyte/peak area of toluene.

PDMS phase, there is a slight increase in selectivity from fluorobenzene to chlorobenzene but the remaining trend shows little change for bromobenzene and iodobenzene. Of all the fibers tested, the PDMS shows the least amount of selectivity, which is to be expected because PDMS is largely a nonselective hydrophobic phase.

In Fig. 8B, the selectivity of the Si-LTGC and F-LTGC fibers for processing temperatures 310 and 1000 $^{\circ}\text{C}$ is shown. Except for fluorobenzene, the selectivities of the LTGC phases are greater than the commercial phases. Also, the general trend for extraction performed with the PDMS/DVB and PDMS/Carboxen fibers are opposite to that of the glassy carbon phases. For all the glassy carbon phases, the trend and magnitude in the selectivity are very similar. The greatest difference occurs for the F-LTGC processed at 310 $^{\circ}\text{C}$. Also, the slight reduction in selectivity of the fluorine phases between the low and high temperature processing is due to the loss of the fluorine atom.

4. Conclusions

Herein is the first application of the fluorine containing low temperature glassy carbon as a coating phase for SPME. The phases were successfully used to extract a series of halogenated benzene molecules from headspace samples. The reduction in oligomer mass during thermal treatment was found to be a result of the loss of fluorine. However, processing of the fluorinated-oligomer at high temperatures produced a more graphitic and homogenous

glassy carbon compared to that produced with the silicon oligomer as indicated by the low level of surface oxides. Also, the glassy carbon surface forms earlier on in the thermal processing for the fluorine oligomer compared to the silicon. Analysis of the extraction mechanism indicates that dispersion is the predominant force during adsorption. A minor contribution from halogen–halogen interactions is only evident for the fluorinated carbon processed at lower temperatures. From the extraction data, it was also evident that the dispersive forces involved during the extractions are established at lower temperatures for the fluorine oligomer and remain fairly consistent through the processing régime. Compared to commercial fibers, the LTGC-SPME fibers display different selectivity trends and are quite unique and complementary to these established phases.

Acknowledgements

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