Polyimide for deactivating gas chromatography vaporising chambers and fixing packing materials

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Abstract

Glass liners serving as vaporising chambers for large volume injection or transfer into capillary gas chromatgraphy were packed with Carbofrit, a carbon material of open structure and low retentive power. Polyimide was used for deactivation of the glass surface with a water-resistant layer, for fixing the Carbofrit material to the insert wall and for binding loose particles.

1. Introduction

For sample introduction into capillary gas chromatography (GC), vaporising chambers must be used if on-column systems fail. They serve for the retention of non-evaporating sample material and to overcome the retentive power of the latter by a relatively high temperature. Furthermore, they may be used for vaporising solvents that do not wet precolumn surfaces or attack their deactivation when present in liquid phase, such as water. Vaporisers are important for the injection of conventional small volumes of liquid samples, but received additional attention for their use in the context of large volume sample introduction [1].

1.1. Deactivation that resists chemical attack

Vaporising chambers must be sufficiently inert to avoid loss of solute material by adsorption or

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degradation. Retentive power should be minimised in order to release the solute material at relatively low temperature. Finally, to make them last, the deactivation of the surfaces exposed to the sample must resist chemical attack by the sample. The latter is a problem when aggressive materials are injected. Water might be the most important of these, especially if samples are acidic or basic.

Most experience concerning degraded deactivation has been gained for uncoated precolumns used for large volume on-column injection or on-line liquid chromatography–GC (LC–GC) [2]. Damage to the deactivation seemed to be caused by liquids, rather than their vapours. In fact, attack, e.g., by water, was only observed in the region of the flooded zone, but not within the retaining precolumn or the separation column. It is, furthermore, more serious if the surface is wetted, i.e., damage is more severe if water is part of a wetting liquid than if it is injected as such [3] (water alone does not wet any surfaces suiting GC [4]). Damage may not become apparent immediately, since water is also one of the most

efficient deactivation agents. During analysis following the injection of a humid sample, adsorptivity may be low, but then water is vaporised and the damage will become obvious as soon as a dry sample is analysed or a smaller volume of sample liquid is injected, only flooding part of the inlet damaged by previous injections.

Even though the inertness of oven-thermostatted uncoated precolumns is more critical than that of injector liners, problems are essentially the same. Injection of large volumes of liquid and on-line transfer require the deposition of the liquid onto surfaces in order to keep it in place and to regulate evaporation, i.e., to avoid "shooting" [5]. Even if the vaporising chamber is thermostatted far above the solvent's boiling point, the surfaces in the region of the evaporation are cooled to a temperature near the boiling point of the sample, which means, at least initially, that they are cooled to the boiling point of the solvent. Hence, if aqueous samples are injected, the region of solvent evaporation is cooled to around 100°C (pressure-corrected boiling point or dew point). At this temperature, water strongly attacks silica [6] as well as the deactivation layer achieved by silylation or thin coatings with silicon [2]. It is from these surfaces that the sample components must evaporate at a later stage.

1.2. Chemically stable deactivation

Modern GC technology largely relies on silicone chemistry: Most stationary phases consist of poly-siloxanes and deactivation is usually achieved by silylation or reaction with siloxane oligomers. This yields excellent thermostability. Chemical stability, however, is rather poor; silylation is reversible and Si-O bonds are easily attacked. In fact, silylated surfaces readily turn into a silylation reagent, derivatising the sample. Water, for instance, reacts with the silyl group and, since the resulting product is volatile, it is removed from the column and leaves an adsorptive silanol group behind. Other reactions split polysiloxane chains and generate free terminal silanols, which are also considered to be adsorptive.

Improvement may be expected from two avenues. If silicone polymers are attached to the surfaces by several bonds, breakage of a few bonds should no longer result in the loss of the deactivation group. It

may be assumed that heating (e.g., during the analysis) reforms the bonds and restores the deactivation. In uncoated precolumns, very thin coatings (0.3–1 nm) of OV-1701 did, in fact, resist water better than silylation with phenyldimethyl groups [7]. A more basic solution to this problem is expected from deactivation with a material that is chemically more stable. Carbowax was considered as a material for the deactivation of precolumns [8], but it did not fulfil our expectations [9]. Since the chemically labile silica support remains, such a deactivation material has to form a skin, shielding the surface. This skin should behave as a solid. Firstly, solids prevent diffusion of sample material through the layer down to the support surface and, secondly, exhibit no retention power by partitioning, i.e., thick films can be applied. In uncoated precolumns, low retention power is particularly important for focusing the initial band that was broadened in space by the retention gap effect [10]. Unfortunately, most organic polymers become permeable when heated to high temperatures. PTFE, for instance, opens its structure for diffusion at about 180°C [11].

In 1984, Balla and Balint [12] described the use of polyimide as a support material for the preparation of capillary columns. They applied it as a layer (several micrometres thick) on the internal wall of fused-silica capillary tubing and coated it with stationary phase. The concept is convincing, but the method was not used.

1.3. Chemically stable packing materials

The introduction of large volumes of liquid into a vaporising chamber presupposes a packing material that keeps the liquid sample in place and regulates vaporisation. In high capacity vaporisers kept at temperatures substantially above the solvent boiling point, packings help to avoid violent delayed evaporation and "shooting" liquid [5]. In gas discharge systems [13], when evaporating the sample liquid in a gas stream, the carrier gas must be able to open a channel through the liquid [14]. Without a packing material, the liquid would form a plug, which was removed by the gas. Solid, inorganic packing materials offer the advantage of exhibiting low retentive power, i.e., of easily releasing high boiling sample components. However, they consist of silica (glass or

fused-silica wool, glass beads) and/or other materials that are attacked by water, such as column packings [15–17]. Organic polymers, such as Tenax or cross-linked polystyrenes, resist water, but strongly retain the solute material. Strong retention may be useful for the analysis of volatile components when the packing also serves for solvent–solute separation, as in Programmed Temperature Vaporizing (PTV) solvent split injection, but hinders the analysis of high boiling compounds. Since our liners were intended for use as hot, high capacity vaporising chambers and systems performing solvent–solute separation by capillary precolumns, high retention power was not of primary interest. Mol et al. [1] found that PTFE wool was a rather inert material. Polyimide wool was determined to be more adsorptive, particularly to compounds like the organophosphorus pesticides.

Restek (Bellefonte, PA, USA) recently introduced "Carbofrit", a material of low gas chromatographic retention power. Although consisting of carbon, it readily releases most high boiling components, with the possible exception of the large polyaromatics to which carbon has a particularly strong affinity [18]. Carbofrit consists of a regular, three-dimensional network, providing lower resistance against the gas flow than most glass wool packings. On the other hand, it is fairly brittle, easily releasing particles that end up being blown into the column by the carrier gas. Fig. 1 shows a photograph of a 1.1-mm I.D. glass liner with a plug of Carbofrit inserted, before and after treatment with a 50% solution of polyimide in dimethylformamide (DMF) and heating to 330°C (see below). The polyimide turned the liner to a light brown, honey colour. Treatment with a 5–10% polyimide solution, as will be suggested, has no visible effect on black and white photographs.

1.4. Objects of this work

The vaporising chambers investigated during this work were of interest as part of the vaporising chamber–precolumn solvent split/gas discharge system [13], which can be regarded as an on-column/precolumn system with a vaporiser at its entrance. It is intended primarily for syringe injection or on-line introduction (e.g., LC–GC) of large volumes of "dirty" or water-containing samples. Samples are introduced into a hot chamber consisting of a packed
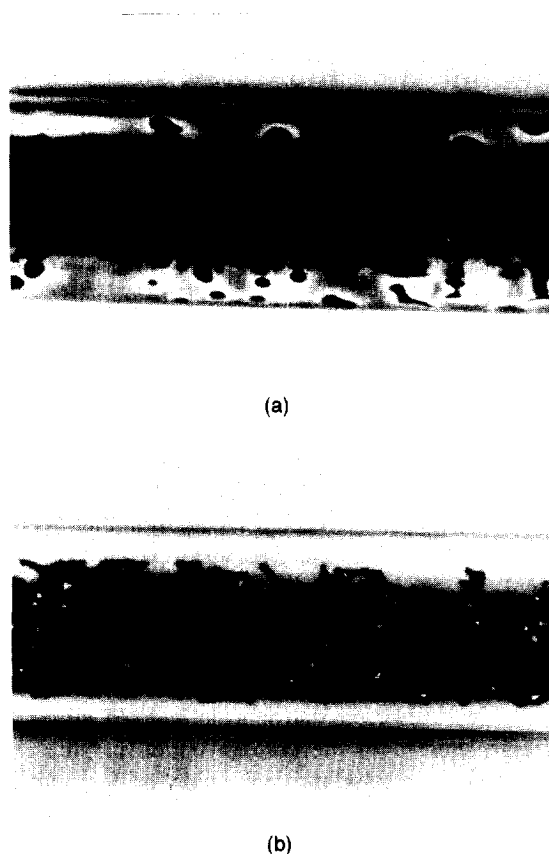

(a)

(b)

Fig. 1. Liner (1.1 mm I.D.) packed with Carbofrit before (b) and after (a) treatment with 50% polyimide in DMF.

glass or deactivated steel liner of 1–2 mm I.D. Vapours are discharged through a precolumn and an early vapour exit. The precolumn may consist of an uncoated precolumn and a retaining precolumn or just one of the two, depending on the technique for solvent/solute separation applied.

The use of polyimide seemed to be promising because it solves two problems at the same time. Firstly, the polyimide coating provides a deactivation of the glass or stainless steel liner (the latter being deactivated with a layer of silica), which resists water better than the methods used previously. Secondly, it acts as a glue, sticking the Carbofrit material to the liner and binding loose particles, i.e., it avoids the need for a glass wool plug to keep the packing in place. Polyimide seemed particularly attractive as it behaves as a solid material up to

temperatures exceeding 340°C, i.e., even large amounts do not build up substantial retention power.

2. Experimental

2.1. Retention power by polyimide

The following experiment revealed that a polyimide layer of 20 μm thickness, on the outside of a fused-silica capillary, exhibits no substantial retention power. A mixture of alkanes ranging from C_{16} to C_{44} in heptane was injected on-column onto a 15 m$\times$0.32 mm I.D. column coated with PS-255 (0.25 μm). Then, a 12-cm piece of 0.17 mm O.D. fused-silica capillary (SGE) with flame-sealed ends was inserted and positioned about 20 cm from the column entrance. The same test run was repeated, with a slightly higher inlet pressure, to compensate for the pressure drop over the inserted piece of capillary tubing. No significant increase in retention times and no broadening of the peaks was observed. Then the column was reversed, causing the inserted tubing to become situated in the column outlet and the test components to pass the polyimide at the elution temperature. Again, even the C_{44} alkane, eluted at 340°C, was not affected by the inserted capillary.

2.2. Instrumental set-up

Further experiments were performed with a vaporising chamber/precolumn solvent split system built into a Carlo Erba (CE Instruments, Milan, Italy) 5300 GC instrument. The gas chromatograph was equipped with an on-column injector and a PTV injector mounted inside the oven to the bottom of the on-column injector. The vaporising chamber consisted of 1.5 mm O.D.$\times$1 mm I.D. liners made from Duran glass with a 20-mm plug of Carbofrit positioned 20 mm from the top. Since the high boiling components were of primary interest, solvent evaporation was performed without partial recondensation, i.e., there was only a retaining precolumn ahead of the early vapour exit (2 m$\times$0.53 mm I.D., coated with 0.2 μm of PS-255, a methyl silicone). Beyond the early vapour exit, there was a 25 m$\times$ 0.25 mm I.D. separation column that was coated with 0.15 μm of PS-255.

The sample was introduced by a syringe pump (Carlo Erba, Phoenix 300) through a ten-port switching valve (VICI, Schenkon, Switzerland) equipped with an injection port and a loop adjusted to the volume to be injected. The sample liquid was delivered through the on-column injector to the top of the Carbofrit packing by a 0.17-mm O.D. fused-silica capillary. This transfer line was permanently left in this position. At the end of the injection, it was emptied backwards by a small flow of carrier gas from the column inlet through the injection valve and a 20 cm$\times$50 μm I.D. fused-silica resistance capillary (as with the on-column interface used in on-line LC–GC [19]). The transfer line passed through a septum that was pressed onto the top of the on-column injector by the syringe guide device in order to prevent loss of carrier gas. The injection rate was determined by the flow-rate of the pump.

2.3. Testing procedure

Injector liners were tested with a mixture containing methyl esters and alcohols from C_{18} to C_{30} (1 ng/μl solution in hexane, prepared from 1 μg/μl solutions of the components in methyl tert.-butyl ether, MTBE). A 100-μl volume was introduced at 100 μl/min in order to reproduce conditions of large volume injection (spreading of the sample and intense contact with the surfaces). The injector was at 300°C. A carrier gas inlet pressure of 1 bar (hydrogen) created a gas flow through the opened vapour exit of 300 ml/min. 3 s after the end of sample introduction, the flow through the vapour exit was restricted by attachment of a 40 cm$\times$75 μm I.D. fused-silica capillary with a press fit connector. Injection occurred at an oven temperature of 40°C, which was then increased at 20°/min to 150°C and at 7°/min to 290°C.

Resistance of the deactivation towards water was tested by introducing water–1-propanol (1:1, v/v) at 100 μl/min over 20 min, with a 2 m$\times$0.53 mm I.D. fused-silica capillary attached to the injector for control of the gas flow-rate. Propanol was added to improve the wettability, i.e., to achieve more intense contact. The injector was kept at 120°C, because this rendered the test tougher. The region of solvent evaporation is cooled to a temperature that is near the boiling point of the solvent. At a high injector

temperature, this region is small, since the heat supply is efficient. At an adjusted injector temperature of 120°C, however, evaporation remained incomplete and non-evaporated solvent was in contact with the whole liner.

2.4. Preparation of the liners

Blocks of Carbofrit were obtained from Restek. Glass liners were packed by cutting several plugs from the block by the liner itself. Packed liners were rinsed with chloroform solutions of EPO-TEK single component polyimide P-10C-1, an almost colourless viscous liquid obtained from Polyscience (Zug, Switzerland), by aspirating it through by vacuum. Concentrations exceeding 30% could only be achieved in DMF. Chloroform was preferred, where applicable, because it readily evaporated by drawing air through the liner. The polyimide was hardened, by turning the liner under an aluminium foil over a heating plate using a slow drilling machine. Initially, the plate was near ambient temperature, then it was heated to 100, 150 and 200°C over 15 min and finally it was heated at 300°C for 30 min. Turning was essential in order to obtain a fairly homogeneous coating of the liner wall. The liner was then installed into the PTV injector and heated at 330°C without carrier gas or mounting of the column.

3. Results

From the experiment with the piece of fused-silica capillary inserted into a column, it was concluded that polyimide maintains its solid properties up to at least 340°C, i.e., it does not allow solute material to diffuse into it. If the 200 μm polyimide coating had behaved as a liquid, it would have performed like a thick-film-trap, from which even the C_{30} alkane hardly would have had a chance to desorb at 340°C. This means that thick layers of polyimide can be applied within the chromatographic path without building up retention power. This is, in fact, a prerequisite if the material is to be useful for gluing the Carbofrit into the vaporising chamber and for shielding the liner wall.

3.1. Deactivation with polyimide

The top chromatogram in Fig. 2 shows the test result of a liner before deactivation with polyimide. Adsorption of the alcohols primarily was by the glass surface, as determined by the following two experiments: injection of a small volume of test solution into a liner without Carbofrit resulted in strong adsorption. A 1-μl injection into the Carbofrit packing of a non-deactivated liner, however, showed little adsorption, because evaporation occurred from the packing.
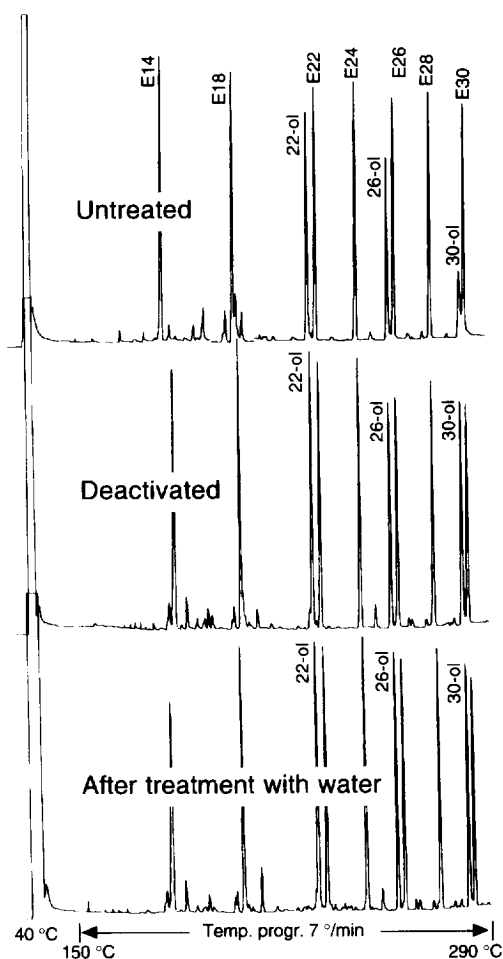

Fig. 2. Test chromatograms of a liner packed with 20 mm of Carbofrit. Top, before deactivation; centre, after treatment with 1% polyimide in chloroform; bottom, after treatment of the deactivated liner with water–propanol. Methyl esters of the C_{14} to C_{30} acids (E) and 1-alcohols C_{22} to C_{30} (-ol).

After treatment with a 1% polyimide solution, adsorption of alcohols was eliminated (middle chromatogram). Treatment with water–propanol did not affect the performance of the liner (bottom chromatogram).

3.2. Water resistance

The GC–flame ionization detection (FID) chromatograms in Fig. 3 are from a glass liner without polyimide treatment, which had little adsorptivity to begin with. The upper chromatogram was obtained with the freshly packed liner, the bottom chromatogram was obtained after treatment of the latter with water–propanol. The deterioration of the alcohol peaks shows increased adsorptivity resulting from attack by water. Emptying the liner and injection of a 1-μl volume of test solution showed strong adsorption, supporting the conclusion that the glass surface had become adsorptive, presumably through opened siloxane bonds and formation of silanols. Using the liner protected with polyimide, the same treatment with water–propanol did not affect the liner's performance (Fig. 2, bottom chromatogram).
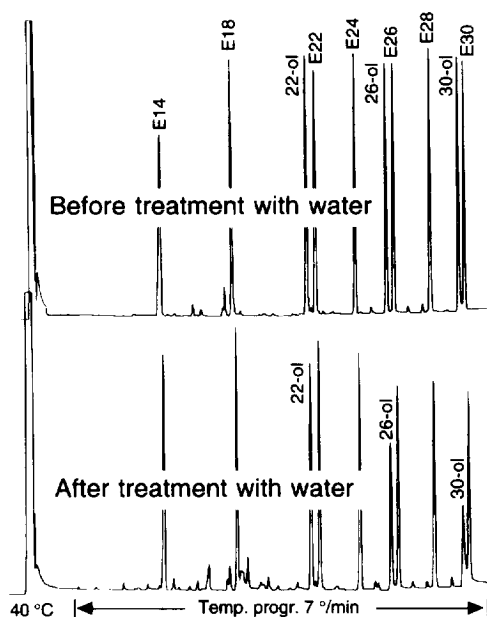

Fig. 3. Increase of adsorptivity through water–propanol for a liner that was not protected with polyimide, but was exceptionally inert without deactivation.

3.3. Optimum amount of polyimide

Treatment with 1% polyimide in chloroform provided good deactivation (Fig. 2). However, the Carbofrit was not fixed well enough; the plugs could be moved and tapping the liner on to the table caused some small particles to fall off. In order to observe possible problems caused by the introduction of large amounts of polyimide, a liner was treated with undiluted polyimide. The high viscosity of the glue caused greater than 100 times more material to be deposited. In fact, after heating, this liner turned black and was no longer transparent. Nevertheless, test results were perfect (Fig. 4), confirming that the polyimide was solid and exhibited no chromatographic retention power. However, it took several hours of heating at 350°C to remove material causing "ghost" peaks, to the extent shown in Fig. 4.

The optimum concentration of polyimide in chloroform for deactivation and mechanical fixation of the packing was 5–10%. It does not increase the resistance against gas flow significantly, i.e., it maintains the openness of the packing. This is important for the discharge of the large volumes of vapours generated during sample introduction at high flow-rates. Using FID, there were no problems with the blank resulting from bleeding of the polyimide.

Once cured at high temperature, polyimide was no longer extractable to a significant extent. A dark brown liner, obtained by treatment with 70% polyim-
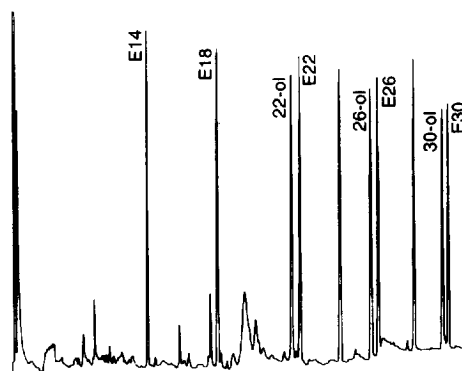

Fig. 4. GC–FID test chromatogram of a liner treated with undiluted polyimide. The extremely large amount of polyimide deposited did not result in increased adsorption or retention power. It is, however, more tedious to remove material causing "ghost" peaks.

ide in DMF, was heated in DMF. Neither was there a visual effect on the liner, nor was there more than a touch of brown in the extract.

4. Conclusion

Vaporising chambers suitable for syringe injection or on-line transfer from sample preparation should be inert and resistant to attack in order to have a long life time when used for "dirty" samples or samples containing aggressive components, such as water. If used for a precolumn solvent split system performing solvent–solute separation apart from solvent evaporation [11], the retention power inside the chamber should be low in order to obtain good performance for high boiling and labile sample components. The proposed glass liner packed with Carbofrit and protected with polyimide bears promises to fulfil these requirements, at least as far as indicated by the testing procedure with esters and alcohols of low volatility.

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