Polydimethylsiloxane as a Packing Material in a Programmed Temperature Vaporizer to Introduce Large-Volume Samples in Capillary Gas Chromatography

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Abstract

The viability of using polydimethylsiloxane (PDMS) as a retaining material inside a programmed temperature vaporizer injector for the introduction of large-volume samples in gas chromatography is assessed. To that end, materials made up of Volaspher A-2 and coated with different percentages of PDMS (5%, 15%, and 50%) are considered. In addition, adsorbent (Tenax TA) and absorbent (PDMS) materials are comparatively studied in terms of their retention capacity. A relative standard deviation lower than 5.0% is obtained from the injection of PDMS, whereas values up to 49% are provided by Tenax TA. Significantly higher amounts of different volatile compounds are retained by PDMS in comparison with Tenax TA. In conclusion, the use of PDMS as a packing material seems to be viable for large-volume sampling and particularly recommendable for minor compounds occurring in complex matrices.

Introduction

Generally speaking, the possibility of introducing a sample directly into the gas chromatograph (GC) with no prior pretreatment improves the reliability of the analysis. In particular, it can be especially useful to determine volatile components occurring at low concentrations, as occasional losses might make their quantitation or even their detection particularly complicated. In this respect, the advantages of using a programmed-temperature vaporizer (PTV) injector for the introduction of large volumes into capillary GC have been reported by several authors (1–4). This procedure involves the use of an adequate packing material inside a glass insert, which is, in turn, placed into the injector body. By using this approach, careful optimization of the involved experimental variables is usually demanded to achieve an efficient retention of the compounds of interest on the packing while the solvent is simultaneously removed. Among these variables, the relevance of considering the sample volume, speed of the sample introduction, the flow rate during sampling, and both the initial and final PTV temperatures was previously pointed out (5–7). However, as far as the packing material is concerned, to our knowledge, only adsorbents (mainly Tenax TA) have been used to date for the introduction of large sample volumes by using a PTV.

Adsorbents are porous materials with a high internal surface area, which causes the analytes to be temporarily retained on the adsorbent superficial active sites. Although these kinds of material usually work quite successfully, they possess some drawbacks, such as their background compounds and the risk of depolymerization and degradation. In addition, adsorptive materials normally result in poor recoveries when combined with thermal desorption. Consequently, adsorbents are easier to recommend when liquid desorption is employed to recover the analytes from the material (8). Taking into account that thermal desorption is normally applied to transfer the solutes retained on the PTV packing material to the GC column, the need for alternative materials that overcome the limitations of adsorbents for the introduction of large volumes is clear. In this context, absorbent materials might be an interesting option for consideration. Generally speaking, absorbents are homogenous, nonporous materials that retain the analytes by dissolution instead of undergoing real bonding with the packing. The most frequently used absorbent is undoubtedly the non-polar polydimethylsiloxane (PDMS). Some of the most outstanding advantages shown by this material are its chemical inertia, stability, and reproducibility.

The objective of this research was to evaluate the viability of using an absorbent material, specifically PDMS, to introduce large volumes of complex mixtures in capillary GC via PTV. A further purpose of this research was to comparatively study the efficiency, in terms of retention capacity, of both adsorbent and absorbent materials.

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Experimental

Standard solutions

Two different test solutions, including compounds of different volatilities, chemical structures, and concentrations, were used in this study: (*i*) the first sample mixture (sample 1) consisted of undecane, ethyl phenyl acetate, 1-octanol, 1,4-butanediol, benzyl alcohol, 2-methyl propanal, and *N*-benzyl dimethyl amine in methanol (concentrations ranged between 280 and 530 mg/L); (*ii*) the second sample mixture (sample 2) contained 800 μL of each of the described compounds, plus 1 μL of α-phellandrene and limonene in 100 mL of methanol. Undecane was purchased from Merck (Darmstadt, Germany) and ethyl phenyl acetate came from Sigma-Aldrich (Madrid, Spain), whereas 1-octanol, 1,4-butanediol, *N*-benzyl dimethyl amine, α-phellandrene, and limonene were obtained from Fluka (Buchs, Switzerland). Benzyl alcohol and 2-methyl propanal were supplied by Carlo Erba (Milan, Italy) and PolyScience (Cham, Switzerland), respectively. Methanol (HPLC grade) was provided by Scharlau (Barcelona, Spain).

Instrumentation

Large-volume injections and subsequent GC analyses were carried out by using a Varian GC (Model CP-3800) equipped with a flame-ionization detector (FID) and a PTV injector (Varian, CA), which acted in the solvent split mode. The data acquisition was performed using a Star Toolbar system (Varian, CA).

Tenax TA (80–100 mesh, Chrompack, Middelburg, the Netherlands) and the synthetic silica-based support Volaspher A-2 (80–100 mesh, Merck), coated with different percentages (5%, 15%, and 50%) of PDMS (PDMS-12M, Sigma-Aldrich), were used as packing materials in the glass liner (a silylated insert of 55 × 3.4-mm i.d., × 6.3-mm o.d., purchased from Varian, CA) of the PTV. The PDMS materials were prepared by dissolving the silicone in 20 mL of CH_2Cl_2 and, subsequently, adding Volaspher A-2 to the obtained solution. The amounts used in each case were 53 mg of PDMS on 1002 mg of Volaspher A-2, 378 mg of PDMS on 2500 mg of Volaspher A-2, and 501 mg of PDMS on 1000 mg

of Volaspher A-2 to prepare the percentages of 5%, 15%, and 50%, respectively. The solvent was finally removed by using a rotary evaporator at room temperature. In all cases, traps were prepared by filling 3 cm of the glass liner with the corresponding packing material. This length corresponded to a 76-mg weight for Tenax TA, as well as 140, 145, and 230 mg for the percentages of 5%, 15%, and 50% of PDMS on Volaspher A-2, respectively. The material was held in place by two plugs of glass wool. Prior to use, Tenax TA and PDMS packing materials were properly conditioned under a stream of helium at 350°C for 2 h and 210°C for 30 min, respectively.
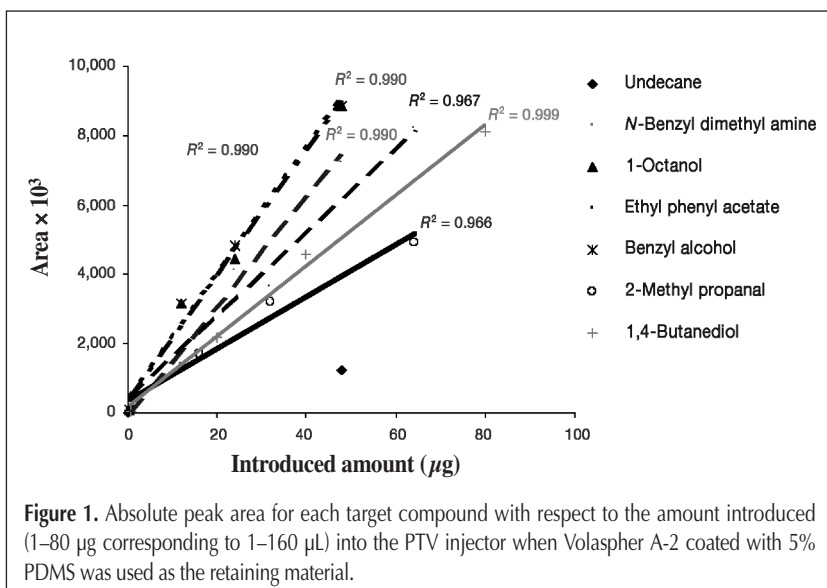
PTV conditions

The introduction of large-volume samples (up to 1500 μL) was accomplished by discharging a 100-μL syringe (Hamilton, Model 710N Bonaduz, Switzerland) into the injector at a speed of 1.1 μL/s. On the basis of previous experience in large-volume introduction (9,10), during sampling, the body injector was maintained at 40°C, and the GC column was withdrawn from the injector body in such a way that the solvent was mostly eliminated through the injector–column connection. As described in the literature (11), a minor proportion of solvent was also removed through the split exit, which was kept open during this step (ratio 50:1, measured with the GC column connected). In addition, in order to eliminate the remaining solvent from the glass liner, helium flows of 1.7 and 2.0 mL/min (the flow was measured with the GC column disconnected) were applied when Tenax TA and PDMS were used as the packing material, respectively. Once the injection was complete, the carrier gas flow was interrupted, the column end was again connected to the injector, and the retained compounds were transferred to the GC column by increasing the PTV temperature (200°C/min from 40°C to either 300°C for Tenax TA or 200°C for PDMS). In all instances, the PTV final temperature was maintained for 10 min.

GC analysis

Chromatographic separations were carried out on a 30-m × 0.25-mm i.d. fused-silica column coated with a 0.25-μm layer of polyethyleneglycol (Carbowax, Quadrex, Woodbridge, CT). The oven temperature was programmed at 6°C/min from 40°C up to 250°C. In all analyses, the FID was set at 250°C and helium was used as the carrier gas.

Results and Discussion

Because previous investigations on the introduction of large sample volumes via PTV (carried out in this laboratory) have demonstrated Tenax TA to be occasionally unsuccessful in terms of retention capacity, evaluating the possibility of using an absorbent material for this purpose was considered. PDMS has already been described by some authors to provide particularly satisfactory results when combined with thermal desorption in a number of sample-

Figure 1. Absolute peak area for each target compound with respect to the amount introduced (1–80 μg corresponding to 1–160 μL) into the PTV injector when Volaspher A-2 coated with 5% PDMS was used as the retaining material.

preparation techniques (12–14), although its use in large-volume sample introduction in GC has not yet been reported. Accordingly, the behavior of PDMS as a packing material inside a PTV injector was studied. To that aim, a standard mixture containing compounds with a differing chemical nature (see sample 1 in the Experimental section) was used.

It is important to point out that the viscosity of the PDMS used (12500 cSt at 25°C) made it necessary to employ a chromatographic support (Volaspher A-2) to prepare a packing material that could be handled and placed into the glass liner. The homogeneity of the obtained material depended on the proportion of PDMS used with respect to Volaspher A-2. For this reason, a percentage as low as 5% was initially prepared. As a starting point, an approximate amount of 0.4 µg for each compound was initially injected. Subsequently, increasing amounts of sample 1 were manually introduced into the PTV, which contained the glass liner filled with a packing material made up of 5% PDMS and 95% Volaspher A-2. The injected amount range was selected in such a way that it enabled the PDMS behavior as a retaining material inside the PTV to be reliably investigated.

Figure 1 depicts the absolute peak areas obtained with respect to the introduced amount (µg) of each analyte. As a first conclusion, it can be stated that the material prepared by coating Volaspher A-2 with PDMS (95:5, w/w) can be used as the packing material inside a PTV injector for the introduction of large volumes. Moreover, each compound included in this study showed a linear behavior ($r^2 > 0.967$) with the injected amount, meaning that the effectiveness of the PDMS did not appear to depend on the chemical structure of the analyte. In this respect, it should be underlined that undecane could not be analyzed by this approach, most likely because of its removal with the solvent during sampling.

The retention observed in the proposed method (i.e., the retention resulting from both the packing material placed inside the PTV injector and the stationary phase used in the chromatographic column) depended on the amount of material used in the injector, the amount of liquid phase contained in the column, and on the vapor pressures and activity coefficients of the target solutes. Furthermore, other variables affecting the overall analysis should also be considered, specifically, the solubility parameter (δ) of helium. It was estimated from its enthalpy of vaporization and molar volume under the experimental conditions tested and resulted to be closer to that of undecane than to those of other solutes (e.g., 1-octanol, 2-methyl propanal, and 1,4 butanediol). Because a helium flow as high as 2.0 mL/min was applied in the PTV to promote solvent removal during the experimentation, it was clear that undecane may have had a more significant inter-action with the gas than the described compounds, and, consequently, it may be more

easily swept from the retaining material and eventually removed with the solvent.

In any case, from the obtained results, it was considered reasonable to evaluate the effect of increasing the percentage of PDMS with respect to Volaspher A-2 in the tested material. In this way, 15% and 50% PDMS were tested. Once more, all target compounds showed a linear behavior with the introduced amount. Actually, better correlation coefficients ($r^2 > 0.996$) than those previously observed were obtained in all instances. It is also worth highlighting that, in contrast to 5% and 15% PDMS, undecane could be properly retained when using Volaspher A-2 coated with 50% PDMS. This was because PDMS seemed to be adequate for all compounds included in this study, as long as a weight of at least 50% was used to prepare the packing material. Figure 2 illustrates a comparison of the retained amount on Volaspher A-2 coated with 5%, 15%, and 50% PDMS for each compound. In general, it can be seen that higher peak areas were obtained when higher proportions of PDMS–Volaspher A-2 were employed to prepare the material tested in the PTV. Nevertheless, despite the satisfactory results provided by the previously mentioned packing materials, a percentage of PDMS higher than 50% was not considered in this study, owing to the lack of homogeneity of the material and, thus, to the experimental difficulty that it involved.
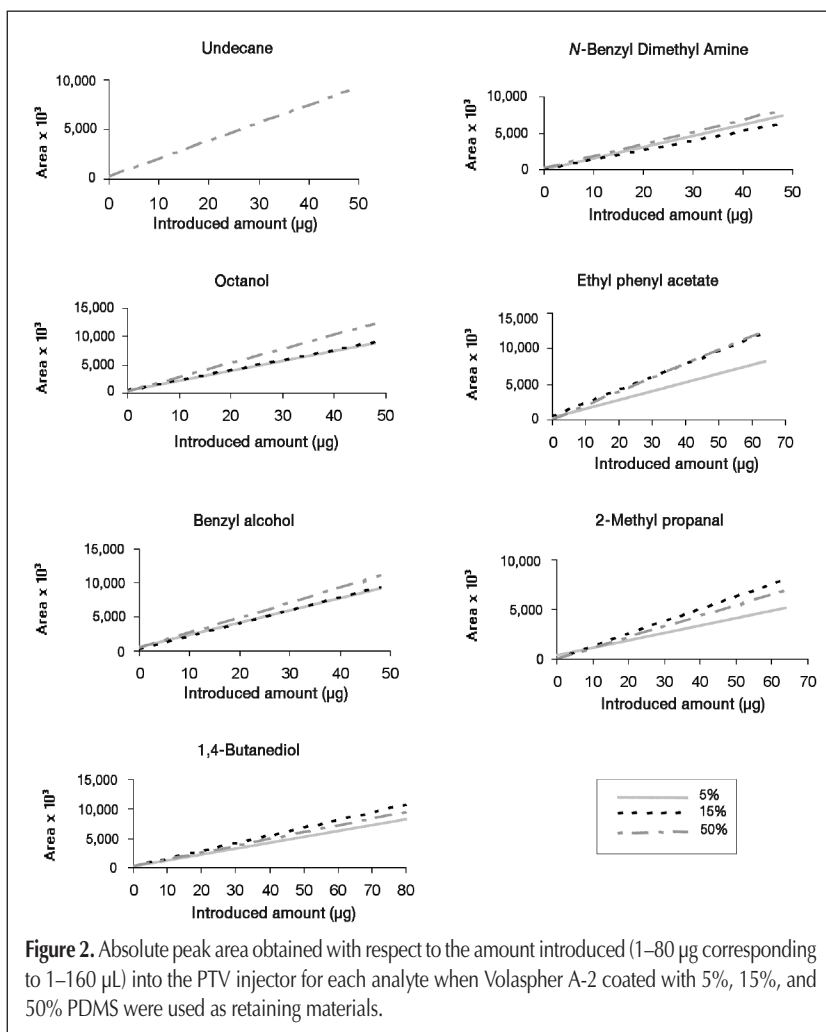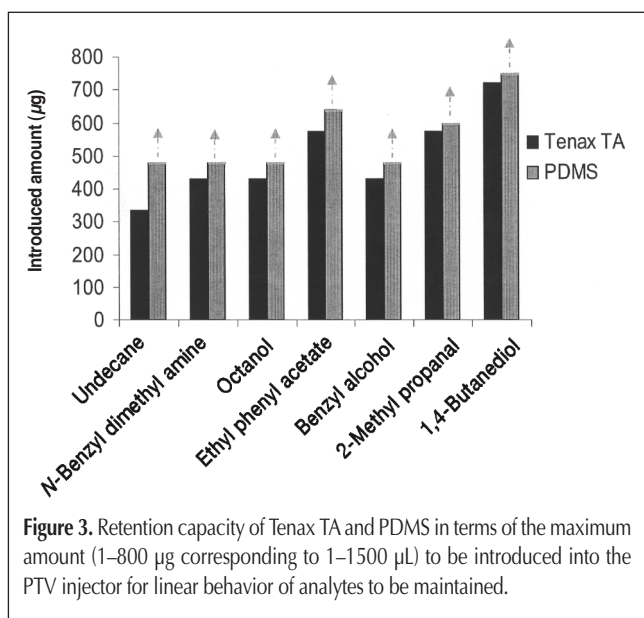

Figure 2. Absolute peak area obtained with respect to the amount introduced (1–80 µg corresponding to 1–160 µL) into the PTV injector for each analyte when Volaspher A-2 coated with 5%, 15%, and 50% PDMS were used as retaining materials.

Figure 3. Retention capacity of Tenax TA and PDMS in terms of the maximum amount (1–800 µg corresponding to 1–1500 µL) to be introduced into the PTV injector for linear behavior of analytes to be maintained.

Table I. RSD Values (%)* Resulting From Internal Concentration into the PTV Injector using PDMS and Tenax TA as Retaining Materials

Compound	PDMS[†]	Tenax TA
Undecane	2.5	20.0
N-Benzyl dimethyl amine	1.3	48.9
1-Octanol	1.1	30.6
Ethyl phenyl acetate	2.9	11.1
Benzyl alcohol	0.3	21.0
2-Methyl propanal	4.9	20.5
1,4-Butanediol	0.2	12.5
α-Phellandrene	0.4	0.8
Limonene	2.2	2.6

* Calculated from three replicates.
[†] Packing material: 50% PDMS in Volaspher A-2.

Once the validity of PDMS as retaining material had been evaluated, a comparative study on the retention capacity of both an absorbent (PDMS) and an adsorbent (Tenax TA) material was performed. To that aim, the linearity range of all compounds contained in sample 1 (see the Experimental section) was estimated by injecting growing amounts into the PTV filled with either Tenax TA or Volaspher A-2 coated with 50% PDMS. As a result of this experiment, a maximum amount, above which the peak area resulting from the analyte introduced in the PTV injector was no longer linear, was encountered for Tenax TA, whereas an upper limit was not observed when the solutes were injected onto PDMS. Figure 3 represents the maximum amount (µg) to be introduced into the PTV injector to assure the linear behavior of the analytes on both tested materials. As can be seen, PDMS appeared to show a higher retention capacity than Tenax TA for all compounds studied. Specifically, amounts higher than 336, 432, 432, 576, 432, 576, and 720 µg for undecane, *N*-benzyl dimethyl amine, 1-octanol, ethyl phenyl acetate, benzyl alcohol, 2-methyl propanal, and 1,4-butanediol, respectively, could not be reliably determined by using Tenax TA. Differences found between Tenax TA and PDMS were most likely because of the different mechanism that retain the solutes on both materials. When an adsorbent was placed into a PTV injector, the compounds of interest were isolated from the matrix by solid-phase extraction (SPE). This differs from absorption, a process based on the partitioning of a compound between two immiscible phases. As briefly mentioned in the Introduction, molecules bind directly to the surface of a solid during adsorption, and they dissolve in the bulk of the material during absorption. Therefore, the amount of molecules that adsorbed onto the surface when an adsorbent was used inside the PTV was proportional to the total surface area of the solid, whereas it depended on the material volume or mass of the material when an absorbent was employed. It should be emphasized that when selecting a packing material, the mechanism that retains the solutes and the chemical structure of the material should be considered. In this regard, because PDMS is a non-polar polymer, it should show, in theory, a high affinity to nonpolar solutes. This

fact was taken into account, as explained later, when selecting the analytes used in the last part of this study.

From the results obtained and considering all aspects mentioned, PDMS seemed to be more recommendable than Tenax TA when amounts greater than those established earlier for each specific analyte were analyzed (see comments to Figure 3). In general terms, when minor analytes occurred together with solutes present in a high concentration, the use of PDMS might have allowed a more reliable detection of low levels.

To study this possibility, a solution made up of compounds with very different concentrations was prepared (sample 2 in the Experimental section). Two compounds, α-phellandrene and limonene, were added in a 1:800 proportion to a mixture containing the same compounds as sample 1. The selection of these two compounds was essentially based on their non-polar nature. In this way, the injection of 400 µL of this solution in the PTV, filled with either Tenax TA or PDMS (50% on Volaspher A-2), was accomplished. The RSD was estimated from three replicates varying from 0.2% to 4.9% for all the studied compounds when PDMS was used, whereas values up to 49% were obtained from injections with Tenax TA (Table I). The higher RSD values observed when using the adsorbent material were most likely because of the fact that several analytes must be adsorbed simultaneously and, therefore, compete for the available adsorptive sites. In this case, as previously reported by other authors (8), matrix compounds occurring at relatively high concentrations can block adsorptive sites, leading to unpredictable and irreproducible results.

As shown in Table I, in view of the RSD values obtained, it is evident that losses are occurring when Tenax TA is used as the packing material. In this regard, there are several possibilities to be considered. The analytes might be either swept during sampling because of low retention in the material, evaporated along with the solvent through the connection of the injector to the GC column, or irreversibly retained in the packing material. On the other hand, although measuring major peak areas was somewhat complicated as a consequence of column overloading, this test allowed the influence of the packing material on the retention of the minor compounds (i.e., α-phellandrene and limonene) to be evaluated. In this regard, absolute peak areas 1.9 and 1.4 times

higher than those obtained from Tenax TA were achieved for α-phellandrene and limonene, respectively, by using PDMS. The increase in the peak areas of minor compounds and the better repeatability attained when PDMS was used as the packing material makes it necessary to carry out a more exhaustive study on the use of absorbent materials for the introduction of large sample volume in GC via PTV. Additional advantages observed for PDMS were its thermal stability and, consequently, a more stable baseline because the intensity of the noise could be reduced 4.4 times with respect to that obtained when using Tenax TA as the retaining material, thus allowing a more reliable trace analysis. Also, a more efficient solvent removal was achieved when using PDMS because it allowed solvent peak areas 3.5 times lower than those corresponding to Tenax TA to be obtained.

An interesting aspect to be considered was that with all the temperatures employed, the PDMS was maintained above its glass transition point. Therefore, the PDMS must be in a gum-like or liquid-like state throughout the experiment, and it must behave similarly to organic solvents, thus allowing the dissolution or partitioning of the target compounds.

Conclusion

In this preliminary study, the approach proposed in this work was considered very promising, as it suggested the possibility of using absorbents as alternative materials to adsorbents for the introduction of large-volume samples in GC via PTV. The results obtained can be used to improve the sensitivity and reliability of the determination of trace compounds occurring in complex matrices by direct injection of the sample and its subsequent internal GC concentration in the trapping material of the PTV. The current aim is to extend the use of absorbents to the online coupling of reversed-phase liquid chromatography with GC via PTV, with the goal of improving the recovery currently obtained with adsorbent materials.

Acknowledgments

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