Characterization of poly(2,6-diphenyl-*p*-phenylene oxide) films as adsorbent for microfabricated preconcentrators

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ABSTRACT

This work aims at evaluating poly(2,6-diphenyl-*p*-phenylene oxide) (Tenax TA), in the form of thin films, as an adsorbent material for various analytical applications. The physical properties of the polymer were studied with regard to surface topography, crystal structure, and thermal stability. Films deposited from solution at different substrate temperatures were studied and compared to the granular form of the polymer. It was found that Tenax TA deposited from solution have a different topography compared to their granular counterpart. The films possess a complex phase composition that includes crystalline and amorphous phases. The films showed high thermal stability (400 °C) similar to the granular form. The adsorption performance of the polymer compared to other possible adsorbent films such as polydimethylsiloxane (PDMS) and layer-by-layer assembled gold nanoparticles (GNPs) were also investigated. Representative volatile organic compound samples were used to compare the adsorption properties of Tenax TA films to that of the granules.

1. Introduction

The polymer of 2,6-diphenyl-*p*-phenylene oxide was patented by General Electric Co. in 1969 as an electrical insulation polymer [1]. The polymer was then developed by AKZO Research Laboratories, Netherlands, as a column packing material for chromatography [2]. It is commonly known by the trademark name "Tenax" with different suffixes. Tenax TA is an improved version of the original Tenax GC. Tenax GR is latest version containing 23% graphitized carbon [3]. The polymer was employed for the first time as an adsorbent for preconcentration of volatile organic compounds (VOCs) by the National Aeronautics and Space Administration (NASA) for monitoring cabin atmosphere in Skylab-4 [4]. Presently, the granular adsorbent is commonly used as a stationary phase in packed column gas chromatography [5] and as an adsorbent material in standard methods from the US EPA and the UK HSE for monitoring air quality and industrial emissions [6]. The adsorption properties of Tenax, in the granular form, have been studied extensively [7–15]. However, quantitative information regarding polymer's physical properties and VOCs adsorption mechanisms are rather scarce with a few studies being found in the literature [16–19].

Recently, Tenax TA, in the film form, has been used as film-based adsorbent for micro preconcentrators (μPCs) by two groups [20,21]. Preconcentrators are concentration amplifiers used to improve the detection limit of analytical systems such as spectroscopy, mass-spectrometry, and chromatography. They are also an integral part of handheld chemical detection systems. Miniaturization of preconcentrators provides high efficiency in terms of sample capacity to device size and the amount of energy needed to release the trapped chemical species. Microfabricated PCs are undergoing a steady evolution resulting in continuous improvement in their performance and capabilities [22–35]. The challenges that arise from miniaturization and batch fabrication of μPCs were the driving force for the efforts on the film-based Tenax TA. One of these challenges is entraining and packing relatively large adsorbent particles within microfabricated structures. It should be noted that the harsh conditions of granular adsorbent packing such as high pressure and the application of ultrasonication which is crucial to achieve good packing density [36] usually cannot be tolerated by microstructures within the μPC or the chip packaging technology. This challenge has also driven the development of several coating methods for μPCs. Some of the coating technologies include spin coating [22], plasma deposition [37], inkjet printing [21], electroplating [38], or conventional static and dynamic

methods used to coat chromatographic open tubular capillary columns [39].

The high molecular weight $(0.5–1\times10^6$ g/mol) [2] polymer in granular form has several attractive features. It is thermally stable (up to 350 °C) [40], has relatively low water retention [10], and is relatively resistant to oxygen (does not require purification of carrier gas) [2]. The film-based adsorbent is deposited on the microstructures from solution (Tenax TA in dichloromethane) under ambient conditions. However, it is not clear if the properties of the adsorbent are retained after this process. The present article describes the characterization of Tenax TA films deposited from solution at different substrate temperatures. The results presented here provide insight on the properties of the film-based polymer in comparison to the granular form. Such information is not only helpful for improving the performance of µPCs, but also in exploring other applications of the film-based polymer. Such applications include solid phase microextraction (SPME) [41], capillary (also microfabricated) chromatography columns, and membrane separation technology. To the best of our knowledge, no systematic characterization of films deposited at different temperatures has been carried out previously.

2. Materials and equipment

All VOC samples used in this work were reagent grade (Sigma-Aldrich Inc., St. Louis, MO). Tenax TA (80/100 mesh, Sigma-Aldrich Inc., St. Louis, MO) was dissolved in dichloromethane (10 mg/mL). For X-ray diffraction measurements, the films were deposited on Kapton at room temperature (20 °C) and at elevated temperature (100 °C). Film thicknesses were in the range of 100–150 µm.

X-ray diffraction (XRD) patterns of the products were recorded using a powder-type X-ray diffractometer (Siemens D5005, Bruker AXS, Inc., Madison, WI) optimized for characterization of thin films. The instrument was operated at 40 kV and 40 mA, producing characteristic $Cu_{K\alpha}$ radiation with an average wavelength of $\lambda = 1.5418$ Å. No background corrections were applied.

Thermal gravimetric analysis (TGA) was done using a research-grade thermogravimetric analyzer (Q 500, TA Instruments, New Castle, DE) for Tenax TA granular and films. The sample sizes for granular, 20 °C film, and 100 °C film were 22.4 mg, and 4.9 mg, and 6.5 mg respectively. The samples were heated from 0 °C to 1000 °C with a rate of 20 °C/min in the air atmosphere of 60 mL/min.

The device testing was carried out using a commercial gas chromatography (GC) system (Agilent Technologies, Inc., Palo Alto, CA). The testing apparatus was installed inside the GC oven in order to maintain isothermal temperature conditions. The setup was supplied with carrier gas via the GC inlet. This configuration enabled the use of the built-in gas flow controller to control the carrier gas entering the setup. The setup was also connected to the built-in flame ionization detector (FID). This permitted signal detection and data collection through the built-in signal processing system of the GC instrument.

The testing apparatus consisted of a six-port zero-dead-volume valve (C6W, VICI Valco Instruments, Houston, TX), and two 250 µm-ID deactivated fused silica transfer lines (Agilent Technologies, Inc., Palo Alto, CA). Using a precision sampling syringe (Pressure-Lok needle, VICI Valco Instruments, Houston, TX), the sample was manually withdrawn from the sample vial and then injected into the GC inlet.

Device testing consisted of a series of three different runs: blank, loading, and heating, all at an inlet pressure of 5 psi. In the blank run, the device was heated to 250 °C at a rate 100 °C/s in order to establish a baseline. In the loading run, the sample was passed through µPC at an isothermal temperature of 60 °C to adsorb the sample. Finally, in the heating run, the µPC was heated to 250 °C at a rate of 100 °C/s in order to desorb the sample. The inlet and FID temperatures were both kept at 280 °C. The µPCs used in this study consisted of an array of 3D micro pillars similar to our previously reported work [21]. Fig. 1 provides a photograph of the µPC showing both front and backside where the heaters and sensors are located. The outer dimensions of the silicon-glass chip were 7 mm × 7 mm × 1 mm. The µPC specific surface area was measured to be 10 m²/g (gas sorption method) with a volume of about 6.5 µL. The dimensions of the high-aspect-ratio pillars were 30 µm × 120 µm × 240 µm. The µPCs used in this study were also coated with (10 mg/mL).

3. Results and discussion

3.1. Tenax TA physical characteristics

To determine if the as-received Tenax TA polymer properties change during the film deposition process, it was necessary to compare the physical characteristics of Tenax TA films to those of the granular form. The granular adsorbent (80/100 mesh) consist of highly porous particles with an average size of 200 µm. The advertised specific surface area of the Tenax TA is 35 m²/g. However, a lower
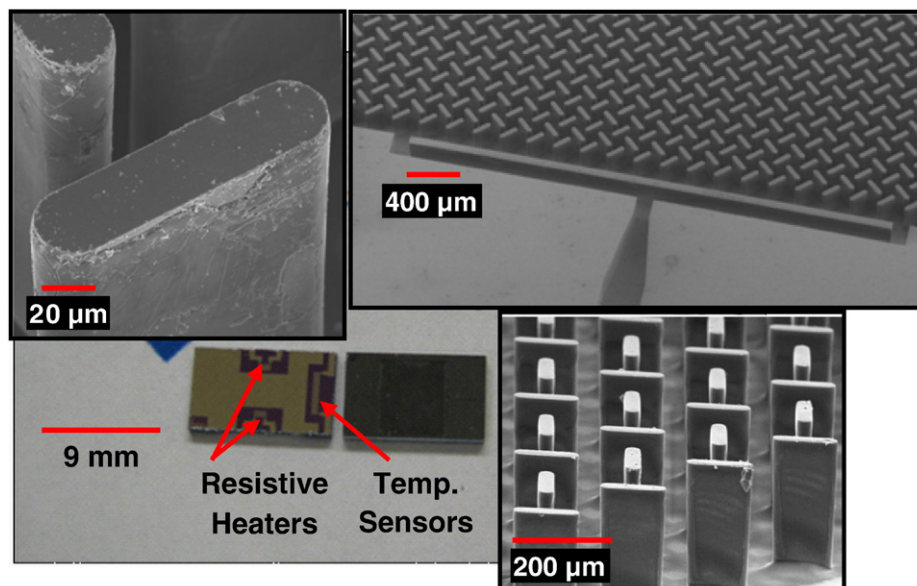

Fig. 1. A photograph of the µPC showing both front and back side where the heaters and sensors are located, insets are SEM micrographs of the microstructures.
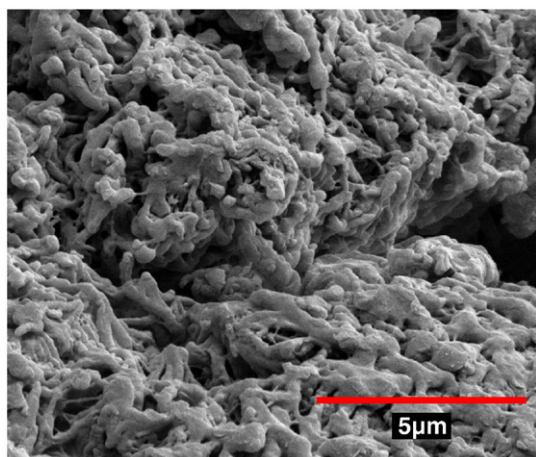
Fig. 2. SEM micrographs of granular Tenax TA.

value was measured (19 m²/g) by other researchers using the Brunauer, Emmett and Teller (BET) gas sorption method [16,42]. Our BET analysis reported specific surface area of 20 m²/g. Moreover, the adsorbent has a density of 0.25 g/cm³, pore volume of 2.4 cm³/g, and an average pore size of 200 nm [43]. Scanning electron microscopy analysis confirmed that the polymer particles had an average size of 200 μm as shown in Fig. 2. Most particles were highly porous but some were found to be partially porous. In fact, the particles consist of highly elongated and entangled solid material with spacing that ranges from 100 nm to 300 nm. The spacing, on average, is consistent with the pore size indicated by the manufacturer. It is notable that Zhao et al. [17] described Tenax TA particles as an assemblage of porous microspheres with an estimated radius of 1 μm and with an average intraparticle pore size of 200 nm. The pore area within each microsphere was estimated by them to be approximately 20 nm².

Figs. 3 and 4 display SEM images of the Tenax TA films deposited at 20 °C and 100 °C, respectively. It is evident that Tenax TA films have a completely different topography compared to their granular counterpart. The film deposited at 20 °C exhibits a repeated spherulitic pattern indicating the crystallization of Tenax-TA. The film deposited at 100 °C lacks such repeated patterns but shows high porosity. It is worth noting that Boon et al. have done a detailed study on the crystalline structure of one of the two crystalline modifications of poly (2,6-diphenyl p-phenylene oxide), specifically α-PPPO modifications obtained by thermal crystallization at 440 °C [44]. However, films

under investigation here are believed to have a different phase compositions that consists of a medley of α-PPPO and β-PPPO crystalline phases as well as an amorphous phase. According to Boon et al., β-PPPO can only be obtained by crystallization from solution whereas α-PPPO can be obtained by either thermal crystallization of undiluted polymer or crystallization from solution. The microscopy data indicate that the film deposited at 20 °C has more crystalline phase than amorphous phase, whereas the film deposited at 100 °C appears to have minimal crystalline phase.

3.2. Tenax TA crystallographic study

The X-ray diffraction patterns of Tenax TA granular and films were recorded in terms of intensity as a function of scattering angle, 2θ. Diffraction from crystalline materials is described by Bragg's law:

$$2\,d\,\sin\theta = n\lambda$$

where d is the spacing between the planes, n is an integer determined by the order given, and λ is the wavelength of the X-rays. The diffraction patterns presented in this article were collected for the granular material, films deposited at 20 °C, and films deposited at 100 °C. Fig. 5 shows the XRD data collected for films of Tenax TA deposited at 20 °C, while the XRD data collected for the granular material and for the films deposited at 100 °C are shown in Fig. 6.

Tenax films formed at 20 °C showed a high level of crystallinity, as illustrated by the sharp diffraction maxima in Fig. 5. Intense, narrow Bragg reflections were observed at 34.7, 38.2, 38.9, and 44.7°2θ. Tenax was previously studied with similar peaks and detailed characterization identified a tetragonal unit cell of a = b = 12.51 Å and c = 17.08 Å [18,44]. Consistent with this previous work, the observed Bragg maxima correspond to 202 lattice plane in the peak that illustrate the tetragonal unit cell in Fig. 5 at 38.2° 2θ, which is also confirmed by Boon et al. with d-spacing values of 2.5 Å [44]. Broader, less intense scattering maxima were observed near 14° and approximately 22° 2θ. These weaker scattering maxima are superimposed on the scattering from the amorphous polymer material, the "amorphous halo", in the semi-crystalline sample and are most likely not related to the structure of the crystalline phase.

In contrast, 100 °C-deposited films provided little evidence of crystallinity, indicating an amorphous material. The main features of interest in the diffraction data for these samples are the peaks located at 14.7, 17.9, and 21.5°2θ. Moreover, the peaks observed are quite weak and broad. The wide peak at 14.7°2θ was previously described as the amorphous halo by Alentiev et al. [18], although here it appears
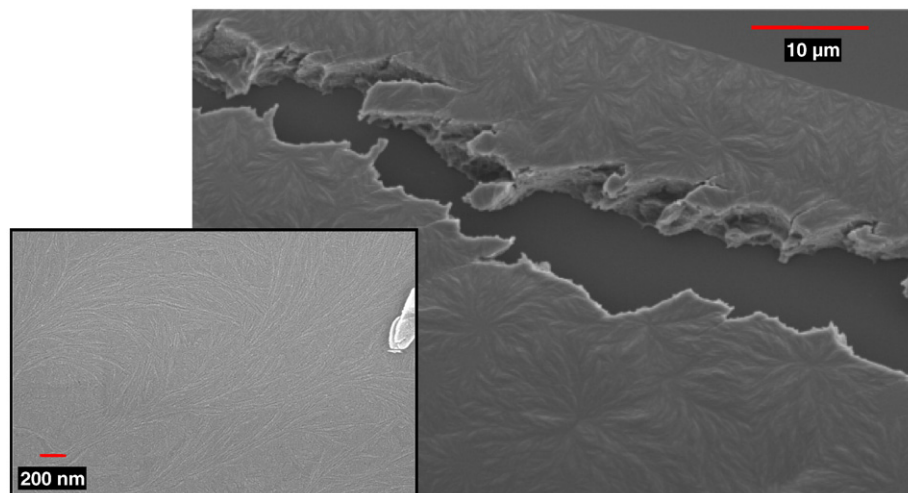

Fig. 3. SEM micrographs of Tenax TA film deposited under ambient conditions, inset is higher magnification micrographs.
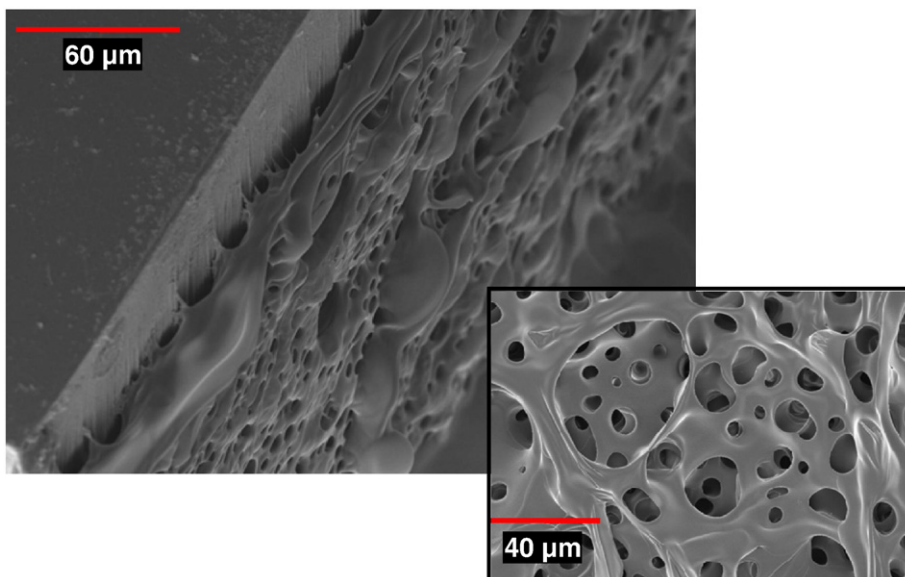
Fig. 4. SEM micrographs of Tenax TA film deposited at 100 °C (side view), inset is direct view.

that the amorphous halo is broadly centered at approximately 20°2θ. The amorphous topography of the 100 °C films is most likely a result of the rapid evaporation of solvent, which prevents polymer crystallization. For the granular sample, maxima are observed at scattering angles of 9.8, 11.2, 17.4, and 20.6°2θ, again coincident with the amorphous halo region of the scattering data and inconsistent with scattering from the tetragonal crystal topography of Tenax.

3.3. Tenax TA thermal characteristics

Thermal stability is a very important property for any adsorbent material for its successful employment in preconcentration devices. Thus, it was necessary to determine the thermal properties of the films in comparison to the granules form of Tenax. This was done by using TGA of the granules and films at identical conditions. The TGA results have shown no weight loss occurs up to 400 °C in all samples. Fig. 7 shows the TGA results of the 20 °C films. The granules and the 100 °C films exhibited similar profile.

3.4. Tenax TA adsorbent films evaluation

To evaluate the adsorption properties of Tenax TA films, different film-based adsorbent materials such as polydimethylsiloxane (PDMS) and layer-by-layer assembled gold nanoparticles (GNPs) were compared with the adsorbent film in question. PDMS is an all-purpose stationary phase commonly used in GC columns [45]. It is also a common adsorbent used in solid phase microextraction applications [46]. PDMS solution (in dichloromethane) was used to coat the µPCs using inkjet printing method similar to Tenax TA coating method described in our previous publication [21]. Tenax TA coating is simpler than PDMS coating as it does not require cross-linking. GNPs were considered due to their recent application in the field of separation science as a stationary phase material [47,48]. The interest in GNPs stems from their ability to form self-assembled monolayers (SAMs) and functionalize them with different functional groups. This allows customization of the µPCs to specific applications. Monolayer-protected gold nanoparticles (MNP) have been successfully employed as a stationary phase for tubular [49] and microfabricated GC columns [50]. The preparation of GNP coated µPCs is similar to the procedure described elsewhere [50] to coat GC columns with GNP films. Briefly, the µPCs were washed with NaOH to charge the surface with OH-groups., which was then followed by treatment with 2 mM solution of aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich Inc., St. Louis,
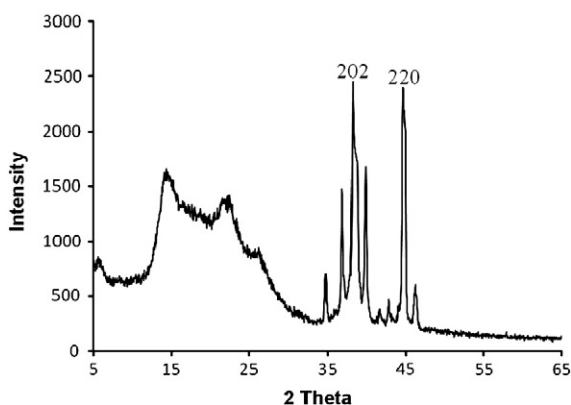

Fig. 5. XRD pattern for a Tenax TA film deposited at 20 °C (peak intensities have been reduced for clarity).
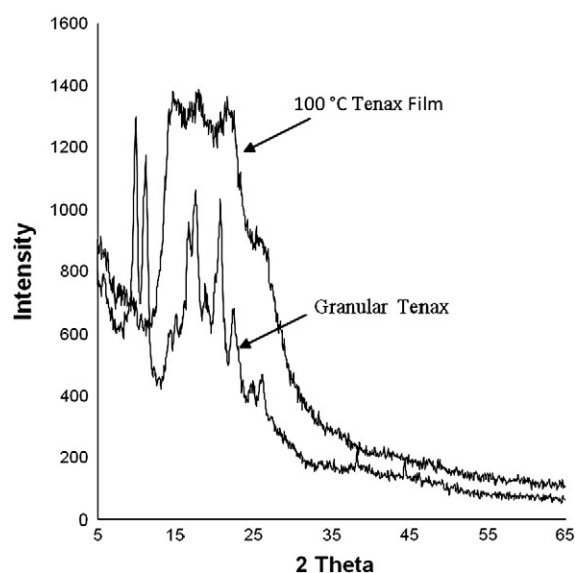

Fig. 6. XRD patterns from granular Tenax TA and films deposited at 100 °C.
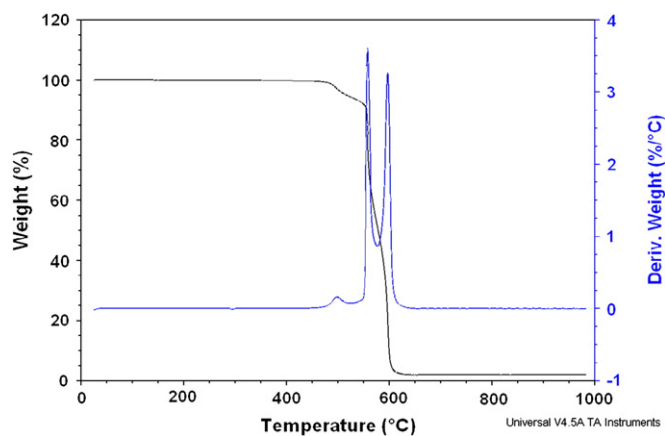
Fig. 7. TGA of Tenax films from 0 °C to 1000 °C.

Fig. 8. FID analysis of desorbed VOC representative samples on Tenax TA films.

MO) in ethanol. GNPs (Ted Pella Inc., Redding, CA) 20 nm in diameter were attached to the amine group of the APTMS by filling the chips with GNP solution. The thiol functional group of alkane was attached to GNPs by introducing a solution of 2 mM solution of octadecylthiol ($C_{18}H_{35}SH$) (Sigma-Aldrich Inc., St. Louis, MO) in hexane to the chip.

Table 1 summarizes the results of the comparison study for different adsorbents under similar conditions by loading the chip with 1 µL of n-nonane and then thermally desorbing it. Coating the µPC with GNPs increased the adsorption capacity by 2440%. However, it was found that the GNPs experience Ostwald ripening under the extreme temperature ramping (100 °C/s). Ostwald ripening degrades the performance of GNPs as an adsorbent over time. Coating the µPC with PDMS increased the adsorption capacity by 7892%. Although PDMS added significant adsorption capacity, extreme temperature variations should be avoided with this material. Thus, it is not suitable for applications where the preconcentrator needs to be heated very rapidly to temperatures close to 250 °C. Furthermore, exposing PDMS to air or oxygen at elevated temperatures oxidizes it, and consequently degrades its performance. Moreover, some solvents can swell the PDMS film, possibly change its surface properties, and may cause the film to detach from the substrate [51]. Tenax TA films provided the highest increase in performance among all adsorbent tested. As demonstrated Figs. 3 and 4, the substrate temperature plays important role in film's porosity. Films deposited below or slightly above the solvent boiling point showed different morphology and thus adsorption performance compared to films deposited temperatures well above the solvent boiling point such as temperatures above 100 °C. The high performance is attributed to both the high porosity of the film and its amorphous phase property.

Representative VOC samples were used to evaluate Tenax TA films as adsorbent material. The samples included alkanes (n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane), ketones (acetone), and alcohols (ethanol, methanol, 1-propanol). Each compound was tested three times in succession on three µPCs. The uncertainties were calculated as a standard deviation. From Fig. 8, it can be concluded that Tenax TA films adsorbs both polar and
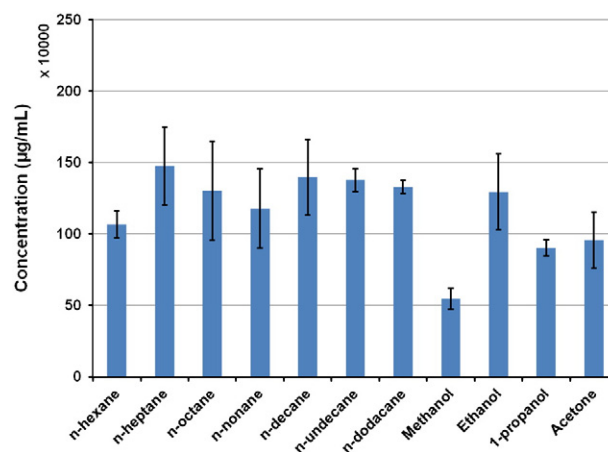
nonpolar compounds The adsorption data is in good agreement with those achieved by Tenax TA particles published elsewhere [10,14,16].

Analyte storage time on Tenax TA films within the µPC was studied to determine analyte life time in the Tenax TA coated µPC. This information is valuable in the case where the analysis could not be done immediately after the sample was collected or in case the µPC is to be utilized as analyte micro storage device. This was done by determining the sample amount loss over storage time. For storage periods of 1 week, 1 month and 3 months, the µPC was loaded with fixed amount of n-nonane at room temperature. After each storage period, the analyte in the µPC was desorbed and analyzed by the FID. The analyte concentration in the desorption plug decreased by about 4% per week. For analyte storage stability, the National Institute for Occupational Health and Safety (NIOSH) recommends that the average quantitative measurements coming from the storage device should not differ from the analysis on day 0 by more than 10% [52]. Conventional Tenax TA preconcentration tubes can hold analytes for up to 14 days according to US EPA method for volatile organic sampling and UK HSE methods for the determination of hazardous substances.

4. Conclusions

This work contributes to the field of analytical chemistry by giving insight into the nature of Tenax TA films in comparison to the common granular form. Tenax TA films have a complex phase composition that includes crystalline and amorphous phases. The phase composition of the film can be controlled by controlling the film's deposition conditions.

In general, our investigation demonstrated the superiority of Tenax TA films over other possible film-based adsorbents for µPCs. The film form of Tenax TA has several advantages over the granular form, especially in micro preconcentration applications. Tenax TA solution allows a simple way of entraining Tenax TA within the small spaces of µPCs. The film also conforms to the complex microfabricated structures, a commodity that is not possible with granules. Moreover, based on the adsorption properties of Tenax TA films investigated here and the published data on Tenax TA granules, it can be concluded that there is no difference in the adsorption properties between the adsorbent polymer in granular and film forms. The effect of phase composition on the properties of the polymer and repeated use on the adsorbent performance will be investigated in future studies.

Table 1
Performance of different adsorbents under similar adsorption/desorption conditions.

Adsorbent	Desorption peak concentration (ppm)	% Increase
Uncoated	606 ± 5%	0
GNP	15,391 ± 20%	2440
PDMS	48,432 ± 5%	7892
Tenax TA 20 °C	19,0517 ± 6%	31,338
Tenax TA 50 °C	214,586 ± 4%	35,310
Tenax TA 100 °C	571,556 ± 5%	94,216
Tenax TA 150 °C	590,225 ± 2%	97,297

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