Short communication

On the performance and inertness of different materials used for the enrichment of sulfur compounds from air and gaseous samples

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Abstract

The performance of the sorbent polydimethylsiloxane (PDMS) is compared to that of the adsorbents Carbotrap and Tenax for the enrichment of volatile and reactive sulfur compounds. These included: 1- and 2-propanethiol, tetrahydrothiophene, 2-thioethanol and 2-ethylthioethanol. Several artifact-forming reactions were identified on both Tenax and Carbotrap including: H_2S elimination and dimerization of thiols. Additionally, permanent adsorption was also observed for heavier solutes. These effects are absent when PDMS is applied. This superior performance is explained by the absence of catalytic or adsorptive activity on PDMS.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most of the analytical techniques presently used for the enrichment of volatile organic compounds (VOCs) in air and gaseous samples are based on adsorption of the analytes of interest on a suitable preconcentration material packed in a short tube followed by either liquid or thermal desorption [1–3]. Commonly used adsorbents include carbon-based materials such as activated carbon and carbon molecular sieves [4,5] and porous organic polymers like Tenax and Chromosorb [6]. These are all relatively strong adsorbents with favorable properties for capturing volatile compounds from gaseous samples.

Trapping of analytes generally does not pose a problem since breakthrough volumes are quite high for most solutes of interest.

Desorption of the analytes can be accomplished in two ways namely: liquid desorption and thermal desorption. Very often, a liquid (organic solvent) is used for desorption of the analytes from the adsorbent. The advantage of this approach is that analytes are desorbed under mild conditions and both polar and apolar compounds can be desorbed using an appropriate solvent. In most cases however, at least 0.5–1 ml of solvent is needed.

Since only an aliquot of the sample is injected in the analytical system (typically 1 μl for capillary GC), sensitivity of this method is rather low. Large volume injection [7] can be used to increase sensitivity but for volatile solutes this is not straight-

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forward, primarily due to the interference of a large solvent peak.

Thermal desorption is increasingly being used as a sensitive alternative to liquid desorption. Here, the trapping material is heated and the analytes are released at temperatures typically in the range of 200–300°C and carried to the analytical column by the carrier gas. The desorbed analytes are refocused in a cold trap prior to the actual transfer onto the analytical column to ensure a narrow injection bandwidth. Thermal desorption allows the complete transfer of the entire sample to the column which results in maximum sensitivity. Therefore, thermal desorption in many cases is far superior to liquid desorption.

Unfortunately, thermal desorption also poses some typical problems of its own. Where in liquid desorption, blank levels are almost solely determined by the purity of the solvent, thermal desorption blanks are determined by the adsorbent itself. At high temperatures, polymeric adsorbents tend to break down, resulting in characteristic adsorbent degradation peaks. In many cases these include analytes of general interest such as benzene, toluene, xylene from Chromosorb [8] and benzaldehyde and acetophenone from Tenax [9]. Additionally, at desorption temperatures of 200–300°C, the adsorbent might react with the analytes to either transform them into other compounds or to permanently bind them onto the adsorbent surface. This is of course highly undesirable. Moreover, the unpredictable sample nature (humidity, concentration, etc.) makes these two effects very troublesome in practice.

The performance of packed polydimethylsiloxane (PDMS) traps as an alternative to adsorbents for air sampling was recently evaluated and compared to that of the adsorbents Chromosorb, Carbotrap 300 and Tenax [8]. For many polar (and/or reactive) compounds much better performance in terms of recoveries was obtained on PDMS [8] because of its inertness. Moreover, PDMS degradation results in a series of cyclic siloxane oligomers which can easily be detected and identified with the use of a mass spectrometer and do not interfere with the solutes of interest. Additionally, permanent adsorption and reactivity of PDMS are suspected to be minimal. In this contribution, adsorbent reactivity and its influence on analyte conversion/stability was studied using several sulfur solutes as model compounds.

2. Experimental

2.1. Thermal desorption cartridges

Three materials namely PDMS, Carbotrap 300 and Tenax are compared. Prepacked Tenax and PDMS traps were obtained from Gerstel (Müllheim a/d Ruhr, Germany) and prepacked Carbotrap 300 cartridges were obtained from Supelco (Bellefonte, PA, USA). The Carbotrap 300 cartridge is a multistage adsorbent trap containing Carbotrap C, Carbotrap B and Carbosieve SIII. PDMS traps were conditioned for 1 h at 300°C and then for 4 h at 250°C. After this procedure, no peaks appear in the blank chromatogram with the exception of the cyclic siloxanes. Tenax traps, obtained in sealed glass containers, were conditioned at 275°C for 2 h before use to guarantee proper blanks. Carbotrap 300 tubes were conditioned at 325°C for 2 h. Conditioning was performed under a flow-rate of 15 ml/min for all materials. Thermal desorption temperatures were 225°C for PDMS, 250°C for Tenax and 300°C for Carbotrap 300 for 5 min if not otherwise stated.

2.2. Experimental set-up

A Gerstel TDS-2 Thermodesorption system mounted on a HP6890-HP5972 gas chromatograph-mass-selective detector (Hewlett-Packard, Little Falls, DE, USA) was used. A CIS-4 programmable temperature vaporizing injector (PTV, Gerstel) is used to cryofocus the analytes, prior to their transfer onto the analytical column. The system was used in a modified form suitable only for split desorption [10]. The modification consists of eliminating the transfer capillary from the thermodesorption unit to the PTV cryotrap. The analytical column is then pushed through the PTV liner and connected directly to the thermodesorption unit. This implies that the analytes are cryotrapped on the analytical column instead of on the glass liner of the PTV. This minimizes component degradation in the analytical system and allows focusing entirely on the thermal desorption process. Observed component loss can thus be totally attributed to processes occurring in the thermodesorption unit.

Analyses were performed on a laboratory-made 50 m×250 μm I.D. fused-silica column coated with a 1-μm film of OV-1 or on a 30 m×250 μm I.D.

Table 1
Composition of the test mixtures

| Mixture	No.	Component	Structure	Concentration (μg/l)	M_r [a]	T_b [a] [12]
1	1	2-Propanethiol	$CH_3CHSHCH_3$	450	76	52.6
1	2	2-Methyl-2-propanethiol	$(CH_3)_2CSHCH_3$	2250	90	88.5
1	3	1-Propanethiol	$CH_3CH_2CH_2SH$	300	76	67.8
2	4	Tetrahydrothiophene	$CH_2CH_2CH_2CH_2S$	1000	88	121
2	5	1-Pentanethiol	$CH_3CH_2CH_2CH_2CH_2SH$	1000	104	126.6
2	6	1-Hexanethiol	$CH_3CH_2CH_2CH_2CH_2CH_2SH$	1000	118	151
3	7	2-Thioethanol	$HSCH_2CH_2OH$	1000	78	158
3	8	Methyl-3-thiopropanoate	$HSCH_2CH_2COOCH_3$	1000	120	
3	9	2-Ethylthioethanol	$CH_3CH_2SCH_2CH_2OH$	1000	106	184

[a] M_r, molecular mass; T_b, boiling point.
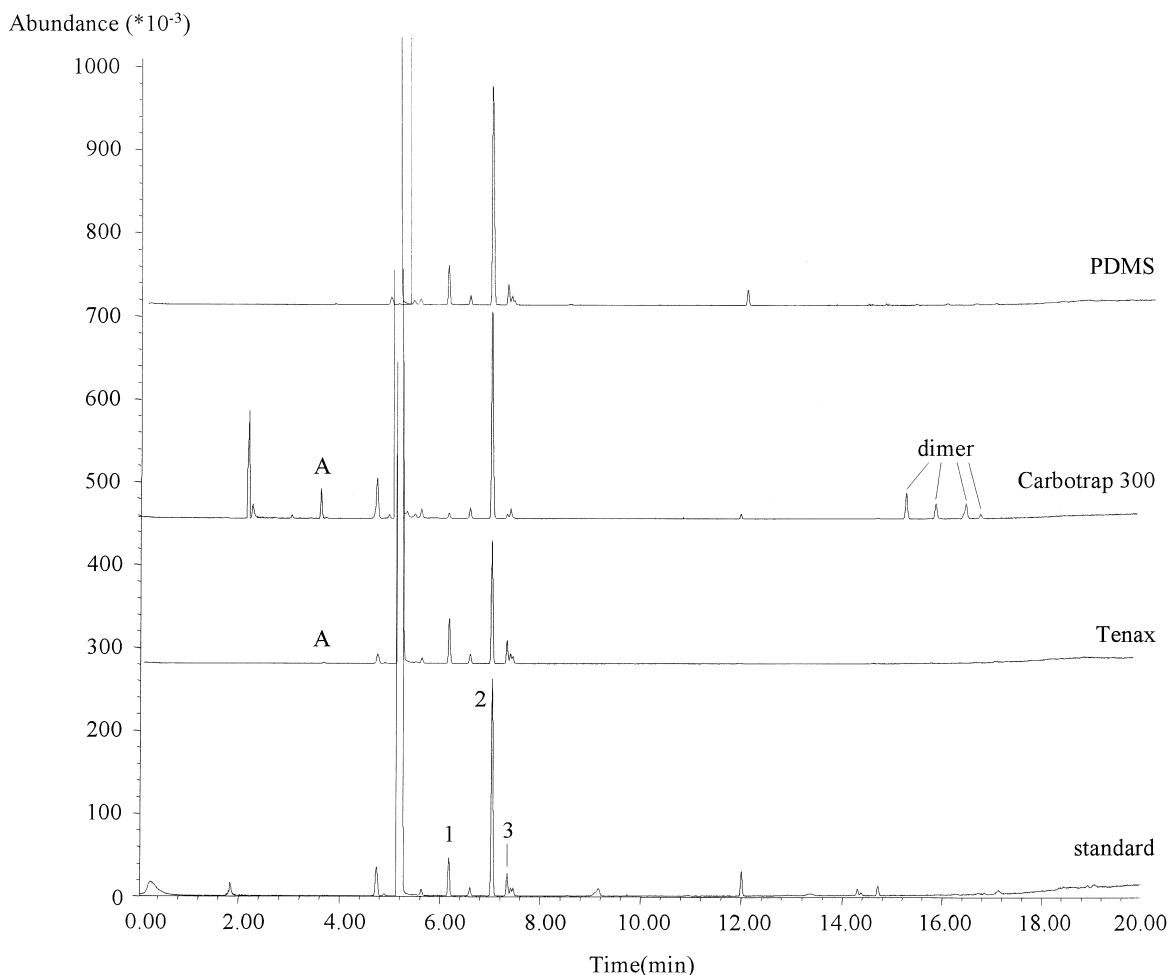
Fig. 1. Chromatograms of mixture 1 injected directly (standard) or enriched from an artificial gaseous sample on Tenax, Carbotrap 300 or PDMS. Sample volume was 150 ml (Carbotrap 300 and Tenax) or 50 ml (PDMS). Peak 1: 2-propanethiol, 2: 2-methyl-2-propanethiol, 3: 1-propanethiol, A: 2-methyl-1-propene. The chromatogram of Carbotrap 300 also reveals the presence of dimers.

0.25-μm HP-5MS column (Hewlett-Packard). Column head pressure was maintained at 50 kPa and the split flow at 15.0 ml/min. For both columns, the temperature program started at 35°C which was kept for 4 min and then programmed to 275°C at 15°C/min. The mass-selective detector was operated in the scan mode, scanning from 40 to 300 u at 2.8 scans/s.

2.3. Standards

For this investigation, three standard solutions in n-pentane were prepared. The first solution contains three 'volatile' thiols (1–3), standard 2 contains three 'heavy' thiols (4–6) and finally standard 3 contains three analytes with both a thiol and an alcohol or ester group (7–9). The compositions of the test mixtures are given in Table 1.

Gaseous standards were prepared by a method described previously [8]. Briefly, a TDS cartridge is connected to a split/splitless injector operated in the splitless mode and the flow is adjusted to 15 ml/min. The injector temperature was maintained at 200°C. After injection of 1 μl of the standard into the GC injector the flow is maintained for 10 min to simulate a sampled volume of 150 ml. Calculation of recoveries is done versus a 1-μl injection into a TDS tube filled with deactivated glass wool and desorbed immediately after spiking.

3. Results and discussion

Initial recovery studies were performed on a 30 m× 320 μm I.D. 4-μm d_f CP-Sil5CB column (Chrompack, Middelburg, The Netherlands) which is a thick-film column specially deactivated for the analysis of volatile sulfur compounds. Incomplete recoveries were observed which could not be attributed to permanent adsorption or artifact formation. Possible artifact solutes can have a relatively high molecular weight which prevents their elution from the thick-film column. Further experiments were therefore carried out on the 1-μm column.

Fig. 1 shows the chromatograms obtained for the analysis of test mixture 1 on the three tubes and the chromatogram obtained by direct injection of the standard solution. Table 2 lists the recoveries on the three sampling tubes. Recoveries are determined relative to the direct injection of the same amounts. For the most volatile solutes in a 150-ml sample, PDMS gives low recoveries. This is due to the fact that the breakthrough volumes for these solutes are lower than 150 ml. If only 50 ml is sampled, good recoveries are obtained, which is in agreement with theoretical predictions [8]. The limitation of the sampling volume on PDMS (and the consequential lower sensitivity) can be overcome by equilibrium sorption [11]. Theoretical and literature data predict that the breakthrough volumes of these solutes are

Table 2
Recoveries for the test solutes from a 150-ml sample on three enrichment materials[a]

No.	Component	Recovery (%)				
		PDMS	Tenax	Carbotrap 300	PDMS[b]	Tenax[c]
1	2-Propanethiol	2	112	28	101	
2	2-Methyl-2-propanethiol	14	53	92	101	
3	1-Propanethiol	25	99	0	103	
4	Tetrahydrothiophene	110	96	100		
5	1-Pentanethiol	100	99	71		
6	1-Hexanethiol	100	99	60		
7	2-Thioethanol	100	98	96		96
8	Methyl-3-thiopropanoate	102	59	69		64
9	2-Ethylthioethanol	98	57	96		51

[a] Desorption temperatures: 225°C (PDMS), 250°C (Tenax), 300°C (Carbotrap 300).
[b] PDMS recoveries from a 50-ml sample.
[c] Tenax desorption at 300°C.

larger than 150 ml for both Tenax and Carbotrap 300. For Tenax, good results are indeed obtained for 2-propanethiol and 1-propanethiol, but 2-methyl-2-propanethiol is partly lost. On Carbotrap 300, both 2-propanethiol and 1-propanethiol show low recovery. It is remarkable that the performance of the adsorbents Tenax and Carbotrap 300 is very poor for the analytes used here, even at the relatively high concentration levels used and in the absence of humidity.

On both adsorbents an early eluting compound (A) is formed. This compound was identified as 2-methyl-2-butene which originates from compound 2 by elimination of H_2S. This artifact tends to occur more on Carbotrap 300 than on Tenax although the loss of compound 2 is more prevalent on Tenax (Table 2). Probably, the 2-methyl-2-butene formed is too volatile to be trapped on Tenax and is lost immediately when formed.

In the case of Carbotrap 300, several peaks are detected between 15 and 17 min. These have been identified as the dimers of the thiols (disulfides) in mixture 1 and are formed by H_2 elimination of two thiols. Between the three thiols from mixture 1, six
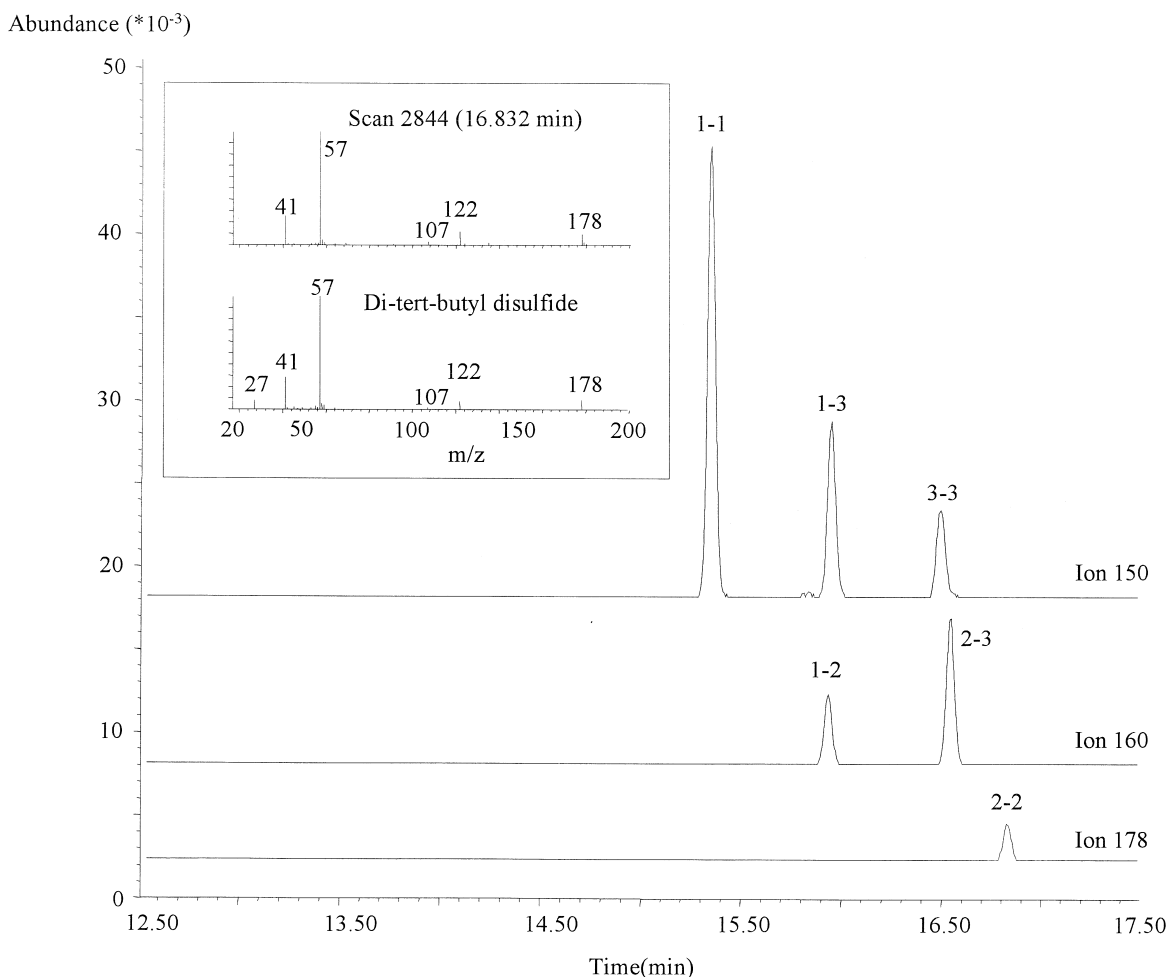

Fig. 2. Extracted ion chromatograms of mixture 1 on Carbotrap 300. Ions correspond to the dimers formed between compounds 1, 2 and 3. Insert shows the spectrum recorded for dimer 3–3 and the library spectrum.

different dimers can be formed and these are all present. This is illustrated in Fig. 2 showing the extracted ion traces corresponding to the molecular masses of the dimers, m/z 150 for dimers 1–1, 1–3 and 3–3, m/z 164 for dimers 1–2 and 2–3 and m/z 178 for dimer 2–2. The insert of Fig. 2 shows the mass spectrum of the 2–2 dimer eluting at 16.83 min together with the library spectrum. If ion extraction is performed on the Tenax chromatogram of mixture 1, the dimers are also observed but at a level 100 times lower than on Carbotrap 300. H_2S and H_2 elimination reactions were not observed on the PDMS sorbent illustrating its superior inertness.

For mixture 2, similar results as for mixture 1 were obtained. Tetrahydrothiophene appeared to be a relatively inert component and was recovered quantitatively from all three materials. 1-Pentanethiol and 1-hexanethiol were quantitatively recovered from both Tenax and PDMS. On Carbotrap 300, significantly lower recoveries were observed. Similar to the observations for mixture 1, this was suspected to be due to dimerization with the formation of disulfides. These dimers could not be eluted from the 1-μm OV-1 column, but their formation was confirmed by using a thin film (0.25-μm) HP-5MS column. Dimers of the 1-pentanethiol and 1-hexanethiol (5–5, 5–6 and 6–6) could easily be detected for Carbotrap 300 and to a lesser extent for Tenax. For test mixture 3, 2-thioethanol was recovered quantitatively from all enrichment materials. The two analytes with the highest molecular mass were only fully recovered from PDMS whereas on Tenax and Carbotrap 300 losses occurred. Since in the case of 2-ethylthioethanol, dimerization cannot occur and for 3-thiomethylpropionate the dimer was not detected, it is assumed that these solutes cannot be completely desorbed from the adsorbent due to their high polarity and relatively high molecular mass compared to the other analytes (permanent adsorption). For these compounds no artifacts were observed, indeed an indication of incomplete desorption or permanent adsorption. It was attempted to improve the recoveries from Tenax by increasing the desorp-

tion temperature but this did not significantly improve the recoveries (Table 2).

4. Conclusion

The 'enrichment performance' of PDMS versus that of the two most popular adsorbents, Tenax and Carbotrap 300, for nine reactive sulfur compounds was investigated. Several artifact-forming reactions were identified and include dimerization, H_2S elimination and permanent adsorption. These reactions occurred on both Tenax and Carbotrap 300 but not on the PDMS phase. The inertness of polydimethylsiloxanes and the absence of catalytic activity and adsorptive sites makes PDMS very interesting for the enrichment of reactive (sulfur) compounds. For the most volatile solutes, the breakthrough volumes on PDMS are, however, much lower in comparison to Tenax or Carbotrap 300. Equilibrium sorption can help to overcome this problem.

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