



Needle trap micro-extraction for VOC analysis: Effects of packing materials and desorption parameters

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ABSTRACT

Combining advantages of SPE and SPME needle trap devices (NTD) represent promising new tools for a robust and reproducible sample preparation. This study was intended to investigate the effect of different packing materials on efficacy and reproducibility of VOC analysis by means of needle trap micro extraction (NTME). NTDs with a side hole design and containing different combinations of PDMS, DVB and Carbopack X and Carboxen 1000 and NTDs containing a single layer organic polymer of methacrylic acid and ethylene glycol dimethacrylate were investigated with respect to reproducibility, LODs and LOQs, carry over and storage. NTDs were loaded with VOC standard gas mixtures containing saturated and unsaturated hydrocarbons, oxygenated and aromatic compounds. Volatile substances were thermally desorbed from the NTDs using fast expansive flow technique and separated, identified and quantified by means of GC-MS. Optimal desorption temperatures between 200 and 290 °C could be identified for the different types of NTDs with respect to desorption efficiency and variation. Carry over was below 6% for polymer packed needles and up to 67% in PDMS/Carboxen 1000 NTDs. Intra and inter needle variation was best for polymer NTDs and consistently below 9% for this type of NTD. LODs and LOQs were in the range of some ng/L. Sensitivity of the method could be improved by increasing sample volume. NTDs packed with a copolymer of methacrylic acid and ethylene glycol dimethacrylate were universally applicable for sample preparation in VOC analysis. If aromatic compounds were to be determined DVB/Carboxen 1000 and DVB/Carbopack X/Carboxen 1000 devices could be considered as an alternative. PDMS/Carbopack X/Carboxen 1000 NTDs may represent a good alternative for the analysis of hydrocarbons and aldehydes. NTME represents a powerful tool for different application areas, from environmental monitoring to breath analysis.

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1. Introduction

Sample preparation is the cornerstone of chemical analysis. Pre-concentration is the crucial step when volatile organic compounds (VOCs) often occurring in concentrations as low as ppbV or pptV are to be determined. Solid Phase Extraction (SPE) and Solid Phase Micro Extraction (SPME) are well established techniques in the field of VOC analysis. Both methods have advantages and limitations [1]. While sensitivity of SPE can be enhanced by increasing sample volume, this method in general requires large sample volumes, thus resulting in long sampling times. In addition, desorption steps, especially those for the analysis of highly volatile VOCs are often sophisticated and time consuming. Therefore, smart

pre-concentration techniques which do not require large sample volumes and sophisticated desorption techniques are desirable [2]. Micro extraction techniques such as SPME can in principle meet these requirements [3]. However, extraction efficiency will depend on physiochemical properties of fiber coatings and analytes since SPME is based on distribution. In addition, sensitivity of this technique cannot be further enhanced by increasing sample volumes.

Needle trap devices (NTDs) represent promising new tools for a robust and reproducible sample preparation, combining advantages of SPE and SPME [4]. Like SPME, NTDs only require very small sample volumes. Nevertheless, sensitivity of the analytical method can be increased by increasing the sample volume since it is an exhaustive technique like SPE. In combination with expansive flow desorption no additional equipment, apart from a heated GC injector, is necessary for application [5]. Several applications of single layer packed sorbents such as Carboxen (CAR), and divinylbenzene (DVB) have been described in the field of environmental monitoring

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(e.g. analysis of BTEX or higher alkanes) [6–9]. Our research group recently proved the applicability of multibed NTDs and expansive flow technique in medical breath analysis [10,11].

This study was intended to investigate the effect of different packing materials on efficacy and reproducibility of VOC analysis by means of NTDs. For this purpose, NTDs with a side hole design and containing different combinations of sorbents were investigated with respect to reproducibility, LODs and LOQs, storage and carry over. The following questions were addressed in detail:

- How does the packing material affect reproducibility, stability, detection limits and linear range?
- Is it possible to use the expansive flow technique for NTDs without generating significant memory effects or carryover of the compounds?
- Is it possible to detect highly volatile VOCs in the ppbV–pptV range when only small sample volumes are used?

2. Experimental

2.1. Chemicals and materials

A standard mixture of C1–C6 reference substances was obtained from Sigma–Aldrich. Aldehyde standard mixtures (C1–C10 aldehydes, 2-propenal and 2-butenal) and a mixture of different volatile organic compounds (formaldehyde, acetaldehyde, methanol, ethanol, 2-methyl-1,3-butadiene, acetone, 2-propenal, acetonitrile, 2-butanone, benzene, 2-butenal, toluene, chlorobenzene, 1,2-dimethylbenzene, 4,7,7-trimethylbicyclohept-3-ene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene) stored in stainless steel canisters were purchased from Ionimed Analytik (Innsbruck, Austria). Substance concentrations were approximately 1 ppmV.

To generate standard mixtures in the required concentration ranges, these mixtures were introduced into clean Tedlar bags and diluted with dry nitrogen.

Gas tight syringes were purchased from Hamilton (Bonaduz, Switzerland) and 0.1 L gas bulbs from Supelco (Bellefonte, CA).

Helium and nitrogen of purity 6.0 (i.e., 99.9999%) were purchased from Linde (Vienna, Austria), and Tedlar bags came from SKC (Eighty Four, PA, USA).

2.2. Needle trap devices

Five different types of needle trap devices, “NeedleEx”, custom manufactured by Shinwa Ltd., Japan, were investigated (Fig. 1). All NTDs consisted of 22 gauge needles with side holes. Triple bed NTDs contained a combination of

- DVB, Carboxen 1000 and Carboxen 1000 or a combination of
- PDMS, Carboxen 1000 and Carboxen 1000

Double Bed NTDs with combinations of

- DVB and Carboxen 1000 and
- PDMS and Carboxen 1000

were also used in the study. In all four cases needles were packed with a length of 1 cm of each sorbent. Furthermore needles equipped with 2 cm of a

- copolymer of methacrylic acid and ethylene glycol dimethacrylate (further referred to as polymer NTDs) [12,13]

were investigated. Sorbents were locked into position within the needles by means of heat-resistant polymer fibers, which were

introduced on both ends of the sorbent packing [12,14,15]. All needles were from the same batch.

Prior to first usage NTDs were conditioned in a special custom-made heating device (PAS Technology, Magdala, Germany) at different temperatures under permanent helium flow (1 bar front pressure) for at least 20 h to eliminate any contaminations from the manufacturing process or shipping. Temperatures were chosen according to the specifications of the different sorbent materials. Needles containing DVB, Carboxen 1000 and Carboxen 1000 or DVB and Carboxen 1000 were conditioned at 250 °C. Needles containing PDMS, Carboxen 1000 and Carboxen 1000 or PDMS and Carboxen 1000 were conditioned at 290 °C, while needles with polymer packing were conditioned at 195 °C, since the polymer is only stable up to 200 °C. Afterwards, both ends of the needles were sealed with Teflon caps. Before the actual use the NTDs were conditioned again for 30 min in the heating device.

Fig. 1 gives an overview of the needle trap design and the different types of NTDs used within the study.

2.3. Sampling procedure

NTDs were manually loaded with gas standards which were prepared in Tedlar bags as described before [10]. Briefly, NTDs were connected to a 1 mL single use sterile syringe. The needle was pierced through the septum of the Tedlar bag and the plunger of the syringe was manually moved up until 1 mL of sample was drawn through the NTD. To ensure pressure equilibration through the needle, the plunger was held in the upright and downward position for 2–3 s. After removing the NTD from the Tedlar bag the plunger of the syringe was moved down again pulling the gas through the needle a second time. One time moving the plunger up within 1 s and down within 1 s was defined as one sampling cycle. One sampling cycle equals a sampled volume of 1 mL.

2.4. Instrumentation

An Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert XL MSD with triple axis detector was used to separate and detect the volatile organic substances desorbed from the needle trap devices. For investigation of storage effects, LOD and LOQ, reproducibility and peak capacity a RTX-624 (60 m; 0.32 mm; 1.8 μm film thickness) capillary column from Restek (Bad Soden, Germany) was used to separate VOCs. In order to investigate carry over and the influence of different desorption temperatures a RTX-624 (30 m; 0.32 mm; 1.8 μm film thickness) capillary column from Restek (Bad Soden, Germany) was used.

The column temperature program for the 60 m column worked as follows: 40 °C for 5 min, 8 °C/min to 120 °C for 2 min, 10 °C/min to 220 °C, 20 °C/min to 250 °C for 4 min.

The column temperature program for the 30 m column was: 30 °C for 2 min, 5 °C/min to 40 °C for 2 min, 5 °C/min to 60 °C, 50 °C/min to 260 °C for 6 min.

NTDs were thermally desorbed using the expansive flow technique in the injection port of the gas chromatograph as described before [11]. Desorption time was set to 30 s. Needles were sealed with a Teflon tip at the Luer lock end and the whole length of the needle was inserted into the GC injector through a septum inlay. Long life non-stick septa from Agilent were used in the experiments. The injector was equipped with a 0.8 mm SPME inlet liner (Supelco, Bellefonte, PA).

Automatic desorption was realized using a GC-Autosampler (Concept, PAS Technology, Germany) optimized for the fast expansive flow technique [11].

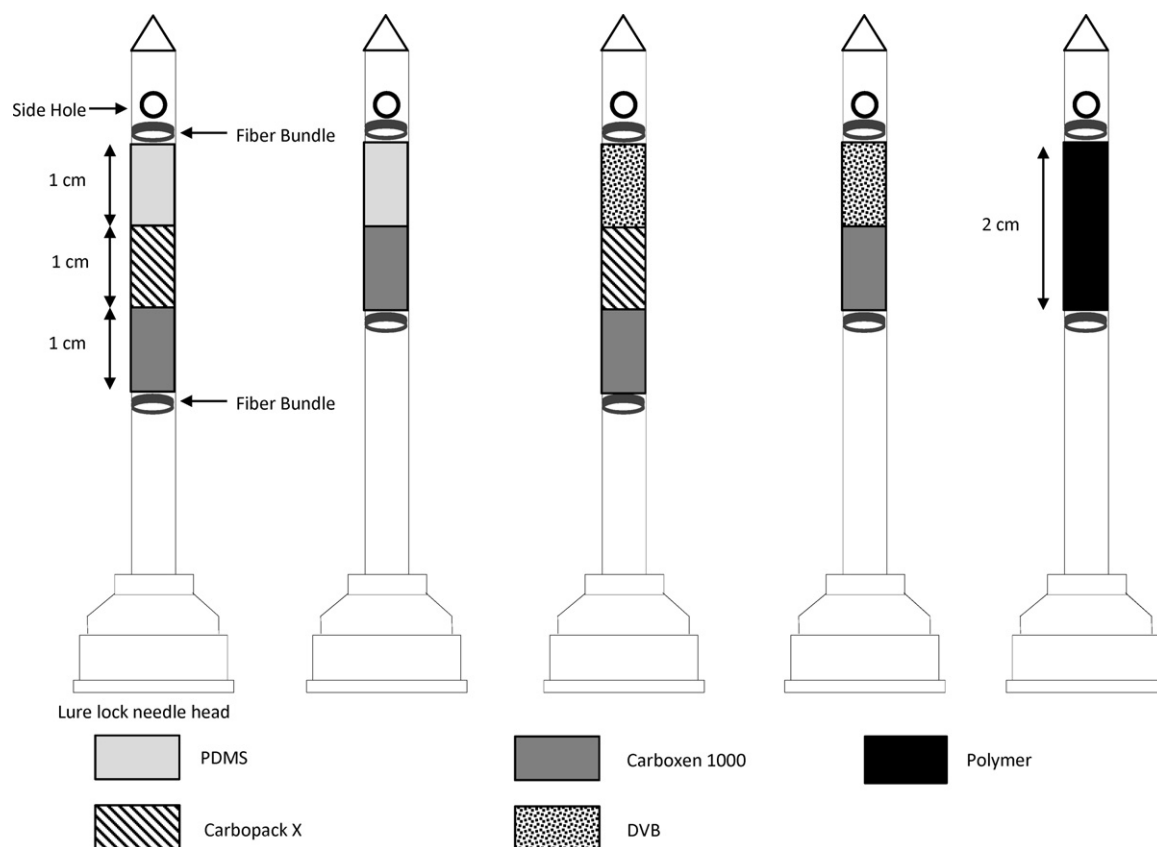


Fig. 1. NTD design and different sorbent packings used in the study.

2.5. Desorption temperature

The effect of five different injector temperatures onto substance desorption from the NTDs was investigated. PDMS and DVB based NTDs were desorbed at 180, 200, 220, 250, 290 °C. Needles with polymer packing were desorbed at 140, 160, 180, 200 and 220 °C. The gas mixture used for that purpose contained volatile substances in the concentration range from 275 ng/L (acetone) to 641 ng/L (E-2-butenal) (≈ 100 ppbV). Three measurements were carried out for each temperature. The number of sampling cycles was 20.

2.6. Carry over

Needles were loaded through 20 sample cycles (20 mL) with volatile substances in the concentration range between 1373 ng/L (acetone) and 3205 ng/L (E-2-butenal) (≈ 500 ppbV). DVB and PDMS based NTDs were introduced into the gas chromatograph at a desorption temperature of 250 °C, NTDs packed with polymer were introduced at 200 °C.

An additional experiment with a desorption temperature of 290 °C was carried out for needles containing PDMS. After 30 s in the injection port, needles were returned to the autosampler rack and injected for a second time after 30 min. The Luer lock end was sealed with a Teflon tip during the whole process. The procedure was repeated for five needles of each kind.

2.7. Reproducibility

Reproducibility of the different NTD types with respect to analysis of different volatile organic compounds was investigated. For intra needle variation, needles were manually loaded with 20 mL of the standard mixture containing the substances in

concentrations of approximately 100 ppbV. NTDs were introduced into the gas chromatograph immediately after sampling. Desorption temperatures for the analysis of intra and inter needle variations were 290 °C for PDMS twin and triple bed NTDs, 250 °C for DVB twin and triple bed NTDs and 200 °C for polymer NTDs. After desorption, needles were conditioned for half an hour. Once the needles had been reconditioned the procedure was repeated. Each needle was analyzed five times.

To investigate inter needle variation five needles of each type were loaded with 20 mL of the standard mixture and analyzed by GC–MS. For DVB and PDMS double bed NTDs only four needles were available. Fresh pre-conditioned needles were used for this study.

2.8. Calibration and LOD/LOQ

In order to assess LOD and LOQ for the determination of different standard substances with different NTD types used for extraction 8 concentration levels were prepared. Concentration ranges used for each substance can be found in Table 3. Needles were loaded with 20 sample cycles (20 mL). In addition, blank samples were analyzed. In these samples needles had been loaded with 20 sampling cycles of nitrogen. For each concentration level two measurements were carried out, the number of measured blanks was five.

LODs and LOQs for the GC–MS method were determined by means of the signal to noise ratio. Noise was determined experimentally from the blank samples. LOD was defined as S/N of 3, LOQ as S/N of 10.

2.9. Effect of sample volume

The effect of sample volumes onto extracted amounts of substances was investigated. For that purpose, polymer NTDs and

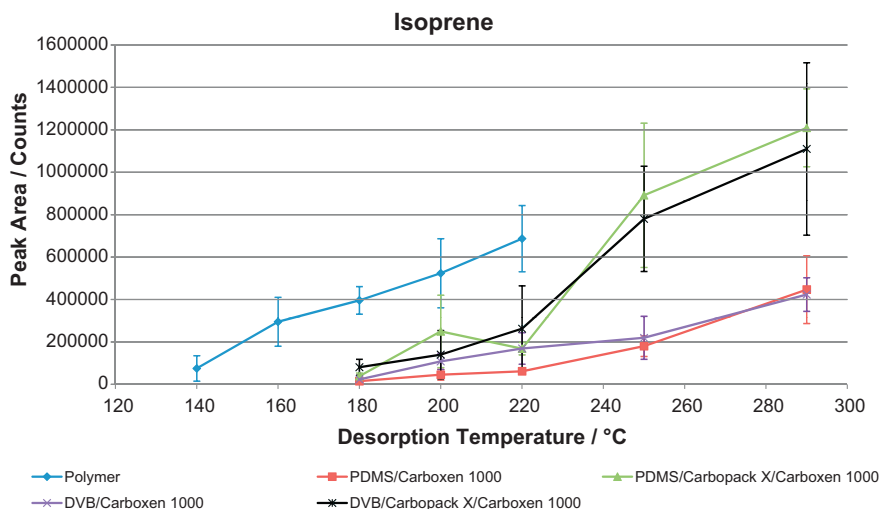


Fig. 2. Effect of desorption temperatures on the detected amount isoprene. NTDs ($n=3$ for each temperature) were loaded with 20 mL of a standard mixture containing substances in concentrations of approximately 100 ppbV. Volatile substances were analyzed by GC–MS. Polymer NTDs were desorbed at 140, 160, 180, 200 and 220 °C. PDMS and DVB double and triple bed NTDs were desorbed at 180, 200, 220, 250 and 290 °C. Mean peak areas for each temperature and NTD type are displayed.

a SPME fiber with 65 μm SPME/DVB/Carboxen (Supelco, Bellefonte, USA) were compared. The standard mixture used for this purpose contained the substances in concentrations of approximately 100 ppbV. Sample volumes were 2 mL, 5 mL, 10 mL, 20 mL and 50 mL. With NTDs triplicate, and with SPME duplicate measurements were performed. Extraction time was 7 min for SPME. Desorption temperature was 200 °C for Polymer NTDs and 290 °C for the SPME experiments.

2.10. Storage

In order to examine the effects of storage onto NTME, needles were loaded with 20 sample cycles (20 mL) of the standard mixture. Substance concentrations were in the range of 275 ng/L (acetone) to 641 ng/L (E-2-butenal, ≈ 100 ppbV) prepared in a tedlar bag directly prior to analysis. Needles were desorbed immediately after sampling, as well as 10 h, 24 h, 48 h and 8 days after loading them with standards. During storage at room temperature the needles were sealed with Teflon tips on both ends. The number of measurements for each storage time was five for polymer NTDs, four for PDMS triple bed needles and three for DVB triple bed needles.

3. Results and discussion

3.1. Desorption temperature

Desorption temperature is a crucial parameter regarding sensitivity and reproducibility. Desorption temperature, therefore, has to be chosen carefully with respect to the sorbent materials applied in the NTDs as well as with respect to the compounds of interest.

Fig. 2 shows the effect of desorption temperatures onto peak areas of isoprene. Detailed results on effects of desorption temperatures are shown in Appendix S1.

Preconcentration by means of double bed NTDs containing PDMS as the first sorbent in the trap yielded largest peak areas at a desorption temperature of 290 °C. Peak areas at a desorption temperature of 250 °C were only 33–70% compared to the peak areas obtained at 290 °C. Aromatic compounds generally showed lower RSDs at 290 °C. Pentane, hexane, isoprene, propanal, E-2-butenal and pentanal had lower RSDs at 250 °C. This could be due to substance decomposition at reactive sites within the Carboxen at higher temperatures.

Triple bed NTDs containing PDMS also showed a better desorption efficiency at 290 °C compared to 250 °C regarding aldehydes and hydrocarbons. Extracted amounts of aromatic compounds, however, were in the same range or even slightly higher at 250 °C, while RSDs were still lower at 290 °C. In order to achieve complete desorption (and minimal carry over, see Section 3.2) a temperature of 290 °C is recommended for both types of PDMS containing NTDs.

With DVB/Carboxen NTDs, peak areas were considerably increasing when desorption temperature was increased from 180 °C to 250 °C. Aromatic compounds, 2-butanone and most aldehydes showed a decrease in measured amount when the desorption temperature was further raised to 290 °C, while the amount of the other investigated substances further increased or stayed at the same level.

DVB triple-bed NTDs with DVB/Carbopack X/Carboxen 1000 sorbent packing showed differing results compared to DVB double bed NTDs. For most substances peak areas further increased at a desorption temperature of 290 °C compared to 250 °C. However, the average increase was comparably small being only about 10%, except for acetone, isoprene and acrolein (30–40%). I.e. introduction of Carbopack X as a second guarding substance for Carboxen further improves extraction efficiency at lower temperatures when compared to double bed NTDs using DVB or PDMS as first sorbent, since irreversible adsorption within the carbon molecular sieve is inhibited.

Preconcentration by means of polymer NTDs yielded largest peak areas at a desorption temperature of 220 °C for most substances. Relative standard deviations, however, were lower at a desorption temperature of 200 °C when compared to desorption at 220 °C. Lower desorption temperatures than 200 °C led to decreasing peak areas and simultaneous increase of relative standard deviations to over 80% for some substances. Since this type of NTD is supposed to be stable only up to 200 °C, this temperature was chosen as the ideal desorption temperature in order to avoid possible damage of the sorbent and impaired reusability. Saito et al. found comparable results for this NTD type using N_2 assisted desorption [12]. On the basis of these experiments desorption temperatures for the five NT types used in the following experiments were chosen as follows:

- 200 °C for polymer NTDs
- 250 °C for DVB containing double and triple bed NTDs

- 290 °C for PDMS containing double and triple bed NTDs

These choices represent a compromise between recovery, error range and potential reusability.

3.2. Carry over

Carry over varied distinctly between the different types of NTDs. PDMS double bed NTDs showed the largest amounts of carry over even at a desorption temperature of 290 °C. Due to the low equilibrium constant of PDMS reactive compounds and compounds with low volatility such as chlorobenzene will accumulate in the Carboxen packing, where degradation (catalyzed by active centres of carboxen) or incomplete desorption is likely to occur [16]. This could be prevented when a second packing like Carboxen X was introduced to guard the Carboxen. Hence, in PDMS triple bed NTDs carry over could be reduced when higher desorption temperatures were applied (Table 1).

When highly volatile substances such as acetone, propanal or isoprene were desorbed from double and triple bed NTDs containing DVB, relatively high carry over was found. This could be due to incomplete desorption from the Carboxen used in the NTDs. Incomplete desorption of unsaturated compounds such as isoprene has been described before for different carbon molecular sieves such as Carboxen 569 or Carboxen 1003 [17] as well as for Carboxen 1000 [18]. Acetone, acrolein and propanal showed even higher carry over when triple bed DVB based NTDs with additional graphitized carbon black located between the DVB and Carboxen were used. The incomplete desorption of polar volatiles such as acrolein from Carboxen has been reported by Rothweiler et al. [19] and seems to be a general problem with graphitized carbon blacks, since it occurred with PDMS triple bed NTDs, too and Sanchez and Sacks also found substance loss using multibed sorbent traps containing Carboxen X [18].

Polymer NTDs provided the best results regarding carry over, since all investigated substances were desorbed nearly to completion (Table 1). When multibed packing was used, triple bed NTDs showed lower carry over than double bed NTDs.

Fig. 3 shows the total ion chromatograms of two subsequent measurements carried out with a polymer NTD. For better understanding the range of retention time from 4 to 10 min is shown on an enlarged scale. Nearly no carry over could be observed with this NTD type.

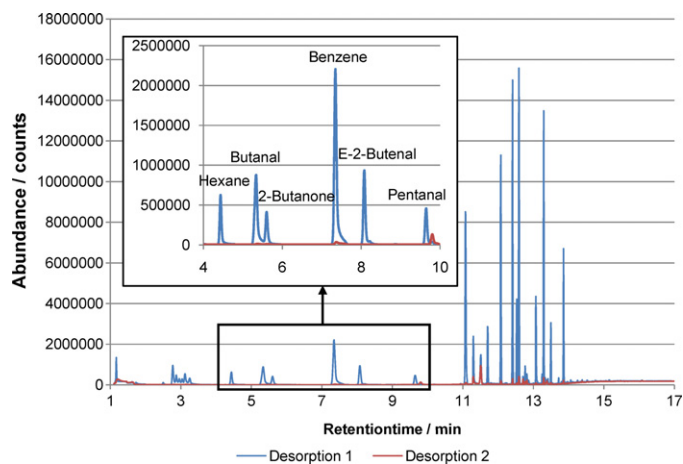


Fig. 3. Total ion chromatograms of two subsequent measurements with polymer NTD after expansive flow desorption (30 s at 200 °C). Blue trace: first desorption, red trace: second desorption of the same NTD. The insert gives a detailed view of the chromatogram between 4 and 10 min of retention time. Peaks in the TIC-chromatogram at 11.26, 11.50, 12.76 and 12.81 min correspond to column material and not to VOCs desorbed from the NTDs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In summary, combined with the results from the evaluation of different desorption temperatures, these results prove that the use of the expansive flow desorption technique is a sufficient and reliable method to desorb the described compounds from NTDs. Except for PDMS double bed NTDs good recoveries and only low carry over was found. In any case, after 30 min of reconditioning at desorption temperature all five types of NTDs could be reused without significant memory effects.

3.3. Reproducibility

Intra Needle RSDs were between 2.5% (α -pinene) and 7.6% (isoprene) for DVB/CarboxenNTDs and between 3.9% (acetone) and 11.9% (E-2-Butenal) for DVB/Carboxen/Carboxen triple-bed NTDs. PDMS/Carboxen NTDs had RSDs between 4.6% (octanal) and 14.5% (pentane) while PDMS/Carboxen/Carboxen NTDs were between 2.7% (pentane) and 7.6% (E-2-Butenal). Results obtained with needles with polymer packing were 1.6% (hexane) to 8.8% (E-2-butanol) RSD.

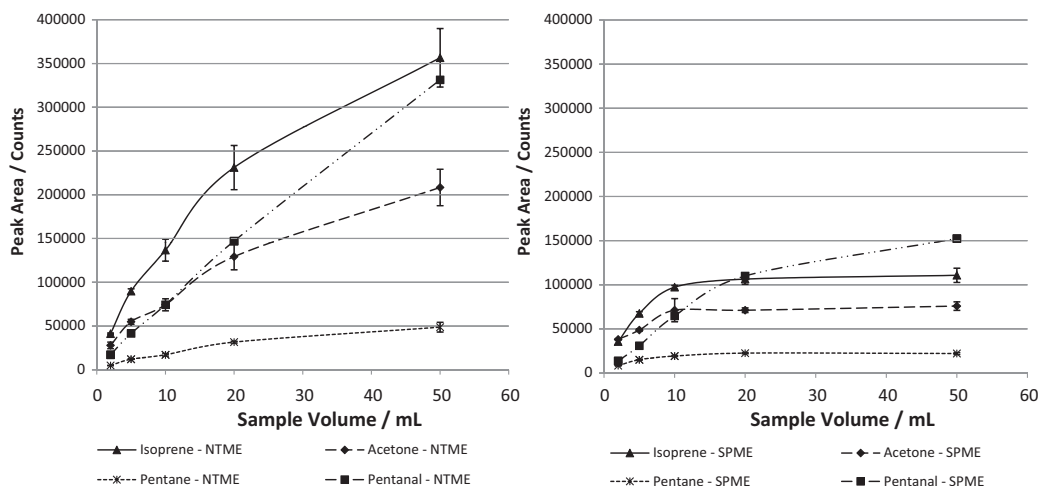


Fig. 4. Peak areas of acetone, pentane, isoprene and pentanal for different sample volumes (2–50 mL) with polymer NTDs (left) and SPME (right). A standard mixture of substances with a concentration of approximately 100 ppbv was used. Desorption temperature was 200 °C for NTME and 290 °C using SPME.

Table 1
Carry over of the different types of needle trap devices after a single desorption of 30 s. NTDs had been loaded with 20 mL of a 500 ppbV standard mixture. Each NTD was desorbed and analyzed two times consecutively by means of GC–MS. The amount of analyte determined after the second desorption was compared to the amount of analyte determined after the first desorption.

	Polymer carry over [%]	DVB/Carboxen	DVB/Carbopack X/Carboxen	PDMS/Carboxen	PDMS/Carbopack X/Carboxen	PDMS/Carboxen	PDMS/Carbopack X/Carboxen
Desorption temperature [°C]	200	250	250	250	250	290	290
2-Butanone	0.90	10.88	3.80	31.29	7.68	23.62	2.76
Acetone	4.57	21.83	27.50	22.44	28.60	30.39	14.67
Acrolein	3.50	23.06	34.95	21.51	27.87	22.73	14.90
α-Pinene	4.27	0.92	1.22	20.49	8.16	8.54	1.32
Benzene	3.63	15.56	16.90	55.51	28.44	48.35	5.77
Butanal	0.69	5.84	2.03	18.42	8.16	20.85	1.89
Chloro-benzene	2.24	0.49	0.97	44.96	10.03	39.82	1.94
E-2-Butenal	0.50	1.96	1.82	18.69	6.17	14.20	1.01
Heptanal	3.06	0.49	0.63	24.10	2.53	6.76	0.43
Hexanal	2.15	0.89	0.98	40.67	8.24	19.49	0.94
Hexane	0.98	2.92	6.50	44.45	18.60	52.30	3.76
Isoprene	3.66	15.69	8.88	24.38	6.91	28.05	3.84
Nonanal	4.82	3.01	2.96	8.02	3.68	7.15	4.63
Octanal	4.25	1.34	1.63	16.89	2.71	3.87	0.79
o-Xylol	2.99	0.30	0.69	23.89	4.15	18.58	1.59
Pentanal	0.82	0.87	0.84	32.24	8.27	22.50	1.02
Pentane	2.67	20.11	10.48	29.61	8.48	44.20	6.00
Propanal	3.09	14.00	22.74	15.54	43.23	12.73	3.69
Toluene	1.53	0.71	1.38	50.46	14.82	46.61	2.28

Inter needle variation was highest for PDMS double bed NTDs. DVB double bed NTDs and PDMS triple bed NTDs performed better, but still had comparably high RSDs varying from 5% to 40%. DVB triple bed NTDs had inter needle RSDs between 10% and 20% for most substances. This was most probably due to limited reproducibility of the packing procedure. The pronounced differences between intra- and inter-needle RSDs further support this hypothesis. In comparison, triple bed needles containing Tenax/Carbopack X/Carboxen 1000 prepared in our own laboratory [10] had RSDs between 4.7% (Acetone) and 14.5% (E-2-Butenal).

Best results could be obtained with Polymer NTDs having inter needle variations between 2% and 6% for all investigated substances. The better performance of polymer NTDs compared to the triple and double bed NTDs might be due the fact that this NTD type contains only one sorbent material resulting in a more homogeneous packing. Furthermore, as flow resistance during sampling

was lower, a more reproducible manual sampling could be realized with the polymer NTDs. Inter needle variation of the double and triple bed NTDs might be improved by applying an optimized, automated packing and sampling procedure.

Table 2 shows intra and inter-needle variations for all investigated needle trap types.

3.4. Calibrations, LOD and LOQ

Table 3 gives an overview of calibrations, LODs and LOQs for all substances analyzed by means of the different NTD types.

When sample volumes of 20 mL were used, LODs and LOQs were found in the typical range of some ng/L. LODs and LOQs were different for different compounds and varied distinctly with different types of NTDs. LODs for the handmade triple pack needles used in the previous study [10] were comparable to LODs determined

Table 2
Intra needle ($n=5$) and inter needle ($n=4$ (double bed), $n=5$ (triple bed, polymer)) variations. NTDs of each type, were loaded with 20 mL of a standard mixture containing substances in concentrations of approximately 100 ppbV. Volatile substances were analyzed by GC–MS.

Substance RSD [%]	Polymer		PDMS/Carboxen		PDMS/Carbopack X/Carboxen		DVB/Carboxen		DVB/Carbopack X/Carboxen	
	InterNTD RSD [%]	IntraNTD RSD [%]	InterNTD RSD [%]	IntraNTD RSD [%]	InterNTD RSD [%]	IntraNTD RSD [%]	InterNTD RSD [%]	IntraNTD RSD [%]	InterNTD RSD [%]	IntraNTD RSD [%]
2-Butanone	3.63	4.26	36.66	9.76	17.53	3.92	6.62	2.83	10.57	7.44
Acetone	3.99	1.96	64.07	8.64	6.91	4.05	26.85	2.93	9.59	3.88
Acrolein	4.34	3.20	20.56	7.93	9.32	4.34	18.52	3.86	12.68	6.33
α-Pinene	2.41	3.38	20.46	7.46	31.07	4.15	29.96	2.47	11.60	4.80
Benzene	4.37	2.69	23.39	10.09	8.04	3.72	4.50	3.47	16.21	7.36
Butanal	3.93	3.29	44.42	11.38	26.93	3.16	14.73	3.02	11.77	6.52
Chloro-benzene	3.39	7.36	17.17	8.65	23.79	5.70	25.75	4.75	19.10	8.49
E-2-Butenal	5.96	8.75	32.41	8.28	7.71	7.60	26.69	4.81	15.55	11.86
Heptanal	4.72	7.33	61.26	5.96	27.06	5.06	6.82	4.64	12.64	8.29
Hexanal	5.77	5.34	27.74	8.93	17.36	4.94	5.17	3.15	20.41	8.47
Hexane	6.46	1.62	26.79	11.12	6.45	3.24	19.20	4.16	20.53	6.30
Isoprene	3.77	3.62	19.61	13.87	12.44	3.45	24.37	7.57	16.89	7.06
Nonanal	16.31	12.12	31.03	3.60	21.66	6.99	12.87	6.65	13.77	10.93
Octanal	4.65	7.96	58.58	4.63	29.20	5.84	10.48	5.09	11.83	11.24
o-Xylol	4.19	5.48	67.66	8.55	29.61	4.59	5.12	4.19	12.50	6.56
Pentanal	6.12	4.47	22.98	9.04	8.05	4.26	15.55	2.68	19.64	8.22
Pentane	5.43	2.92	38.06	14.54	19.52	2.67	27.60	6.30	15.51	5.96
Propanal	3.18	4.37	24.01	9.58	8.02	5.51	40.14	4.28	13.78	5.41
Toluene	4.21	4.81	35.16	10.45	16.47	4.11	10.14	2.70	21.08	6.80

Table 3
Linear range, LODs and LOQs for VOC determination with different NTD types.

Substance	NTD type	Range (ng/L)	Slope	R ²	LOD/ (ng/L)	LOQ (ng/L)
Acetone	Polymer	2.75–1373.3	38.27	0.99	18.51	61.71
	DVB/Carbopack/Carboxen	13.73–412.00	48.21	0.98	63.64	212.14
	DVB/Carboxen	0.27–412.00	47.61	0.99	84.91	283.04
	PDMS/Carbopack/Carboxen	0.27–412.00	65.60	0.98	43.09	143.62
	PDMS/Carboxen	0.27–412.00	46.41	0.97	103.53	345.11
Isoprene	Polymer	0.31–460.43	28.30	0.99	1.81	6.04
	DVB/Carbopack/Carboxen	0.31–460.43	117.48	0.98	5.04	16.79
	DVB/Carboxen	0.31–230.22	65.09	0.99	18.04	60.14
	PDMS/Carbopack/Carboxen	0.31–460.43	330.95	0.99	0.88	2.93
	PDMS/Carboxen	0.31–460.43	36.13	0.96	16.92	56.41
2-Butanone	Polymer	0.35–530.80	83.71	0.99	1.78	5.93
	DVB/Carbopack/Carboxen	0.35–530.80	106.54	0.99	4.84	16.14
	DVB/Carboxen	0.35–265.41	60.43	0.98	11.94	39.78
	PDMS/Carbopack/Carboxen	0.35–530.80	128.06	0.99	5.21	17.38
	PDMS/Carboxen	0.35–265.41	19.69	0.98	63.36	211.18
Pentane	Polymer	16.42–492.5	12.47	0.98	8.46	28.21
	DVB/Carbopack/Carboxen	3.28–492.50	19.92	0.96	9.64	32.13
	DVB/Carboxen	16.42–492.5	8.76	0.99	45.00	150.01
	PDMS/Carbopack/Carboxen	0.33–492.50	54.82	0.99	4.28	14.27
	PDMS/Carboxen	0.33–492.50	5.48	0.94	93.86	312.88
Hexane	Polymer	0.38–576.73	108.66	0.99	1.38	4.60
	DVB/Carbopack/Carboxen	0.38–576.73	180.12	0.99	3.46	11.54
	DVB/Carboxen	0.38–576.73	89.16	0.99	13.08	43.59
	PDMS/Carbopack/Carboxen	0.38–576.73	236.45	0.99	3.69	12.31
	PDMS/Carboxen	0.38–576.73	15.41	0.94	96.37	321.22
Chlorobenzene	Polymer	0.54–806.01	512.57	0.99	0.24	0.80
	DVB/Carbopack/Carboxen	0.54–806.01	538.53	0.98	0.33	1.10
	DVB/Carboxen	0.54–403.00	415.41	0.99	0.94	3.12
	PDMS/Carbopack/Carboxen	0.54–806.01	535.61	0.99	0.32	1.07
	PDMS/Carboxen	0.54–403.00	73.06	0.97	4.55	15.28
Benzene	Polymer	0.37–559.32	483.71	0.99	4.49	14.95
	DVB/Carbopack/Carboxen	0.37–559.32	661.96	0.99	6.42	21.38
	DVB/Carboxen	0.37–559.32	455.48	0.98	5.75	19.16
	PDMS/Carbopack/Carboxen	0.37–559.32	929.55	0.99	13.67	45.56
	PDMS/Carboxen	0.37–279.66	52.98	0.98	23.20	533.45
Toluene	Polymer	0.43–647.45	775.23	0.99	2.00	6.68
	DVB/Carbopack/Carboxen	0.43–647.45	912.25	0.99	1.56	5.19
	DVB/Carboxen	0.43–647.45	844.02	0.98	1.30	4.33
	PDMS/Carbopack/Carboxen	0.43–647.45	847.05	0.99	4.21	14.03
	PDMS/Carboxen	0.43–323.72	56.90	0.90	39.54	131.81
o-Xylene	Polymer	0.48–717.62	780.19	0.99	0.82	2.74
	DVB/Carbopack/Carboxen	0.48–717.62	706.97	0.99	1.07	3.55
	DVB/Carboxen	0.48–358.81	705.43	0.99	1.31	4.37
	PDMS/Carbopack/Carboxen	0.48–717.62	770.46	0.99	1.36	4.52
	PDMS/Carboxen	0.48–358.81	48.37	0.99	15.47	51.56
alpha-Pinene	Polymer	0.55–829.63	526.79	0.99	0.22	0.74
	DVB/Carbopack/Carboxen	0.55–829.63	526.94	0.99	0.35	1.18
	DVB/Carboxen	0.55–829.63	701.56	0.99	0.44	1.45
	PDMS/Carbopack/Carboxen	0.55–829.63	463.09	0.99	0.42	1.40
	PDMS/Carboxen	0.55–414.81	32.07	0.99	10.83	36.11
Propanal	Polymer	0.27–412.01	36.03	0.99	7.73	25.77
	DVB/Carbopack/Carboxen	0.27–412.01	20.62	0.95	51.02	170.06
	DVB/Carboxen	0.27–206.00	35.35	0.98	45.10	150.33
	PDMS/Carbopack/Carboxen	0.27–412.01	45.09	0.98	31.83	106.10
	PDMS/Carboxen	0.27–412.01	40.98	0.98	63.27	210.90
Butanal	Polymer	0.32–482.58	60.41	0.99	2.18	7.26
	DVB/Carbopack/Carboxen	0.32–482.58	73.36	0.99	10.61	35.36
	DVB/Carboxen	0.32–242.29	46.56	0.99	25.07	83.56
	PDMS/Carbopack/Carboxen	0.32–482.58	102.67	0.99	9.83	32.77
	PDMS/Carboxen	0.32–241.29	14.37	0.96	153.29	510.96
E-2-Butenal	Polymer	0.64–961.57	105.84	0.99	0.87	2.90
	DVB/Carbopack/Carboxen	0.64–961.57	130.12	0.99	1.94	6.47
	DVB/Carboxen	0.64–480.79	62.96	0.96	8.19	27.29
	PDMS/Carbopack/Carboxen	0.64–961.57	151.81	0.99	4.10	13.66
	PDMS/Carboxen	0.64–480.79	15.88	0.98	48.27	161.18
Pentanal	Polymer	0.37–553.35	82.21	0.99	4.74	15.81
	DVB/Carbopack/Carboxen	0.37–553.35	105.96	0.99	15.62	52.08
	DVB/Carboxen	0.37–276.67	61.64	0.99	48.18	143.93

Table 3 (Continued)

Substance	NTD type	Range (ng/L)	Slope	R ²	LOD/ (ng/L)	LOQ (ng/L)
Hexanal	PDMS/Carbopack/Carboxen	0.37–553.35	105.10	0.99	26.80	89.34
	PDMS/Carboxen	0.37–553.35	14.72	0.96	58.92	196.38
	Polymer	0.44–663.59	126.84	0.99	8.96	29.88
	DVB/Carbopack/Carboxen	0.44–663.59	135.15	0.99	41.25	137.49
	DVB/Carboxen	0.44–331.80	94.13	0.99	142.26	474.21
	PDMS/Carbopack/Carboxen	0.44–663.59	131.58	0.99	46.74	155.78
Heptanal	PDMS/Carboxen	0.44–663.59	19.59	0.99	102.98	509.96
	Polymer	0.46–695.41	123.82	0.99	5.12	17.05
	DVB/Carbopack/Carboxen	0.46–695.41	109.11	0.98	41.14	137.13
	DVB/Carboxen	0.46–347.71	84.71	0.99	104.65	348.84
	PDMS/Carbopack/Carboxen	0.46–695.41	123.36	0.99	39.28	130.93
	PDMS/Carboxen	0.46–695.41	16.61	0.99	89.84	898.45
Acrolein	Polymer	0.51–757.84	25.46	0.99	4.73	15.91
	DVB/Carbopack/Carboxen	0.51–757.84	14.99	0.96	41.52	138.39
	DVB/Carboxen	0.51–757.84	28.96	0.98	30.27	100.92
	PDMS/Carbopack/Carboxen	0.51–757.84	42.61	0.99	28.99	96.64
	PDMS/Carboxen	0.51–378.92	24.95	0.99	90.19	300.64
	Octanal	Polymer	0.46–694.99	61.89	0.96	13.27
DVB/Carbopack/Carboxen		0.46–694.99	56.21	0.94	64.59	215.31
DVB/Carboxen		0.46–347.50	38.39	0.99	196.06	653.52
PDMS/Carbopack/Carboxen		0.46–694.99	70.76	0.98	60.12	200.40
PDMS/Carboxen		23.16–378.92	11.55	0.99	88.05	899.25
Nonanal		Polymer	0.47–704.41	48.31	0.93	37.53
	DVB/Carbopack/Carboxen	0.47–704.41	51.78	0.89	194.26	647.55
	DVB/Carboxen	0.47–704.41	54.21	0.90	411.87	1372.91
	PDMS/Carbopack/Carboxen	0.47–704.41	66.29	0.94	146.81	489.37
	PDMS/Carboxen	0.47–704.41	15.36	0.98	168.24	946.15

for polymer and triple bed NTDs in the present study. For most substances LOD on double bed NTDs were higher.

Polymer, PDMS triple bed, as well as DVB double and triple bed NTDs had LODs and LOQs in the same concentration range when aromatic compounds were analyzed. PDMS/Carboxen 1000 NTDs produced significantly higher values. This can be explained by their low overall capacity combined with large carry over.

Among the investigated substances aldehydes had the highest LODs and LOQs. Poorest results were obtained with PDMS/Carboxen 1000 NTDs. PDMS triple bed NTDs and DVB containing NTDs (double and triple bed) performed better, on average LODs/LOQs were lower by a factor of 5–10. For aldehydes analyses by means of polymer NTDs resulted in the lowest LODs and LOQs.

When hydrocarbons and oxygenated compounds were analyzed LODs and LOQs were considerably higher for double bed NTDs than for triple bed and polymer NTDs. This may be due to lower adsorption capacities and higher carry over in double bed NTDs.

From these results the following practical conclusions can be drawn:

- Polymer NTDs are universally applicable for sample preparation in VOC analysis. These NTDs represent a sound combination of low carry over, good reproducibility and acceptable sensitivity for most substances.
- If aromatic compounds are to be determined double and triple bed DVB devices could be considered as an alternative.
- Triple bed PDMS NTDs may represent an acceptable alternative for the analysis of hydrocarbons and aldehydes.
- For analysis of hydrocarbons and oxygenated compounds in the ppbV to pptV range PDMS double bed NTDs cannot be recommended.

3.5. Effect of sample volume

Fig. 4 shows the effects of increasing sample volume ($C_{\text{STANDARD}} = 100 \text{ ppbV}$) onto pre concentration of acetone, pentane, isoprene and pentanal. Polymer NTDs as well as a

PDMS/DVB/Carboxen SPME fiber and sample volumes from 2 to 50 mL were used. Appendix S2 shows a selected ion chromatogram of polymer NTME measurement with low sample volumes (2, 5 mL).

An increase in sample volume led to an increase of measured peak areas when NTME was used. SPME led to a significant increase of peak areas only when sample volumes were increased from 2 to 10 mL. When sample volumes were increased beyond 10 mL no, or only small increases of measured peak areas (of e.g. pentanal) could be observed.

Hence, sensitivity of the NTD–GC–MS assay can be increased using higher sample volumes. I.e. LODs and LOQs shown in Table 3 could be improved by increasing sample volume. However, a sample volume of 20 mL as used in these experiments represents a reasonable compromise between sensitivity and sampling time.

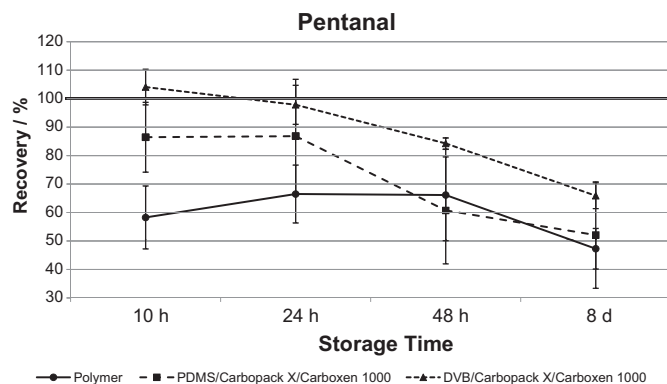


Fig. 5. Effects of storage onto recovery for pentanal. Recoveries in percentage relative to immediate analysis are displayed for four different storage times (10 h, 24 h, 48 h and 8 days). 20 mL of a standard containing substances in concentrations of approximately 100 ppbV were sampled. Dots and solid line: polymer NTDs ($n = 5$); squares and dashed line: PDMS/Carbopack X/Carboxen NTDs ($n = 4$); triangles and dotted line: DVB/Carbopack X/Carboxen NTDs ($n = 3$).

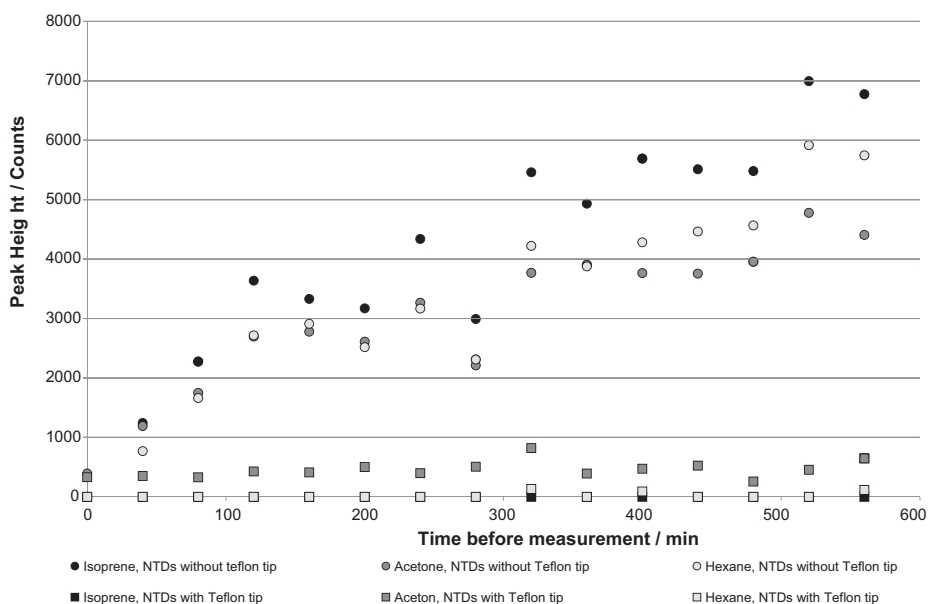


Fig. 6. Time course of peak heights determined for isoprene, acetone and hexane on polymer NTDs during storage in the autosampler rack. Squares represent NTDs sealed with Teflon tips, circles represent NTDs not sealed with Teflon tips.

3.6. Storage

Fig. 5 shows recoveries for pentanal after 10 h, 24 h, 48 h and 8 days of storage of sealed triple bed needles and polymer NTDs. Detailed results on effects of storage are shown in Appendix S3.

DVB/Carbopack X/Carboxen 1000 needles in general showed poor recoveries for oxygenated compounds and hydrocarbons after only 48 h. Aromatic compounds, however, had recoveries of over 90% even after 8 days, except for benzene, which only showed a recovery of 26%.

PDMS/Carbopack X/Carboxen 1000 needles showed recoveries of less than 80% for all investigated compounds after only 48 h. After 8 days of storage, recoveries varied from about 50% (toluene, butanal, benzene, E-2-butenal, 2-butanone, pentanal) to 80% (octanal, pentane).

Polymer NTDs showed recoveries between 46% (toluene) and 83% (octanal) after 8 days of storage. After storage of 24 or 48 h recoveries were between 60 and 87%.

It is mandatory that NTDs are thoroughly closed on both ends during storage as well as during hold-up in the autosampler rack before the actual measurement. Fig. 6 shows the accumulation of isoprene, acetone and hexane over a period of ten hours, which represents a typical duration of a GC run with 15–20 samples in our laboratory. NTDs which were not sealed on the lower end with a Teflon tip showed almost linearly increasing amounts of isoprene, acetone and hexane over time. In contrast, this effect could not be observed with NTDs which were sealed with an additional Teflon tip on the lower end of the needle. This has to be taken into account if NTDs are stored and if high sensitivities are required.

4. Conclusion

- Sorbent materials had distinct effects onto reproducibility, stability, detection limits and linear range of VOC analysis by means of needle trap micro-extraction.
- Volatile substances could be desorbed from the polymer NTDs by means of expansive flow technique without generating significant memory effects or carryover of the compounds.
- PDMS double packed needles are not well suited for reproducible trace analysis of VOCs.

- Polymer and triple pack needles enabled highly reproducible detection of VOCs in the ppbV–pptV range with sample volumes as low as 20 mL.

If analytical parameters were chosen properly, NTME provided excellent results for the detection of VOCs in the pptV to ppbV range. Low sample volumes, straightforward sampling and desorption and good reproducibility facilitate various applications of this technique. However, analytical performance of NTME crucially depends on sorbent materials, desorption temperatures and storage times. Intrinsic properties of sorbent material such as PDMS, DVB, graphitized carbon and molecular sieves have carefully to be taken into account. Monophasic polymer materials exhibited excellent performance in terms of reproducibility, reusability and sensitivity for all compounds and therefore represent the best choice for screening studies. For special applications, such as the detection of breath aldehydes, other packing materials such as PDMS/Carbopack X/Carboxen 1000 may be better suited. Therefore packing materials for NTME should be adapted to the problem under investigation. Limits of detection and limits of quantification could be achieved in the pptV range with sample volumes as low as 20 mL. Higher sample volumes can be used to further improve the sensitivity of the method. Without the need of any further equipment for the desorption of the NTDs, expansive flow technique resulted in sharp peaks and low carry over for most materials and the majority of investigated substances.

In conclusion, NTME represents a powerful tool for different application areas, from environmental monitoring to breath analysis, whenever VOC trace levels need to be detected.

Conflicts of interest

Shinwa Industries Ltd. (Mr. Ellwood Sean James) is producer and PAS Technology (Mr. Dietmar Hein) is distributor for Needle Trap devices (“NeedlEx”).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2011.10.077](https://doi.org/10.1016/j.chroma.2011.10.077).

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