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Determination of airborne, volatile amines from polyurethane foams by sorption onto a high-capacity cation-exchange resin based on poly(succinic acid)

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Abstract

A high-capacity carboxylic acid-functionalized resin prepared by ring-opening metathesis polymerization based on cross-linked *endo,endo*-poly(norborn-2-ene-5,6-dicarboxylic acid) was used for the sampling of volatile, airborne amines from polyurethane (PU) foams. Six tertiary amines which represent commonly used promotors for the formation of PUs from diisocyanates and polyols, namely pentamethyldiethylenetriamine, diazabicyclooctane, N-methylmorpholine, N-ethylmorpholine, 1,4-dimethylpiperazine and N,N-dimethylethanolamine, were sorbed onto the new resin. The sorption behavior of the new material was investigated in terms of loading capacities, the influence of concentration, flow-rate as well as of the amount of resin. Breakthrough curves were recorded from each single component as well as of mixtures thereof. Finally, the resin was used for the sampling of amines evaporating from PU foams applied in buildings. Further information about time dependent concentration profiles were obtained using a combination of GC–MS and Fourier transform IR spectroscopy. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Poly(succinic acid)-based sorbents; Sorbents; Extraction methods; Air analysis; Amines

1. Introduction

Polyurethane (PU) foams are widely used in construction work. They exist as high-speed and low-speed reacting foams, with chemical compositions depending on their actual application. In general, high-speed PU foams contain significant amounts of tertiary amines which are known to catalyze [1] the reaction between the polyol and the diisocyanate (Fig. 1). As this reaction is exothermic, low-boiling amines tend to evaporate during this process. As a consequence of their sometimes toxic nature, they

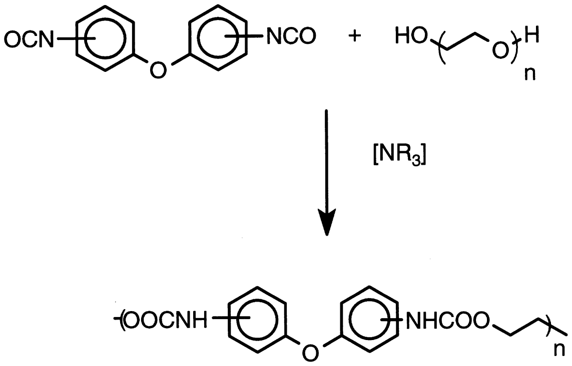

Fig. 1. Formation of PU foams from reaction of a diisocyanate and a polyol.

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need to be quantified in order to fulfil certain legal restrictions. While many methods such as thermodesorption [2] or pyrolysis–gas chromatography (GC)–mass spectrometry (MS) [3] allow the determination of ‘‘permanent’’ foam components, few reports [4–7] describe the sampling of volatile amines. Aromatic amines [8], dansyl- [9] or *o*-phtalaldehyde-derivatized [10] aliphatic amines are easily extracted by apolar sorbents such as charcoal or silica-C_{18}. The adsorption of tertiary aliphatic amines onto these sorbents suffers from low recoveries because of poor extraction efficiencies [11]. The derivatization and subsequent quantification of aliphatic amines using isothiocyanates [12] has been reported earlier. Nevertheless, this procedure is restricted to ammonia, primary and secondary amines. The use of ion exchangers based on silica for the enrichment of tertiary aliphatic amines encounters several problems, as the sorbent is often at least partially destroyed during the process of elution. Thus, organic fragments are formed, coelute with the amines and very often aggravate their subsequent analysis. Sulphonic acid-derivatized polystyrene–divinylbenzene (PS–DVB) materials provide excellent materials for the sampling process. Unfortunately, the sulfonic acid groups form rather stable salts with strong bases such as tertiary aliphatic amines. Elution is significantly impeded from this type of resins [13] and requires the use of eluents containing strong acids such as HCl [14] in order to obtain high recoveries. To circumvent this problem, strong cation exchangers are usually used only for weak bases [15,16]. As a consequence, a polymer-based high-capacity, weak cation-exchange resin based on a carboxylic acid-functionalized resin must be regarded as a suitable solution to the present problem [17]. To the authors knowledge, the system presented in this contribution allows for the first time a quantitative and reproducible determination of airborne tertiary aliphatic amines using a high-capacity weak cation-exchange resin based on cross-linked poly-(norborn-2-ene-5,6-dicarboxylic acid).

2. Experimental

2.1. Reagents and chemicals

The analytes studied were of >99% purity and used as obtained from Fluka (Buchs, Switzerland) and Aldrich (Milwaukee, WI, USA). All solvents and reagents (acetone, methanol, ethylacetate, diethyl amine, triethylamine, hydrochloric acid) were of analytical grade. Laboratory distilled water (DI water) was further purified using a Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA). Carboxylic acid functionalized resins (3.75 mequiv. COOH/g, specific surface area 14 m^2/g, pore volume 750 μl/g) was prepared as described elsewhere [18,19].

2.2. Equipment

For GC measurements, a GC 8030 (Fisons Instruments) system with MD 800 mass spectrometer (Fisons Instruments) was used in the splitless mode. The stationary phase consisted of a J&W capillary column DB-5 (30 m×0.25 mm I.D., 0.25 μm film thickness, 5% phenyl–95% dimethylpolysiloxane, flow 1.1 ml/min) and a HP capillary column HP-1 (60 m×0.25 mm I.D., 0.25 μm film thickness, 5% phenyl–95% dimethylpolysiloxane, flow 1.2 ml/min).

2.3. Procedure for solid-phase extraction (SPE) of amine solutions

For SPE experiments, 1.5-ml polypropylene–SPE columns (Iso-Lute) were used. COOH-resin particles were employed as the SPE adsorbent and slurry packed using suspensions in methanol or methanol–water (20:80). The amount of polymer used is indicated in the Tables. Samples were prepared by adding aliquots of a methanolic solution containing 1000 ppm of the corresponding analyte to the corresponding amount of methanol. Solutions containing the analytes were passed over the columns filled with the resin, using positive pressure to force liquids through the adsorbents.

2.4. Procedure for sampling of amines from air

Two different devices were used for sampling. The first one, used for the sampling of the high-boiling diazabicyclooctane (DABCO), consisted of a 500-ml three-necked beaker. It was loaded with a known amount of amine (2–10 mg), closed and heated to 150°C. The air containing the corresponding evaporated amine was passed at a constant stream (200 ml/min) over an extraction column filled with polymer using a pump (GS 312 gas sampler, Desaga). The whole set-up was designed in a way, that a closed system was generated. Sampling of the air through a septum and quantification by means of GC–MS allowed the determination of the current concentration of the amine in air. For low-boiling amines, a 50-l box was used, which was equipped with a thermometer, a small ventilator and two outlets. One outlet was connected to an extraction column filled with polymer which itself was connected to the pump in a way that the exhaust was reintroduced into the box (outlet 2). The actual amine concentration was again determined by sampling through a septum which was located right before the extraction column and subsequent quantification by means of GC–MS (Fig. 8). An average concentration was calculated by determining the concentration of the amine at the beginning, during and after the sampling procedure. The drop of amine concentration (if any) was found to be linear within the time of sampling. A detailed description of the box as well as its connection to the Fourier transform (FT) IR are available upon request.

2.5. Breakthrough volumes and breakthrough curves

Slurry-packed SPE columns containing 30–50 mg of resin were used throughout. Organic solutions containing one ore more amines were passed over the resin at a rate of 1.00 ml/min. The amount of resin indicated in the Tables was treated with 2–5 ml portions of the standards and the effluent was checked for analytes by means of GC–MS. An overview over the maximum loadings for each amine at the point of breakthrough is given in Table 1.

2.6. Recoveries

Recoveries for all analytes were calculated as an average of at least two trials by comparing the relative peak areas with standards (pentaoxapentadecan, *n*-hexylamine, 2,6-diisopropyl aniline) that were not subjected to SPE. Elution of all compounds from the columns was performed with diethyl- or triethylamine in the indicated solvent. Unless stated otherwise, relative standard deviations (R.S.D.s) were less than 2%.

2.7. FT-IR measurements

A MIDAC FT-IR gas cell (10 m) with an internal pump was used. It was connected to the 50-l box in a way that the air, which was pumped through the IR spectrometer was reintroduced into the box (outlet 2). The sampling device for GC–MS measurements was installed between the box and the FT-IR spectrometer (Fig. 9). This set-up ensures the most

Table 1
Maximum loadings (in % of theoretical capacity) at point of breakthrough for single compound standards in ethylacetate

Amine	pK_B	b.p. (°C)^{Pa}	Concentration (ppm)	Max. loading (%)$^a \pm \sigma_{n-1}$	Total amount (mg/g resin)
PMDTA[b]	4.6	198	70	22.8±0.5	48.0
	5.6				
	11.6				
DABCO[b]	5.4	158.16	50	4.9±0.2	22.5
	11.1	(m.p.)	100	5.3±0.3	24.1
NMM[c]	4.3	280^{8700}	42	15.8±0.2	33.8
	8.8				
NEM[c]	4.1	133	48	13.3±0.4	44.6
DMP[c]	6.6	155.3	50	4.7±0.2	17.8
DMEA[c]	6.3	138.6	50	4.0±0.2	17.5

[a] Expressed in % of capacity based on the assumption that each amine functionality is protonated by the resin.

[b] Thirty mg resin.

[c] Fifty mg resin. $n=3$.

accurate correlation between both analytical methods. The limit of detection (LOD) for pentamethyldiethylenetriamine (PMDTA) was found to be 0.15 ppm (signal-to-noise ratio=3).

3. Results and discussion

Ring-opening metathesis polymerization (ROMP) was used for the preparation of a new COOH-functionalized resin. It consists of an inert, cross-linked interior and a molecular fur, bearing the linear chains formed by the functional monomers, at the outside [18,19]. The structure of the resin is given Fig. 2. As a consequence, all functionalities are readily available for ion pairing. Additionally, the carboxylate groups provide sufficient hydrophilicity [20]. Electron microscope investigations revealed, that the material consists of irregularly shaped, agglomerated particles with a mean particle diameter of approximately 40±10 µm. This results in a low backpressure (5–10 p.s.i.; 1 p.s.i.=6894.76 Pa) during all experiments and positively influences the sampling of the amines from air. The specific surface of the 3.75 mequiv. COOH/g resin was 15 m^2/g, indicating a non-porous structure. Nevertheless, a non-permanent porosity was found in the conditioned state. The pore volume of 750 µl/g and the resulting higher specific surface of 80 m^2/g account for the considerable swelling (+40%) upon treatment with polar solvents such as methanol or water. The material is entirely pH stable and reusable for at least 30–40 times without any loss of performance.

3.1. Sampling of amines from solution

In order to characterize the resin in terms of its retention behavior versus the amines of interest, solutions thereof in methanol were passed over the resin. Breakthrough curves were recorded (Fig. 4) and maximum loadings of the resin with each amine were calculated. Table 1 gives an overview of these values and the concentrations of the corresponding amines using single compound standards. The structures of the amines are shown in Fig. 3. As expected, the monoamines [N-methylmorpholine (NMM), N-ethylmorpholine (NEM)] elute prior to the diamines [DABCO, 1,4-dimethylpiperazine (DMP)] and the triamine (PMDTA). Additionally, the order of elution of the monoamines correlates strongly with their pK_B values. Surprisingly, N,N-dimethylethanolamine (DMEA), a monoamine, is retained quite strongly. This effect is believed to result from some additional hydrogen-bonding between the carboxylic acid moieties and the alcohol functionality. High loadings for each of the amines were achieved (Table 1, Fig. 4) which allows the use of significantly reduced amounts of resin (usually 50 mg). The influence of the different compounds upon each other was determined by passing a mixture containing four different amines (NEM, NMM, DMP, DMEA) over the same amount of resin. In order to be able to compare these results with those obtained from single component standards, the same concentrations for each amine were chosen. As expected, the order of elution did not change (Fig. 5) and was strictly related to the pK_B value of the corresponding amine. In a next step, recoveries were determined by passing known amounts of the amines over the resin using single compound standards (Table 2). High recoveries for all six amines were obtained over a concentration range of 5 to 100 ppm (v/v). The di- and triamines PMDTA and DABCO were even retained efficiently up to a concentration of approxi-

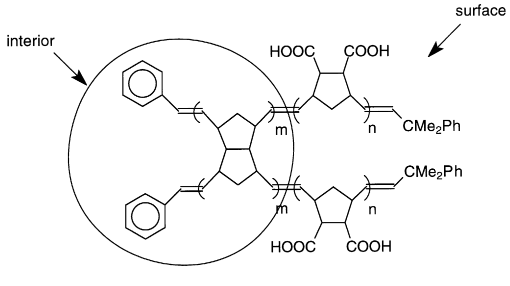

Fig. 2. Structure of the new resin.

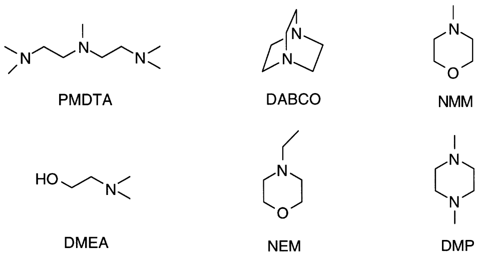

Fig. 3. Structure of tertiary amines.

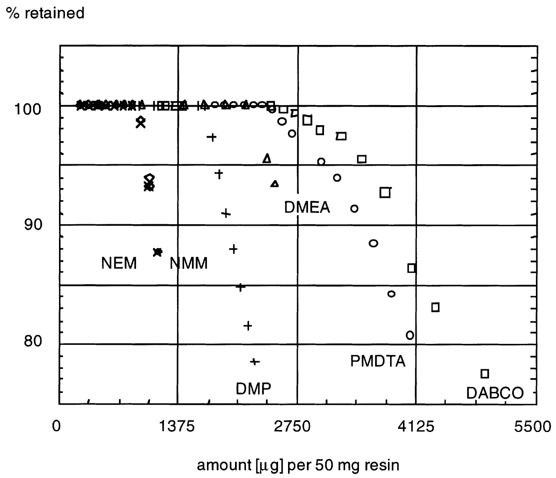

Fig. 4. Breakthrough curves for amines using single compound standards (40 ppm DMP, 50 ppm NEM, NMM, DMEA, 70 ppm DABCO, 90 ppm PMDTA) in ethyl acetate. Fifty mg COOH resin (3.75 mequiv./g).

mately 300 ppm (v/v). Finally, it should be noted, that recoveries were identical or within a range of 5% for each amine using both single compound as well as mixed standards.

3.2. Sampling of amines from air

The efficiency of a sampling method for volatile compounds from air strongly depends on the concentration of the corresponding analyte as well as on the extraction efficiency of the resin. So far, the resin used for the present investigations, showed excellent extraction efficiencies and high recoveries for all six amines in SPE experiments carried out in solution. In order to develop a method for the sampling of these amines from air, a suitable concentration in air of each analyte had to be chosen. Preliminary experiments revealed, that concentrations of the corresponding amine of approximately 5–50 ppm (v/v) had to be expected. Using the set-up described in Section 2.4, a total volume of 1.0–3.0 l of air (corresponding to a sampling time of 5–15 min) containing one of the amines was passed over the resin at a flow-rate of 200 ml/min. Using only 50 mg of the new resin, almost quantitative recoveries for amines at concentrations of 2 to 140 ppm (v/v) were achieved within sampling times of 5 to 15 min. Table 3 gives an overview of the results. While PMDTA, DABCO were retained quantitatively within a concentration range of 2 to approximately 140 ppm, significant losses of the monoamines DMP, NEM and MMM were observed at elevated concentrations. This is in accordance with the results from the breakthrough curves determined for all amines from solutions in methanol. Finally, it is worth mentioning that DMEA is again retained effectively, despite that fact that this compound is a monoamine. Again, the high retention is attributed to some additional hydrogen bonding between the alcohol moiety and the carboxylate groups. In general, the applied sampling rate of 200 ml/min proved to be suitable for PMDTA, DABCO, DMEA up to concentrations of at least 100 ppm (v/v). Nevertheless, using this sampling rate, MMM, NEM as well as DMP are adsorbed quantitatively up to 10 ppm (v/v).

3.3. Sampling of amines from PU foams

A variety of different high- and low-speed PU products were investigated. They contained one or more of the above-mentioned amines at various concentrations. While all low-speed foams did not release any detectable amounts of amines, several high-speed products emitted considerable amounts of one or more amines above their LOD yet below their limit of quantification (LOQ) according to DIN 32645 [21] (Table 4). Nevertheless, one type of high-speed PU foam was found to release rather large amounts of PMDTA. It showed a strongly exothermic reaction resulting in temperatures around 95°C at the interior of the foam.

One cartridge containing 200 g of the PMDTA emitting high-speed reacting PU foam was brought out at room-temperature. Sampling was performed in a way, that the sampling device, consisting of a SPE cartridge filled with 50 mg of resin was positioned right over the surface of the foam. After 5 min of sampling, the cartridge was eluted with triethylamine–methanol (50:50) and quantified by GC–MS. The actual PMDTA concentration in air right above the foam was found to be 2.5 ppm (v/v). In order to be able to estimate the total emitted amount of PMDTA, five cartridges of the same PU foam were brought out in a closed 35 m^3 room. Sampling was

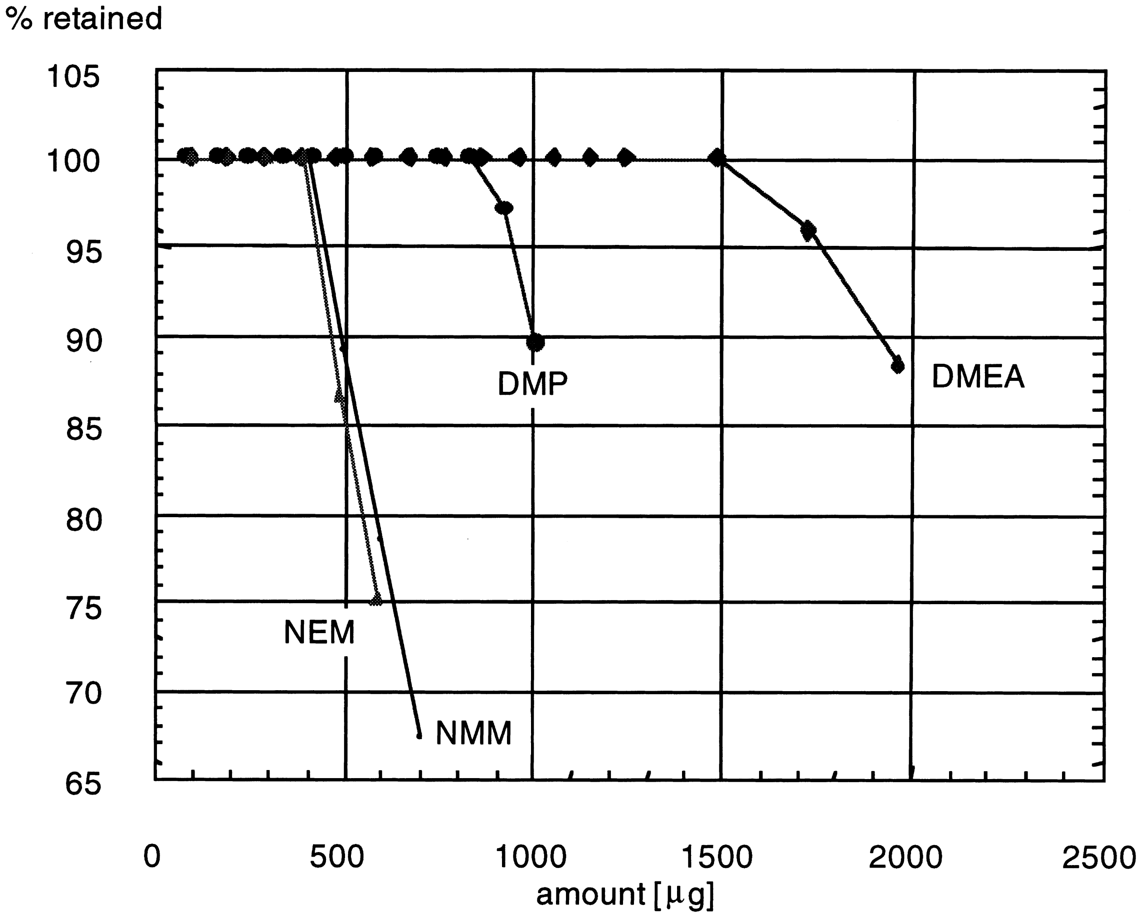

Fig. 5. Breakthrough curves for amines using a mixed standard (50 ppm of DMEA, NMM; NEM, 40 ppm of DMP) in ethyl acetate. Fifty mg COOH resin (3.75 mequiv./g).

performed over a period of 32 h using 50 mg of the resin. The average PMDTA concentration over that time was calculated to be 10 ppb, which corresponds to a total amount of approximately 60 mg PMDTA. This value represents only a rough estimation due to a fast decrease of the PMDTA concentration in air. Nevertheless, it significantly differs from the PMDTA concentration found right above the PU foam. This putative inconsistency is explained by the chemical nature of the amine. While the rather low boiling point of PMDTA (198°C) and its low polarity, respectively, lead to the release of large amounts of the amine during the exothermic polymerization reaction, the amine gets readsorbed onto any cold surface upon cooling, which causes a fast concentration drop in air. This proposal was supported by an experiment described in the following.

3.4. Concentration profile of PMDTA

The determination of a time-dependent concentration profile requires a quick data acquisition as well as processing. GC does not allow the recording of such a profile due to the rather time-consuming separation. FT-IR represents an ideal method for such a data acquisition. In a first step, a FT-IR calibration curve for PMDTA was recorded by measuring the actual concentration by GC–MS. This was necessary, as neither liquid-film nor any solution spectra represent adequate sources for such a cali-

Table 2
Recoveries for amines using single compound standards in methanol (50 mg resin)

Amine	Concentration (ppm)	Recovery (%)	Loading (% of capacity)
PMDTA[a]	300	117.9	10.8
	100	98.0	1.8
	5	102.7	0.9
DABCO[a]	275	103.3	12.1
	100	101.2	1.9
	5	100.6	1.0
NMM[b]	100	95.7	1.1
	66	93.4	1.4
	5	92.7	0.5
NEM[b]	100	96.7	0.9
	70	91.5	1.3
	5	89.7	0.5
DMP[b]	100	95.4	1.9
	65[c]	93.3	3.6
	5	95.3	0.9
DMEA[b]	100	101.2	1.2
	75[c]	90.0	3.6
	5	95.1	0.6

[a] Elution with 3 ml Et_3N–MeOH (50:50).
[b] Elution with 2 ml Et_2NH–MeOH (50:50).
[c] One hundred mg resin.

Table 3
Recoveries for amines after SPE from air using 50 mg resin

Amine	Concentration (ppm, v/v)	Sampling time ([22])	(%)
PMDTA[a]	140	5	107.5
	75	10	107.6
	13.4	10	102.9
	6.8	10	107.8
	2.1	10	103.4
DABCO[a]	95	5	94.8
	50	5	98.3
	13	10	99.3
NMM[b]	300	3	37.7
	120	5	68.3
	5	15	98.8
NEM[b]	170	5	87.1
	5	15	97.1
	3	15	95.3
DMP[b]	70	5	80.7
	9	15	104.9
DMEA[b]	113[c]	10	107.5
	90	10	101.2
	35	10	103.2
	15	10	110.2

[a] Elution with 3 ml Et_3N–MeOH (50:50), $n=3$.
[b] Elution with 2 ml Et_2NH–MeOH (50:50).
[c] One hundred mg resin.

bration due to changes in the absorption wavelength as well as intensity. A plot of the peak-height (expressed in AU) determined by FT-IR versus the peak area of PMDTA determined by GC–MS is shown in Fig. 6. The good correlation factor ($R^2=0.991$) justifies the concept of the combination of both methods. Limits of detection for PMDTA by FT-IR were defined on a signal-to-noise ratio of 3 which corresponds to concentration of 0.15 ppm (v/v). Finally, the PU foam was placed into the 50-l box, the system was closed and data acquisition was started. Fig. 7 shows the time dependent PMDTA concentration inside the box (50 l). It can be seen, that the high amine concentration rapidly drops to about 0.2 ppm within approximately 2 h. This is in accordance with the low average amine concentration in large rooms.

4. Conclusions

The new carboxylic acid derivatized resin provides excellent properties for the sampling of airborne aliphatic mono-, di- and triamines. The resin allows the sampling of non UV-absorbing, non-derivatizable, polar amines with high extraction efficiencies and recoveries. These high recoveries which were obtained over a broad range of concentration in SPE experiments using solutions of the amines were again observed in the sampling of the same compounds from the gas phase. Applications in the area of polymer analysis have been given by the quantifica-

Table 4
Limits of detection and limits of quantification for amines in air according to DIN 32645 [21] based on a 500-μl injection volume

Amine	LOD (ppm, v/v)	LOQ (ppm, v/v)
PMDTA	0.70	2.38
DABCO	1.51	4.86
NMM	1.1	3.19
NEM	0.18	0.60
DMP	0.64	2.08
DMEA	0.98	2.89

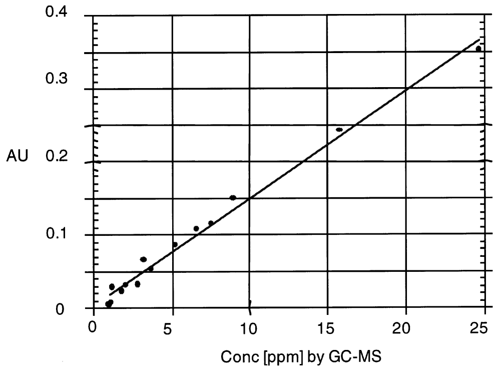

Fig. 6. Peak-height of FT-IR signal (expressed in AU) vs. concentration of PMDTA (determined by GC–MS).

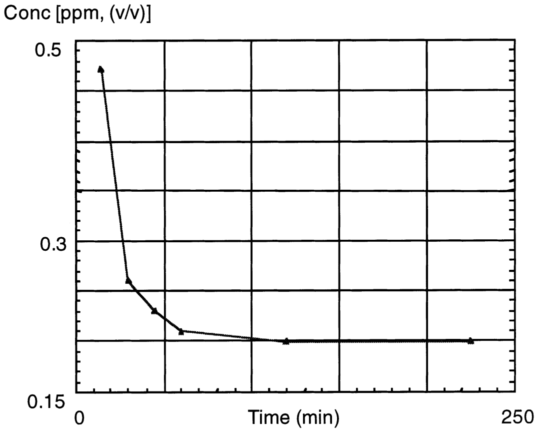

Fig. 7. Concentration profile of PMDTA (neat) in a closed system. Quantification by FT-IR (ν=1030 cm^{-1}).

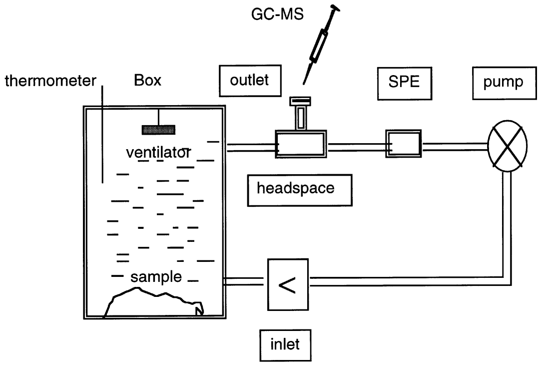

Fig. 8. Box connected to the sampling device for GC–MS.

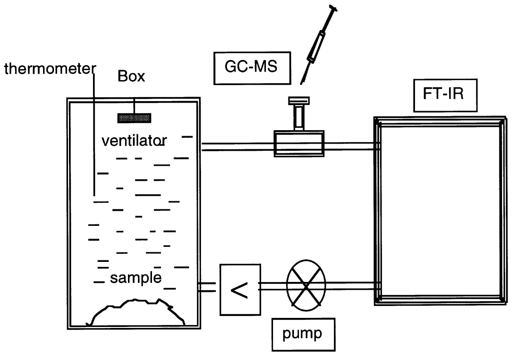

Fig. 9. Set-up for simultaneous FT-IR and GC–MS measurements.

tion of volatile promotors in the PU foam formation. The combination of GC–MS with FT-IR (see Figs. 8 and 9) additionally allows the fast recording of concentration profiles. In general the entire set-up allows the fast routine analysis of volatile, basic compounds. Additionally, the high stability of the resin as well as the high loading capacities make it highly attractive as filter materials for air clean-up. Possible large-scale applications are currently under investigation.

Acknowledgements

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