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Journal of Chromatography A, 809 (1998) 47–63

JOURNAL OF CHROMATOGRAPHY A

Development and application of a thermal desorption method for the analysis of polar volatile organic compounds in workplace air

Rainer A. Hallama, Erwin Rosenberg*, Manfred Grasserbauer

Institute of Analytical Chemistry, Vienna University of Technology, Getreidemarkt 9/151, A-1060 Vienna, Austria

Received 17 June 1997; received in revised form 3 March 1998; accepted 4 March 1998

Abstract

The application of a newly developed thermal desorption method for the analysis of workplace air to the analysis of polar compounds is reported. The method was validated for both pumped and diffusive sampling of test gases containing polar volatile organic compounds (esters, alcohols, ketones or aldehydes) on adsorption tubes and subsequent analysis of these tubes. Carbosieve SIII, Carboxen 569, Carbopack B and Tenax TA were used as solid adsorbents. Analysis was performed by thermal desorption of the analytes from the adsorbent tubes followed by gas chromatography–flame ionisation detection (GC–FID). It could be demonstrated that thermal desorption–GC–FID is feasible also for the analysis of polar compounds and that problems arising from the high concentration levels of some analytes in workplace air could be solved.

Keywords: Thermal desorption; Sample preparation; Air analysis; Adsorbents; Volatile organic compounds; Esters; Carbonyl compounds; Alcohols

1. Introduction

Monitoring of volatile organic compounds (VOCs) is an important analytical task not only because of their contribution to atmospheric pollution [1,2] but also in the field of industrial hygiene. Since certain VOCs are known to be hazardous to human health [3–5], exposure to these compounds in the workplace is subject to regulations and has to be monitored regularly [6–8].

A large number of methods has been reported to date for this purpose: ambient VOC monitoring can be carried out by either on-line gas chromatography [9–11] direct spectroscopic measurement [12,13] whole air sampling (e.g. in passivated canisters [14–16] or sampling on solid adsorbents [17,18] and subsequent analysis in the laboratory.

As the first three methods are very costly and experimentally difficult, they are mainly applied in environmental monitoring studies and/or where a high resolution time for the monitored compounds is required. In the field of industrial hygiene, however, personal exposure measurements are done with low-cost equipment to yield a time-weighted average of the worker's exposure. In the vast majority of cases, solid adsorbents are used for sampling.

Sampling of the VOCs can be achieved by either active (pumped) or passive (diffusive) [19,20] sam-

*Corresponding author.

0021-9673/98/$19.00
PII: S0021-9673(98)00220-9

pling. Whether thermal desorption [18] or solvent desorption [6] is used is mainly dependent on the choice of adsorbent material, the sampler design and the analytical task. Provided that universal adsorbent materials and appropriate sampler designs are used, both thermal and solvent desorption can be used alternatively [21].

When selecting from the different possibilities for sampling and desorption, a number of aspects have to be considered. Some of them relate to the convenience of the workers, such as ease of use, size and portability of samplers; others relate to the method performance, such as requirements for accuracy and precision, validation and storability. Ease of operation for the analyst, such as handling of toxic or flammable solvents, required skill, potential for automation is also a consideration. Finally there is the cost aspect [20,22,23].

It is common practice to monitor the workplace atmosphere for VOCs by adsorptive sampling and solvent desorption [6–8]. This can be realised by sucking with a pump a defined volume of workplace air through a tube filled with a suitable adsorbent, e.g. an active charcoal or silica gel tube. Prior to analysis, the adsorbent is extracted with carbon disulphide or solvent mixtures containing polar components; analysis is done by gas chromatography–flame ionisation detection (GC–FID). One of the main disadvantages of this method — apart from being rather labour-intensive — is the fact that there is no universally usable solvent for the quantitative desorption of polar compounds such as e.g. esters, ketones and alcohols. Diethyl ether has been examined for this purpose [8], but the results have not been satisfactory. Desorption is less efficient or slow in many cases. In addition, the solvent desorption method is not suitable for automation. Sensitivity and detection limits suffer from the fact that only a very small fraction of the extract can be analysed. While a few millilitres of solvent are used for desorption, only a few microlitres can be injected into the GC.

Thermal desorption is better in some of the aspects mentioned above. Active sampling has preferentially been used in environmental analysis due to its sensitivity down to the ppb- and ppt-range [24–26]. However, it has also demonstrated its feasibility in workplace air monitoring, and a number of applications, especially in combination with diffusive sampling, have been reported [27–29]

The present work reports on the use of a recently developed thermal desorption method [30,31] that has been applied and validated for the analysis of workplace air with special emphasis on polar compounds, namely esters, alcohols, ketones and selected aldehydes. Due to the difficulties encountered in thermal desorption of polar compounds, these have not been included in routine analytical schemes [32,33].

The method presented here is generally applicable and can be used in combination with both active and passive sampling without any modification. Since greatly differing amounts of analyte are trapped with active and passive sampling, one important achievement of this work was to eliminate the problems associated with thermal desorption analysis of such large amounts of substance. This is important since some of the polar analytes (e.g. ethyl acetate, ethanol) are less toxic and thus have to be monitored up to very high concentrations in workplace air.

The problems encountered with high sample loads are: nonquantitative adsorption of the analytes during the sampling, nonlinearity of the calibration curve caused by overload of the internal trap and peak distortion in the chromatograms caused by overload of the GC column.

Optimisation of the parameters for both the sampling (active/passive) and the thermal desorption, results in an analytical method that complies with the requirements that are laid down for methods for monitoring of VOCs in workplace air based on pumped [19] and diffusive sampling [37] for most of the investigated compounds. The main advantages of thermal desorption over solvent desorption are: higher sensitivity, lower detection limits (important especially when doing passive sampling); elimination of the use of carbon disulphide (which is toxic and may cause interfering peaks in the chromatogram) and potential for automation [18,34].

2. Experimental

2.1. Test gases

Test gases were prepared by a syringe injection

apparatus, which allowed generation of test gases with defined concentrations of the VOCs. The appropriate regulations for the development and evaluation of techniques for monitoring VOCs in workplace air [19,35–37] require the methods to be applicable in the range of 0.1–2 times the threshold limit value (TLV) and at different relative humidities (RH). Therefore, test gases with different concentrations of analytes (at 0.1-fold TLV and 2-fold TLV) and different RHs (20, 50 and 80%) for each class of compounds were used. Four to eight tubes were sampled under either of these conditions with the test gas containing 3–8 components of one class of compounds and subsequently analysed and quantitatively evaluated. The substances investigated in this study were grouped according to chemical class, and only compounds belonging to one class of compounds were sampled and analysed at one time. Samples were collected by pumped sampling and diffusive sampling [38] on custom-made adsorption tubes. The sample loadings of the substances investigated were dependent on their individual TLVs, which means that lower loadings were obtained for more toxic and higher loadings for less toxic substances. For the C_3–C_6-aldehydes, arbitrary values (of 12.5, 125 and 250 mg m^{-3}) were assumed, since TLVs have not been established in Austria for these compounds. The highest test gas concentration was 9450 mg m^{-3} of esters (corresponding to an atmosphere containing the investigated esters at their twofold TLVs). Therefore, at a sampling volume of 1 dm^3, the highest loading was 9.5 mg of esters on one sampling tube. Sample loadings of individual substances were between 1.6 μg (corresponding to 1 dm^3 of air containing benzene at 0.1 TLV) and 3.8 mg (corresponding to 1 dm^3 of air containing ethanol at 2 TLV) when carrying out active sampling. The loadings obtained with passive sampling were lower by a factor of approximately 30. The tubes were analysed by the thermal desorption method. The test gas concentration was calculated from the absolute amount of analytes trapped on the solid adsorbent bed and from the sampling volume (for active sampling) or the uptake rate and sampling time, respectively (for diffusive sampling). The so-obtained concentration values (mg analyte/m^3 test gas) were divided by the values known from the test gas generation to obtain the recovery rates. Calibration of the thermal desorption method was performed by repeatedly (n=5–6) injecting a liquid mixture of the same components into an empty tube which was mounted in the oven of the thermal desorption unit instead of an adsorbent tube.

2.1.1. Test gas generator

A syringe injection apparatus [30,39,40] was used for generating test gases over a wide range of volatility (b.p.=20–192°C) and concentration (ppb up to thousands of ppm) of the components. With the option of (even multistep) dilution by the zero gas, VOC mixtures of almost deliberate composition can be generated, provided that the analytes are in the liquid state at the operating temperature. In principle, the apparatus operates by slowly and continuously injecting a liquid mixture of the components into an exactly defined gas stream. The injection is done by a syringe which is driven by a computer-controlled stepper motor and a micrometer screw. A schematic view of the apparatus is given in Fig. 1.

2.2. Substances

The substances investigated in this work are listed in Table 1 with formula, molecular mass, TLV in Austria [41], boiling point [42] and diffusion coefficient (at 25°C) [44]. TLVs are concentration limits of substances which are likely to appear at the workplace; they are established to protect the employees from adverse effects on their health and usually imposed by the government on the employers.

The diffusion coefficients of the aldehydes have been calculated as described elsewhere [43]. The substances were obtained from Merck, Aldrich and Fluka with purities of higher than 98% in all cases.

2.3. Adsorbent tubes

The adsorbent tubes were custom-made of glass, ~12 cm×6–6.2 mm O.D. and a wall thickness of ~1 mm. They were filled with solid adsorbents up to a bed length of 8 cm for active sampling or 6 cm for passive sampling. Silanised glass wool plugs were used to hold the adsorbents in place. The tubes were end-closed with 1/4 in. brass caps and PTFE ferrules (Swagelok) or Vespel ferrules (Supelco). For active sampling, tubes filled with a combination of 250 mg

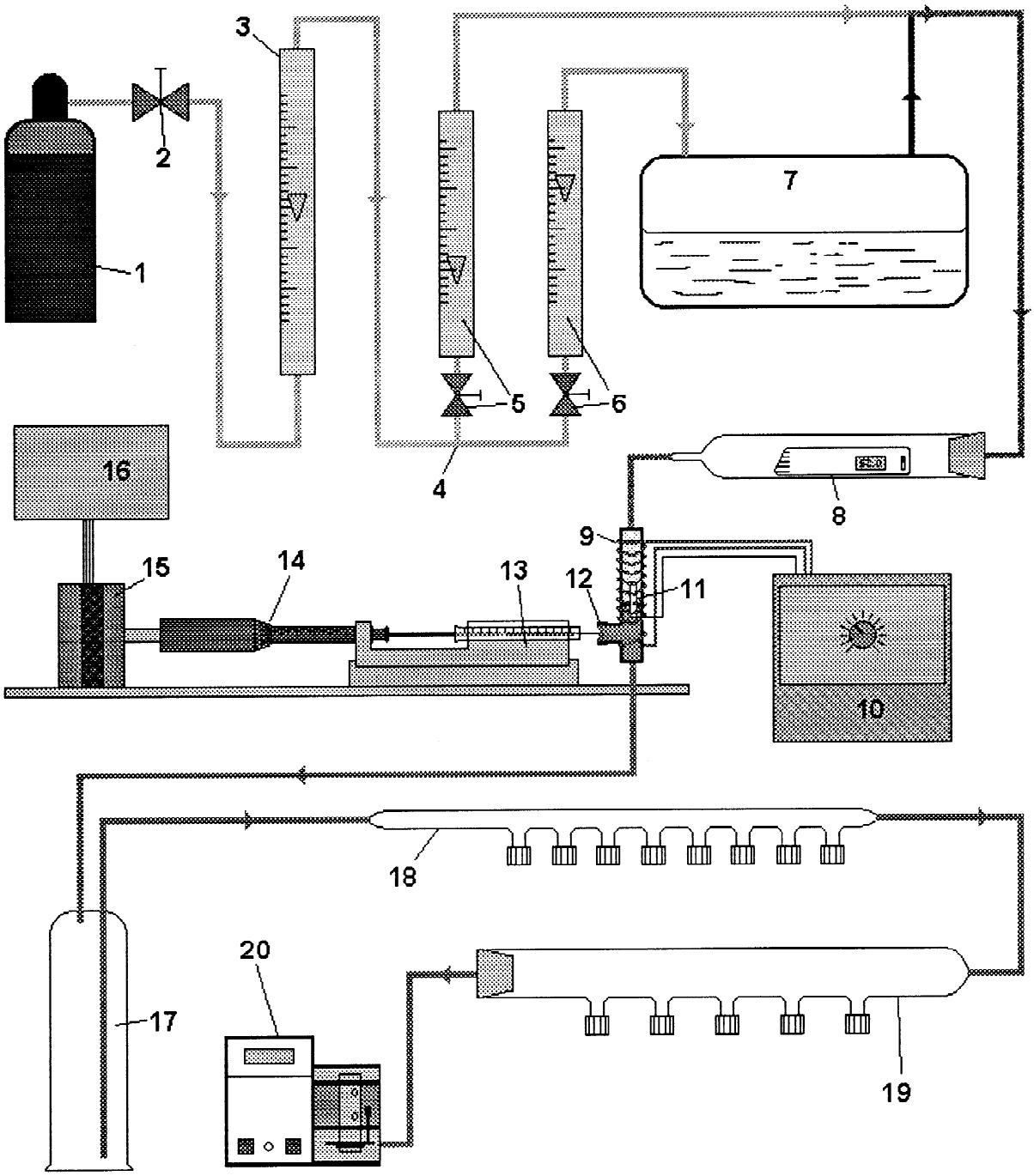

Fig. 1. Schematic view of the custom-made injection apparatus. Gas tank with (1) synthetic air, (2) needle valve, (3) rotameter for monitoring the total gas flow, (4) tee, (5) needle valve and rotamer for the dry gas stream, (6) needle valve and rotameter for the humidified gas stream, (7) humidifier, (8) hygrometer, (9) heater for the injection chamber, (10) temperature control, (11) thermoelement, (12) injection chamber, (13) syringe with carriage, (14) micrometer drive, (15) stepper motor, (16) control electronics of the stepper motor, (17) mixing chamber, (18, 19) chambers with sampling ports, (20) air flow calibrator.

Table 1
List of substances investigated in this work[a]

Name	Formula	M_r	TLV		B.p. (°C)	D_{298} ($cm^2\ s^{-1}$)
			($ml\ m^{-3}$)	($mg\ m^{-3}$)		
Ethyl acetate	$CH_3CO_2C_2H_5$	88.11	400	1400	77	0.0861
Isopropyl acetate	$CH_3CO_2CH(CH_3)_2$	102.13	200	840	89	0.077
n-Propyl acetate	$CH_3CO_2C_3H_7$	102.13	200	840	102	0.0768
Isobutyl acetate	$CH_3CO_2CH_2CH(CH_3)_2$	116.16	150	700	116	0.0663
1-Butyl acetate	$CH_3CO_2C_4H_9$	116.16	150	700	126	0.0672
2-Ethoxyethyl acetate	$CH_3CO_2C_2H_4OC_2H_5$	132.16	20	110	156	0.061
2-Butoxyethyl acetate	$CH_3CO_2CH_2CH_2OC_4H_9$	160.21	20	135	192	0.0585
Ethanol	C_2H_5OH	46.07	1000	1900	78	0.1181
2-Propanol	$(H_3C)_2CHOH$	60.10	400	980	82	0.1013
2-Methyl-1-propanol	$(H_3C)_2CHCH_2OH$	74.12	50	150	108	0.081
1-Butanol	C_4H_9OH	74.12	50	150	118	0.0861
2-Ethoxyethanol	$C_2H_5OC_2H_4OH$	90.12	20	75	136	0.0788
2-Butoxyethanol	$C_4H_9OCH_2CH_2OH$	118.18	20	100	171	0.0634
Acetaldehyde	CH_3CHO	44.05	50	90	20	0.1234
Propanal	CH_3CH_2CHO	58.08	–	–	48	0.1008
2-Methylpropanal	$(CH_3)_2CHCHO$	72.11	–	–	64	0.0872
2-Methylbutanal	$(CH_3)_2CHCH_2CHO$	85.13	–	–	92	0.0769
Hexanal	$CH_3(CH_2)_4CHO$	100.16	–	–	131	0.0690
Acetone	CH_3COCH_3	58.08	750	1780	56	0.1049
2-Butanone	$CH_3CH_2COCH_3$	72.11	200	590	80	0.0903
4-Methyl-2-pentanone	$(CH_3)_2CHCH_2H_3$	100.16	100	400	116	0.0702

[a] Since no threshold limit values have been issued in Austria for some aldehydes, an arbitrary value of 125 $mg\ m^{-3}$ was assumed.
M_r, molecular mass, TLV, threshold limit value, b.p., boiling point, D_{298}, diffusion coefficient at 25°C.

Carbopack B and 300 mg Carbosieve SIII (sampling of esters, alcohols and ketones) or a combination of 320 mg Carboxen 569 and 320 mg Carbosieve SIII (for aldehydes) were used. Tubes filled with about 200 mg Tenax were used for passive sampling of all compounds investigated. Before sampling, all tubes were conditioned at 300°C for >2 h at a flow-rate of 30–50 ml/min He (purity 99.999%). The rather short conditioning time as compared to other studies [24] seemed to be sufficient since the blank value is actually determined by the carryover of the internal trap of the thermal desorption unit and not by the adsorbent tubes. Before and after sampling, all tubes were stored at room temperature.

2.4. Active sampling

Densely packed thermal desorption tubes show a significant flow resistance which makes them difficult to use with commercially available sampling pumps. Since these pumps are designed for the less densely packed active charcoal tubes, they can be operated only at a small flow resistance. Besides, it is very difficult to achieve a constant flow at a flow-rate of about or less than 10 $ml\ min^{-1}$ with these pumps. For these reasons, an appropriate sampling pump was custom constructed [30]. It consists of a membrane pump and an expansion vessel (serving at the same time as a flow dampener) to which the four sampling channels are connected. The flow in each channel is regulated by a needle valve and monitored by a calibrated rotameter. This allows simultaneous sampling of up to four adsorption tubes at individually set (and even very small) flow-rates and precise monitoring of the actual flow-rate. For active sampling, a defined volume of test gas was sucked through the adsorption tube by the sampling pump. The adsorption tubes were connected to the sampling chamber of the test gas generator by stainless steel tubes of 4 cm×2 mm I.D. These tubes act as a diffusion barrier and avoid errors due to passive sampling superimposed on active sampling at low

flow-rates. The gas flow is measured before and after sampling by an air flow calibrator at the inlet of the pump. The sampled volume is calculated as the product of the average gas flow through the adsorption tube and the sampling time. Active sampling was carried out over a period of 2–2.5 h at a sampling rate of 6–8 ml/min, leading to a sample volume of ~1 dm^3 in order to avoid sample breakthrough. All sampling was done at ambient temperature (21±3°C).

2.5. Passive sampling

Passive sampling was done perpendicular to the gas flow with tubes which were filled with Tenax TA (Fig. 2). The diffusion path consists of a stainless steel tube of precisely determined length and I.D., the dead volume of the brass screwing (which connects the steel tube with the glass tube) and the distance between the beginning of the glass tube and the beginning of the adsorbent bed. The values of L/A (length divided by the cross-section area) for each of the three sections were summed up to get a total value of L/A which can be used for the calculation of the results (for the respective values, see Table 4, wide tube). The linear air velocity was 5.0 cm s^{-1}. To test the influence of the position of sampling tubes relative to the test gas flow, passive sampling was done with tubes positioned in the direction of the gas flow in one case, unlike the arrangement shown in Fig. 2.

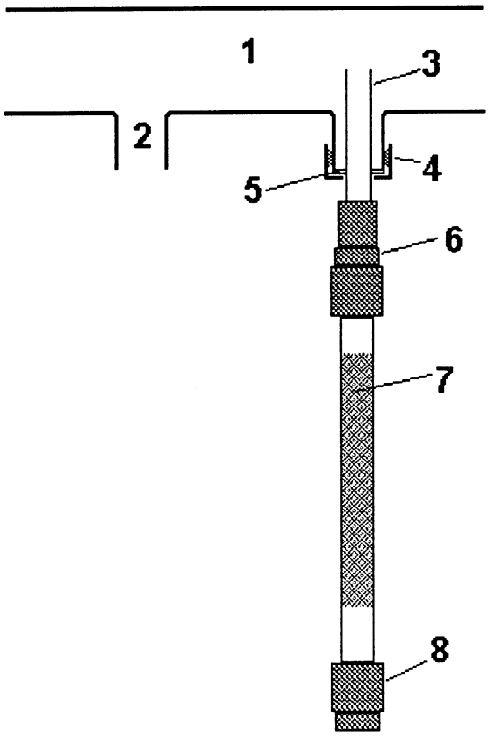

Fig. 2. Sketch of the set-up for passive sampling on thermal desorption tubes: sampling chamber of the test gas apparatus (1), sampling port (2), stainless steel tube (3), cap nut (4), sealing ring (5), brass screw (6), sampling tube (7), brass cap (8).

2.6. Analysis

Analysis was carried out by using an OI 4460 A thermal desorption unit (OI Analytical, College Station, TX, USA) coupled to a HP 6890 gas chromatograph with electronic pressure control equipped with a flame ionisation detector (Hewlett-Packard, Palo Alto, CA, USA). The thermal desorption unit was mounted in the supply gas line of the GC system. Thus, the GC carrier gas line was routed to the thermal desorption unit, passed through its six-port-valve and was then redirected to the split injector. The analytes were desorbed from the adsorption tube onto a focusing trap which was at room temperature. The trap (OI No. 6) 2 mm I.D. and a bed length of ~24 cm. It was packed with approximately equal volumes of Tenax, silica gel and active charcoal. After the focusing step, the analytes were desorbed from the trap by rapid heating (400°C min^{-1}) in the backflush mode into the split injector of the GC. A HP 624 thick film column (30 m×0.32 mm×1.8 μm, Hewlett-Packard) was used for the separation of the analysed compounds. The parameters for thermal desorption are listed in Table 2, those for GC are listed in Table 3.

Certain modifications were made to the thermal desorption unit to make it more suitable for the present task: the heater block in which the adsorbent tubes are mounted was made longer to accommodate adsorbent tubes with a bed length of 80 (instead of 65) mm. Adsorbent tubes with a longer adsorbent bed length are necessary to avoid analyte breakthrough during sampling. For calibration, an empty stainless steel tube was mounted onto the heater block instead of an adsorption tube, and 2 μl of a

Table 2
Parameters for thermal desorption

Step	Parameter	Value
Adsorbent tube desorption		
	Temperature of the focusing trap	25°C
	Desorption temperature	300°C
	Desorption time	5 min
	Drying step	No
Desorption from the focusing trap		
	Desorb preheat	No
	Temperature of the focusing trap	220°C
	Time	2 min
Bake		
	Temperature of the internal trap	220°C
	Time	4 min
Auxiliary temperatures		
	Valves and transfer line	180°C

calibration mixture of the components which were to be analysed were injected into this tube. For this purpose, a stainless steel T-piece with a silicone rubber septum on one side was used. Injection was done through this septum directly into the heated stainless steel tube where the analytes were evaporated completely. The same mixture of compounds (containing only the investigated compounds and no additional solvent) was used for both calibration and sampling. In order to minimise the volumetric error of a (comparatively slow) manual injection into the heated zone of the thermal desorption unit, one has to consider that part of the liquid in the dead volume of the needle is also evaporated into the gas flow. Thus, a correction for the actual injected volume has to be made in order to minimise the calibration error. Usually, six calibrations were done before starting the analysis of loaded adsorption tubes. When adsorption tubes with very small loadings of analytes were measured after tubes with high sample loadings, blank values were measured in between to avoid sample carryover.

2.7. Investigation of the effect of back-diffusion

An important criterion for the suitability of an adsorbent material and a sampler design is whether the adsorbed compounds tend to desorb from the adsorbent bed upon exposure to clean air for an extended period. To this aim, experiments were carried out in which 12 passive samplers were sampled with a test gas for 30 min. Six of them were then left uncapped and exposed to clean air (relative humidity: 80%) for 7.5 h, while the control set of samples was closed directly after sampling. After analysis of the 12 tubes, the results of the two sets of samplers were compared. If those samplers which were left uncapped and exposed to zero air 7.5 h after sampling yielded significantly lower recovery rates, back-diffusion of the adsorbed compounds had

Table 3
GC parameters

Parameter	Value
Carrier gas	He (purity 99.999%)
Inlet temperature	250°C
Inlet pressure	6.4 p.s.i. (0.44 bar)
Total gas flow	243 ml min^{-1}
Split ratio	200:1
Split flow	239 ml min^{-1}
Gas saver mode	Off
Column flow (setpoint)	1.2 ml min^{-1}
Linear velocity of the carrier gas in the column	22 cm s^{-1}
Oven temperature (start)	45°C over 4 min
First ramp	15°C min^{-1} up to 135°C
Second ramp	90°C min^{-1} up to 225°C
Oven temperature (end)	225°C over 2 min
Detector temperature	250°C
Hydrogen flow (FID)	40 ml min^{-1}
Air flow (FID)	264 ml min^{-1}
Nitrogen flow (make-up gas, FID)	30 ml min^{-1}

occurred and the adsorbent strength was classified as insufficient.

3. Results and discussion

Although the absolute amounts of substance that were introduced onto the column are rather high for capillary chromatography, the resulting chromatograms showed very satisfactory peak shape and resolution due to the optimised separation conditions (high split ratio and use of a thick film column). A chromatogram for the determination of alcohols on an actively sampled tube at the highest concentration level investigated in this work is shown in Fig. 3. Although the amount of ethanol on the column (first peak) was 18 μg, the chromatogram exhibits an acceptable peak shape and good resolution, which makes quantitation straightforward. Recovery rates, *r*, and their standard deviations, *s*, for active and passive sampling, respectively, are listed in Tables 5 and 6. Concentration values are given as multiples of the TLV. The relative overall uncertainty (ROU), calculated as $(r-1+2s)\cdot 100\%$, is significantly below 30% in most cases (for both sampling methods), and therefore meets the requirements given in the regulation EN 482 [35]. In the following sections, the influence of concentration, humidity and storage time (of the adsorbent tubes between sampling and analysis) on the recovery rates are discussed for 21 polar organic compounds. An analysis of variance (ANOVA) was done to confirm the interpretations statistically. The obtained results were statistically supported by the ANOVA. The particular modifications made to simplify the application of the ANOVA are presented elsewhere [31]. Using directly the standard deviations given in Tables 5 and 6 to determine whether two mean values and the respective standard deviations differ significantly is not meaningful for the following reason: since sampling and analysis of a set of adsorption tubes was usually carried out within 1 day, the figures given for the standard deviations are only a measure of the short-time repeatability. In order to account for different sources of variability that influence the results from day to day (e.g. precision/reproducibility of test gas generation), the day-to-day reproducibility has to be considered by estimating the total uncertainty of the whole procedure. Therefore, the standard deviations mentioned above have to be extended by a contribution to the random errors from test gas generation etc. This contribution to uncertainty was calculated with 4.1% as square root of the sum of squares of the estimated contributions of test gas concentration and calibration [31].

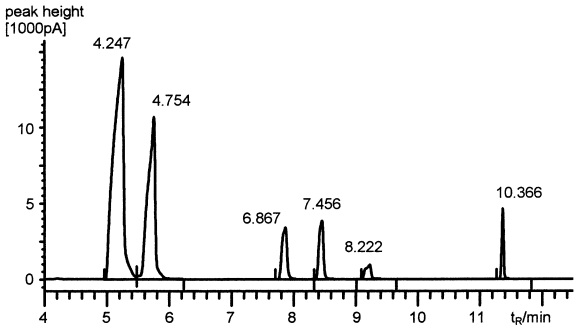

Fig. 3. Chromatogram of a set of alcohols thermally desorbed from a sorbent tube which had been sampled by pumped sampling at the highest concentration level investigated. The alcohols (in the order of increasing retention time) are: ethanol, 2-propanol, 2-methyl-1-propanol, 1-butanol, 2-ethoxyethanol and 2-butoxyethanol. The concentration of ethanol in the test gas was 3800 mg m^{-3}, therefore its amount on the sorbent tube was 3.7 mg. Since a split ratio of 1:200 was used, 18 μg of ethanol were transferred onto the column.

3.1. Esters

The 30% criterion for the relative overall uncertainty is met for all esters under all conditions examined in this work; the only exception is the recovery rate of butoxyethyl acetate after passive sampling and 2 weeks storage.

Active sampling yields recovery rates between 91 and 104% for humidities of 50% or lower. At the TLV, recovery rates between 98 and 101% were found (exception: 94% for isopropyl acetate), whereas at the other concentration levels recovery rates were slightly lower for alkyl acetates (about 5%). For the alkoxyethyl acetates, recovery only decreased at the lowest concentration level (8–10%). A humidity of 80% (active sampling) causes a slight decrease (about 5%) of the recovery rates of the two branched esters (isopropyl acetate and isobutyl acetate), whereas it has no effect for the other esters. An explanation for this observation might be a possible

breakthrough of these esters through the first adsorbent layer (Carbopack B) during sampling; from the second layer (Carbosieve SIII) they cannot be desorbed quantitatively. A 2-week storage does not affect the recovery rates after active sampling significantly, except for the recovery rate of butoxyethyl acetate, which decreases dramatically after storage. This behaviour indicates that decomposition takes place; the investigation of decomposition products will be subject to further investigations in order to elucidate the reasons and to possibly improve its recovery.

Passive sampling yields recovery rates between 85 and 105%. A decrease in the recovery rate for increasing concentration values was observed for isopropyl acetate, but no trend can be seen for the other esters. The lowest recoveries were found for ethyl acetate under most experimental conditions. Since ethyl acetate is the most volatile ester investigated in this work, this indicates nonideal adsorption behaviour. No significant effect of humidity on the recovery rates can be found. No significant effect of storage can be found for alkyl acetates, either. The recovery rate of ethoxyethyl acetate decreases by 7% after storage, which is not significant. Butoxyethyl acetate shows the same lack of storage stability as with active sampling. Passive sampling of esters on Carbopack B yielded no substantial improvements and results are thus not reported.

3.2. Alcohols

3.2.1. Active sampling

The 30% criterion is met in all cases for all alcohols except the alkoxyethanols. All recovery rates of ethanol and 2-propanol lie between 92.8 and 103.2%, which is very satisfactory because of the extremely high concentrations of these alcohols (ethanol: up to 2000 ppm, v/v). Most of the recoveries of the butanols also lie in this range; exceptions are the recoveries at the lowest concentration level (about 10% higher than expected) and the recovery of 2-methyl-1-propanol (isobutanol) after 2 weeks storage. It is noteworthy that in contrast to isobutanol, storage has no significant effect on *n*-butanol. Except for the higher than expected recoveries of the butanols at the lowest concentration level no influence of concentration or humidity can be found for the alcohols without an ether group. The influence of humidity on the recoveries was found to be not significant; this might be explained by the low affinity of the adsorbents to water. For the two alkoxyethanols the method is not suitable yet, because of their very high recovery rates (15–25% higher than expected in many cases), and because of the strong effects of high humidities (ethoxyethanol) and storage (butoxyethanol) on the recoveries. While the higher than expected recovery rates might be attributed rather to the calibration than to the analysis, the notable decrease of recovery at high humidity and after storage indicates decomposition of the alkoxyethanols. Again, further investigations have to be carried out in order to identify possible decomposition products.

3.2.2. Passive sampling

Passive sampling yields very good recoveries for the butanols (93.7–110%), but seems not to be suitable for the more volatile alcohols. The recoveries for ethanol and 2-propanol are below 80% in many cases, thus reflecting nonideal adsorption behaviour. The use of stronger adsorbents or a longer diffusion path (which reduces the amount of analyte reaching the adsorbent bed) might solve this problem; further work will be devoted to this question. The problems with alkoyethanols are completely different: the recovery of ethoxyethanol decreases at low concentrations possibly because the chromatographic peak of ethoxyethanol is very broad and therefore integration underestimates the peak area. A smaller split ratio (e.g. 1:80 instead of 1:200) or a different internal trap (packed with weaker adsorbents) might solve this problem. High humidities seem to lower the recovery, too, although Tenax TA has a very low affinity to water. Perhaps the problems with high humidities might be solved by the use of a different thermal desorption unit with a completely inert inner surface. The problems with butoxyethanol are high recovery rates that exceed the theoretically expected value in most cases (up to 126%) and the bad storage stability, whereas the recoveries of the other alcohols on Tenax TA are not affected by storage at all. Considering the results for esters and alcohols, it seems as if the butoxyethyl group is prone to decomposition.

3.2.3. Influence of the length of the diffusion path on the recovery rates of alcohols

Diffusive sampling was done for alcohols on Tenax TA again, where passive samplers with two differently sized diffusion paths were compared. The dimensions of the two different diffusion paths are given in Table 4; the sampling tubes themselves were identical, however. The recovery rates of the alcohols increase while the absolute amount of analyte sampled on the adsorption tubes decrease with increasing diffusion path length. This change in the sampler design brings a great improvement for the most volatile alcohols, ethanol and 2-propanol (Fig. 4). The fact that the overestimation of the recoveries is more pronounced for the more volatile alcohols and the wider diffusion tube indicates that this is an adsorption, rather than a desorption-related problem. The desorption efficiency can be assumed for all compounds to be similar and high. The trapping efficiency, however, is lower for the more volatile alcohols and this effect seems to be the more pronounced the higher the absolute amount of adsorbed compound. Since a narrower diffusion path reduces the absolute amount of analyte trapped on the adsorption tube, it also reduces the deviation from quantitative recovery.

3.3. Ketones

The 30% criterion for the relative overall uncertainty is met for all ketones under all conditions examined in this work with the exception of the recovery rate of 4-methyl-2-pentanone after active (pumped) sampling and 2 weeks storage.

3.3.1. Active sampling

The maximum deviation of the recovery rates from 100% is 7% for all ketones at 50% humidity and 10% under all conditions if the samples were not stored longer than a few days. In most cases the deviation is not significant; no trend for the deviations was found. At the TLV the recovery rates seem to have a maximum (significant influence of the concentration on the recoveries of acetone and 2-butanone), whereas no significant influence of humidity was found. The effect of storage (decomposition) increases with decreasing volatility.

3.3.2. Passive sampling

The maximum deviation of the recovery rate from 100% is below 10% for the two less volatile ketones. The recoveries of 4-methyl-2-pentanone are in three cases significantly higher than unity, whereas those of 2-butanone are significantly lower than unity in two cases. The recoveries of acetone are about 85%, which can be explained by the insufficient strength of the adsorbent used. A solution to this problem could be achieved by using a stronger adsorbent and/or a longer diffusion path. In contrast to active sampling, no influence of concentration on the recovery rates was found, but a significant influence of humidity. At medium humidity (50%) the recoveries are about 6% higher than at low (20%) or high humidity (80%). Storage on Tenax TA has no

Table 4
Physical dimensions of the components forming the diffusion path of the two different diffusion tube designs

Part	Length L (mm)	I.D. (mm)	Cross-sectional area A (mm^2)	L/A (mm^{-1})
Narrow tube				
Steel tube (narrow)	45.0	2.24	3.94	11.42
Brass screwing, 1st section	5.67	2.29	4.12	1.38
Brass screwing, 2nd section	6.0	4.0	12.57	0.48
Glass tube with adsorbent (typical dimensions)	30	4.1	13.2	2.27
Total				15.55
Wide tube				
Steel tube (wide)	80	4.57	16.41	4.88
Brass screwing	11.9	4.76	17.80	0.67
Glass tube with adsorbent (typical dimensions)	30	4.1	13.2	2.27
Total				7.82

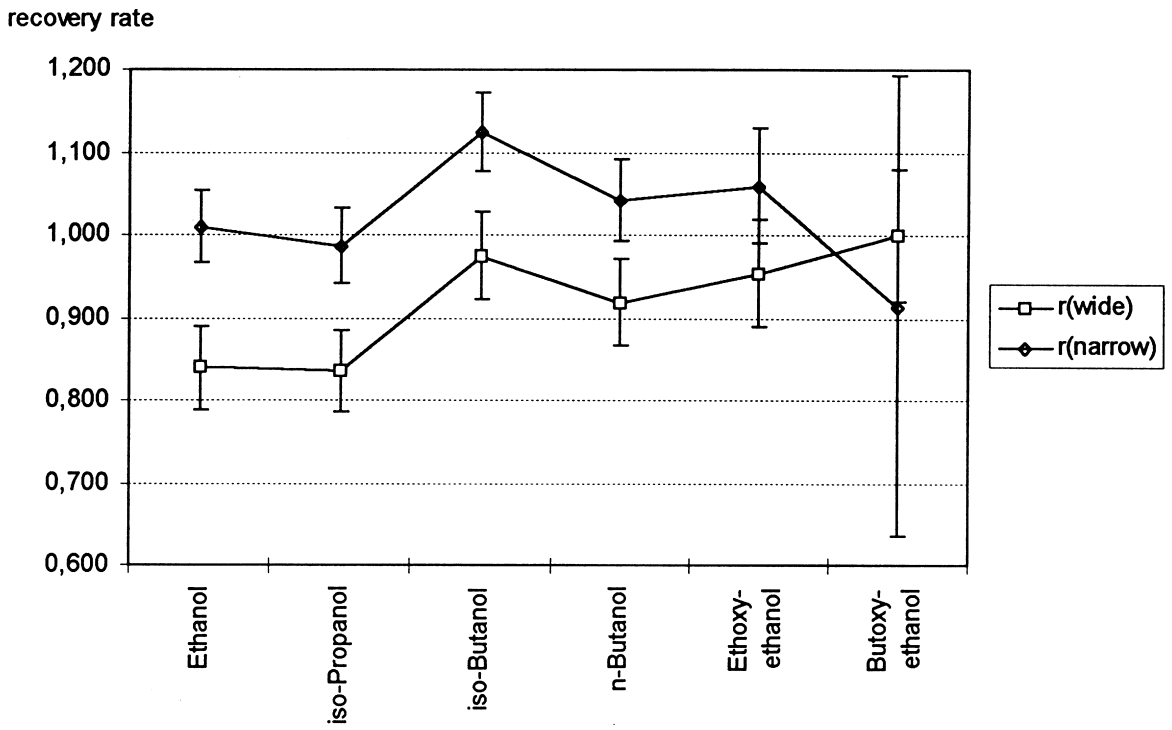

Fig. 4. Recovery rates (with bars indicating the total uncertainty) of two different types of passive samplers (wide and narrow diffusion path). It can be clearly seen that a larger uptake rate achievable with a wide diffusion path leads to a decrease in the recovery rates especially for the very volatile substances.

effect on recoveries. The storage stability of 4-methyl-2-pentanone is much better on Tenax TA than on the Carbopack B/Carbosieve SIII-combi tube, on which adsorption might be stronger and therefore chemical decomposition (notably during the desorption) might be favoured. In summary, active sampling of ketones does not yield better results than passive sampling as it does for the other classes of compounds.

3.4. Aldehydes

3.4.1. Active sampling

The recovery rates and standard deviations for active sampling and thermal desorption analysis of polar compounds under different conditions can be found in Table 5.

The 30% criterion could be met for the C_2–C_5-aldehydes when the adsorption tubes were analysed within a few days, whereas even without prolonged storage the method cannot be recommended for hexanal. The reason may be incomplete desorption from the adsorbent tube or from the focusing trap, decomposition on the hot metal surfaces inside the thermal desorption unit or wall adsorption. Interestingly, the recovery rates of most of the aldehydes decrease with increasing concentration (significantly for C_3-, C_4- and C_6-aldehydes) and with increasing humidity (significantly for C_2- and C_3-aldehydes, for the others only slightly). Fig. 5 shows the difference between the recovery rate at 20% and at 80% humidity as a function of the number of carbon atoms. The difference of recovery rates decreases with the number of carbon atoms. It may be that a long aliphatic chain protects the molecules of the higher aldehydes at a humidity of 80% from decomposition (higher stability) or from being displaced by water molecules. At the TLV, recovery rates of 96–99% were found for the C_2–C_5-aldehydes, which is highly satisfactory. As the aldehydes are very reactive, a 2-week storage causes a drastic decrease in the recoveries for all aldehydes investi-

Table 5
Recovery rates and standard deviations for active sampling and thermal desorption analysis of polar compounds under different conditions

Compound	Concentration/TLV:	0.1		1		2		2		2		2	
	Humidity/%:	50		50		50		20		80		80	
	Storage time/weeks:	0		0		0		0		0		2–2.5	
		r	*s*	*r*	*s*	*r*	*s*	*r*	*s*	*r*	*s*	*r*	*s*
Ethyl acetate (1400)		0.940	0.033	0.998	0.012	0.949	0.015	0.988	0.009	0.936	0.016	0.975	0.003
Isopropyl acetate (840)		0.938	0.032	0.943	0.008	0.924	0.009	0.944	0.010	0.866	0.016	0.878	0.008
n-Propyl acetate (840)		0.947	0.036	0.992	0.012	0.951	0.014	0.990	0.009	0.930	0.017	0.960	0.003
Isobutyl acetate (700)		0.953	0.038	0.982	0.012	0.953	0.014	0.983	0.010	0.903	0.022	0.883	0.016
1-Butyl acetate (700)		0.947	0.040	0.996	0.012	0.958	0.015	1.011	0.010	0.938	0.024	0.967	0.003
2-Ethoxyethyl acetate (110)		0.924	0.041	1.006	0.010	0.985	0.020	1.029	0.008	0.971	0.037	0.934	0.002
2-Butoxyethyl acetate (135)		0.912	0.081	1.005	0.015	1.015	0.042	1.043	0.015	0.988	0.031	0.738	0.009
Ethanol (1900)		1.004	0.044	0.978	0.051	1.013	0.025	1.032	0.019	1.031	0.019	1.030	0.015
2-Propanol (980)		0.997	0.036	0.928	0.054	0.941	0.046	0.989	0.024	1.002	0.022	0.980	0.021
2-Methyl-1-propanol (150)		1.134	0.055	0.932	0.055	0.995	0.055	1.005	0.009	1.026	0.014	0.827	0.019
1-Butanol (150) 1.094		0.047	0.994	0.048	1.012	0.036	1.029	0.023	1.023	0.014	0.969	0.014	
2-Ethoxy ethanol (75)		1.136	0.040	1.128	0.062	1.142	0.056	1.161	0.018	0.672	0.044	0.633	0.107
2-Butoxy ethanol (100)		1.455	0.103	1.265	0.089	1.243	0.045	1.141	0.058	1.113	0.103	0.801	0.057
Acetone (1780)		0.939	0.092	1.040	0.037	0.988	0.029	0.924	0.030	0.962	0.016	0.921	0.029
2-Butanone (590)		0.934	0.042	1.008	0.034	0.961	0.025	0.904	0.029	0.958	0.015	0.890	0.033
4-Methyl-2-pentanone (400)		1.008	0.091	1.060	0.038	0.954	0.042	0.942	0.035	0.995	0.016	0.781	0.084
Acetaldehyde (90)		0.908	0.035	0.964	0.023	0.919	0.038	0.979	0.016	0.882	0.042	0.553	0.044
Propanal (125[a])		1.040	0.027	0.972	0.023	0.841	0.035	0.972	0.013	0.865	0.039	0.472	0.020
2-Methylpropanal (125[a])		1.035	0.022	0.988	0.021	0.932	0.037	0.961	0.014	0.915	0.032	0.622	0.029
2-Methylbutanal (125[a])		0.982	0.018	0.978	0.017	0.949	0.039	0.952	0.012	0.922	0.033	0.886	0.024
Hexanal (125[a])		0.968	0.042	0.803	0.063	0.771	0.036	0.811	0.015	0.786	0.044	0.536	0.059

TLV (threshold limit values) are given with each compound name in brackets (unit: mg m^{-3}). *r*=recovery. *s*=standard deviation (*n*=4–8).
[a] Arbitrary values were taken for all aldehydes except acetaldehyde.

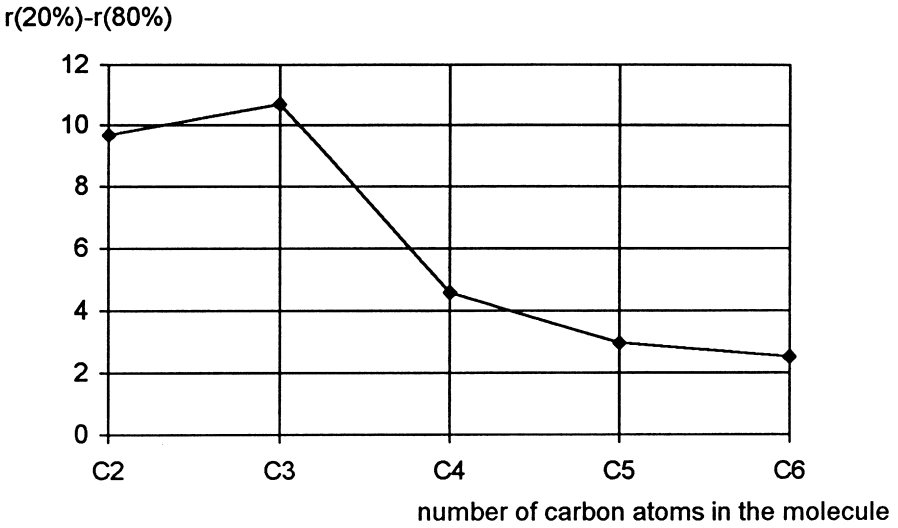

Fig. 5. Difference between the recovery rates at low (20%) and high (80%) humidity as a function of the number of C-atoms in the aldehyde molecule.

gated except for 2-methylbutanal. In the chromatograms some additional peaks appear which can be attributed to decomposition products, but their areas are too small to explain the dramatic losses of aldehydes during storage. A fraction of the aldehydes may be either adsorbed irreversibly or some of the decomposition products are very volatile and may be lost before analysis. Another explanation might be an oxidation (to form e.g. an α-hydroxyketone) which would result in a decrease of the peak area sum (the FID response decreases in the following order: aliphatic C>C–OH ≫ C=O).

3.4.2. Passive sampling

The recovery rates and standard deviations for diffusive sampling and thermal desorption analysis of polar compounds under different conditions can be found in Table 6.

Whereas acetaldehyde is too volatile to be sampled with this type of diffusive samplers, the recoveries of the C_3–C_5-aldehydes do not differ more than 7.1% from 100% under all conditions except for 2 weeks storage. The method cannot be recommended for hexanal, because the recoveries are quite low (dropping to 84% without storage) and the standard deviation of the recovery rate at the lowest concentration is too high to be acceptable. Except for the recovery rates of acetaldehyde and propanal at the lowest concentration, no influence of concentration or humidity on the recovery rates can be found, which is in contrast to the results of active sampling. The main problem with aldehydes is their poor storage stability. The recovery rates of all aldehydes investigated in this work showed a decrease of between 14% and 33% after 2 weeks storage of the passive samplers before analysis. The only difference between the storage stability on active sampling tubes and passive sampling tubes is the good stability of 2-methylbutanal on active sampling tubes; this result is surprising, because it was not expected that an aldehyde would be less stable on a weak adsorbent (Tenax TA) than on a strong adsorbent (Carboxen 569).

3.5. Back diffusion of volatile compounds

Back diffusion of compounds only weakly adsorbed on the adsorbent bed (sometimes also referred to as ‘nonideal adsorption behaviour’ [44] was found for very volatile substances for which the recovery rates were far below 1.0 in Table 5. It is thus appropriate to state that the passive sampling method requires some improvement for very volatile substances (less than three carbon atoms). Since active sampling of these compounds with the resulting higher absolute amounts of analytes generally led to

Table 6
Recovery rates and standard deviations for diffusive sampling and thermal desorption analysis of polar compounds under different conditions

Compound	Concentration/TLV:	0.1		1		2		2		2		2	
	Humidity/%:	50		50		50		20		80		80	
	Storage time/weeks:	0		0		0		0		0		2–2.5	
		r	*s*	*r*	*s*	*r*	*s*	*r*	*s*	*r*	*s*	*r*	*s*
Ethyl acetate (1400)		0.861	0.019	0.903	0.033	0.858	0.022	0.886	0.022	0.879	0.023	0.855	0.021
Isopropyl acetate (840)		1.076	0.085	0.963	0.035	0.885	0.025	0.915	0.023	0.908	0.025	0.880	0.018
n-Propylacetate (840)		0.947	0.018	0.945	0.035	0.896	0.026	0.923	0.023	0.918	0.027	0.891	0.023
Isobutyl acetate (700)		1.002	0.014	1.016	0.033	0.965	0.026	0.990	0.025	0.992	0.030	0.961	0.024
1-Butyl acetate (700)		0.962	0.019	1.003	0.036	0.957	0.028	0.978	0.024	0.979	0.031	0.944	0.026
2-Ethoxyethyl acetate (110)		0.953	0.045	1.048	0.029	1.016	0.032	1.019	0.016	0.992	0.042	0.920	0.033
2-Butoxyethyl acetate (135)		0.889	0.044	1.020	0.033	0.922	0.034	0.899	0.017	0.880	0.044	0.646	0.030
Ethanol (1900)		0.701	0.100	0.516	0.171	0.650	0.177	0.759	0.028	0.598	0.181	0.723	0.022
2-Propanol (980)		0.694	0.026	0.789	0.073	0.803	0.064	0.888	0.024	0.774	0.077	0.823	0.026
2-Methyl-1-propanol (150)		1.050	0.021	1.034	0.043	1.021	0.023	1.100	0.027	0.997	0.041	1.020	0.024
1-Butanol (150)		0.937	0.021	0.974	0.035	0.963	0.021	1.029	0.024	0.941	0.029	0.944	0.023
2-Ethoxyethanol (75)		0.731	0.080	0.917	0.058	0.942	0.029	1.012	0.041	0.880	0.038	0.861	0.028
2-Butoxyethanol (100)		1.040	0.133	1.232	0.074	1.164	0.038	1.263	0.124	1.105	0.056	0.794	0.033
Acetone (1780)		0.847	0.068	0.882	0.032	0.874	0.014	0.813	0.016	0.827	0.015	0.839	0.016
2-Butanone (590)		0.952	0.087	0.985	0.038	0.974	0.016	0.903	0.016	0.920	0.015	0.933	0.022
4-Methyl-2-pentanone (400)		1.015	0.027	1.066	0.043	1.065	0.017	0.992	0.016	1.008	0.018	1.023	0.028
Acetaldehyde (90)		0.610	0.062	0.709	0.028	0.712	0.018	0.704	0.017	0.729	0.017	0.589	0.029
Propanal (125[a])		1.065	0.054	0.955	0.025	0.945	0.025	0.929	0.018	0.963	0.020	0.772	0.038
2-Methylpropanal (125[a])		0.967	0.050	0.958	0.024	0.966	0.025	0.970	0.019	0.981	0.013	0.745	0.037
2-Methylbutanal (125[a])		0.993	0.035	0.973	0.026	0.976	0.024	0.987	0.017	0.991	0.014	0.664	0.045
Hexanal (125[a])		0.914	0.378	0.837	0.039	0.867	0.052	0.920	0.028	0.957	0.059	0.674	0.054

TLV (threshold limit values) are given with each compound name in brackets (unit: mg m^{-3}). *r*=recovery, *s*=standard deviation (*n*=4–8).
[a] Arbitrary values were taken for all aldehydes except acetaldehyde.

higher recovery rates, breakthrough of the analytes through the focusing trap can be excluded as a source of error for this underestimation. The complete results are listed and discussed in greater detail in [30].

3.6. General remarks on the results of ANOVA (statistical evaluation of the influence of concentration and humidity on the recovery rates by analysis of variance)

Very little influence of concentration and humidity on recovery rates was found for the esters, whereas the recovery of alcohols, aldehydes and ketones was influenced by these parameters in many cases. Compared to the results on apolar compounds [31], concentration and humidity have much more influence on the recovery of polar compounds.

When carrying out diffusive sampling, humidity has an influence on the recoveries of more compounds than with active sampling, which is remarkable since the adsorbent used for passive sampling (Tenax TA) is a weak adsorbent, but has a very low affinity to water.

The behaviour of the recovery rates and their dependence on concentration and humidity after active sampling is very different from that after diffusive sampling, but different adsorbents were used for active and passive sampling.

3.7. Investigation of blank values

To determine the blank values, some of the adsorbent tubes were analysed after appropriate conditioning, but without a preceding sampling step. The peak areas in the resulting chromatograms (A_{Blank}) were divided by those of chromatograms which were obtained by analysing tubes that were sampled at the lowest concentration level (0.1 TLV) by passive sampling (A_{passive}). The peak areas from the analysis of active sampled tubes were not considered, because they are about two orders of magnitude higher than those from the analysis of passive sampled tubes ($A_{\text{active}} \gg A_{\text{passive}}$). The quotient $A_{\text{Blank}}/A_{\text{passive}}$ was below 0.03 for all substances except for 2-butoxyethanol ($A_{\text{Blank}}/A_{\text{passive}}=0.09$). It could also be shown that most of the peaks found in these measurements are memory effects from the internal trap of the thermal desorption unit. These problems are likely to be solved with the use of a different internal trap (e.g. Vocarb 3000) which can be baked out at higher temperatures (max. 350°C). In the design usable with the OI thermodesorber, this trap has an I.D. of 2 mm and a length of 24 cm, containing 1 cm of Carboxen 1001, 6 cm of Carboxen 1000 and 10 cm of Carbopack B.

3.8. Analysis of measurement uncertainty

3.8.1. Systematic errors

The analysis of the total uncertainty budget of the proposed method identified the following possible contributions of systematic errors whose magnitude is given as an estimation in brackets:

- memory effects in the test gas chamber (Fig. 1): overestimations up to 10% (e.g. alcohols at the lowest concentration level)
- calculation of diffusion coefficients (about 5%, passive sampling only)
- determination of the cross-section of the diffusion path (<3%, passive sampling only)
- nonideal adsorption behaviour of the employed adsorbents (10–40%, passive sampling of very volatile compounds)
- insufficient desorption (up to 10%, less volatile compounds)

3.8.2. Random errors

The uncertainties (random errors) have been estimated to be about 3.4% for test gas generation, 3.0% for active sampling, 5.0% for passive sampling and 3.1% for thermal desorption analysis; this was done by either measuring (where possible) or estimating (where inaccessible to measurement) and summing up the variances of the most important single contributions to uncertainty, e.g. the uncertainty of the gas stream, of the liquid injection, of the diffusion path dimensions, of the calibrations etc. Therefore the total uncertainties for the complete sequence of test gas generation, sampling and analysis are 5.5% (active sampling) and 6.8% (passive sampling).

For solvent desorption analysis after active sampling the random error has been estimated to be 2.5%; therefore the total uncertainty (test gas generation+active sampling+analysis) for the solvent desorption method was estimated to be 5.2%.

Table 7
Comparison of the sensitivity and limits of detection (LOD) for the proposed techniques[a]

Sampling and desorption method	Active sampling+ thermal desorption	Passive sampling+ thermal desorption	Active sampling+ solvent desorption
LOD/effective carbon (C_{eff})	2 μg m^{-3} (4 ppb)	60 μg m^{-3} (120 ppb)	250 μg m^{-3} (500 ppb)
Sensitivity/effective carbon (C_{eff})	100 pA s mg^{-1} m^3 (50 pA s ppm^{-1})	3.3 pA s mg^{-1} m^3 (1.7 pA s ppm^{-1})	0.4 pA s mg^{-1}m^3 (0.2 pA s ppm^{-1})

[a] 1 pA s=10^{-12} ampere×s (unit of peak area).

Both solvent and thermal desorption are thus equivalent in terms of measurement uncertainty.

3.9. Sensitivity and limit of detection

Sensitivity and limits of detection for the proposed methods are listed in Table 7. It is evident that the sensitivity is much higher and the LOD (limit of detection) is much lower for thermal desorption (even in combination with passive sampling) than for solvent desorption and active sampling. The calculation of these values is based on the signal-to-noise ratio of the peaks (3σ criterion) and described in [31] in more detail.

4. Conclusion

Esters, alcohols, aldehydes and ketones can be determined by a recently developed thermal desorption method for the analysis of solvents in workplace air. The method is therefore suitable for analytes of a wide range of polarity and it can easily be used in combination with both active sampling and passive sampling. The method was validated by sampling adsorption tubes with test gases containing polar compounds and analysing the tubes subsequently. The requirements of the EN 482 regulation are met for most of the recovery rates for three different concentrations, for three different test gas humidities and for 2 weeks storage of the sampling tubes. Good, in some cases excellent results were achieved for active sampling as well as for passive sampling. The detection limit (as determined by the 3σ criterion) not only of active sampling and subsequent thermal desorption (2 μg m^{-3} effective carbon), but even for passive sampling and thermal desorption (60 μg m^{-3} eff. C) is lower than the detection limit of active sampling and solvent desorption (250 μg m^{-3}). The sensitivity of the method developed in this work is higher than that of the solvent desorption method. Some problems still remain to be solved, such as:

- the poor storage stability of some less volatile aldehydes, ketones, butoxyethyl compounds and isobutanol which cannot be explained by evaporation from weak adsorbents
- incomplete trapping (‘nonideal adsorption behaviour’) of some volatile compounds on the weak adsorbent Tenax TA
- systematic bias for the analysis of some higher-boiling polar compounds (overestimations of the alkoxyethanols, underestimation of hexanal)

Solving these problems will be the aim of further investigations, but already thermal desorption has proved to be an excellent and universally applicable alternative to solvent desorption.

Acknowledgements

Financial support of this work by the Allgemeine Unfallversicherungsanstalt (AUVA), Vienna, is gratefully acknowledged.

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