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TOPAS / TDS D – Badge-Type Thermodesorption Passive Sampler Based on Tenax for Air Sampling - Development Study

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ABSTRACT

The TOPAS / TDS D system combines the advantages of the passive sampling of badge-type passive samplers with thermal desorption for sample transfer to the gas chromatography system. The large surface and the sampler's short diffusion path permit high sampling rates. Use of thermal desorption as a sample transfer technique avoids the necessity for time consuming sample preparation and allows low detection limits, since the entire sample can be used for gas chromatography analysis. The system is suitable as a

personal dosimeter or environmental monitor.

The outstanding feature of the TOPAS system is its completely new designed desorption gas flow path which is built of a spiral-shaped groove. This offers a great diffusion cross section (5.25 cm²). With this new badge geometry high sampling rates equivalent to 3 L/h for volatile aromatic and halogenated hydrocarbons were achieved.

A study is presented in which the TOPAS /TDS D system is compared with active sampling on Tenax tubes for determining emissions of volatile organic compounds from a rubber flooring. With both types of sampling, active and passive, the same spectrum of compounds was detected. The sampling rates of TOPAS for these compounds were in the range of 0.5 to 2.5 L/h, so during a 5 h sampling period the total enriched amount allows a secure identification and quantification with a GC-MSD system.

The TOPAS / TDS D system has been developed recently by GERSTEL GmbH & Co. KG and the ICB (Institut für Chemo- u. Biosensorik). The present system is still a prototype, but future development is planned to make the system easier for routine use.

INTRODUCTION

Passive Sampling - The TOPAS /TDS D System. Conventional procedures usually involve eluting the passive collectors with solvents, whereby only an aliquot of the extract is analysed. This process is costly as the samples need to be prepared manually. Furthermore, only a portion of the sample is used. On this basis, sampling times for emission concentration measurements amount to several weeks in some cases in order for the requisite amount of analytes to be enriched. With the TOPAS system on the other hand, sampling cycles of a few hours are possible even with the lowest concentrations. The outstanding feature of the TOPAS system is its completely new designed desorption gas flow path. Figure 1 shows the basic aluminium body with its spiral-shaped groove. This groove contains the adsorbent (Tenax). The entire surface of the groove represents the diffusion cross section and is thus used for sampling. A microporous Teflon membrane assures a pure diffusion-controlled enrichment of the analytes. For thermal desorption, the badge is set membrane-side down in the holder (see Figure 1). The desorption gas inlet and outlet are located on the reverse of the badge. Only the narrow cross-section of the groove is used for desorption, ensuring a complete flow-through of the

adsorbent bed and thus a complete sample transfer.

A special badge holder is provided for fixing the badges for sampling and storage and to carry out the gas chromatography analysis later. Clips can then be added to this holder for personal sampling. For passive sampling, the exposure time is the decisive value. The detection limits of the method depend on the air concentration and the sampling rate of the sampler as well as the limits of determination of the gas chromatography system. Currently, the sampling rates for the BTEX (benzene, toluene, ethylbenzene, xylene) and halogenated hydrocarbons are available for TOPAS. Sampling time of 1 hour is sufficient even for a concentration of 5 x 10⁻⁴ mg/m³. Similar sampling rates are to be expected for comparable non polar and volatile analytes. However, due to the utilisation of Tenax and the Teflon membrane, sampling of extremely polar analytes such as methanol is only possible to a limited extent.



Figure 1. TOPAS badge: basic aluminium body with cut groove (left), badge fitted for measuring, filled with Tenax and encapsulated with the microporous Teflon membrane (middle) and reverse view of badge fitted for storage and GC analysis; view of desorption gas inlet and outlet (right).

Thermal desorption. The corresponding thermal desorption injector was based on GERSTEL®'s already well-known TDS 2. GERSTEL®'s cooled injection system (CIS) is used for cryogenic focussing of the desorbed analytes. Both thermal desorption and the transfer of analytes from the cryogenic trap to the GC column can be performed in split or splitless mode. This possibility of multiple sample splitting permits a split ratio of 1:10,000, even with moderate gas flows, so that overload of the gas chromatography system can be avoided.

Aim of this study. The aim of this study was to determine if the TOPAS /TDS D System is suitable for indoor air inspection during expert appraisals. Emissions of volatile organic compounds (VOC) from materials

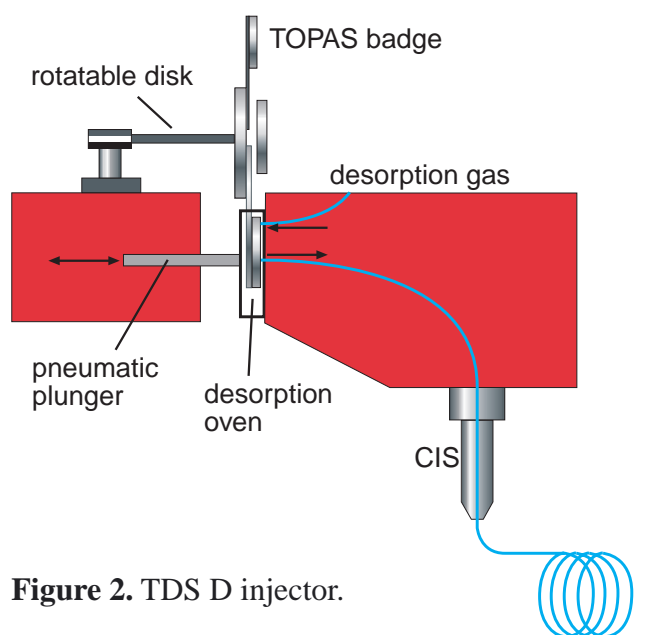


Figure 2. TDS D injector.

especially from floorings in new buildings or after renovation often lead to complaints about unpleasant odours or even about injuries to health. For risk assessment air samples are taken by independent experts or laboratories. In these cases active or passive enrichment of the air samples are usual. For active sampling all equipment including sampling pumps have to be carried to the location. Passive samplers don't need pumps and can be shipped by post, but long sampling times for passive sampling are time consuming and allow fraudulent manipulations.

From earlier studies with the TOPAS / TDS D system it was known that sampling rates from 1–3 L/h for non-polar and volatile compounds like BTEX and halogenated hydrocarbons can be achieved. The time limit for an expert appraisal can be fixed for one day, so assuming a concentration level of $10 \mu\text{g}/\text{m}^3$ 5 h sampling periods with the TOPAS badges should be adequate to enrich a sufficient amount for identifying and quantifying the analytes with a GC / MSD, even for semi volatile or polar compounds like glycol derivatives.

In this study it was checked if TOPAS can be used as an alternative for active sampling to determine the emission of a flooring material. First the recovery for the thermal desorption step with the TOPAS badges was determined for a number of typical compounds. Then a real flooring sample was fixed with original glue on a glass plate in an emission test chamber. Active and passive samples were taken from the atmosphere of the test chamber and compared to each other in order to calculate the sampling rates.

EXPERIMENTAL

The emission test chamber consists of a 500 L acrylic glass cube with a small opening for inserting the passive samplers and with a gas connection for fresh air ($22^\circ\text{C} \pm 2\text{K}$, 50% relative humidity $\pm 5\%$, constant air change ratio 0.5 per hour) and a $1/8''$ connector for active sampling tubes (Figure 3). The flooring sample was a rubber flooring (styrene butadiene elastomer; $0.5 \times 0.4 \text{ m}$) fixed with the original glue on a glass plate.

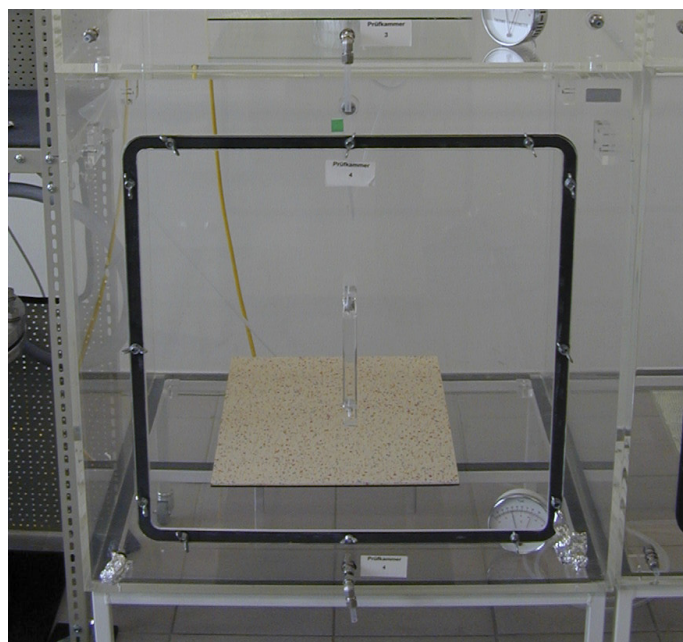


Figure 3. Emission test chamber.

All GC experiments were performed with an Agilent GC 6890 with Agilent MSD 5973. A GERSTEL® Cooled Injection System (CIS) was used for liquid injections and as cryo-trap for thermal desorption experiments. For gas chromatographic separations a Agilent HP-642 column with 30 m length x 0.25 mm ID x $1.4 \mu\text{m}$ film was chosen.

Analysis conditions active sampling.

Sample volume: 5-10 L, with 100 ml/min
 Thermal desorption: 310°C (10 min), splitless
 Cryogenic trap: -150°C , on glaswool
 Sample transfer to GC: 310°C , split 30:1

Analysis conditions passive sampling.

Sampling: 5 h
 Thermal desorption: 250°C (10 min), splitless
 Cryogenic trap: -100°C , on Tenax
 Sample transfer to GC: 250°C , split 30:1

RESULTS AND DISCUSSION

First the thermal desorption recoveries from the TOPAS badges were determined. Therefore 0.2 μL of liquid standard solutions of typical compounds in pentane/ethanol 1:1 were injected in the CIS and on the Tenax layer of a TOPAS badge. Figures 4 and 5 show typical chromatograms. The recovery data were calculated by comparing the peak areas from the thermal desorption experiments with calibration functions from liquid injections into the CIS. In order to determine the independence of the recovery levels from the total amount the experiments were carried out by injecting approximately 200 ng and 1000 ng total amount for each compound, 5 times for each level. The results are shown in Figure 6.

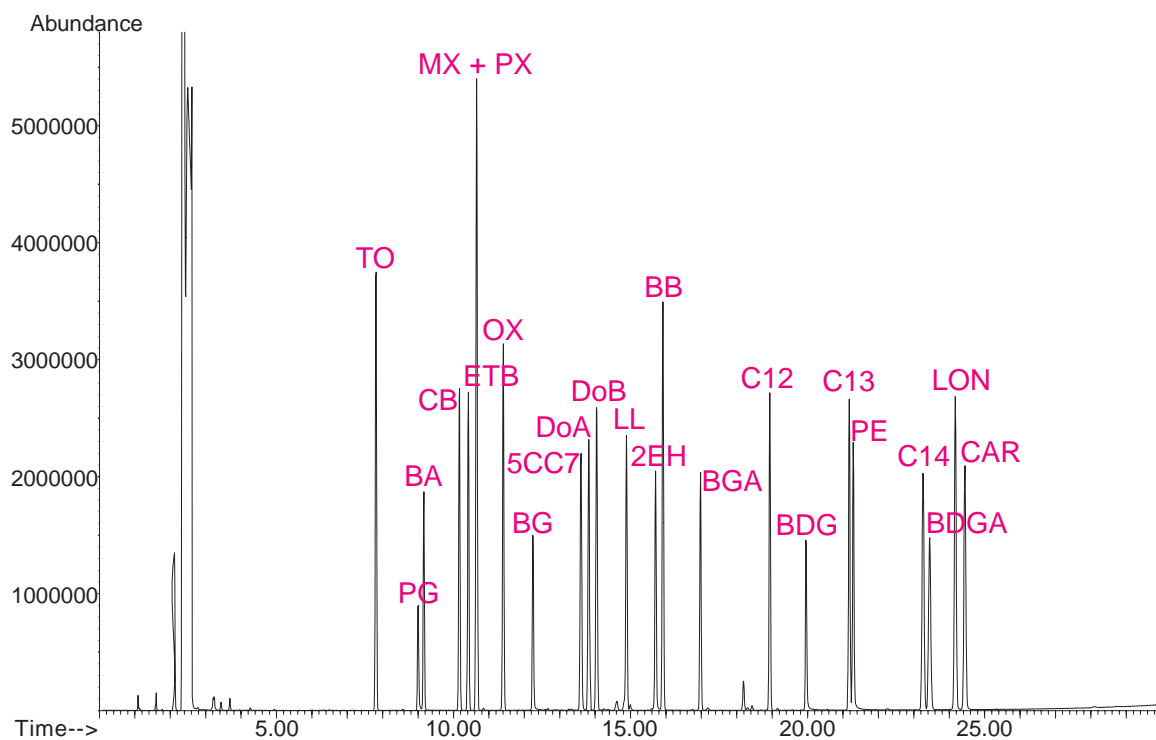


Figure 4. Liquid injection of standard solution into the CIS.

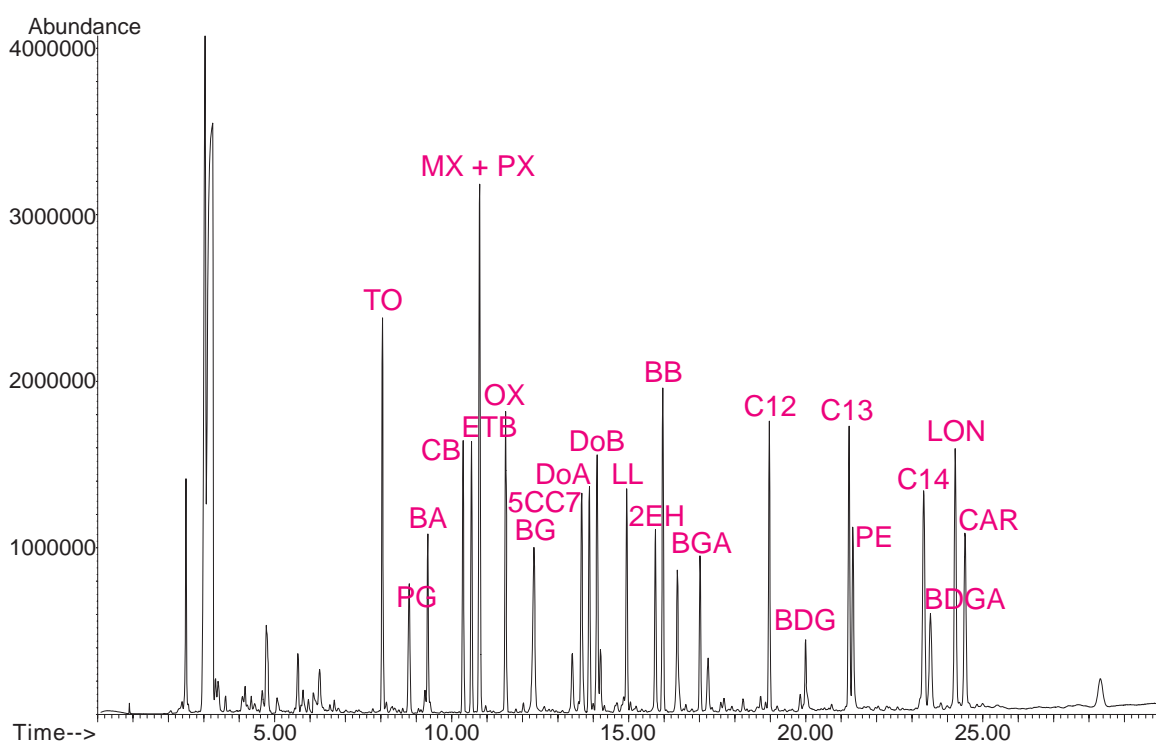


Figure 5. Liquid injection of standard solution into the TOPAS badge.

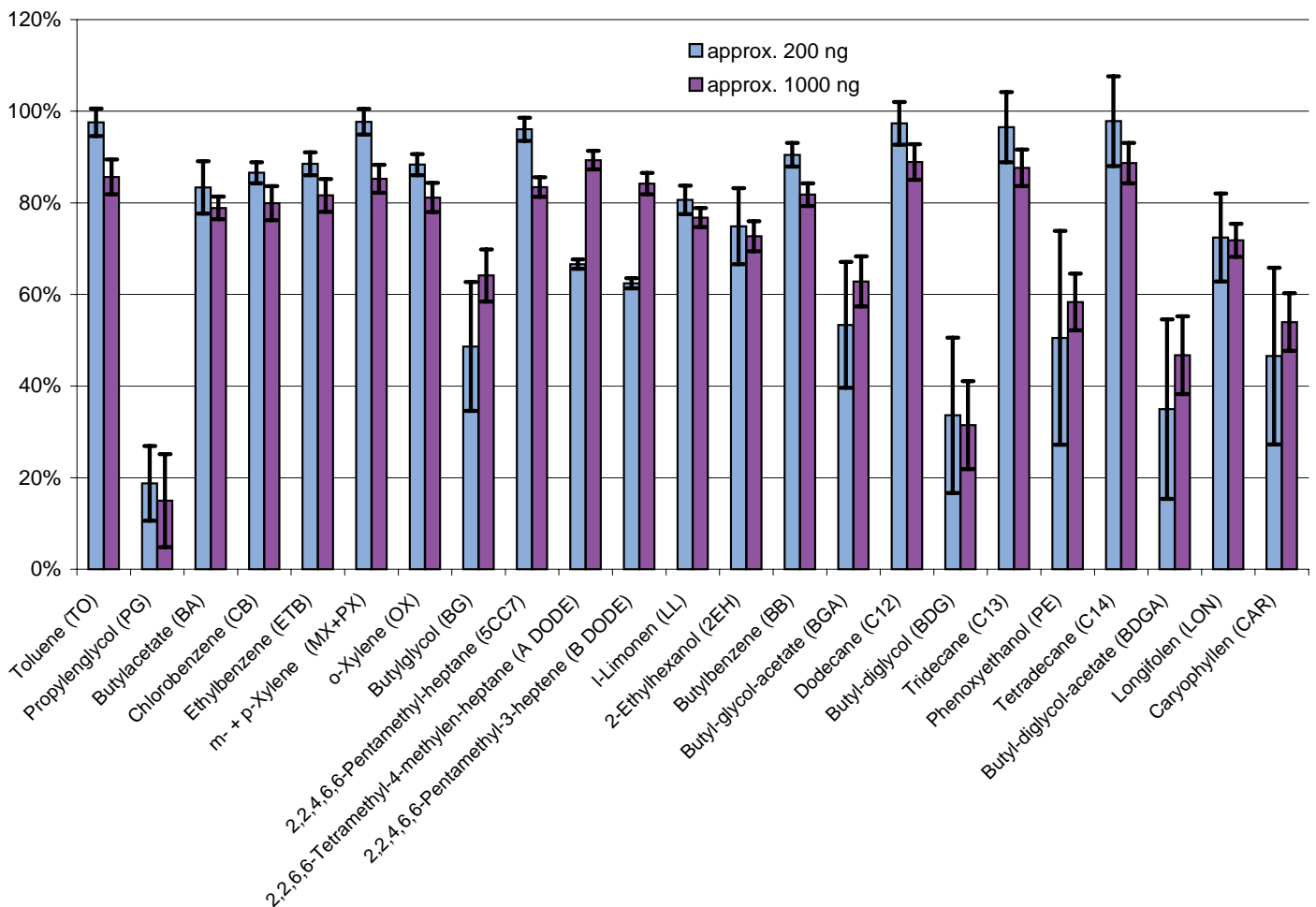


Figure 6. Recovery data of thermal desorption from TOPAS badges at 250°C.

As initial results, the analysis of air samples accumulated on adsorbents simply indicate the adsorbed mass of analyte. To calculate the related air concentration the air volume data are needed. For passive samples these data have to be calculated from an experimentally determined sampling rate and the sampling period (equation 1).

$$(1) S = M / (t * c)$$

S = Sampling rate [L/h]

M = Accumulated mass [ng]

t = Exposure time [h]

c = Test chamber concentration [ng/L]

Sampling rates indicate the volume of air from which the analytes are accumulated in the sampler within a given unit of time. They depend of the properties of the analytes, especially their diffusion coefficients, and on the geometry of the sampler, in other words the diffusion layer and diffusion cross-section. Sampling rates are substance specific device constants which need to be determined once.

In this study determination of the sampling rates were carried out with a real flooring sample in an

emission test chamber. A few days after inserting the flooring sample in the chamber the emission rate and therefor the air concentration is constant. During the following 3 days 6 samplers were exposed in the chamber, each for 5 h. Simultaneously the air concentration was checked by active sampling. Chromatograms obtained by thermal desorption of active and passive samples are shown in Figures 7 and 8. The calculated sampling rates are summarized in table I.

Table I. Sampling rates for TOPAS (exposition time 5 h).

Compound		Sampling Rate
STY	Styrene	0,9 L/h ± 0,2 L/h
ON	Cyclohexanone	2,4 L/h ± 0,2 L/h
BG	Butylglycol	n.a. (coelution)
A DODE	2,2,6,6-Tetramethyl-4-methylenheptane	0,5 L/h ± 0,1 L/h
B DODE	2,2,4,6,6-Pentamethyl-3-heptene	0,7 L/h ± 0,1 L/h
2EH	2-Ethylhexanol	1,3 L/h ± 0,1 L/h
BDG	Butyl-diglycol	2,1 L/h ± 0,3 L/h
PE	Phenoxyethanol	1,2 L/h ± 0,2 L/h
BTL	Benzothiazole	2,6 L/h ± 0,2 L/h
4PCH	4-Phenylcyclohexene	1,2 L/h ± 0,2 L/h
BDGA	Butyl-diglycol-acetate	1,4 L/h ± 0,4 L/h
LON	Longifolen	1,1 L/h ± 0,5 L/h
BHT	Methyl-di-tert.butyl-phenol	0,7 L/h ± 0,1 L/h

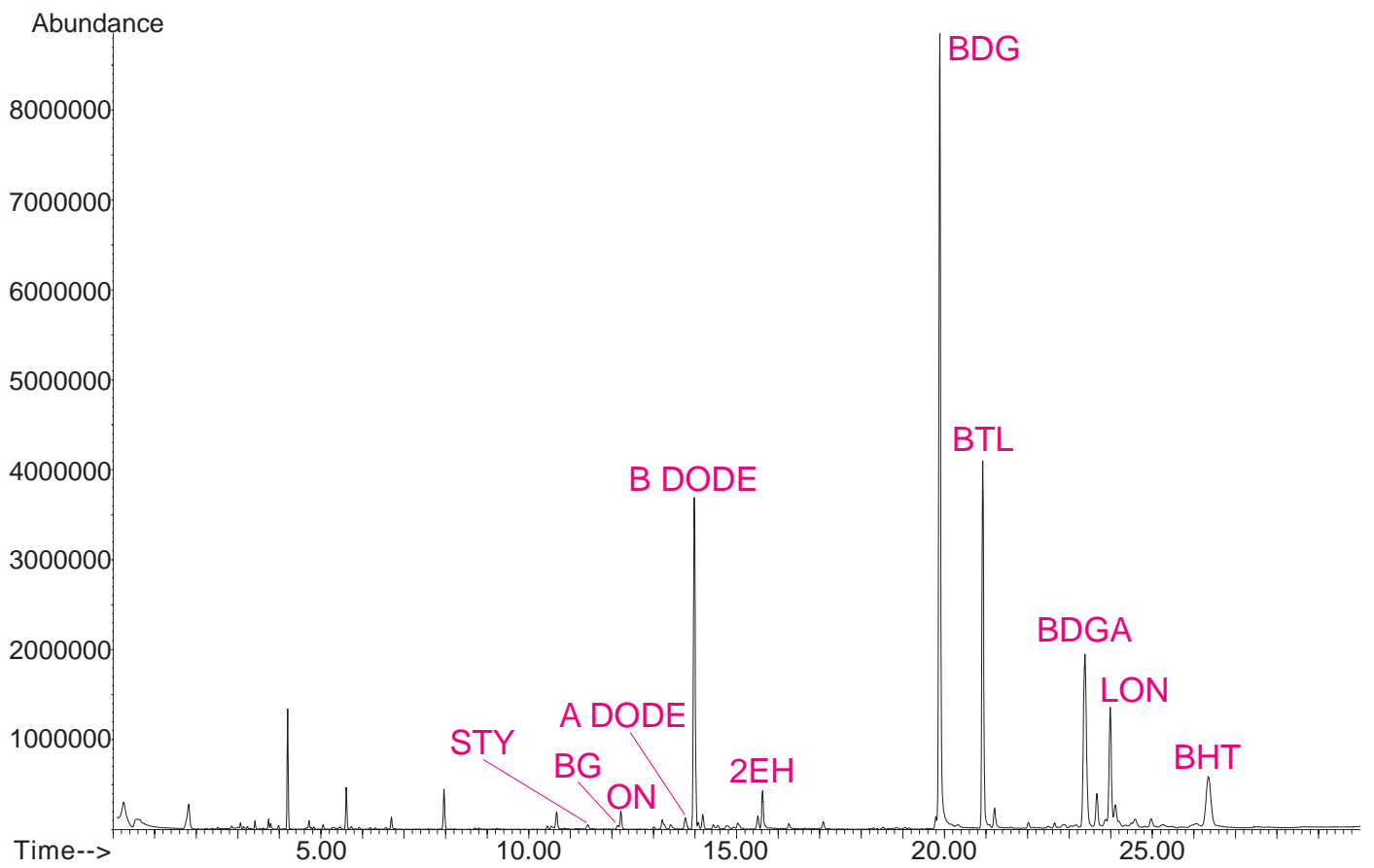


Figure 7. Active sampling (5.4 L) from rubber flooring emission in a test chamber.

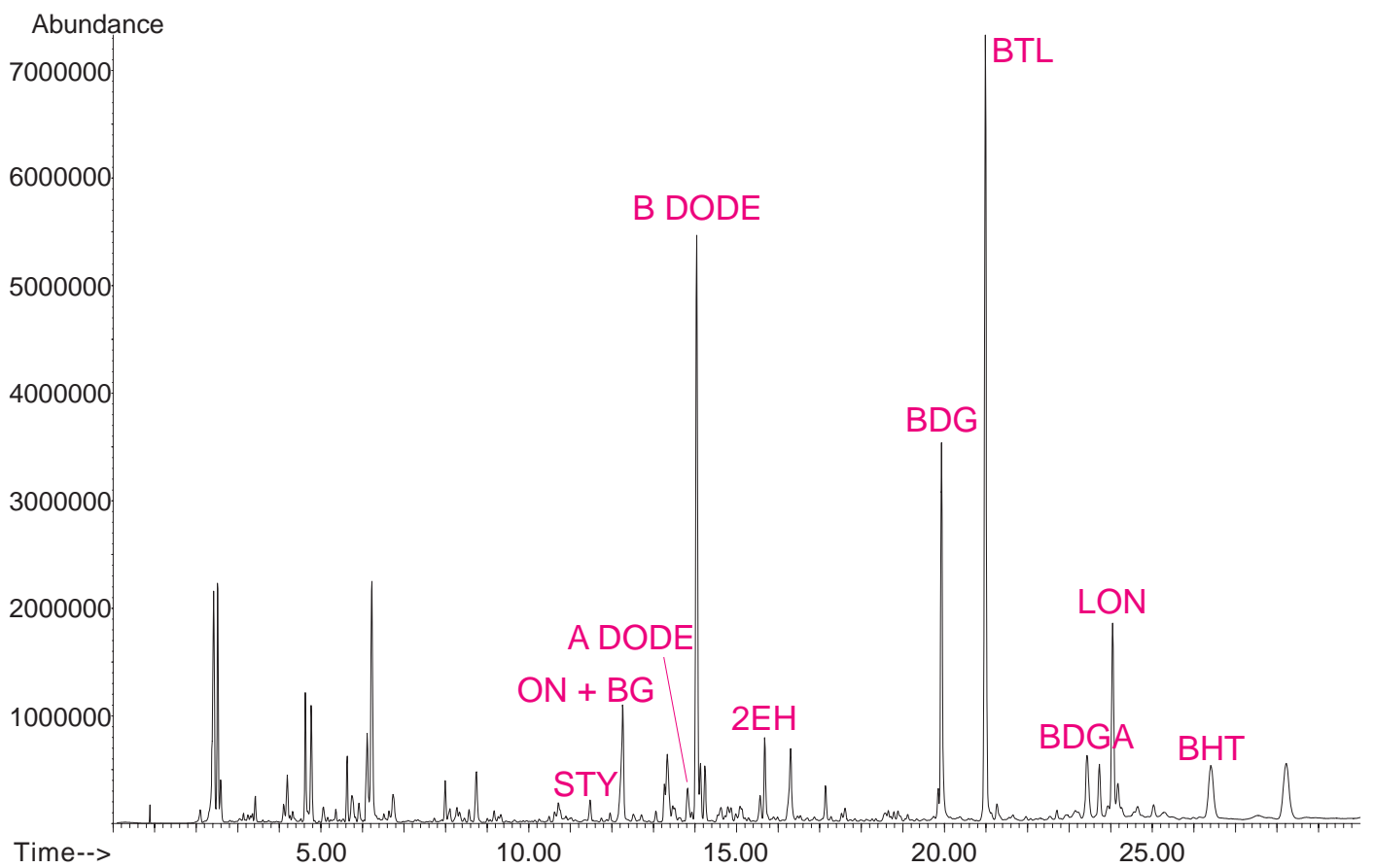


Figure 8. Passive sampling (5 h) from rubber flooring emission in a test chamber.

CONCLUSIONS

Except for polar compounds like the glycol derivatives the recovery for the thermal desorption step is satisfactory. Thus the first condition for further usability of the TOPAS / TDS G system is fulfilled. For the polar compounds like the glycol derivatives or phenoxyethanol the recovery is less than 70% and it is independent of the total injected amount. So it is possible to work with these recovery levels even if the resulting detection limits are higher.

The comparison of the chromatograms obtained from thermal desorption of an active and a passive sample from the emission test chamber shows no difference in the substance spectrum for both types of sampling. This indicates that in this case it is possible to use the TOPAS / TDS D system as an alternative for active sampling. With calculated sampling rates from 0.5 up to 2.5 L/h a sufficient amount of analytes for identifying and quantifying can be enriched within 5 h sampling periods.

Although this study showed quite impressive potential for the TOPAS / TDS D system, changing the badges and working with the badge holders is very cumbersome. In future developments these problems of handling the system components have to be improved.

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