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World first at Analytica 2000

1000 times more sensitive
than SPME:
GERSTEL Twister™

New passive air sampler

GERSTEL® TOPAS
Field tested

ICB presents GERSTEL at Achema

Practical knowledge
converted to advanced
technology

Emmission measurement

Comparison of classical
and thermal desorption
methods for air monitoring



GERSTEL technology at Analytica 2000

Pointing the way for decades

We have to admit, that after looking through some old documents recently, we were somewhat surprised when we realized that this year we presented our range of products at the Analytica trade fair in Munich for the tenth time. This means we have been presenting our innovative systems and complete solutions for chromatographic analysis to scientists at Analytica for the last 20 years now.

Where has the time gone?

All modesty aside, there can only be one answer to that question: it has been spent working on high-quality, technically perfected and unique analytical systems, building a highly skilled and qualified workforce and developing first-class service. In short, the name GERSTEL stands for quality. It is because of this that internationally renowned companies work closely with us to develop innovative solutions to their analysis needs, and why the number of these companies placing their trust in our Global Analytical Solutions technology is constantly growing.

This year, as in the past, we showed pioneering product innovations for gas and liquid gas chromatography at Analytica 2000. Quite outstanding in this regard was the GERSTEL Twister™. Without taking too much away for the article appearing later in this issue of GERSTEL Solutions Worldwide, we will simply say that this simple and ingenious technique revolutionizes the preparation of aqueous samples for GC analysis. Further innovations include the GERSTEL MPS 3 C and the ultra-versatile GERSTEL MPS 3, which are fully automatic LC samplers. We also introduced the GERSTEL TDS D, a thermal desorption system specially developed for evaluating new types of Tenax-based passive collectors (TOPAS).

for decades

Of course, we presented the latest developments in our time tested cooled injection and thermal desorption systems – products that are inextricably linked with the name GERSTEL, and our company's history.

We hope that you had a chance to visit our booth at Analytica 2000, but if you did not, we hope this latest issue of GERSTEL Solutions Worldwide will give you some idea of what you missed.

Eberhard G. Gerstel

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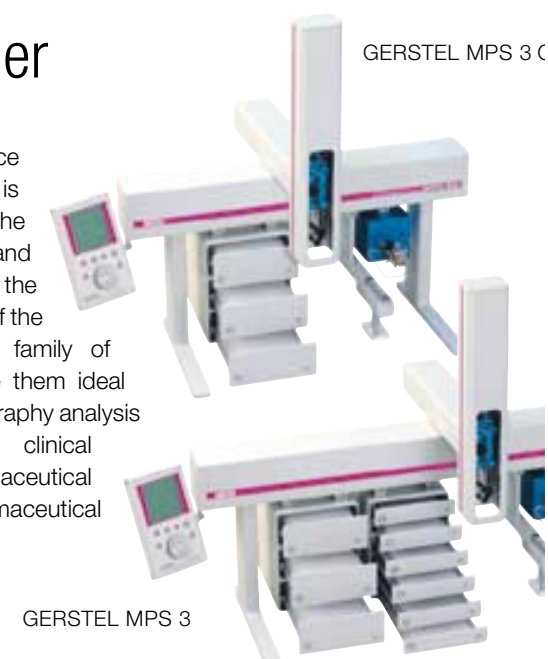
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The GERSTEL MPS 3 provides new dimensions

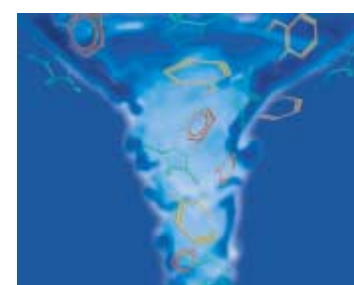
The ultra-versatile LC autosampler

Regardless of whether a sample needs derivatized, have an internal standard edit, of simply diluted – the GERSTEL MPS 3 and the space saving version, the MPS 3 C, set a new standard for automated sampling in liquid chromatography. The sample can accommodate 96-well or 384-well microtiter plate formats, or more traditional 0.7-20 ml. Two HPLC systems can be run simultaneously from one autosampler. A further advantage of the MPS 3/3 C is that samples can be cooled and heated or agitated. This eliminates the need for additional preparation of samples such as tablets since

dissolution takes place automatically. All that is needed is to place the sample in the vial and let the sampler do the rest. The versatility of the GERSTEL MPS 3 family of autosamplers make them ideal for liquid chromatography analysis in the areas of clinical chemistry, pharmaceutical research and pharmaceutical production.

**Up to 100 times more sensitive than SPME**

The GERSTEL Twister creating a stir in sample preparation



Determination of organic compounds from aqueous matrices with no sample preparation, but up to 1000 times more sensitive than SPME? An innovative product developed by GERSTEL GmbH &

Co.KG makes this possible. The GERSTEL Twister looks and functions like a conventional stir bar, but with an important difference: as the stir



bar spins in the sample, organic compounds are extracted into its polydimethylsiloxane (PDMS) coating. The Twister can be used with matrices as diverse as drinking or wastewater, body fluids, beverages, dairy products, and processed foods. After sample extraction, the Twister can be directly transferred to the GERSTEL TDS 2 thermal desorption system where the extracted compounds are thermally desorbed and determined by gas chromatography. For a more detailed look at Twister, see pages 4 – 8.

**New thermodesorbable passive collector - tested in practice**

Faster and more sensitive on a Tenax base

The combining of a badge-shaped passive collector with thermal desorption for transferring atmospheric constituents to GC analysis forms the basis of an innovation developed by GERSTEL in co-operation with the Institut für Chemo- and Biosensorik (ICB) in Münster, Germany. TOPAS



is the name of the system, which comprises a badge-shaped, Tenax-based passive collector the size of a large coin (a German five-mark piece) and the GERSTEL thermal desorption system TDS D specially developed for it. This combination enables comparatively simple, fast and extremely sensitive measurements of harmful pollutants as

well as the monitoring of limit values in the workplace. The outstanding feature of the TOPAS system is that, in contrast to its active carbon-based counterparts, the harmful substances enriched on the Tenax can be desorbed completely and without any sample preparation through thermal desorption and analysed by gas chromatograph. Furthermore, compared with other Tenax-based passive collectors, the new system developed by GERSTEL and the ICB offers the added advantage of being suitable for interior short-time measuring. TOPAS permits sampling cycles of just a few hours even for the lowest of pollutant concentrations.



Stir Bar Sorptive Extraction (SBSE)

A Novel Extraction Technique for Aqueous Samples

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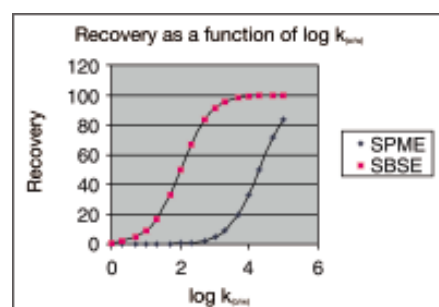
The analysis to determination organic compounds in aqueous environmental, biomedical, food and fragrance matrices is normally performed after extraction and enrichment of the solutes from the matrix (drinking water, waste water, body fluids, beverages,...). Most sample preparation methods are based on liquid-gas equilibrium or extraction

lower solvent consumption, less manpower in sample preparation, while maintaining or even improving limits

Some 10 years ago, a new micro-extraction method was developed by Arthur and Pawliszyn (1), namely solid-phase micro-extraction (SPME). Extraction of organic compounds from aqueous samples (or from a gas phase) using a polydimethylsiloxane (PDMS) sorbent as extraction medium was already described by different groups in the mid 80s using open tubular traps coated with thick PDMS films. Extraction using PDMS media is based on sorption instead of adsorption. Sorptive enrichment offers several advantages over adsorption processes, as described by Baltussen et al (2). These advantages include predictable sorption, absence of displacement effects, inertness and faster and milder desorption. Practical limitations (low sample capacity, low breakthrough volumes,...), however, limited the applicability of PDMS coated open tubular traps. SPME, on the other hand, is a very simple and fast technique. A relative thin layer of PDMS (7-100 μm) on the outside of a needle device is used as extraction medium. After sorption, the compounds are thermally desorbed in a GC inlet or liquid desorbed in a LC inlet. In contrast to PDMS coated open tubular traps, SPME is by nature an equilibrium technique, based on the partitioning of the solutes between the silicone phase and the aqueous (and/or gas) matrix. Recent studies (3-5) have correlated this equilibrium with octanol/water distribution coefficients ($k_{(o/w)}$). These studies demonstrated that for solutes with low $k_{(o/w)}$

Figure 1

Recovery as a function of $\log k_{(o/w)}$; comparison SPME and SBSE



(headspace, purge and trap), liquid-liquid extraction or solid phase extraction (SPE).

During the past years, miniaturization has become a dominant trend in analytical chemistry. Typical examples of miniaturization in sample preparation techniques are micro liquid-liquid extraction (in-vial extraction), ambient static headspace and disk cartridge SPE. In combination with state-of-the art analytical instrumentation, this resulted in faster analysis, higher sample throughput,



Figure 2

GERSTEL Twister™



($k < 10000$), low recoveries are obtained. This is mainly due to the phase ratio between the aqueous and PDMS phase. The amount of PDMS used in SPME is typically in the order of 0.5 μL or less. For a 10 mL water sample, this corresponds to a phase ratio of 20000. Consequently the enrichment on the PDMS fiber is limited. This is illustrated in Figure 1 showing the recovery of solutes on the SPME fiber in function of the $\log k_{(o/w)}$. A 50 % recovery is only obtained for compounds with a $k_{(o/w)}$ larger than 20000.

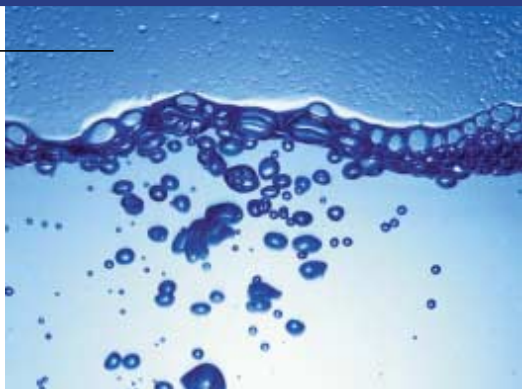
Based on these observations, a new approach using stir bars coated with PDMS was recently developed (2). The technique is called stir bar sorptive extraction (SBSE). In this approach, 50-300 μL PDMS coatings are used. This corresponds to phase ratios of 33-200 for 10 mL samples. Consequently, the sensitivity is increased by a factor of 100 to 1000 in comparison to SPME. This is demonstrated in Figure 1 for a 10 mL water sample and a stir bar coated with 100 μL PDMS. More than

50% recovery is obtained for solutes with $k_{(o/w)}$ larger than 100 and the SBSE curve reaches 100% recovery at much lower $\log k_{(o/w)}$ values in comparison with SPME. Solute with $k_{(o/w)}$ from 10 to 100 can also be analysed using calibration as is done in SPME.

In this paper some applications demonstrate the applicability of stir bar sorptive extraction for the analysis of aqueous matrices.

Experimental

PDMS coated stir bars (Twister™) are commercially available from GERSTEL GmbH. Magnetic stirring rods are incorporated in a glass jacket and coated with a 1 mm layer of PDMS (Fig. 2). Two Twisters are available: 10 mm L x 3.2 mm o.d. and 40 mm L x 3.2 mm o.d. PDMS coated stir bars. Typically the 10 mm stir bars are used for 1-50 mL sample volumes and the 40 mm stir bars are used for 100-250 mL sample volumes.



Sample extraction is performed by placing a suitable sample amount (typically 10 mL) in a vial, adding a stir bar and stirring for 30-120 min. After extraction, the stir bar is introduced in a glass thermal desorption tube (4 mm i.d. x 187 mm L), placed in a thermal desorption unit and thermally desorbed. Desorption temperatures are application dependant and are between 150-300°C. Alternatively, liquid desorption can be used.

Two typical applications are shown to illustrate stir bar sorptive extraction. First, an orange juice drink was analysed. A 20 mL sample was placed in a headspace vial and extracted using a 10 mm stir bar for 90 min. The stir bar was then thermally desorbed at 240°C for 10 min in splitless mode using a TDS-2 system (GERSTEL GmbH), installed on a HP 6890 GC – HP 5973 MSD combination. The desorbed solutes were cryofocussed in a CIS 4 PTV inlet at –150°C. After the stir bar desorption, the PTV was programmed to 240°C at 12°C/s and held for 5 min to transfer the trapped solutes in the GC column. Injection was done in split mode (split ratio 1:20). The

carrier gas was helium at 1 mL/min constant flow. The compounds were analysed on a 30 m x 0.25 mm i.d. x 0.25 µm Stabilwax (Restek) column. The oven was programmed from 40°C (1 min) to 230°C at 5°C/min. Detection was done using a HP 5973 MSD in scan mode (35-500 amu).

Secondly, pesticides were analysed in a wine sample. A 25 mL wine sample (dry white wine) was spiked at the 1 ppb level with a mixture of organochlorine pesticides, placed in a 40 mL vial and extracted with a 10 mm stir bar for 40 min while stirring at 1400 rpm. The stir bar was desorbed at 300°C for 10 min in a TDS-2 system installed on a HP 6890 GC – HP G2350 A Atomic Emission Detector combination. The solutes were cryofocussed in an CIS 4 PTV inlet at –50°C. After the stir bar desorption, the PTV was programmed to 300°C at 10°C/s and held for 5 min to transfer the trapped solutes in the GC column. Injection was done in splitless mode. The carrier gas was helium at 170 kPa constant pressure. The compounds were analysed on a 30 m x 0.25 mm i.d. x 0.25 µm HP-5 MS column. The oven

Figure 3

SBSE-TDS-GC-MS
analysis of
orange juice

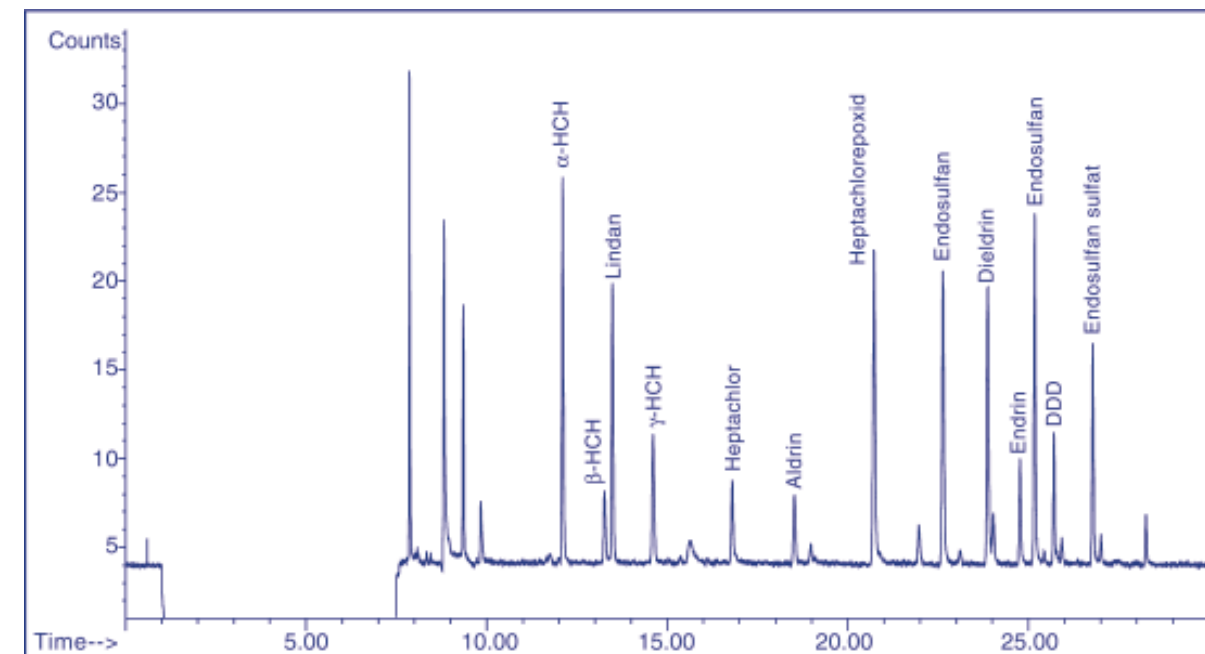
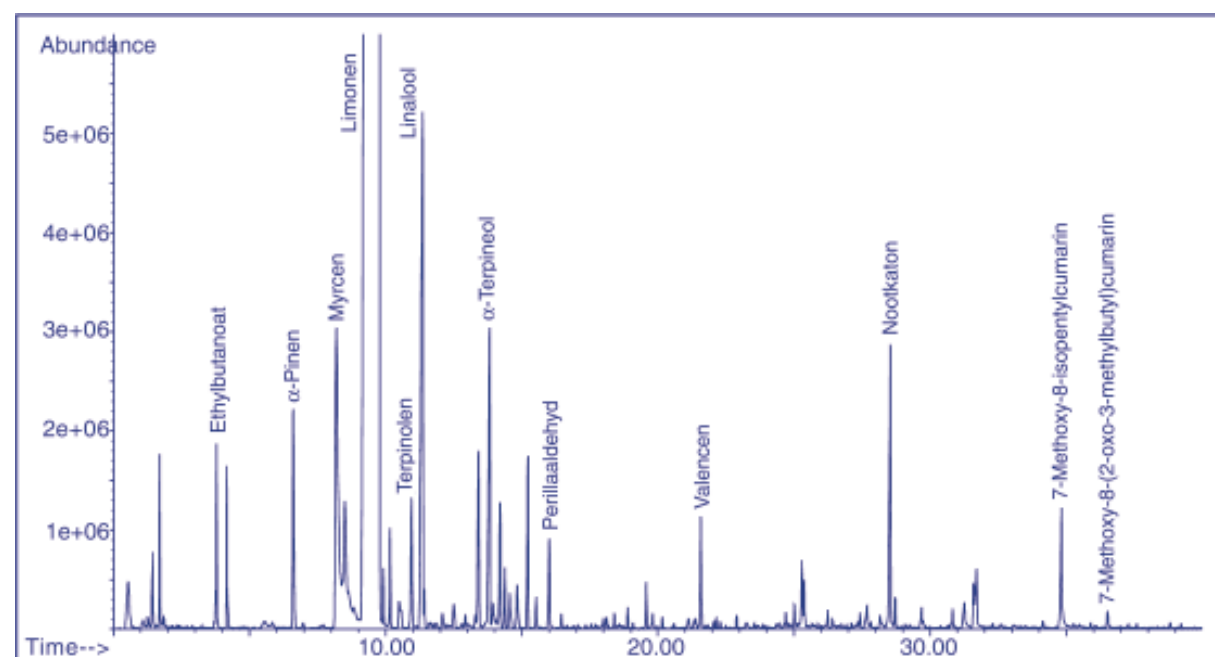


Figure 4

SBSE-TDS-C
AED analysis
pesticides in

was programmed from 70°C (2min) to 150°C at 25°C/min, to 200°C at 3°C/min and to 280°C at 8°C/min. Chlorine and bromine emission lines were monitored.

Results and Discussion.

The analysis of an orange juice sample is a typical quality control application. The PDMS coated stir bar extracts apolar and semi-polar solutes from the aqueous matrix. Thermal desorption of the stir bar and on-line GC-MS analysis gives a very detailed picture of the flavour and fragrance compounds present in the sample. The chromatogram obtained by SBSE-TDS-GC-MS of the orange juice sample is given in Figure 3. The chromatogram shows excellent peak shapes and resolution. Peaks ranging from the very volatile esters (ethyl butanoate) to semivolatile coumarins are identified.

The second application is the analysis of pesticide traces in wine. Classical sample preparation methods involve liquid-liquid extraction or solid phase extraction, followed by a clean-up prior to GC analysis. Figure 4 shows the chlorine trace obtained by SBSE-TDS-GC-AED analysis. All spiked pesticides are easily detected with good peak shapes. The spiked level of 1 ppb is well below the accepted levels for wine (or grapes), so the obtained sensitivity is more than sufficient. Sample preparation time is low and not labor intensive. Several samples can be extracted simultaneously and thermal desorption – GC-AED analysis is fully automated.

Conclusion.

Stir bar sorptive extraction is a powerful technique for the extraction and analysis of organic compounds in aqueous matrices. The system can be used for fast quality control of food and fragrance samples and for trace analysis in environmental, food and biomedical samples.

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Analysis of Volatiles in Wet Samples by Direct Thermal Desorption GC

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Abstract

The analysis of volatiles in solids is a common analytical problem. Examples include volatile aroma compounds in foods (coffee, tea, herbs), residual fragrances from soaps and fabric softeners on textiles, and volatiles in polymer resins, films and plastic products. When high sensitivity analysis is needed, many of these sample types can be analyzed by direct thermal desorption with cryotrapping before the GC column.

A wide variety of sample types can contain significant levels of water. This poses significant challenges when doing direct thermal desorption and cryotrapping for analysis of volatiles, since water can accumulate and freeze in an inlet or at the head of a column. Introduction of significant levels of water into the GC column can degrade chromatographic performance and shorten column lifetime.

There are several strategies that are useful to reduce the introduction of water into a GC when doing thermal desorption. These range from offline thermal extraction with trapping of volatiles on adsorbent beds to incorporating drying steps into the thermal desorption process itself. Estimating the amount of water that can be eliminated with each of these approaches is a challenge.

Volatiles in solid samples containing up to 90% water were analyzed by direct thermal desorption incorporating different drying strategies. Offline thermal extraction utilizing Tenax TA™ adsorbent was the most effective approach for eliminating large amounts of water while effectively retaining low boiling analytes. Small amounts of water (tens of milligrams) can be eliminated from samples by using Tenax TA™ packed inlet liners cooled to 20–40°C. General guidelines for choosing appropriate steps for eliminating different levels of water are summarized.

Keywords

Thermal Desorption, Tenax TA™, Sample drying, Herbs, Peppers

Introduction

Direct analysis of wet samples has often been limited to Static Headspace GC or SPME, both of which tolerate water reasonably well. Both of these approaches are usually much less sensitive than thermal desorption, however, sometimes by factors of 100 or more.

There are strategies available to trap volatile components while eliminating water, the most common of which uses Tenax TA™ adsorbent. Tenax TA™, an adsorbent based on 2,6-diphenylene oxide polymer has long been used for air sampling in humid environments and purge & trap applications since it has a very low affinity for water. Tenax adsorbent can also be used to facilitate Thermal Desorption of wet samples.

Offline Sampling. One approach to managing water in wet samples is offline thermal extraction of a sample, trapping the volatiles on adsorbent tubes packed with Tenax TA™. Under appropriate conditions, enough water can be eliminated from the adsorbent tube to allow Thermal Desorption of the trapped volatiles with cryofocusing in a cold inlet. There is a need to define drying conditions that eliminate water interference in the subsequent GC analysis.

Online Sampling. A second and more easily automated approach is to attempt to dry the sample at low temperature prior to thermal extraction of the analytes of interest. This is possible for semivolatile analytes that will not be lost during the drying step. It is necessary to define starting conditions that provide adequate sample drying, and determine which volatiles can be lost during the drying step. A third automated strategy uses Tenax TA™ adsorbent in the GC

inlet liner to trap volatiles from wet samples while allowing water vapor to pass out the split vent.

This paper will define conditions necessary to eliminate water from wet samples using the above three strategies. Examples illustrating the high sensitivity analysis of volatiles in wet samples by Thermal Desorption are shown.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with Flame Ionization Detection. The GC was equipped with a Thermal Desorption unit with autosampling capacity (TDS 2 & TDS A, Gerstel) and a PTV inlet (CIS 4, Gerstel). Offline extraction of wet samples onto Tenax TA™ adsorbent tubes was done using a heated Thermal Extractor unit (TE, Gerstel).

Sample Preparation. Fresh Peppers and Herbs. For offline extraction of volatiles, fresh samples (100–500 mg) were weighed into large (14 mm ID x 178 mm) glass extraction tubes. Samples were then extracted under 50 mL/min helium flow in a Thermal Extractor unit (Figure 1).

trapping volatiles at ambient temperature on 4 mm ID x 178 mm Tenax TA™ adsorbent tubes. Adsorbent tubes were then thermally desorbed in the TDS A unit, cold trapping the volatiles in the inlet. For online extraction of volatiles, fresh samples (25–50 mg) were weighed directly into glass Thermal Desorption tubes. Samples were extracted under 45 mL/min helium flow, trapping volatiles in the CIS 4 inlet on Tenax TA™ packed liners.

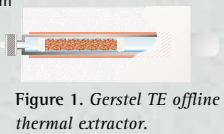


Figure 1. Gerstel TE offline thermal extractor.

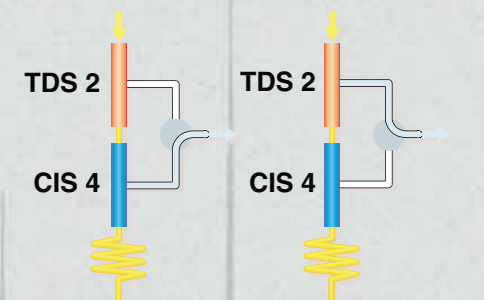


Figure 2. Pneumatics diagram for Gerstel TDS 2/CIS 4 in splitless (left) and solvent venting desorption modes.

| Analysis conditions. | |
|--|--|
| Column: | 30m HP 5 (Agilent) d _i =0.25 mm d _i =0.25 µm |
| Pneumatics: | He, P _i =91.7 kPa, constant flow = 1.2 ml/min |
| Oven: | 40°C (2 min); 10°C/min; 280°C (2 min) |
| Offline thermal extraction conditions. | |
| TE 1: | 50 ml/min (10–30 min); 40°C or 60°C |
| TDS 2: | solvent venting / splitless 20°C; 60°C/min; 60°C (20 min); 60°C/min; 280°C (3 min) |
| Offline thermal extraction conditions. | |
| PTV: | 0.1 min solvent vent (45–60 ml/min) split: see figures -70°C; 12°C/sec; 290°C (5 min) |

| Online thermal extraction conditions. | |
|---------------------------------------|---|
| TDS 2: | splitless -20°C; 60°C/min; 60°C (10–30 min) |
| PTV: | 1 min solvent vent (45 ml/min) split 1:10 5–60°C; 12°C/sec; 60°C (1 min); 12°C/sec; 275°C (3 min) |

Results and Discussion

Model Drying Studies.

Dried cotton terrycloth towel samples (50 mg) were placed into glass Thermal Desorption tubes (4 mm ID x 178 mm) and spiked with 10 mg or 25 mg water. Wet samples were then dried under helium flow at 30°C in the TDSA to simulate drying a sample prior to thermal extraction. Table I summarizes the percent water removed under different time and flow conditions.

| Drying Time (Minutes) | 10 mg water | | 25 mg water | |
|-----------------------|-------------|------------|-------------|------------|
| | 50 ml/min | 150 ml/min | 50 ml/min | 150 ml/min |
| 5 | 68 % | 33 % | 60 % | |
| 10 | 98 % | 45 % | 97 % | |
| 20 | 108 % | 78 % | N.D. | |
| 40 | 105 % | 100 % | N.D. | |

Table I. Percent Water Removed from Terrycloth Towel @30°C.

The same terrycloth towel samples were spiked with 25 mg water + 10 µl of a low boiling C₅–C₁₈ hydrocarbon mix in methanol (5080–8768, Agilent). Wet samples were then dried at 30°C under

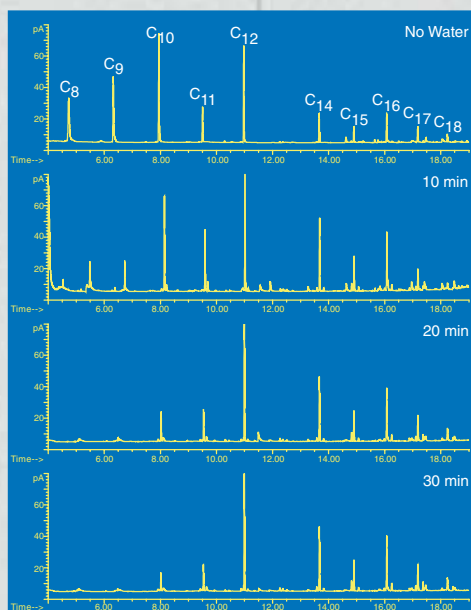


Figure 3. Loss of hydrocarbon mix spiked onto towel at different drying times. Boiling points in parentheses. C₈ (126°C); C₉ (151°C); C₁₀ (174°C); C₁₁ (196°C); C₁₂ (216°C).

40 mL/min helium flow in the TDSA solvent venting mode (Figure 2) prior to desorption at 150°C for 10 minutes. Hydrocarbons were trapped onto a Tenax TA™ packed inlet liner at 5°C.

Figure 3 shows that drying for 10 minutes results in some loss of C₈–C₁₀ hydrocarbons compared to the upper trace with no water present. At 10 minutes drying there is also evidence of the presence of water, which affects the chromatography of the early eluting C₈ and C₉ peaks. Longer drying times result in almost complete loss of C₈ and C₉ hydrocarbons and significant reduction of C₁₀–C₁₁. This is consistent with the general rule for large volume liquid injection solvent venting, which states analytes that boil >100°C higher than the solvent will be retained while lower boiling analytes will be lost at rates related to their boiling point.

Tenax TA™ adsorbent tubes (4 mm ID x 178 mm) were spiked with 25 mg or 50 mg water. Wet tubes were then dried under 50 mL/min helium flow at room temperature (25°C) or 60°C in the TDS A solvent venting mode to simulate drying prior to thermal desorption. Table II summarizes the percent water removed under different time and flow conditions.

| Drying Time (Minutes) | 25 mg water | | 50 mg water | |
|-----------------------|-------------|------|-------------|------|
| | 25°C | 60°C | 25°C | 60°C |
| 5 | 25 % | 97 % | 11 % | 97 % |
| 10 | 71 % | N.D. | 36 % | N.D. |
| 20 | 95 % | N.D. | 80 % | N.D. |
| 40 | N.D. | N.D. | 98 % | N.D. |

Table II. Percent Water Removed from Tenax TA™ Adsorbent Tubes.

It is clear that despite the low affinity of water for Tenax TA™, at low temperatures it is quite possible for adsorbent tubes to retain enough water to adversely affect thermal desorption results. It is therefore necessary to warm the adsorbent to assure elimination of water prior to analysis.

High Water Content Samples

Offline Thermal Extraction. Fresh peppers and basil can contain 50–90% water depending on their age and storage conditions. This precludes direct thermal desorption with direct cold trapping of volatiles in the inlet.

Offline thermal extraction of 250 mg fresh habanero pepper at low temperature (30 min, 40°C) minimized overloading the

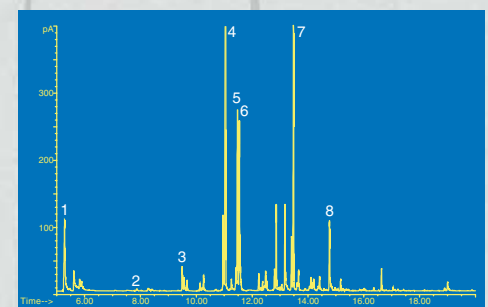


Figure 4. Offline thermal extraction of fresh habanero pepper volatiles, 10:1 split. 4-methyl-1-pentanol (1); benzaldehyde (2); 2-methyl propionic acid ethyl ester (3); hexyl pentanoate isomer (4); cis-3-hexenyl-3-methyl butanoate (5); hexyl pentanoate isomer (6); 2,5-dimethyl-2,4-hexadiene (7); α-gurjunene (8).

residual water before thermal desorption. Volatiles were cold trapped in the inlet at -70°C without freezing the inlet (Figure 4). This procedure resulted in analysis times in excess of 1 hour.

To try to speed analysis, 500 mg fresh basil was thermally extracted offline (15 min, 60°C) trapping volatiles on Tenax TA™ adsorbent tubes. The Tenax TA™ tube was then heated to 60°C for 12 minutes in the TDS solvent vent mode to eliminate residual water before thermal desorption. Volatiles were cold trapped in the inlet at -70°C. Although excellent separation was obtained (Figure 5), an increase in inlet pressure during trapping and shifts in early peak retention time indicate some water still remained on the Tenax TA™ adsorbent tube. Analysis time was reduced to 47 minutes.

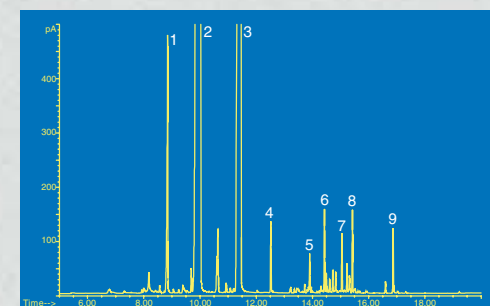


Figure 5. Offline thermal extraction of fresh basil volatiles, 100:1 split. Octene-ol isomer (1); 1,8-cineole (2); α-terpinolene (3); 1-α-terpinol (4); 2-methoxy-4-(2-propenyl)-phenol (5); α-bergamotene (6); β-cubebene (7); δ-cadinene (8); epi-bicyclosesquiphellandrene (9).

Online Thermal Extraction. The CIS 4 inlet liner was replaced

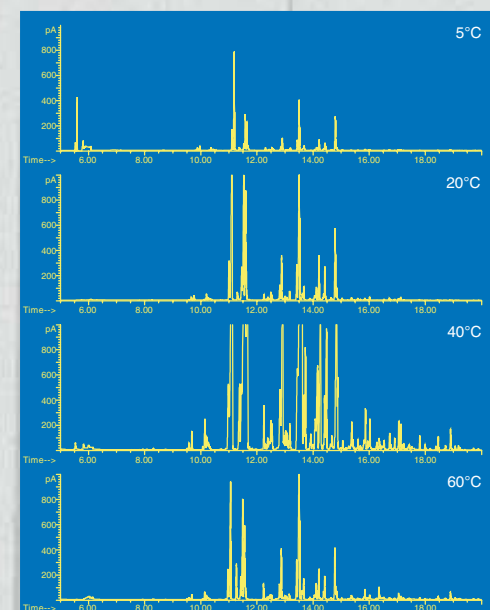


Figure 6. Online direct thermal extraction of fresh habanero pepper volatiles. Inlet liner Tenax TA™, 10:1 split. Inlet temperature listed in figure.

with a liner packed with Tenax TA™ adsorbent to allow above 0°C for direct thermal extraction of fresh habanero. Since previous drying studies had shown Tenax TA™ cold water, inlet temperature was varied to optimize volatile while eliminating water as vapor. 50 mg samples of fresh pepper were thermally extracted for 30 minutes at 60°C, 45 mL/min flow in the TDS splitless mode. The inlet solvent mode was used to allow high desorption flow while trapping volatiles at 5–60°C. To minimize water entering the column trapping, column flow was reduced by setting the inlet to zero (stopped flow mode).

Figure 6 shows maximum trapping efficiency of the Tenax TA™ packed inlet is near 40°C. Increasing the inlet temperature water condensing in the adsorbent, maximizing trapping efficiency. Above 40°C the trapping efficiency of the Tenax TA™ cold reducing sensitivity.

The optimized inlet conditions were then used for direct extraction of fresh basil for 10 minutes at 60°C (Figure 7). separation and peak shape were obtained for the full volatiles present. Compared to offline thermal extraction (Figure 2) online direct thermal desorption showed improved for both early and late eluting compounds. Analysis reduced to 30 minutes.

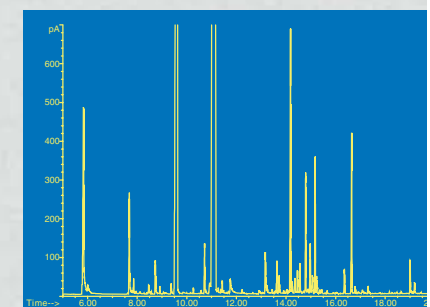


Figure 7. Online direct thermal extraction of fresh basil volatiles. Inlet liner Tenax TA™, 10:1 split, temperature listed in figure.

Conclusions

Drying hydrophilic substrates (cotton) under a helium flow at 30°C can effectively remove water from the sample without analytes with boiling points above 200°C.

Tenax TA™ adsorbent tubes can be used offline to trap and eliminate water from wet samples containing hundreds of milligrams of water. This approach may be useful for inhomogeneous samples must be analyzed. Drying the sample at 60°C for 20 minutes or more may be necessary to reduce interference from water.

Volatiles in wet samples up to 50 mg can be analyzed by direct thermal desorption using Tenax TA™ packed adsorbent. Maintaining inlet temperature near 40°C during trapping provides optimal sensitivity.

Acknowledgements

The author wishes to thank Ms. Jackie Whitecavage for her technical work generating the GC data and Mr. Andreas for providing technical suggestions toward optimized conditions, and graphics design.

New calibration method for thermal desorption

■ Suitable sampling and measuring methods are required to determine organic compound contamination of interior and exterior air. Enrichment on thermally desorbable sorbents is a widely-used method, offering the advantage over solid-liquid extraction of allowing the entire sample to be injected for GC analysis all at once, which results in low detection limits. It also does not require the use of toxic solvents.

The calibration of the measuring process is particularly important. In co-operation with Reinhard Keller, Head of the Department at the Institute of Medical Microbiology and Hygiene at the Medical University of Lübeck, GERSTEL has designed a calibration unit taking six TDS tubes to make this stage faster and simpler.

Using a knurled nut, the TDS tubes can be fixed to the bottom of the unit via a Teflon ferrule, with six septumless sampling heads (SLHs) located on the top for contamination-free injection of the calibration solution. The entire unit is purged with carrier gas and the volumetric rate of flow can be regulated separately for each channel.

The pre-conditioned TDS tubes were clamped into the calibration unit. In his tests, Keller used analytes which are listed in VDI 4300, Sheet 6 for determining the overall concentration of volatile organic compounds and which also span a relatively broad boiling-point range (66 – 287°C). Between 10 ng and 2000 ng were selected for the concentrations to be examined so as to take account of all problematic concentrations occurring in interior spaces. The analytes were dissolved in methanol and doped at the rate of 1 µl was injected into the system to provide the proper loading of the compounds into the Tenax™.

The advantages of the process developed by Keller compared with conventional methods are obvious: less instrument equipment and time needed, easy handling and easy to integrate into laboratory practice. This means that an alternative to the established procedures, such as the use of test gases, now exists.

The GERSTEL Twister™ tested in practice

Waste-water analysis made easy

Differing TOC concentrations were found in the waste-water tanks of two plants producing under the same conditions, although the concentrations were virtually identical at the inlet to the tanks. In the troubleshooting process, the GERSTEL Twister proved to be the ideal means of identifying the constituents quickly and economically after thermal desorption, gas chromatography separation and mass-selective detection.



A chemical company in the German region of North Rhine-Westphalia manufactures a certain product in two different plants using an oxidation process, with the waste water accumulating fed into two separate tanks. Although the products and production conditions were identical, the waste water had differing TOC concentrations (Fig. 1), with tank 2 displaying higher values than tank 1. In order to be able to identify the cause quickly, an analytic method was required which would provide qualitative information about the constituent. The TOC concentration alone was not sufficient.

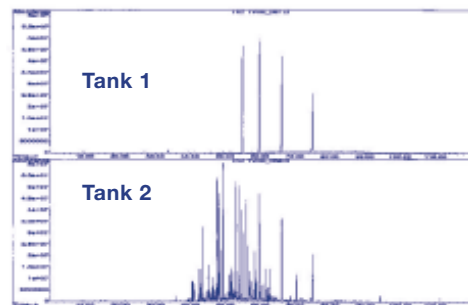


Figure 1 Waste-water tank TOC concentrations

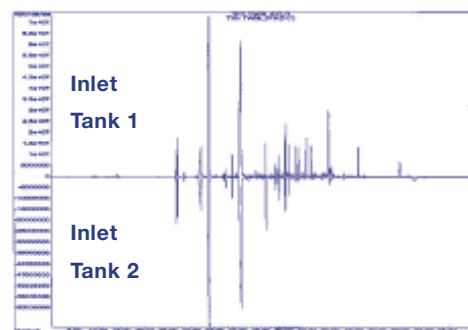


Figure 2 Waste-water tank TOC concentrations in the inlet pipes

Measuring method

The GERSTEL Twister was put directly into 20 ml of the samples taken from the inlet pipes and the waste-water tanks, with these then agitated for 30 minutes at a time. The constituents were sorbed in the Twister's polydimethylsiloxane (PDMS) coating. Analysis was then carried out by direct thermal desorption by placing the Twister in a GERSTEL

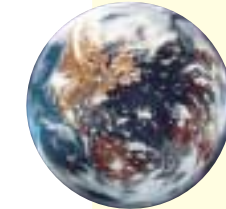
TDS 2 in combination with the GERSTEL CIS 4, an Agilent GC 6890 and a GERSTEL MCS column switching system (column 1: 60 m RTX-1, ID 0.32 mm, FD 1.5 µm; column 2: 90 m Agilent VOC, ID 0.32, FD 1.0 µm) and mass-selective detection (Agilent MSD 5973).

Evaluation

While the chromatograms of the samples from inlet pipes 1 and 2 were virtually identical (Fig. 2), those of the tank samples displayed distinct differences (Fig. 1). The source of the discrepancy therefore had to be in the waste-water tank. As the Twister and the MSD allowed the components to be identified, potential causes of the additional contamination could be determined using available piping plans. This meant that there had to be at least one more inlet pipe to tank 2. This was located, after which a sample was taken and compared with the existing results. When the components found were added to tank 1, the chromatogram showed the same picture as in the analysis of the sample from tank 2 (Fig. 3 and 4). The cause of the additional waste-water contamination could then be established.

Result

With the help of the GERSTEL Twister, it proved possible to implement a process which, compared with conventional sample preparation for GC analysis, enables an organic waste-water contaminant to be detected much more quickly and economically while retaining the same measuring sensitivity. The advantages of using the Twister: the costs were only one third of those normally incurred and the time required for the analysis was, after optimization, reduced to a quarter of that previously needed. Following identification with a mass-selective detector (MSD), the quantifying process can be carried out using a flame ionisation detector (FID). This possibility is currently being tested.



ICB presents
GERSTEL at
Achema 2000

World's first through innovation

■ In the development of innovative marketable products, the transfer of know-how between industry and research institutes can often be the key to developing technologies for the future. An excellent example of this is the co-operation between GERSTEL and the Institut für Chemo- und Biosensorik (ICB) in Münster, Germany in developing the TOPAS system: a badge shaped Tenax-based passive collector combined with thermal desorption for direct transfer to GC analysis (see page 3).

While TOPAS has left the experimental stage and is currently undergoing practical testing, everyone is now talking about yet another new innovation resulting from GERSTEL's co-operation with the ICB: the Automated Speciation Analyser (ASA), a new type of analytical instrument which thanks to its special column technology and an element-selective detector, provides for much faster GC analysis than hitherto facilitated by conventional systems. As Reinhard Bremer, technical director at GERSTEL says: »The ASA is designed to enable high toxic metallo-organic compounds to be detected for the first time in a manner that is fast, reliable, sensitive and extremely economical.«

Bringing these attributes together in a single product was an analytical challenge. »It took a huge amount of technical and time resources,« comments Dr. Wolfgang Buscher, ICB's analyst. With the ASA, organic mercury compounds, for example, can be detected five times more quickly than with conventional methods. The detection limit is 2 picogrammes in absolute terms. The analyst is convinced that future prospects are bright.

Further information is available from ICB Münster: w.buscher@izb-online.de.

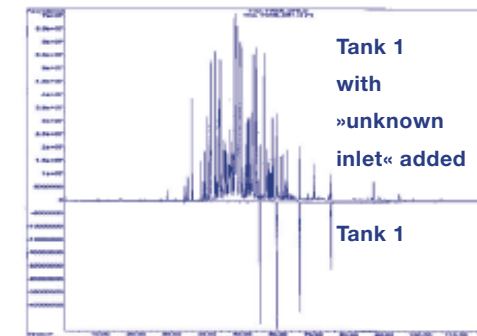


Figure 3 Waste water contaminant load with and without the components detected in tank 2

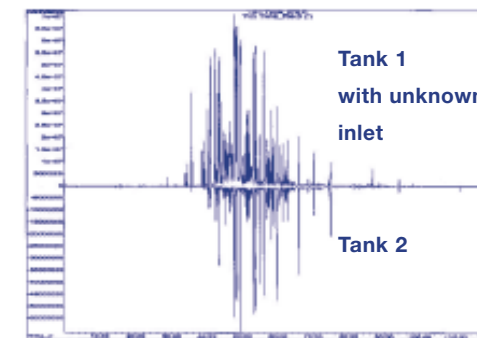


Figure 4 Comparison of contaminant load in tank 2 with unknown inlet

Analytic conditions

- TDS:
 - Starting temperature: 5 °C
 - Heating rate: 60 °C/min
 - Final temperature: 240 °C
 - Final retention time: 5 minutes
- Purge flow: 100 ml/min
- CIS 4:
 - Glass evaporator tube with TENAX
 - splitless mode
 - Starting temperature: -100 °C
 - Heating rate: 12 °C/s
 - Final temperature: 240 °C
 - Final retention time: 20 minutes

Volatile Organic Compounds from Adhesives and their Contribution to Indoor Air Problems

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Keywords

Indoor Air Pollution, Thermal Desorption, Adhesives, Floor Coverings, Emissions, Bromophenol

Abstract

Carpets for office use are nowadays in most cases applied with water-based adhesives. During the last decade the complaints about odors and emission of volatile organic compounds from these fitted carpets have increased dramatically, causing a major problem for indoor air quality. In a series of investigations it has been established that in many cases the adhesives used were the primary cause of complaints. This is initially surprising, since usually solvent-free water-based dispersion adhesives were used.

This paper describes the analytical approach of analyzing a broad variety of volatile compounds within a wide boiling point range with thermal desorption GC/MS.

Introduction

In the early 90's, due to a German worker safety regulation (TRGS 610), solvent based adhesives for floorcoverings were changed to water-based dispersions. To realize this change in technology, instead of low boiling solvents such as methanol and toluene high boiling components such as Phenoxy ethanol, miscellaneous glycols and glycolethers were used. These components still do have the function of a solvent, but due to the solvent definition of the regulation (boiling point < 200°C), the adhesives have been declared solvent-free.

These high boiling and polar components have been identified as a major source of problems caused by glued carpets. Due to their low vapor pressure, the high boiling components diffuse only very slowly from the adhesive through the textile floorcovering, but can cause long-term indoor air pollution. Adhesives for textile floorcoverings do not only contain these high boiling components but also other components, such as terpenes or other volatile organic compounds as shown in Table I.

For the analysis of volatile organic compounds in indoor air, various sampling techniques and different adsorbing materials are in use (Figure 1). The sampling strategies depend on the boiling point of the components.

As a common adsorbent, activated charcoal tubes are regularly used for the determination of volatile organic compounds. However, this type of adsorbent is not suitable for the detection of high boiling and polar compounds, such as glycols and glycolethers found in water-based adhesives.

As shown in Figure 2, the use of activated charcoal for the sampling of these components will lead to severely biased analytical results and incomplete information for the interpretation of the indoor air situation.

According to these data, for the determination of volatile organic com-



Figure 3 GERSTEL TDS system with autosampler mounted on 6890 GC with 5973 MSD

ponents from adhesives the adsorption on Tenax TA, in combination with Thermo-desorption and GC/MS analysis is nowadays state of the art (Figure 3: GERSTEL Thermo-desorption system). Only this technique is suitable for the analysis of a broad variety of volatile compounds with a wide range of boiling points and different polarity.

Experimental

Instrumentation. The analytical system consists of a thermal desorption system with autosampler (TDS A, TDS 2, GERSTEL GmbH & Co.KG, Mülheim an der Ruhr, Germany, Figure 3), a temperature programmable vaporization inlet (CIS 4, GERSTEL), a gas chromatograph (6890, Agilent Technologies, Little Falls, USA) and a mass selective detector (5973, Agilent).

Operation. The air samples are drawn on a Tenax TA tube, which is then introduced into the thermal desorption unit and thermally desorbed to release the trapped organic compounds into the cryogenically precooled PTV for subsequent GC/MS analysis.

Results and Discussion

As shown above, these high boiling and polar compo-

| Adsorbents | Suitable Compounds | Unsuitable Compounds | Desorption |
|------------------|---|-----------------------------------|-----------------|
| Activated Carbon | Aromatics Aliphatics Terpenes | Glycol Ethers Polars (Phenols) | Carbonbisulfide |
| Silicagel | Polars | Non-Polars | Ethanol |
| Tenax TA | Compounds of a wide boiling point range with different polarities | Boiling points below 60°C | Thermal |

Analysis conditions

| | |
|-------------------|--|
| Tube | Tenax TA, 60/80 mesh, 160 mg |
| Column | 30 m HP VOC (Agilent), $d_i = 0.2$ mm, $d_f = 1.1$ μ m |
| Pneumatics | He, $P_i = 170$ kPa, constant pressure TDS-desorption flow = 50 ml/min (splitless) PTV-splitflow = 50 ml/min |
| TDS | 10°C (2 min), 30°C/min, 250°C, 40°C/min, 300°C (6 min) |
| PTV | -150°C (1 min), 8°C/s, 250°C, 10°C/s, 320°C (6 min) |
| Oven | 35°C (2 min), 25°C/min, 70°C, 6°C/min, 150°C, 10°C/min, 280°C (20 min) |
| Detector | MSD, 230°C / 150°C, Scan 34-450 amu |

Figure 2

Comparison of different adsorbents for indoor air analysis

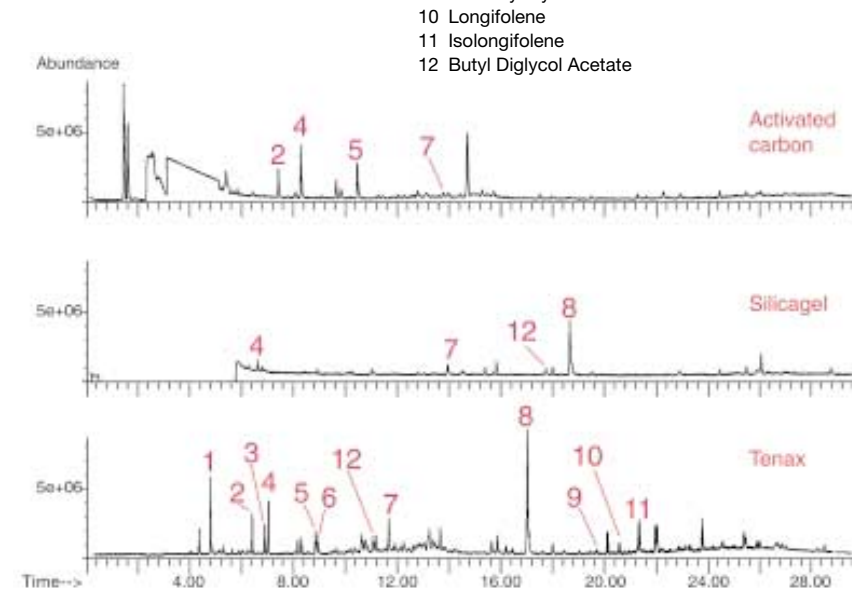


Figure 1
Boiling point range of VOC's and applicable adsorbents

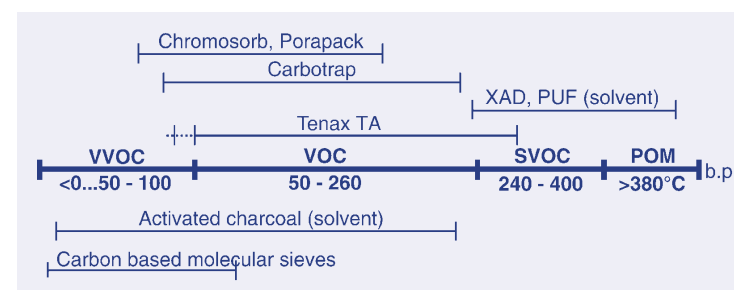


Table I

Volatile organic compounds from water-based dispersion adhesives

| | Compound | Source |
|---------------|---|-----------------------------|
| Terpenes | Pinene Limonene Carene Longifolene Isolongifolene | Colophony Resin |
| Glycol Ethers | Butyldiglycol Butyldiglycol Acetate Phenoxy Ethanol Phenoxy Propanol | Soft Resins and Solubilizer |
| Alcohols | 2-Ethyl Hexanol | Emulgators and Defoamers |
| Esters | Acrylic Acid Esters | Acrylic Resins |

Table II

Comparison of different adsorbents and their suitability for different compound classes

Table III

Analysis conditions

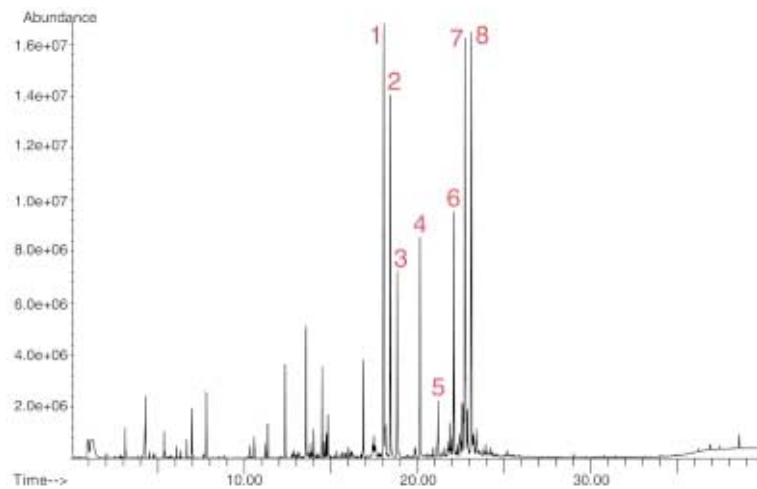


Figure 4
Adhesive after
7 days

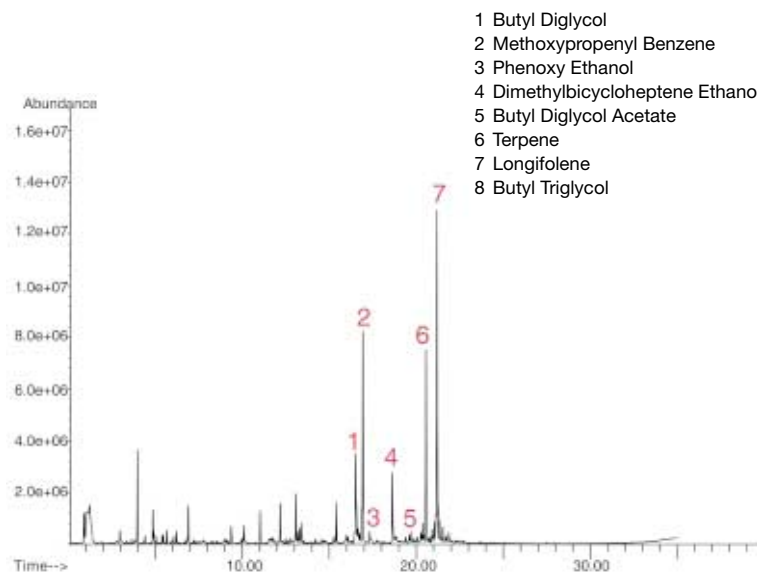


Figure 5
Adhesively fitted
carpet after 7 days

nents are not only difficult to detect, but can also influence the ambient indoor air to a great extent. Compared to low boiling solvents, these chemicals tend to migrate slowly out of the adhesive into the textile floorcovering and will furthermore lead to ongoing emissions of the material. Figure 4 shows a chromatogram of an air sample taken in a test chamber above a pure adhesive in comparison to one of a fitted carpet containing the same adhesive after 7 days (Figure 5).

Another experiment is shown in Figure 6. For the determination of long-term emissions from adhesives (prediction for real rooms), a chamber measurement has been performed over 100 days. A carpet, glued on a glass plate was measured for this long

Figure 6
Long-term
emission (TVOC)
of a glued carpet
in a test chamber

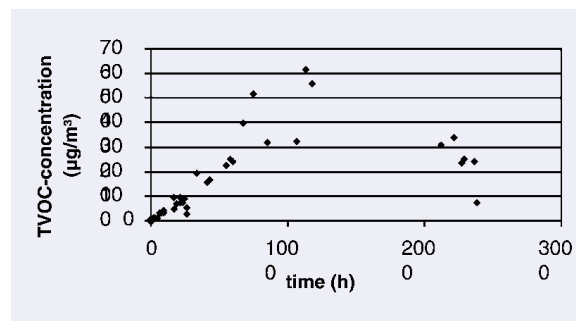


Figure 7
Test chamber



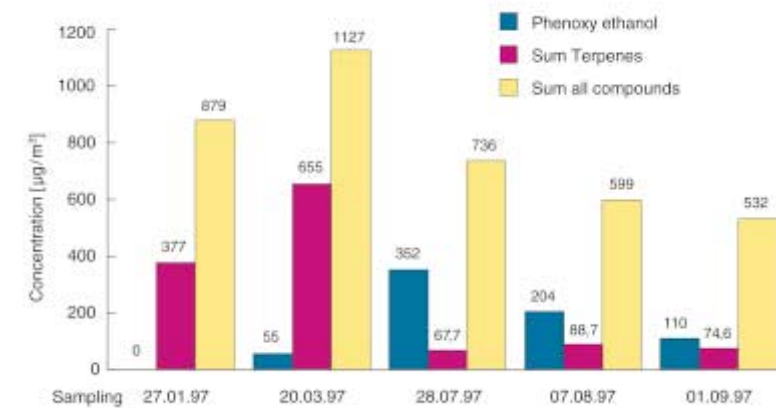
period of time in a test chamber (Figure 7) to obtain more information concerning the long-term emission behavior of glycols and glycol ethers.

An actual situation similar to the test chamber compounds, has lead to a long lasting emission of volatile components into the indoor air. As shown in Figure 8 in a real room situation these high-boiling components, such as phenoxy ethanol, do not appear immediately, but instead after a period of time after installation. In this particular case, the office had to be renovated after nine months due to the complaints of the users and according to the emission data.

Another example shows that air analysis alone does not necessarily solve indoor air odor problems. In this case an extremely annoying bad smell was reported in an office room. Indoor air analysis resulted in the detection of bromophenol (Figure 9), but neither the floor covering nor the adhesive contained even traces of this compound. The combination of carpet and adhesive led to the formation of bromophenol and placing a piece of carpet (with the

Figure 8

Real room
situation in a
newly
constructed
office building



adhesive applied) in the thermal desorption unit and performing thermal extraction could reproduce the bad smell.

Figure 10 shows the mechanism of formation: phenoxy propanol (from the adhesive) is hydrolyzed to phenol, which itself reacts with inorganic bromide (from the latex back of the textile covering) forming bromophenol.

Conclusions

Volatile organic components from water-based adhesives have a major influence on the indoor air quality. Due to the use of high-boiling and polar compounds, the impact of the problem has been shifted from the installation process to the consumer or inhabitant of the office. The emissions of these compounds are a major problem of indoor air pollution. As shown in this paper, the influence of adhesive components on the long-term emission is substantial and by using the wrong analytical technique the true magnitude of the problem for the indoor air situation can be severely underestimated.

After having learned about the situation, a new testing scheme for the long-term emission of adhesives was developed by the association of adhesive manufacturers and the association of environmentally friendly carpets.

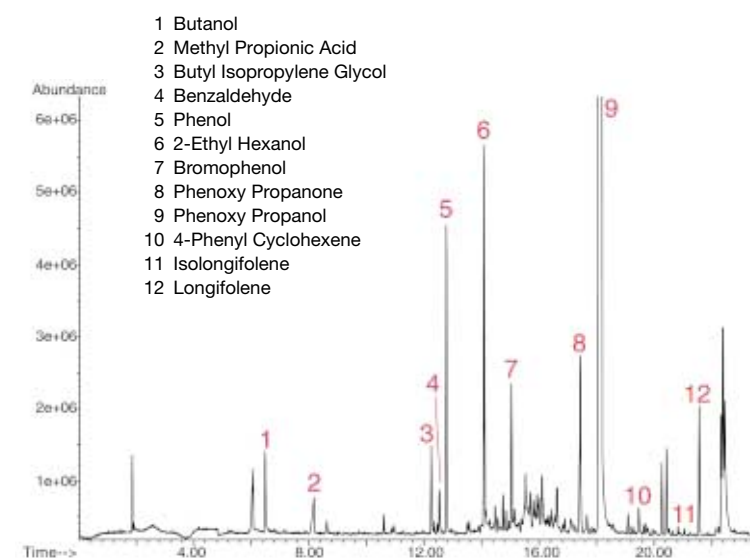


Figure 9
Direct thermal
extraction of
carpet material
and an adhesive

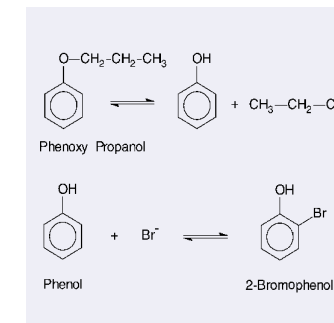


Figure 10 Mechanism of
formation of bromophenol



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Our man in Asia: Dr. Fred Schwarzer



**Dr. Fred
Schwarzer**

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