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MPS 2 with Automated Liner EXchange (ALEX)

Sample Preparation by mouse-click

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Emission testing

GERSTEL TDS hunts down hidden office pollutants



Fast capillary GC

GERSTEL MACH analyzes C₅ - C₄₄ in less than 1.5 minutes



GERSTEL Twister

Efficient multi-residue analysis of Endocrine Disrupting Chemicals (EDCs) in drinking water



GERSTEL TDS hunts down hidden office pollutants

* www.blauer-engel.de



Printers and copiers emit volatile organic compounds (VOCs); some, mainly older models, generate ozone. VOCs and ozone form a reactive cocktail that can bring tears to anyone's eyes in the office – in addition to causing wheezing, coughing and general irritation of mucus membranes. Recently, changes were made to the requirements for obtaining “Der Blaue Engel” (The Blue Angel) – the German environmental label. Copiers and printers must now meet emission standards for a whole list of VOCs that can heavily influence indoor air quality. While testing printers and copiers, the German Federal Institute of Materials Research and Testing (BAM) recently found an unexpected source of semi-volatile organic compounds (SVOCs): Recycled paper! Kaj Petersen reports.

Well done to all those printers and copiers with very low emissions of chemicals – they've really earned the German environmental seal of approval: “Der Blaue Engel” (The Blue Angel). Recycled paper also can be given the “Blue Angel” label for being environmentally friendly if it meets test criteria specified in the German regulations for recycled paper RAL-UZ 14.

A brief search of the internet confirms that the Blue Angel has been awarded to a staggering 212 types of recycled paper for various uses including copying and printing. However, printers, copiers and

multi-purpose office machines that currently wear the Blue Angel badge of honor are barely mentioned. Here's why.

At the beginning of 2004, new test criteria came into force for printers and copiers. According to the German Federal Environmental Ministry, it is no longer sufficient just to test for ozone, dust and styrene emissions. As of late, testing includes how much benzene and other volatile organic compounds (VOCs) these machines emit into their environment during operation. Based on an article released by the German Federal Institute of Materials Research and Testing (BAM),

the question arises whether current test criteria for granting the Blue Angel for recycled paper are adequate, or if they are due for revision as is the case for printers and copiers.

Thermal Desorption using the GERSTEL TDS led to the discovery

While performing emissions testing using environmental test chambers, the BAM scientists came across not only VOCs emitted from laser printers and copiers, but also large amounts of semi-volatile organic compounds (SVOCs) that were not emitted from the machines themselves. Further detailed testing revealed the source of the emissions: The recycled paper being used.

The analytical method used for emissions testing of printers and copiers is based on the Standard Method 328 from the European Computer Manufacturers Association (ECMA). The ECMA 328 method was developed to measure VOC emissions from electronic and semiconductor products in order to determine the impact of such products on indoor air. A GERSTEL Thermal Desorption System (TDS) in combination with a GERSTEL Cooled Injection System (CIS) is required in order to comply with the ECMA 328 method parameters.

Official documentation in English is available from BAM for the Blue Angel test-method for printers and copiers: Text 88/03; ISSN 0722 186X
 "Development of a test method for an investigation into limiting the emissions from printers and copiers within the framework of assigning the environmental label". The official test method is included: "Test Method for the determination of emissions from hardcopy devices with respect to awarding the environmental label for office devices RAL-UZ 62, RAL-UZ 85 and RAL-UZ 114. (BAM, June 2003)". Further information:
 Werbung und Vertrieb, Wolframstraße 95-96, 12105 Berlin, Germany, fax: +49 30 218 13 79; E-mail: berlin@wundv.com.

To track down the source of SVOC emissions from the recycled paper, the BAM scientists relied on the GERSTEL TDS 2 and direct thermal extraction inside the TDS tube.

The paper was cut into strips that were placed inside TDS tubes and subsequently thermally extracted. The tubes were heated to 180°C inside the TDS 2 in a flow of inert gas that is used to transfer extracted VOCs and SVOCs to the GC for analysis. The desorption temperature was set at 180°C since this is the temperature used for toner fixation in laser printers and copiers.

An efficient and inexpensive alternative to environmental test chambers

As emission measurements of various solids have already shown (see page 4), direct thermal extraction leads to results comparable to those coming from environmental test chambers under properly controlled conditions.

The main difference is that emissions can be determined much more easily – and much less expensively – using direct thermal extraction. Using the TDS to determine materials emissions requires only small amounts of sample (approximately 5-12 mg).

The sample to be analyzed is placed inside the TDS tube, which is then transferred to the GERSTEL TDS 2. Thermal extraction takes place by heating the tube and sample inside the TDS 2 in a flow of inert carrier gas. Emitted analytes are swept from the TDS to the GERSTEL CIS 4, where they are concentrated prior to GC/MS analysis. Following the thermal extraction and concentration step, the CIS 4 is rapidly heated and analytes are transferred to the GC column for separa-

tion and mass spectrometric (MS) detection. Using this method, emitted organic compounds are easily identified and quantified.

When the BAM scientists analyzed the recycled paper, they found not only VOCs, but also SVOCs, including isopropyl laurate – an ink binding agent – and isopropyl naphthalene.

According to the scientists, these chemicals are probably residues of printing inks applied to the original recycled paper.

However, not only was the presence of SVOCs surprising, but also the amount: Depending on the printer or copier, up to ten times more SVOCs than VOCs were emitted.

A further aspect: Modern printers may produce little or no ozone, but many offices still have older equipment. Ozone reacts readily with unsaturated organic compounds to form free radicals that are known to irritate the eyes and respiratory tract even at low concentrations.

Reduce the temperature of the printing process or get rid of the chemicals

Perhaps one should not be overly concerned, but the BAM scientists still believe the emission of SVOCs from printing and copying with recycled paper needs monitoring.

The scientists have the following suggestions: Inks and toners should be developed that enable fixation to take place at lower temperatures. In addition, only printing inks should be used that can easily be removed from paper in the recycling process.

Questions still remain about what to do with recycled papers that have already been awarded the Blue Angel label. Should these be allowed to keep their stamp of approval in spite of these new findings, or should the supposedly environmentally friendly paper share the same fate as printers and copiers and be sent back to the environmental test bench?

The environmental labelling agency will have to come up with an answer. It is safe to say that if the rules for awarding the Blue Angel are tightened, then direct thermal extraction using the GERSTEL TDS will enable the efficient and sensitive determination of VOC and SVOC emissions according to the new regulations.

The TDS is a proven tool for determining emissions from not only paper, as in this case, but also from solid materials in general and from viscous samples such as sealants and glues.

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Kaj Petersen
 Marketing Manager,
 GERSTEL GmbH & Co. KG.

Direct thermal extraction vs. emission test chambers

Fast and reliable determination of emissions from carpet adhesives

Upholstery, carpeting, adhesives, sealants, paints and various building materials can contain and emit volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), which impact indoor air quality and can contribute to “sick building syndrome” (SBS).

SBS is a term used when bad indoor air quality leads to health problems or even illness among occupants. In order to test materials used inside our homes and workplaces, their VOC and SVOC emissions are determined using an emission test chamber under controlled conditions. Direct thermal extraction with the GERSTEL Thermal Desorption System (TDS) leads to comparable results, as testing of carpet adhesives shows.

Authors

Olaf Wilke Ph.D., Oliver Jahn Ph.D. and Doris Brödner, Federal Institute for Materials Research and Testing (BAM), Germany

lium) to simulate test chamber conditions. Determination of the analytes is performed by GC/MS.

Emission Test Chamber

The Emission test chambers used for analysis of the adhesives comply with the European standard EN 13419-1.

The operating temperature was kept at $23 \pm 0.5^\circ\text{C}$, the relative humidity

$50 \pm 3 \%$ and the area-specific air flow rate set to $q = 1.25 \text{ m}^3/\text{m}^2 \text{ h}$ (loading $0.4 \text{ m}^2/\text{m}^3$, air exchange 0.5 h^{-1}).

Chamber air sampling

Air sampling from the test chamber was performed using GERSTEL TDS glass tubes (length 178 mm, outside diameter 6 mm, inside diameter 4 mm), filled with Tenax TA (200 mg, 60/80 MESH) mounted with plugs of deactivated glass wool. Between 1 and 2 L of chamber air was sampled at a flow of 100 mL/min.

Just before the sample was drawn, the glass wool was spiked with $1 \mu\text{L}$ internal standard containing cyclodecane in methanol. For calibration, a blank tube was spiked with $1 \mu\text{L}$ of a standard mixture in methanol. After adding the internal

Figure 1
Loading a 1 m^3
test chamber
with adhesive on
glass plates



Figure 2
GERSTEL TDS 3
and TDS A with
samples for
direct thermal
extraction

Emission testing of materials is generally performed in test chambers. An emission profile is generated over a period of 28 days under well-defined conditions. This process is time-consuming and extremely costly. The process can be simulated by direct thermal extraction: A large number of extractions are performed in a much smaller volume and over a much shorter period of time.

Thermal extraction is an extremely efficient method for determining the emission potential of a material or product, for example, in the development phase. To perform a thermal extraction determination using the GERSTEL TDS, only 5 to 20 mg sample is required. The sample is introduced into a TDS glass tube and then heated to the specified temperature in a controlled gas flow (he-

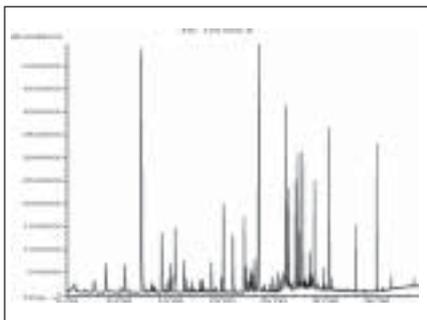
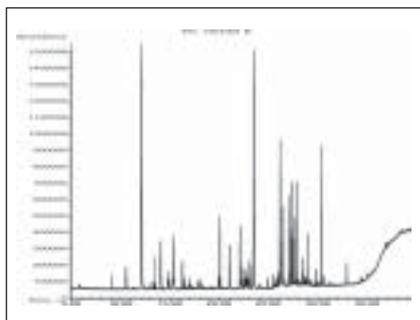


Figure 3 Chromatograms from test chamber air analysis after 24 hours (left) and from direct thermal extraction analysis after 1 h (right)



standard, 1 L of clean air from an empty emission test chamber was drawn through the tube to purge out the methanol.

Analysis of the Chamber Air

The analysis was performed by thermal desorption GC/MS using a TDS 2 coupled to a GC 5890 II Plus / MSD 5972 GC/MS system. The thermal desorption conditions were: Heating from 40°C to 280°C at 40°C/min, hold time 5 minutes at 280°C. Cryofocussing at -150°C in the GERSTEL Cooled Injection System (CIS 3). Helium desorption flow 20 mL/min. Following tube desorption, the CIS 3 was heated to 280°C at a rate of 12°C/s in splitless mode to transfer the analytes to the GC column. A Restek Rtx-200 column was used, length 30 m, film thickness 1 µm, i.d. 0.25 mm.

Direct Thermal Extraction

Using a spatula, the adhesives were applied to aluminum foil between two adhesive strips, which were used to get a defined film thickness.

After 1 hour of drying, a small strip (3 mm x 20 mm) with 5-10 mg of adhesive was cut out and transferred to an empty glass TDS tube. Thermal extraction was performed at 23°C for 12.5 minutes under a helium flow of 20 mL/min. Multiple thermal extractions were performed by repeating the extraction at the end of each GC run, enabling a rate of one extraction per hour.

Between extractions, the glass tube containing the adhesive was sealed airtight by the GERSTEL TDS A autosampler (Fig. 2). The only difference in analysis parameters from the chamber air analysis is that the TDS 2 temperature is kept constant at 23°C for thermal extraction.

Results

The chromatograms in Figure 4 show that direct thermal extraction and test chamber measurements for flooring adhesives yield comparable results. Chromatograms obtained with the two methods show the same compounds and peak pattern. Our results also show that multiple thermal extraction can simulate the long term emission behavior of a material measured in a test chamber.

Discussion

The method of direct thermal extraction was first used at higher temperatures (up to 200°C) as a screening tool for VOC and SVOC emissions from building products. The results for flooring adhesives show that keeping the temperature at 23°C, as in the chamber experiments, gives a good correlation to the chamber measurements.

The differences between test chamber measurement and direct thermal extraction using a TDS are the gas used, the different specific flow rate (q) and the mass of the applied adhesive. In the chambers, humidified air is used with $q = 1.25 \text{ m}^3/\text{m}^2 \text{ h}$ and $300 \text{ g}/\text{m}^2$ adhesive applied. For direct thermal extraction, helium is used with $q = 20 \text{ m}^3/\text{m}^2 \text{ h}$ with $100 \text{ g}/\text{m}^2$ adhesive applied. These parameters are compensated by using different test times: 1 hour after application for thermal extraction, 24 hours after application for chamber measurements. Using the TDS for direct thermal extraction analysis of inhomogeneous or thick materials such as floor coverings showed no such correlation to test chamber measurements. When using 4 mm i.d. tubes for thermal extraction, test conditions such as emitting surfaces and edges are too different. For inhomogeneous or thicker materials, we will test the GERSTEL Thermal Extractor TE 2 with its larger 14 mm i.d. extraction tube.



Toyota uses GERSTEL TE 2 for materials emission testing

When leading automobile manufacturers and their suppliers world-wide perform materials emission testing, they turn to a method from the German association of car manufacturers (VDA). Before a material is accepted for use in a car interior, it is tested for emission of volatile organic compounds (VOCs) as well as for emission of organic compounds in the boiling point range corresponding to the range from n-C₁₆ to n-C₃₂.

The amount of higher-boiling compounds in a material is expressed in a so-called fog-value, a name derived from condensation of these compounds forming a film on the windshield (fogging).

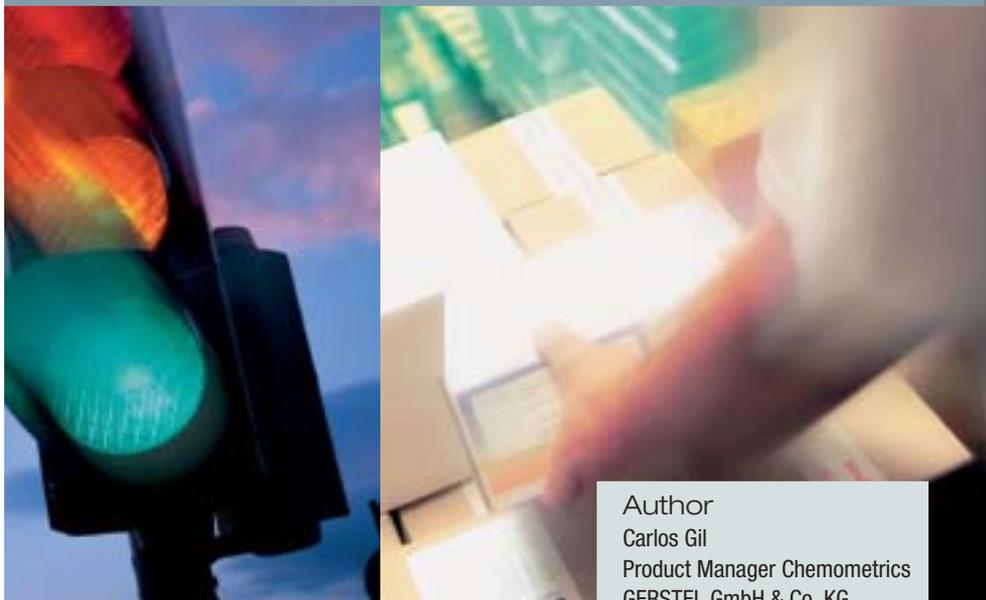
The VDA 278 method describes the "thermal desorption analysis of organic emissions for the characterization of non-metallic materials used in automobiles".

The method is based on the use of the GERSTEL Thermal Desorption System (TDS 2) that incorporates the GERSTEL Cooled Injection System (CIS 4) as well as a twenty position autosampler.

TDS tubes, which are used for the VDA 278 method, have an internal diameter of 4 mm. Sample size is thus limited, making it difficult to analyze representative samples of foams, molded plastics and inhomogeneous materials.

Toyota has now optimized the VDA 278 method for larger samples by using the GERSTEL Thermal Extractor (TE 2) with its larger inner tube for the thermal extraction step. Thanks to the larger internal diameter of its extraction tube, the GERSTEL TE 2 facilitates direct thermal extraction of a representative sample amount.

Thermal extraction is performed at temperatures that could be encountered in your car interior when parked in direct sunlight on a warm summer's day.



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**Yes/no. Good/ bad:
 Chemometrics offer efficient
 evaluation and classification of chromatograms.**

When you need a fast decision

You are faced with a substantial number of chromatograms, and want to know which ones fall into certain classes, for example good or bad, ship or hold. What do you do? Normally, you would download the data to your chromatography data handling software, generate a peak area report for each chromatogram, and begin the process of comparing the reports - a laborious and tedious process. The exploratory analysis of reduced data could make your work significantly easier.

Chromatography data analysis is normally performed based on the peak areas of identified compounds or on area percent reports. Especially in the case of complex chromatograms, evaluation and classification becomes a difficult and time-consuming exercise that requires highly qualified and experienced personnel. There are alternatives, however, especially when quick decisions are needed, for determining whether a sample is good or bad or whether it can be shipped, yes or no.

Chemometric analysis using pattern recognition algorithms can provide clear answers quickly and easily. The data

analysis procedure can be fully automated. Chromatograms and/or mass spectra of samples are subjected to a sophisticated screening process and only outliers subsequently need to be evaluated in the traditional way.

GERSTEL offers chemometrics software packages – either within the scope of a complete analytical solution package, or as a retrofit for existing systems.

GERSTEL co-operates with Infomatrix, one of the leading developers of chemometric software, as well as with Agilent Technologies, a leading manufacturer of analytical systems.

Complete Solution Packages: The GERSTEL ChemSensor Systems

The product family of the GERSTEL ChemSensors is far superior to conventional electronic noses. By coupling an autosampler directly to a mass spectrometer, a highly flexible analytical system is produced with a large number of fully independent sensors: every detected variable (m/z) is equivalent to the sensor of a conventional electronic nose. Apart from this, the ChemSensor offers the user the possibility of correlating both GC/MS data and their chemometric evaluation.

The principle of chemometric evaluation is based on reducing 3-dimensional data (intensity, fragment m/z and retention time) acquired with the mass-selective detector (MSD) to two dimensions. This means that either the total combined mass spectrum of the sample over the course of the analysis, also called the fingerprint mass spectrum (intensity vs. m/z) or the total ion current chromatogram (TIC intensity vs. retention time) is used.

ChemSensor: Fingerprint Mass Spectrum without GC Separation

The ChemSensor is the MS-only configuration. It comes with an interface through which samples can be directly injected into the MSD – without chromatographic separation. The injection is done via the GERSTEL Cooled Injection System (CIS 4 Plus), which can be operated in split and splitless modes using various injection techniques. In combination with the GERSTEL MultiPurpose Sampler (MPS 2) (cf. pp 14-15), either headspace injection or solid phase microextraction (SPME) can be applied.

As compounds are not separated, retention times are irrelevant. The influence of retention time is removed from the data by summing up the intensities of m/z value over the complete time period of the run. The evaluation is performed based on fingerprint mass spectra.

ChemSensor System: Fingerprint Mass Spectrum plus GC Separation

The ChemSensor System consists of a GC coupled with a Mass Spectrometer. The sample is injected via a conventional GC, not through the ChemSensor inter-

face. The ChemSensor system can be operated both as a ChemSensor and as a conventional GC/MS system with free choice of the injection technique. The system is extremely flexible: During ChemSensor operation, the column is mainly kept isothermal (hot) and serves as a transfer capillary. Samples identified as outliers can be investigated further by performing a full GC/MS analysis using the system in exactly the same configuration. For ChemSensor operation, chromatographic separation is irrelevant, and analyte retention is minimal. The aim is to reduce analysis time and increase sample throughput. Chromatograms, though, are helpful for closer investigation of outliers.

If a GC separation is performed, the ChemSensor software can be used to evaluate both the fingerprint mass spectrum and the total ion chromatogram (TIC) profile. The TIC profile shows the total intensity of all fragments as a function of the retention time.

Pirouette Software for Chemometric Analysis

Regardless of how the user reduces the data (intensity vs. m/z or TIC intensity vs. retention time), the result is a two-dimensional matrix. Using the Pirouette Software, the data can be depicted as a line plot and normalised.

Chemometric analysis is based on linear combinations of the original variables (m/z values or retention times). The data is listed in the columns of the data tables. The first step after visualizing the data is an exploratory analysis employing two algorithms: hierarchical cluster analysis (HCA) and principal component analysis (PCA).

The aim is to identify groups within the data, and to determine whether classifications can be established. PCA searches simultaneously for correlations between all variables, and extracts linear combinations of strongly correlated variables, the so-called principal components, which describe the main variability of the sample. The PCA Scores Plot (Figure 1) shows quickly and simply which samples are similar and which fall outside the pattern.

In parallel to the exploratory analysis, two further algorithms are used to construct the classification models and assign unknown samples to the groups: K Nearest Neighbors (KNN) and the so-



GERSTEL ChemSensor System

called SIMCA (Soft Independent Modeling of Class Analogy) algorithms.

KNN classifies unknown samples depending on their proximity to samples already assigned to categories (classes), whereas SIMCA uses principal component analysis (PCA) to model the position and distribution of the samples. Classifications of this type can be automated with the ChemSensor software.

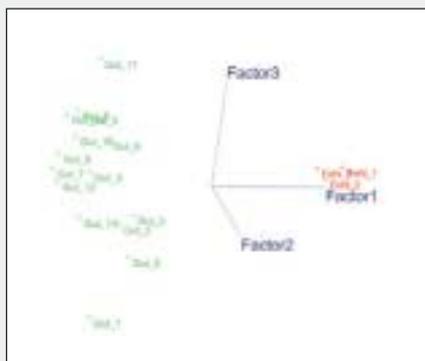


Figure 1 PCA Scores Plot

Rapid Data Interpretation

For existing Agilent GC/MS systems, the Rapid Data Interpretation Software is a convenient add-on tool that implements many ChemSensor features. Its main application is to search datasets for outliers or to investigate the natural grouping of samples based on the fingerprint mass spectrum or on the TIC profile. A Pirouette Lite Explore software is included, comprising the HCA and PCA algorithms.

Chemometric Analysis of GC and LC Data from non-MS detectors

GC and LC data based on detectors other than mass spectrometric can also be analyzed and classified using automated chemometric analysis. The analysis can be based on either a peak table or raw data (intensity vs. retention time). When using raw data, which is normally acquired at a high sampling rate, it is advisable to reduce the number of data-points (bunching).

GC and LC Retention Time Correction

Concentration differences, ageing of the column and changes in carrier gas flow are factors that can cause a shift in retention time. To compensate for this, the Agilent Technologies Retention Time Locking (RTL) software can be employed. Alternatively, the new InfoMetrix LineUp software, Version 2.0 can perform purely software-based corrections. The software uses a multivariate correlation method to shift and align the retention time axis of a chromatogram with a reference chromatogram. LineUp supports various file formats, for instance Agilent ChemStation (*.CH files) and AIA data interchange format (*.CDF files). In combination with the ChemStation, this process can be automated.

Modular Accelerated Column Heater for fast Capillary GC

Analyze C₅ – C₄₄ in less than 1.5 minutes

Increased efficiency, increased sample throughput, lower operating expenses – there are many reasons why GC labs invest in new technology. Often this requires a sizeable investment, which can be a stumbling block in itself – but that doesn't have to be the case – as the following report demonstrates.

In addition to financial aspects, changes in laboratory equipment and techniques often involve worrying about parting with established methods and investing valuable energy into developing and validating new methods. Such changes need not be of great concern to users of Agilent Technologies 6890 GCs, says Ralf Bremer, general manager of GERSTEL GmbH & Co. KG in Mülheim an der Ruhr, Germany.

GERSTEL offers its customers a new heating module that is quickly retro-fitted to the 6890 GC, increasing the efficiency of the system and cutting operating costs at the same time. The analytical method is left almost unchanged, ensuring a smooth transition. The Modular Accelerated Column Heater (MACH) significantly increases sample throughput while requiring only 1% of the power needed to operate a conventional GC oven in temperature-programmed mode.

Separation of a mixture of hydrocarbons covering a wide boiling-range from n-C₅ to n-C₄₄- alkanes is performed in as little as 1.5 minutes. Rather than develop-

ing all new GC methods, the user just has to perform slight modifications. No new injector or detector is needed. "The only thing the user has to get used to", says Bremer "is the speed at which the GC system gets ready for the next analysis".

MACH was developed by RVM Scientific Inc., located in the United States. MACH is based on LTM technology, as Robert Mustacich Ph.D. of RVM explains. The acronym LTM stands for Low Thermal Mass, a term which aptly describes why the module temperature can quickly be changed using very little energy.

The module contains almost no insulation material or void volumes which would have to be heated or cooled over the course of a temperature program. "No energy is wasted, the module heats and cools extremely fast and is quickly ready for the next analysis", says Mustacich.

"The concept of the MACH heating module is quite simple: A heating wire and a sensor wire run parallel to the entire capillary column. The temperature is measured over the entire length of the column and a thin ceramic insulation



Figure 1. MACH GC Module based on Low Thermal Mass (LTM) technology (covers removed); Inside, the specially packaged column can be seen along with the heated transfer line connectors and high-temperature interface. The 3.5" Floppy Disk is shown for size comparison.

layer prevents short circuits in the heating wire, ensuring an even temperature profile over the complete length of the column", explains Mustacich.

"The column and heating-wires are wound together in a coil and wrapped tightly with metal foil. In essence, LTM technology is a kind of repackaging method, realized within the smallest space. The use of energy for heating and cooling is reduced to a minimum, and the heating/cooling speeds are increased to a maximum – at the same time making sure that all commercially available capillary columns of any length can be used", says Mustacich.

“The spatial construction of the LTM-system is far more efficient than, for example, two-dimensionally etched tubes in planar substrates”, explains the developer. Due to the low surface area, the heat loss in MACH is negligibly small, which, by the way, is especially noticeable for the user in summer. Mustacich: “Room temperature in the lab is less influenced by MACH GC operation, reducing the need for air conditioning and consequently reducing your utility bills.”

The analysis requires less energy, yet the temperature program runs much faster than in standard gas chromatographs. “The amount of energy needed to heat an 18 m fused silica capillary column with a diameter of 0.32 mm from 40 to 400°C with a ramp rate of 60°C/min is only 23 Watts, i.e. only 1.3 W/m of column”, says Mustacich.

MACH is cooled by ambient air using fans that are mounted in the module below the column. A fused silica column of 2 m length with an inside diameter of 0.10 mm, used for example with GC/Time-of-Flight MS, cools from 350°C to 50°C in 30 seconds, dramatically reducing the cool-down time when compared to a traditional GC instrument. This leads to better productivity and much improved return on investment for the complete system.

Cool-down in an LTM module for a 15 m column with an inside diameter of 0.32 mm from 350°C to 50°C takes 140 seconds. Due to its low thermal mass and fast cool-down, fused silica capillary columns are preferred, but short metal capillary columns with a diameter of 0.53 mm can also be used.

Upgrading an existing GC takes only a few moments

MACH is mounted on the outside of the GC using a special replacement oven door. Mounting on the outside instead of inside the GC oven has distinct advantages, Bremer explains:

“The GC oven can be operated isothermally at the maximum temperature needed for the analysis.” This means that no special steps have to be taken to heat injector and detector connections inside the oven.

The oven door with the integrated control module can be exchanged very quickly. One control module operates up to four MACH column modules, which can be programmed independently of each other, Bremer explains, and continues: “In multi-column applications, the GC separation on each column can be optimized independently without affecting other columns. The user is not forced to work with a single temperature program for all columns.”

Running a MACH analysis is exactly like running a standard GC analysis; there is no difference in how the GC is oper-



Figure 2. Two MACH modules installed in the oven door of an Agilent Technologies 6890 GC.

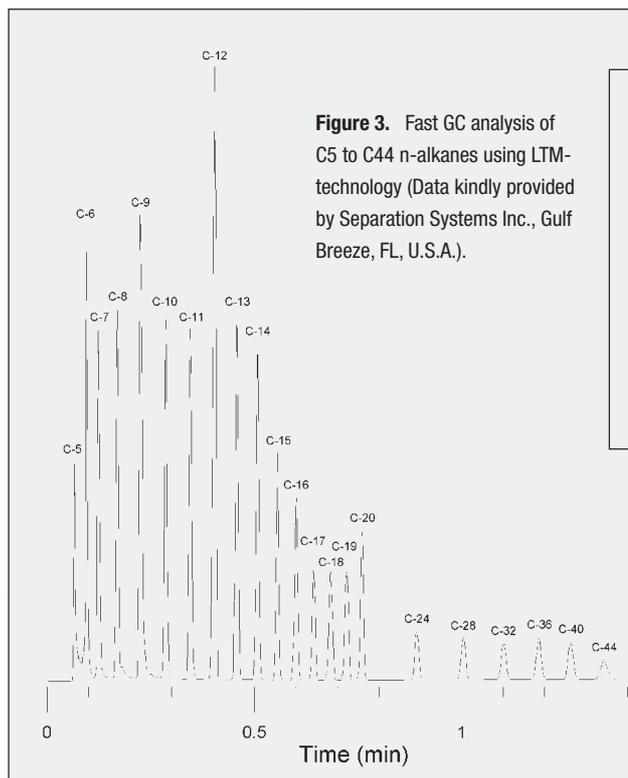


Figure 3. Fast GC analysis of C5 to C44 n-alkanes using LTM-technology (Data kindly provided by Separation Systems Inc., Gulf Breeze, FL, U.S.A.).

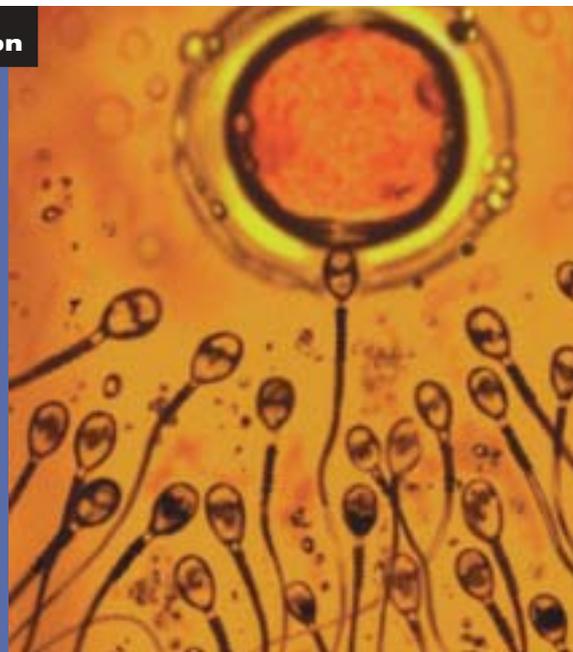
		Retention Time Repeatability for n-Alkanes (%RSD)									
		Ramping Rate	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₂	C ₁₂	C ₁₈	C ₂₀	C ₂₂ *
Conventional GC	30°C/min	0.06	0.05	0.04	0.04	0.03	0.03	0.02	0.02	0.02	0.02
	50°C/min	0.04	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.01	0.03
LTM GC	100°C/min	0.07	0.03	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03
	200°C/min	0.04	0.00	0.00	0.03	0.02	0.00	0.03	0.02	0.03	
	400°C/min	0.06	0.04	0.00	0.02	0.03	0.00	0.02	0.03	0.03	
	800°C/min	0.04	0.03	0.00	0.02	0.03	0.00	0.03	0.03	0.05	
	1200°C/min	0.00	0.00	0.00	0.02	0.00	0.03	0.04	0.02	0.05	

* Peak broad and low in amplitude resulting in uncertainty in apex location

Figure 4. %RSD for Alkane-Retention times comparing the MACH System with an Agilent 6890 GC using the same GC column.

ated. “The system is highly transparent to the host GC, the user can continue to work with the same software, injectors and detectors as before”, says Bremer, and adds: “Everything is comfortably operated from the ChemStation from Agilent Technologies using just one method and just one sequence list.”

Twister provides efficient multi-residue analysis of endocrine disrupting chemicals in drinking water



In the early 1990s a discovery stirred up the scientific community: The quality of human sperm was found to have seriously deteriorated over a period of 50 years. Millions of dollars were subsequently invested in research to determine the causes, with researchers initially focusing on synthetic hormones used in contraceptive pills. Such hormones are excreted in urine and returned to the environment through the sewage system. Soon, another group of chemicals was under scrutiny: Endocrine Disrupting Chemicals (EDCs). EDCs include a wide range of chemicals such as some pesticides, industrial chemicals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and several other types of compounds.

EDCs are suspected of blocking or replicating the functions of natural hormones, with negative impact on reproduction, development and growth in a variety of organisms. Unfortunately, a lot of proof has been found in real-life samples in our environment.

“In sole and codling, PCBs caused atrophy of the ovaries, and reduced fertility in male fish. Similar effects were discovered in mink, otter, beluga whales and in seals”, says Oliver Lerch, Ph.D., application chemist at GERSTEL. Lerch wrote his dissertation on “Automated Detection of Endocrine Disrupting Substances by GC/MS” at the Ruhr University in Bochum, Germany.

While the negative influence of EDCs on wildlife is considered proven, there is little concrete proof of negative effects on humans. Still, reports on infertility, prostate-, testicular-, and breast-cancer, retarded intellectual development in children or premature puberty, point time

and time again to influence of EDCs, which reach us in food and drinking water. Due to the severe consequences, the mere suspicion of a possible threat is considered enough justification for banning suspected EDC type pollutants. Food and drinking water needs to be thoroughly analyzed for traces of EDC compounds. From a list of 553 suspected EDC agents, 300 potential active compounds have been identified.

According to the German Drinking Water Regulation (TrinkW2001), which is based on the EU Drinking Water Regulations (98/83/CE), the maximum allowable concentration for any single EDC compound is 0.10 µg/L and the sum of all EDC compounds is not allowed to exceed 0.50 µg/L.

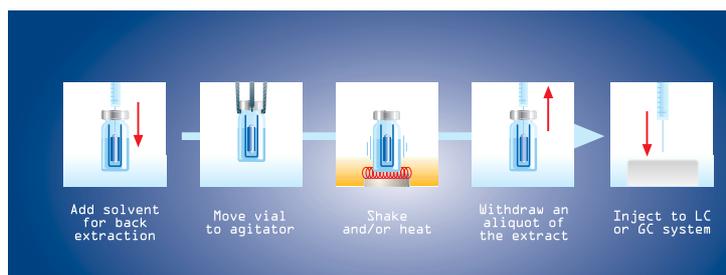
Reliable determination of different EDC classes

Some screening and analytical methods for a limited number of EDCs are available. Analytical laboratories are, of course, looking for efficient multi-residue EDC analytical methods. These need to cover as many target compounds as possible, using only one sample preparation method and one chromatographic

technique. Equally, labs are striving to eliminate or reduce the use of toxic solvents such as acetonitrile for sample preparation.

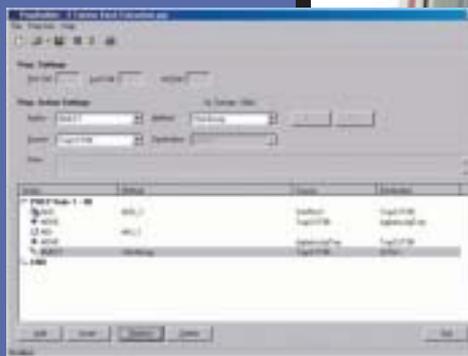
According to Lerch, existing methods for the detection of EDCs are based on solid phase extraction (SPE) or liquid-liquid extraction (LLE) which require relatively large volumes of solvent in the order of 500 to 1000 mL. In addition, the degree of automation of existing methods is limited.

A comprehensive analysis method for EDCs was recently published in ‘Analytica Chimica Acta’ by scientists working with José Manuel Nogueira from the Institute of Chemistry and Biochemistry at the University in Lisbon, Portugal. Relatively small sample volumes (30 mL) were used. Such a volume is easy to handle, even for automated equipment, while offering sufficient detection limits. Sample extraction was performed by SBSE, using the GERSTEL Twister, followed by GC/MS analysis. 60 different EDCs were determined, including herbicides, organophosphate pesticides, polychlorinated biphenyls, phthalates, and alkylphenols.



Twister Back Extraction A solvent is used to desorb analytes from the Twister and subsequently transfer these to the GC or LC for analysis. This technique is used for thermally labile analytes that cannot be thermally desorbed.

Endocrine Disrupting Chemicals (EDCs) have long been suspected of interfering with the hormonal systems of humans and other species. A new multi-residue method based on Stir Bar Sorptive Extraction (SBSE-Twister) allows reliable trace analysis of more than 60 EDCs in drinking water while meeting the requirements of European Union guidelines.



Increased extraction efficiency with SBSE due to the large PDMS volume

SBSE is a relatively new sample preparation method based on the same basic principle as solid phase micro-extraction (SPME). SBSE is especially suitable for quick and reliable detection of trace level organic contaminants in water and other polar matrices. Extraction is performed using a special glass coated magnetic stir bar, the GERSTEL Twister, which is coated with polydimethylsiloxane (PDMS). A major difference between SPME and SBSE lies in the volume of the available PDMS sorption phase: While the SPME fibre has a maximum volume of 0.5 μL PDMS (100 μm film thickness), the Twister is available with between 24 μL and 126 μL PDMS. The larger volume of sorption phase used in SBSE ensures a much better phase ratio for extraction, resulting in better recovery, and up to 250 times better detection limits, (as low as sub-ng/L for many compounds). The Twister stirs the sample during extraction, making the process faster and more efficient. Compared to SPME, larger sample volumes can therefore be efficiently extracted, leading to further lowering of detection limits.

The SBSE sample extraction process is independent of the GC/MS system. Any number of samples can be extracted simultaneously without having to wait for the GC to become ready, ensuring higher sample throughput. For GC/MS analysis, compounds that are absorbed in the PDMS phase of the Twister are transferred directly to the GC column by thermal desorption, enabling quantitative transfer of the extracted compounds to the analytical system, resulting in the

lowest possible detection limits. Thermally labile compounds that cannot be thermally desorbed from the Twister, can be extracted using a liquid solvent. This process is called Twister Back Extraction (TBE) and it can be fully automated using a suitable autosampler. The liquid extract is transferred to a GC/MS system, for example using Large Volume Injection, or to an LC or LC/MS system for analysis.

Efficient monitoring of EDCs using the GERSTEL Twister

Nogueira and his colleagues used Twisters coated with 47 μL PDMS, letting them stir at 750 rpm for 60 minutes at 20°C in the water sample (30 mL). The Twisters were removed from the samples and the absorbed compounds back-extracted with a small amount of acetonitrile. The scientists reported that SBSE coupled with back extraction and GC/MS resulted in "high sensitivity and remarkable reproducibility (<18.4%) when monitoring EDCs at trace levels (0.10 $\mu\text{g/L}$)". Experiments demonstrated excellent linearity in the dynamic range for almost all trace compounds investigated (0.025 – 0.400 $\mu\text{g/L}$).

According to the scientists, the method (SBSE/TBE/CGC-MSD) is an effective, reliable and cost-effective tool for routine analysis of trace amounts of various classes of EDCs in water samples. The EDCs determined include herbicides, organochlorine and organophosphate pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, biocides, phthalates and alkylphenols. The published method meets the requirements of the European Union guidelines for drinking water analysis.



More information on the internet

Original article in *Analytica Chimica Acta*:
 "Multi-residue screening of Endocrine Disrupting Chemicals in water samples by stir bar sorptive extraction-liquid desorption-capillary gas-chromatography-mass spectrometry detection",
 by P. Seródio and J.M.F. Nogueira.
http://www.dqb.fc.ul.pt/docentes/jmfnogueira/jmfn_web/Artigos/ACActa2.pdf

European Commission website information pages on EDCs. (Detailed background information, topical studies):

http://europa.eu.int/comm/environment/endocrine/index_en.htm

U.S Environmental Protection Agency EPA website. Extensive background information on EDCs,
<http://www.epa.gov/ebtpages/pollchemicendocrinedisruptors.html>

Background information on SBSE and the GERSTEL-Twister: http://www.gerstel.de/produkt_twister.htm

Anatune Ltd. – New GERSTEL Distributor in the UK and Ireland

Anatune joined the world-wide network of GERSTEL distributors in 2004 and is now responsible for distribution and support of GERSTEL products in the UK and Ireland.

Anatune is located in Cambridge and was formed in 1995. Specializing in providing analytical solutions to users of GC and GC-MS, the company has had rapid growth. Today, Anatune is the UK market leader in this sector.

As the principal Value Added Reseller for Agilent Technologies in the UK, Anatune uses the Agilent 6890 GC and 5973 MSD for its systems and solutions.

This provides a perfect match when offering complete solutions based on GERSTEL products. For especially demanding applications, the LECO Pegasus III GC-TOFMS or Pegasus 4D GCxGC-TOFMS can also be offered.



Ray Perkins (left) and his team from Anatune



Ray Perkins, Anatune's managing director, describes Anatune's business philosophy as follows: "Our business is centered around the belief that customers don't buy instrumentation – they buy what the instrumentation does. This belief influences everything we do. We focus our attention on the application rather than the hardware. The Anatune application laboratory is very well equipped and staffed with experienced analysts. We work together with customers to devise the best way of tackling analytical problems".

When offered to represent GERSTEL products and solutions, Anatune welcomed the opportunity to complete its product portfolio with GERSTEL sample preparation technology.

"We are now able to offer exciting new techniques such as Stir Bar Sorptive Extraction using the GERSTEL Twister", Ray Perkins says.

While Anatune serves customers in all market sectors, it is particularly strong in water, environmental and food analysis. It is here that a combination of demanding requirements are encountered; large numbers of target compounds, low limits of detection, complex and variable matrices, tight analytical QC requirements, large numbers of samples and constant pressure to reduce cost.

Anatune's approach is to automate as much of the analytical process as possible. Together, Anatune and GERSTEL can now offer analysts in the UK and Ireland new and better ways of doing this.

Bob Green, Anatune's Sales and Service Manager comments: "I think it is fair to say that the high quality of support that Anatune offers its customers, both pre and post sale, is a significant factor in our success. We are keen to further strengthen our offering based on GERSTEL Sample Prep technology".

For information about Anatune and its range of products and solutions, please visit: www.anatune.co.uk.

Diane Turner working with a GERSTEL MPS 2 in Anatune's Cambridge Laboratory

GERSTEL and RVM - Scientific Form Fast GC Partnership

GERSTEL and RVM Scientific, Inc., USA, have formed a partnership to develop, market, and distribute products that provide fast gas chromatography capabilities. Core products include low thermal mass GC column modules that incorporate direct resistive heating and integrated temperature sensing rather than convection oven heating.

For example, the new Modular Accelerated Column Heater (MACH) module incorporates low-thermal-mass (LTM) technology, direct resistive heating and integrated temperature sensing. MACH modules provide fast temperature ramping and fast cooling, ensuring high throughput, even for complex samples.

MACH is based on standard capillary column technology, so that existing analysis methods can be directly transferred and accelerated. Modules are externally mounted onto an Agilent 6890 GC, providing a simple and cost-effective upgrade. The complete system is controlled through the Agilent ChemStation software.

Up to four independently controlled MACH modules can be mounted on one GC for efficient multidimensional GC analysis or for independent dual-column confirmation methods. GERSTEL will provide value-added product and applications development, including integrated software, multidimensional GC capabilities, and multi-column confirmatory analysis capabilities. GERSTEL will further provide sales and distribution channels throughout the world.



Opening ceremony GERSTEL management (middle), seated with senior management of the joint venture partner AMR Inc., celebrating the GERSTEL K.K. opening in Tokyo



Dr. Fred Schwarzer

An important milestone in GERSTEL's world-wide expansion

GERSTEL K.K. established in Japan

Six years ago, Fred Schwarzer moved from Germany to Japan for GERSTEL. The mission: "To support GERSTEL partner Yokogawa Analytical Systems, Inc. and help establish GERSTEL in the Japanese market." Because of his efforts, GERSTEL is now well established in Japan, and the software expert and Ph.D. food chemist recently returned to Germany to fill the position of Software Development Manager at GERSTEL's headquarters.

Dr. Schwarzer's work in Japan and the cooperation with Yokogawa has been extremely successful. In fact, so successful that, GERSTEL management recently visited the land of the rising sun for

the official opening of GERSTEL's third subsidiary, GERSTEL K.K.

GERSTEL K.K. has been established in Tokyo as a joint venture with the Japanese company AMR. Eight employees cover the fields of service, applications support and marketing. The GERSTEL K.K. application laboratory develops customer applications and analysis methodology for the Japanese market.

GERSTEL has succeeded in obtaining the services of Hirooki Kanda as director of the Japanese subsidiary. Mr. Kanda was previously responsible for Japan-wide sales of Gas Phase products for Agilent Technologies, covered by more than 100 sales representatives.



Hirooki Kanda



200 installed TDS systems in Japan: Hirooki Kanada congratulates the satisfied customer, Nissan Arc Ltd., Nissan Analysis and Research Center, presenting a gift from GERSTEL to Laboratory Engineer Ms. Hiroko Saito.

250th TDS installed in Japan

In the summer of 2004, GERSTEL K.K. reached an important milestone. The GERSTEL subsidiary installed Thermal Desorption System (TDS) number 200 in Japan at the Nissan Analysis and Research Center, Nissan Arc Ltd., a key customer of GERSTEL. Representatives of GERSTEL K.K. and the local distributors visited Mr. Hiroyuki Koyama and his staff at the Nissan Arc Organic Analysis Section. Mr. Hirooki Kanda, General manager of GERSTEL K.K., presented employees of Nissan Arc with a gift to celebrate the occasion. Meanwhile, GERSTEL K.K. has passed yet another milestone by selling TDS number 250.



Shoulder to shoulder: Representatives of GERSTEL K.K. and GERSTEL distributors in Japan join Mr. Hiroyuki Koyama (standing second from right) and his staff at the Organic Analysis Section. Further cooperation projects are planned.

Efficient automated sample prep and sample introduction

Optimized automated GC analysis

Atlanta / USA, Mülheim an der Ruhr / Germany: The US Centers for Disease Control and Prevention (CDC), have placed an order with GERSTEL worth 3.2 million USD.

The order entails the delivery of more than 40 GERSTEL PrepStations for fully automated determination of potentially toxic substances in a variety of samples. The PrepStation consists of two Multi-Purpose Samplers (MPS 2) mounted on top of each other, fully controlled by GERSTEL MASTer Software.



Dr. Hans-Peter Schlegelmilch, imat-uve, Mönchengladbach, Germany: "With the MPS, I can fulfill the many requests from my customers more quickly and flexibly."

An outstanding feature of the control software from GERSTEL is its PrepBuilder function (see also page 16). It was the first of its kind to enable intuitive operation combined with fully automated sample preparation: Individual steps are simply selected and combined from straightforward menu-lists with a click of a mouse. Maximum productivity is achieved while reducing potential sources of errors.

At first glance, the MPS seems similar to samplers supplied by other manufacturers. As is so often the case, appearances can be deceiving. The differences are significant and are found when the MPS 2's capabilities are studied in more detail.

The performance and flexibility, the wide range of possible application areas and the extremely efficient operation of the MPS 2 are directly related to the control software, which is based on the proven GERSTEL MASTer software.

Save time and get more done

The GERSTEL MASTer software is integrated completely into the GC and MS ChemStation software from Agilent Technologies. This feature is highly valued by users, due to the efficient and reliable instrument control.

In addition, system integration eliminates potential sources of error. The user only needs to enter one sequence table and one method to control the entire system – i.e. the sampler, the injector, the GC and MS detector – from the ChemStation software.

The MPS 2 offers the user a lot more depending on the user-specified configuration.

Even the basic version of the MPS 2 provides convenient sample handling



Andreas Koblitz, BP, Cologne-Worringen (right):

"The MPS 2 gives us efficient automation and complete flexibility. We perform automated tests of all liquid samples by liquid injection and of solids by headspace GC. Our gas samples can still be injected manually without having to modify the system"

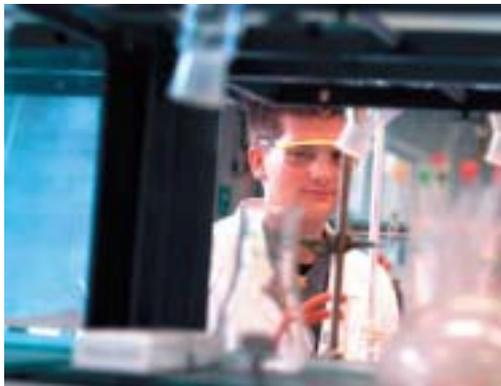
and sample introduction. All injection parameters such as sample volume, fill and injection speed, as well as sample preparation steps (standard addition and derivatization) can be programmed and controlled using MASTer software. However, the MPS 2 with MASTer software is compatible with all standard GC models that use Windows™ based operating systems.

Modular expansion: One autosampler for all tasks

As the user's requirements grow, the MPS 2 can be expanded into a multifunctional system for sample preparation and sample introduction by adding various modules. Depending on the configuration, the injection of liquid samples (basic version), headspace injections, solid phase microextraction (SPME) and fully automatic analysis of the GERSTEL Twister are possible with the MPS 2. The extent of the MPS 2's capabilities is defined by the user and his or her individual analytical requirements.

GERSTEL PrepStation

In combination with the PrepBuilder software: efficient automated sample preparation and GC analysis.



This is what the GERSTEL MultiPurpose Sampler has to offer you

Liquid And Large Volume Injections

All MPS 2 samplers can be used for liquid injections, including large volume injection (LVI). The control software includes special LVI software for fast method development.

The MPS 2 is easily upgraded to include automated headspace, SPME and Twister techniques. Twister analysis requires the MPS 2 Twister Option, the GERSTEL Twister Desorption Unit TDU and the GERSTEL Cooled Injection System CIS.

Headspace Technique

The MPS 2 enables automated headspace analysis of volatile and semi-volatile compounds from solid and liquid matrices. For increased sensitivity, a special type of headspace analysis, Headspace Sorptive Extraction (HSSE), can be performed. A GERSTEL Twister is placed into a headspace vial above the sample and analytes concentrated in the Twister. It is easy to switch from headspace to liquid injection; the headspace syringe holder is simply replaced with a liquid syringe holder.

Heating or Cooling Samples

The MPS 2 sample trays and agitator can be optionally cooled or heated. Cooling is required when analyzing thermally labile compounds or in order to reduce microbial activity in samples.

Analyte concentration

Using the proven GERSTEL Cooled Injection System CIS as cold trap, analytes can be concentrated from a large volume injection prior to the analysis. This applies to liquid, headspace and thermal desorption injections. Example: headspace analysis of BTX or halogenated hydrocarbons in water.

Solid Phase Microextraction

Due to its high performance, for example for extraction and enrichment of a large variety of components, SPME has

So that you can form your own picture of the applications scope of the MPS 2, we have once again summarized for you the most important features and innovations of this outstanding GC autosampler.

proven itself in numerous GC laboratories for environmental as well as food and flavor analysis. The MPS 2 enables fully automated SPME analysis including derivatization before or after the extraction.

GERSTEL Twister Option

Automated analysis of up to 196 GERSTEL Twisters – even this can be done by the MPS 2 with the click of a mouse. Twister analysis requires the Twister Desorption Option, Twister Desorption Unit TDU as well as the Cooled Injection System CIS.

Simple Handling

The MPS 2 is controlled through the GERSTEL MASTer Software, which is completely integrated into the Chem-Station software from Agilent Technologies. One method and one sequence list controls the entire system: MPS 2, GC and MSD.

MPS 2XL – more Space, more Possibilities

The MPS 2XL sampler is enlarged by 40 cm, offering more room for additional sample trays. The MPS 2XL accommodates up to 128 headspace vials (20 mL) for high-throughput automated headspace or SPME analysis. The MPS 2 XL can be mounted on any standard GC. Due to its length, the MPS 2 XL can also be positioned above two GCs. This means that with just one autosampler, the user can operate two gas chromatographs.

Online sampling or LC/GC coupling

The MPS 2 can be fitted with a flow-cell, which enables on-line sampling from a liquid process stream or LC/GC coupling. Samples can be taken automatically from the flow-cell. The sampling time is user-defined in the GC method. The sample can be injected into the GC for analysis – or parked in a vial for further sample preparation.

Automated Headspace Analysis in 100 mL Vials

A new sample tray enables the MPS 2 to perform automated headspace analysis using 100 mL vials. Larger vials are useful when analyzing inhomogeneous samples such as coffee beans. When combining the MPS 2 and a GC 6850 from Agilent Technologies, an 8-position sample station can be positioned next to the unit. For the GC 6890, the larger MPS 2 XL is required.



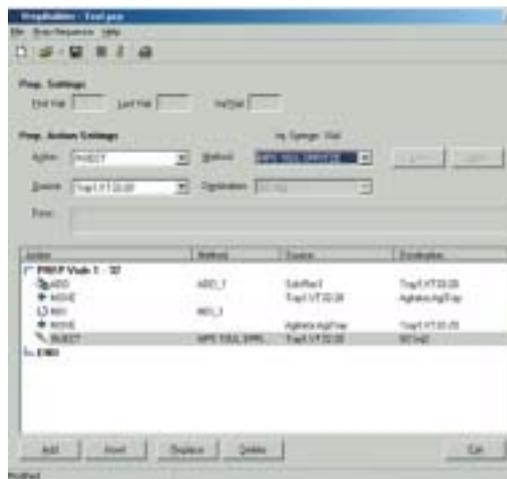
25-position heated tray for headspace GC

For standard headspace analysis using the MPS 2, incubation is performed in the 6-position heated agitator. When incubation times are very long, simultaneous incubation of up to six samples may not offer sufficient productivity. For this reason, a heated tray with 25 positions for simultaneous incubation is available. This accessory is used in the pharmaceutical industry for headspace analysis of extended release pharmaceuticals.



GERSTEL MPS PrepBuilder Software

Sample Prep by mouse-click – easier than ever



The new GERSTEL PrepBuilder Software, in combination with the GERSTEL MultiPurpose Sampler (MPS 2), makes it simple to automate the complete GC analysis including sample preparation.

Most steps in sample preparation are reduced to short commands such as add, mix or move. These and more commands are found in a menu-list. The user selects and combines these commands by mouse-click into tailor-made sequences for different sample preparation procedures.

“To automate sample preparation steps using the MPS 2 you don’t need macro programming”, says Stefan Bobinger, Ph.D., software expert in the GERSTEL R&D department. “All the user needs to do is to select the required sample preparation steps from a menu in the MPS PrepBuilder Software.”

The user is not limited to standard parameters, however. Dr Bobinger adds: “The parameters hidden behind the program steps can be edited and tailored to individual needs.”

“Although the addition of an internal standard can be automated with the PrepBuilder Software in combination with

the MPS 2 – provided the sampler is configured for liquid injection – the software unleashes its full power when combined with the MPS PrepStation”, says the software engineer.

“Dilute, add an internal standard, adjust the temperature, shake, sample using headspace or SPME and then inject. The two rails mounted on top of each other and the two robotic arms enable the GERSTEL MPS PrepStation to combine a number of sample preparation and introduction techniques”, Bobinger says.

The PrepBuilder Software makes work with the MPS extremely reliable and efficient. Appropriately chosen incubation parameters ensure maximum sample throughput.

By performing sample preparation during the GC run, the time required for analysis can be reduced by 50 percent or more, depending on the application.

For example, The Institute for Forensic Science at the University of Zurich uses the MPS 2 in combination with MASTer Software for the analysis of blood alcohol levels (see GERSTEL Solutions Worldwide, issue 31, pp 13-15).

Here, the headspace technique is used. For this application, the GC analysis time is much shorter than the required incubation time for each sample. If incubation and analysis were performed sequentially, throughput would be dramatically reduced. The MPS 2 enables overlapping incubation and analysis; up to six samples can be incubated in the agitator while the GC analysis is running. This ensures maximum productivity since the next headspace sample is always ready to be injected every time the GC becomes ready.

>ADD<
Add an aliquot of liquid from a solvent reservoir to a vial at a specified location.

>MOVE<
This command is used to move a vial from location X to location Y.

>MIX<
The sample vial is shaken in the agitator and/or incubated at a set temperature for a specified period of time.

>INJECT<
An aliquot of sample or standard is injected into the GC.



New technology for handling dirty samples

Automated liner exchange for GC injectors

Authors

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Keywords

Gas Chromatography, Injector, PTV, Automated Liner Exchange, Sample Preparation, Sample Clean-up, Large Volume Injection (LVI).

Introduction

Sample clean-up steps needed to prepare environmental or food samples for determination of pesticides are time-consuming and are potential sources of errors. Simplification or elimination of such procedures is often the motivation for development of new analytical methods and new instrumentation. Unfortunately, analytical instruments do not normally tolerate introduction of "dirty" samples or even "dirty" extracts.

For example, extracts containing suspended matter or high-molecular-weight compounds contaminate a GC inlet after a few injections, causing peak broadening or even loss of sensitive compounds. Reducing or eliminating clean-up steps will result in dirty extracts and daily – or even hourly – maintenance of the GC system.

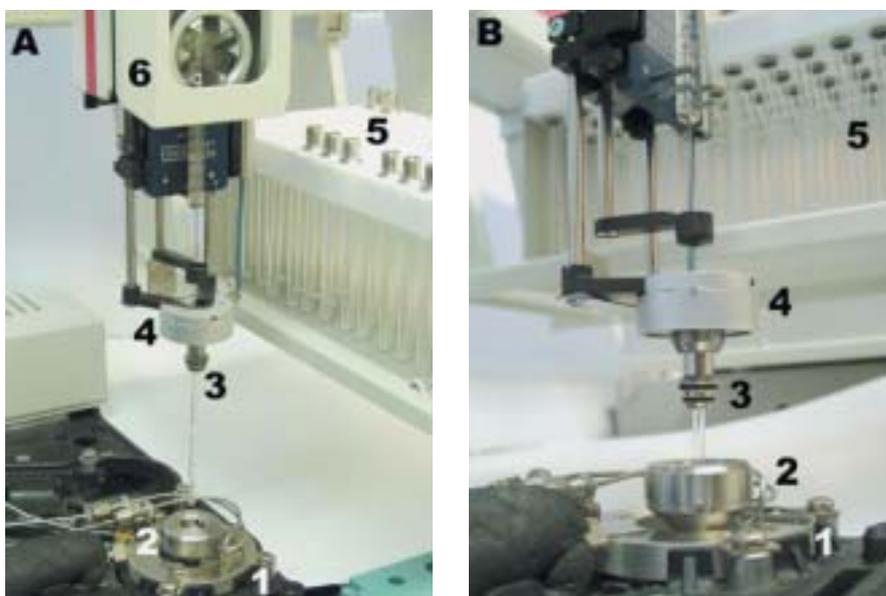


Figure 1 A. Automated Liner Exchange (ALEX) installed on an Agilent 6890 GC equipped with a CIS 4 programmed temperature vaporization (PTV) injector (1), ALEX support head mounted on CIS 4 (2), transport adapters for PTV liners with septum (3), electrical gripper for transport adapters (4), tray for storage of a total of 97 clean liners and used liners (5), autosampler tower with liquid syringe (6).

B. Detailed view of the ALEX System

System Design for Automated Liner Exchange

A simple and automated liner exchange system is able to overcome most chromatographic problems caused by "dirty" samples in GC analysis. A solution is presented that uses a commercially available programmable temperature vaporizing (PTV) inlet in combination with an autosampler, which can automatically perform a liner exchange at any time during a sample sequence. Every liner is equipped with a transport adapter, which

also allows liquid injection through a septum. Adapters fitted with liners are transported by means of the autosampler which also performs the liquid injection. The system is based on the Cooled Injection System (CIS 4) inlet and the MultiPurpose Sampler (MPS 2) (GERSTEL, Germany). Instead of the septumless head normally used on the CIS 4 for liquid injection, a special support head is mounted. This support head seals the transport adapters, providing an uncompromised carrier gas flow through



the adapter and liner. The support head and the transport adapters are conical. In order to provide a perfect seal, every transport adapter is fitted with two o-rings, between which the carrier gas inlet is placed. Such a sealing system has been proven through years of use in other systems where glass tubes are automatically exchanged, such as the GERSTEL Thermal Desorption System (TDS).

In order to grip and transport the adapters, the autosampler has been modified slightly and fitted with an electrical gripper. Up to 97 conditioned liners are stored in a special tray; the transport adapters provide a gas-tight seal for contamination-free storage.

For liquid injections, every transport adapter is equipped with a 5 x 3 mm septum that is commercially available and is, for example, used in Agilent's cool on-



Figure 2 Left: Exploded view of transport adapter for automated liner exchange with liner, adapter, 3 x 5mm septum and septum screw; a hole for carrier gas entry can be seen between the o-rings of the transport adapter. Right: Assembled transport adapter with liner

column inlet. The top of the injector, and the transport adapter in particular, remain cool during the analysis due to effective heat decoupling between the body and the top of the PTV.

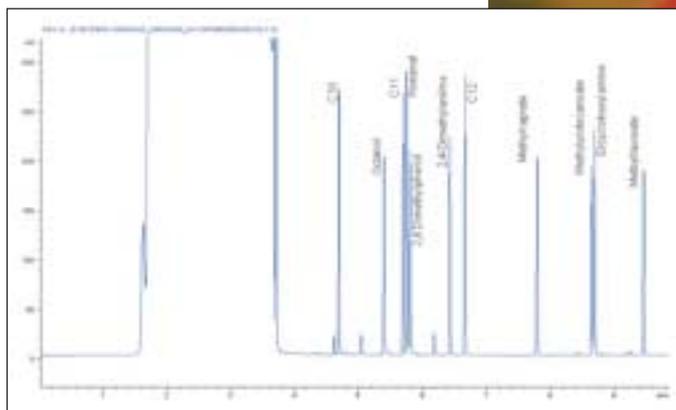
As a result, no septum bleeding or bleeding of the o-rings of the adapters can be observed.

The body of the injector is identical to the CIS 4 inlet and all commercially available types of liners for this inlet can be used (empty liners or liners filled with glass wool or adsorbents). The automated liner exchange head doesn't affect the analytical performance of the CIS 4 inlet. As an example, Fig. 3 shows a chromatogram of a Grob test mixture with uncompromised peak resolution and peak shapes.

Tests with n-alkane mixtures proved that recovery of high boiling substances

Figure 3

GC FID chromatogram of a Grob test mixture (1 μ L splitless) injected into a CIS 4 equipped with the ALEX system



is comparable to a normal CIS 4 system. It is clearly seen that this new Automated Liner EXchange (ALEX) system has no influence on CIS 4 performance. Methods developed for CIS 4 system can be transferred to the ALEX system without any modifications.

A software solution was developed that enables the user to exchange liners at any point in time during the analysis sequence. The software can be operated stand-alone or integrated into the Agilent GC or MS ChemStation. This means that only one sequence list is needed for the complete system. Fig. 4 shows a screen shot of such a sample sequence.

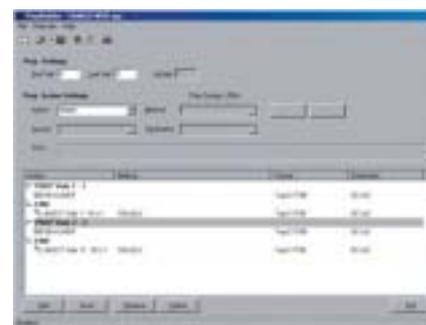


Figure 4 Screen shot of a control sequence for ALEX embedded in Agilent GC ChemStation and MS ChemStation; In this example the sequence starts with a liner exchange, followed by liquid injections from vial 1 to 10. After the 10 sample injections, the liner will be exchanged and the system is ready for the next 10 sample injections from vial 11 to 20.

Pesticide analysis of non-fatty foods with reduced sample preparation

Recently a new multi-residue method for pesticide analysis in fruits and vegetables was presented (QuEChERS, Quick Easy Cheap Effective Rugged Safe) [1]. Compared to previous methods, the QuEChERS method enables rapid sample preparation for determina-

tion of pesticides such that 8 samples can be prepared in less than 30 minutes. Table 1 summarizes all necessary steps of the QuEChERS method.

The main benefit of this sample preparation method is a less time-consuming analysis, which is also less error-prone. Unfortunately, extracts obtained following this procedure often have a high matrix content, which causes chromatographic problems for GC analysis due to residue build-up in the liner.

Fig. 5 shows a picture of a 2 mL vial containing a bell pepper extract and a glass wool packed liner in which 5 μ L of this extract has been injected.

Residue build-up in the GC liner very quickly affects the analysis of many pesticides, as can be seen in Fig. 6. A 5 μ L standard solution made up in a bell pepper matrix was injected 20 times into a deactivated baffled liner. Peak area trends for three different pesticides are presented. For endosulfane sulphate and chlorothalonil, peak areas decrease over

Table 1: QuEChERS method sample preparation steps for multi-residue analysis of pesticides in non-fatty foods such as fruits and vegetables

- **Weigh 10 g of sample**
→ Add 10 ml of Acetonitrile (AcN)
- **Shake vigorously 1 min**
→ Add 4 g $MgSO_4$ and 1 g NaCl
- **Shake vigorously 1 min**
→ Add internal standard solution
- **Shake 30 sec and centrifuge**
- **Take Aliquot of supernatant**
→ Add $MgSO_4$ and sorbent
- **Shake 30 sec and centrifuge**
- **GC-MS and LC-MS**

**Figure 5**

2 mL Vial containing a QuEChERS method bell pepper extract and a liner packed with glass wool in which 5 µL of this extract has been injected.

the course of the 20 injections. This can be explained with increasing matrix contamination of the liner, leading to loss of analytes. For dichlorophos the situation is different; the peak areas increase. This effect is described in the literature as “matrix-induced chromatographic response enhancement” [2]. This means that matrix components cover remaining active sites in the chromatographic system leading to higher response for sensitive analytes.

Fig. 6 shows clearly that when analyzing extracts obtained with the QuEChERS method, a liner exchange is required after 10 or at least 15 runs for vegetables like bell peppers. In order to implement the QuEChERS method in a laboratory for a routine automated analysis, it is absolutely necessary to have the capability of exchanging liners automatically as is provided by the new GERSTEL ALEX system.

The following is an example of a sequence for routine analysis:

- 1 Liner Exchange**
- 2 Standard Injections for recalibration (3 or 5 concentration levels)**
- 3 Sample Injections (7 up to 10 runs)**
- 4 Liner Exchange**
- 5 ..Steps 2-4 are repeated..**

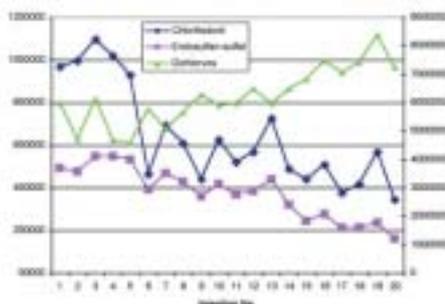


Table 2 Standard deviations for different pesticides achieved under optimized injection conditions (see Table 3) for 10 injections in one liner. Even though only 10 injections per liner are performed, standard deviations are still high for several pesticides. Apart from the specific chemistry of some pesticides, this is due to the fact that 5 µL of the acetonitrile extract had to be injected into an empty liner. Acetonitrile is known not to be a suitable solvent for GC analysis. Normally for such a solution, and such an injection volume, a liner with glass wool should be used. Unfortunately, some substances are very sensitive and show discrimination on glass wool liners. On the other hand a 5 µL injection volume is necessary in order to meet required detection limits of 0.01 mg/kg.

Compound	sd	Compound	sd
1 Cyhalothrin	9.5%	Imazalil	7.2%
2 Cyhalothrin	6.7%	Cresoxim-methyl	6.7%
Atrazine	9.0%	Methamidophos	6.5%
Azoxystrobin	5.9%	Permethrin	7.0%
Bifenthrin	6.8%	Permethrin 2	6.8%
Carbaril	12.9%	Procymidone	4.7%
Chloropyrifos-methyl	6.9%	Tebuconazol	6.8%
Chlorpyrifos-ethyl	8.5%	Thiabendazole	6.8%
Chlorthalonil	29.3%	Tolyfluanide	8.2%
Cyprodinil	7.7%	Trifluraline	6.9%
Dichlorvos	12.0%	Tritane	3.5%
Endosulfan sulphate	12.7%	o-Phenylphenol	6.8%
Ethion	8.0%	p,p'-DDD	6.1%

Table 3: Injection conditions for Pesticide Analysis after QuEChERS sample extraction method, GERSTEL MPS 2 with ALEX system, GERSTEL CIS 4, Agilent 6890 GC, Varian FactorFour XMS column (30 m, 0.25 mm ID, 0.25 µm film), Leco Pegasus 3 TOF-MS; Liner: Empty baffled liner, deactivated.

Liner	Empty baffled liner (deactivated)
Injection Volume	5 µL (AcN solutions)
Injection Speed	10 µL/sec
Injection Mode	Solvent vent for 15 sec (50 mL/min; 8.2 psi), Splitless sample transfer, Purge Flow 50 mL/min @ 150 sec
CIS 4 Temp. Program	50°C (0.25 min) - 12 °C/sec - 280 °C (30 min)

Conclusions

The system described herein for automatic exchange of PTV inlet liners enables automated GC analysis of samples or extracts with a high content of high boiling substances or suspended matter.

The chosen application, determining pesticides in fruits and vegetables with QuEChERS sample preparation, demonstrates that a reduction of sample preparation steps combined with a GC system which tolerates injection of solutions with

a high matrix content is a powerful solution. Laboratory time for sample preparation is reduced dramatically and at the same time a high sample throughput for the analytical instrument is ensured.

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ALEX tackles a traditional bottle-neck in GC analysis: Sample clean-up. Samples that contain a large amount of high-boiling or solid residue normally require extensive clean-up steps prior to injection into a GC. An alternative is to frequently replace GC liners; until now this has been a manual operation step, incompatible with modern automated analysis.

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