GERSTEL solutions worldwide

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No. 17

Tattoo Ink: A Closer Look

Automated Sample Preparation
Efficient Doping Control with DBS

Water Analysis
Monitoring Disinfection Byproducts

Material Analysis
VOC Emissions from PU Foam

Dear Reader,

Eberhard G. Gerstel

Holger Gerstel

Ralf Bremer

The time when only groups on the margins of society had tattoos is over and long gone. Instead of just adorning sailors and identifying members of criminal gangs, tattoos are now prominently displayed by respected members of society from all walks of life, not just sports stars, artists and musicians. The works of art range from the very small to larger canvasses covering major portions of the body.

But what happens if your personal tastes change and the tattoo no longer fits your life style or your next career move? It takes time and is very costly, and dare we say not without risk, to have a tattoo removed as we report in our cover story on page 7. In the investigations of side effects of tattoo laser removal, GERSTEL thermal desorption solutions played a key role.

Apart from the skin deep investigation, the 17th issue of the GERSTEL Solutions Worldwide Magazine offers several interesting reports on application areas in which GERSTEL instruments and -systems are being used. For example, we report on the use of our Dried Blood Spot Autosampler (DBS A) in doping analysis (page 4) and on the highly efficient determination of disinfection byproducts in drinking water from page 10 onwards. Incidentally, the cover picture for the article was taken by Jan Garbe-Immel from GERSTEL, Germany, an avid photographer who frequently takes the plunge with his kids in the neighborhood swimming pool.

Our report on material emissions brings a more volatile note: Polyurethane (PU) is widely used in building and vehicle interiors. When developing an automated method for the characterization of VOC emissions from PU foams, the GERSTEL DHS Large was the key player as can be seen in the article on page 15. But wait, there's more: Just like the GERSTEL DHS, our thermal desorption solutions offer solvent free analysis, one of the major strengths in the GERSTEL portfolio. Why? Read more on page 19.

From the beginning we have made a habit of visiting laboratories and reporting on their use of GERSTEL technology for a wide range of applications. Starting on page 20, we report on a visit to the State Office for Consumer Protection and Food Safety (LAVES) in the State of Lower Saxony, Germany, a highly interesting visit that offered much insight into automating the generation of standards and standard addition for improved quality of analysis results.

What else is left to say? – GERSTEL celebrates its 50th anniversary in 2017! More on the matter on page 3.

We wish you an enjoyable and interesting read of the 17th GERSTEL Solutions Worldwide Magazine.

Sincerely,

GERSTEL Management

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On the Wings of the Condor

The State Office for Consumer Protection and Food Safety (LAVES) in Lower Saxony, Germany, came out on top with the best results in a Europe-wide round robin test of pesticide laboratories for the determination of pesticides residues in cereals. GERSTEL Solutions Worldwide magazine visited the LAVES pesticide laboratories where we joined the staff at work to gain some insight. **20**

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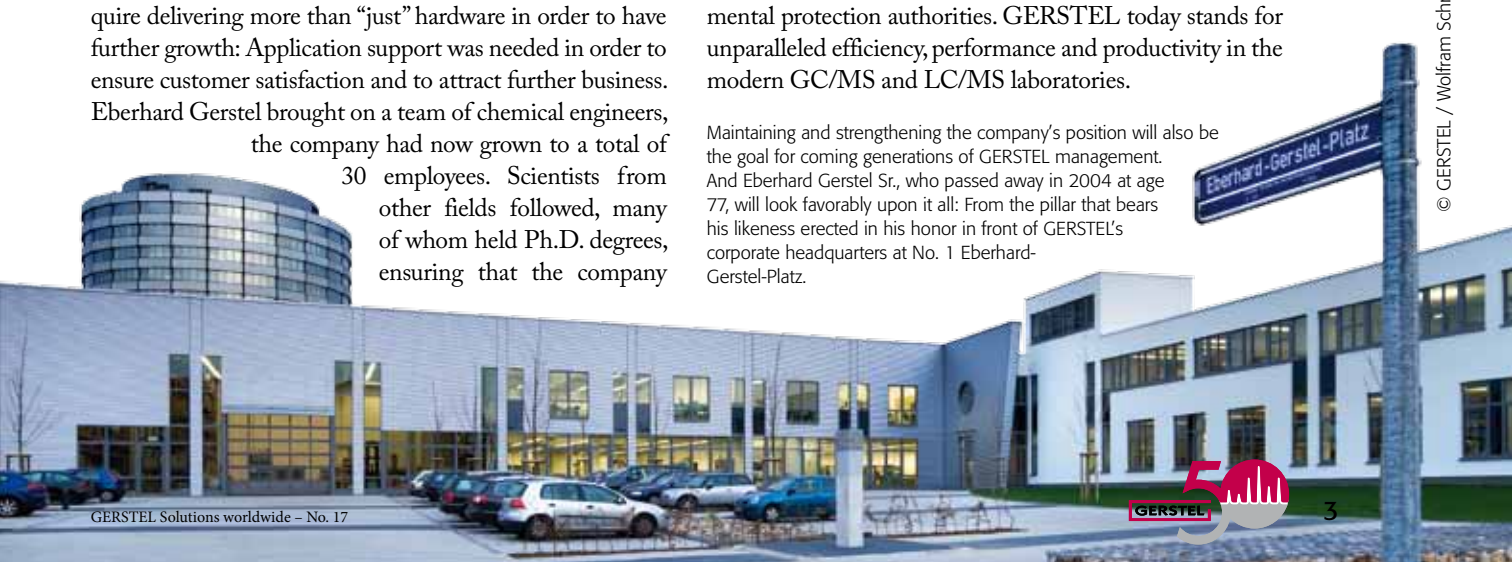
GERSTEL celebrates its 50th anniversary

From one-man show to internationally acclaimed laboratory solutions provider: the story of GERSTEL can be summarized in just those few words. The company will be celebrating its 50th anniversary in October 2017. A fitting occasion to reflect on our roots, celebrate our achievements and venture a guess on what the future may hold.

By Guido Deussing

Eberhard Gerstel, born in 1927, husband and father of three sons, worked at the venerable Max Planck Institute (MPI) for Coal Research in Mülheim an der Ruhr, Germany. A talented craftsman and creative precision mechanic, he developed and built measurement and control instrumentation as well as laboratory equipment for the MPI scientists. At the time, demand for sophisticated equipment was soaring and not only at the MPI. Eberhard Gerstel resigned his position at the MPI in 1967 at age 43 to start his own business. In a garage-turned-fine mechanical workshop in Mülheim an der Ruhr, the company „Labormechanik Gerstel" was born. The first devices created were all custom built. Initially, his precision mechanics and engineering skills were fully enough to meet his customers' demands, but technology is constantly evolving and after only three years, Eberhard Gerstel's team counted four employees, including experts in electronic control technology. The trend was plain to see: Growth. Eberhard Gerstel developed humidity sensors, contact thermometers and soon filed his first patent; the company would go on to file a total of around 200 patent applications by 2017. In the mid 1970s, gas chromatography (GC) became GERSTEL's main line of business. The entrepreneur broke into the GC market with a patented seal technology and a highly specialized GC inlet system. Eberhard Gerstel successfully eliminated major limitations of conventional gas chromatographs of the time, adapting them to the newly developed capillary columns and helping to improve their overall sensitivity significantly. His Cooled Injection System (CIS) became the world's most successful means of introducing and analyzing samples by GC using programmed temperature vaporization (PTV). The opportunities for GERSTEL continued to present themselves, but they seemed to require delivering more than "just" hardware in order to have further growth: Application support was needed in order to ensure customer satisfaction and to attract further business. Eberhard Gerstel brought on a team of chemical engineers, the company had now grown to a total of 30 employees. Scientists from other fields followed, many of whom held Ph.D. degrees, ensuring that the company had expertise equal to its customers. The company expanded its laboratories and entered into several strategic partnerships, for example with Hewlett-Packard in 1986, one of the world's leading manufacturers of gas chromatographs and detectors, a business area which was later split off under the name of Agilent Technologies. Now GERSTEL was finally able to offer clients complete analytical solutions, opening up a wealth of opportunities. Eberhard Gerstel Sr. handed the company over to his sons Eberhard. G. Gerstel and Holger Gerstel who took the reins along with longtime employee Ralf Bremer in 1998. The new generation of leadership quickly accelerated the company's growth by focusing on international expansion. As early as 1994, the company's first US subsidiary, GERSTEL Inc., had opened its doors. In short order, GERSTEL AG in Switzerland was founded in 2000, GERSTEL K.K. in Japan in 2004, and GERSTEL LLP in Singapore in 2010. The company was additionally represented in more than 70 countries worldwide using a network of dedicated and trained distributors. In the new millennium, GERSTEL followed the trend toward automation and miniaturization in the laboratory while critically expanding and deepening our software development capabilities. The steadily growing company has now become one of the world's leading providers of innovative solutions for automated sample preparation and sample introduction for GC/MS and LC/MS. 50 years after Eberhard Gerstel Sr. founded his company, GERSTEL's solutions are well-established in in a broad range of markets and fields of application. Our systems are used across many key industries, in academic research, as well as by food safety and environmental protection authorities. GERSTEL today stands for unparalleled efficiency, performance and productivity in the modern GC/MS and LC/MS laboratories.

Maintaining and strengthening the company's position will also be the goal for coming generations of GERSTEL management. And Eberhard Gerstel Sr., who passed away in 2004 at age 77, will look favorably upon it all: From the pillar that bears his likeness erected in his honor in front of GERSTEL's corporate headquarters at No. 1 Eberhard-Gerstel-Platz.



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Automated Sample Preparation

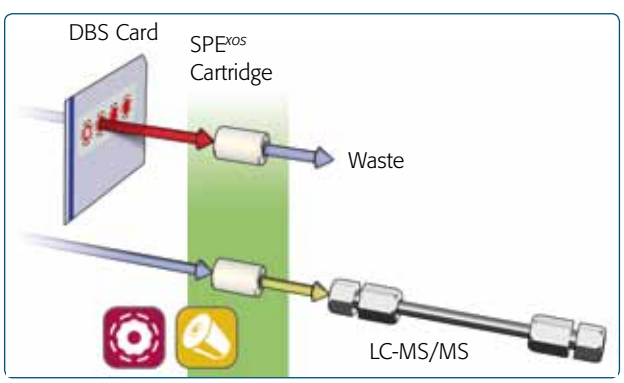
Efficient Doping Control

Automated determination of nicotine and its metabolites in blood

In the race to keep up with new and suspected doping agents, the Centre for Preventive Doping Research at the German Sport University Cologne, Germany is upgrading their laboratory with performance enhancing technologies and automation: The institute is betting on a fully automated Dried Blood Spot (DBS)-LC-MS/MS analysis system.

By Guido Deussing

The pressure to achieve record-breaking results in sports has become extremely intense, advances in technologies that can effectively guide an athlete to peak performance has made achievement of new records an almost routine occurrence. However, even after all aspects of an athlete's training regime have been optimized and the seemingly endless hours of preparation have been put in, some athletes still cannot achieve the desired results. This is when the temptation to use performance enhancing substances rears its head.



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Principle of Flow Through Desorption (FTD) of a DBS card (left hand side).

Not every chemical means of enhancing physical or mental performance is currently listed as illegal. But the World Anti-Doping Agency (WADA) has a watchful eye on many substances that they suspect are being used to gain an unfair advantage in sports. In 2015, the watch list sported names of active pharmaceutical ingredients such as Bupropion, Phenylephrine, Phenylpropanolamine, Pipradol, and Synephrine, along with stimulants such as caffeine and nicotine that are naturally present in coffee and tobacco.

Doping with nicotine – more than just a suspicion

In 2011, the German daily Süddeutsche Zeitung reported that scientists at the University of Lausanne, Switzerland, had found elevated levels of nicotine in urine samples from athletes from various disciplines.

"Nicotine doesn't improve stamina or muscle power, but it affects the brain and places the athlete in a different state of mind", says the pharmacologist Fritz Sörgel, a recognized doping expert and Head of the Institute of Biomedical and Pharmaceutical research (IBMP) at the University of Nuremberg, Germany. In those sports, in which reaction time and concentration are especially important to performance, an increased nicotine level could help athletes gain an advantage. While smoking tobacco could have significant detrimental health and performance effects, e-cigarettes or chewing tobacco could present an attractive alternative without the negative side-effects.

The same applies to snuff, an orally consumed form of tobacco, which is widely used in Norway and Sweden. "The suspicion is that snuff is being abused for doping purposes", states Professor Mario Thevis from the Centre for Preventive Doping Research at the German Sport University Cologne, Germany. No clinical studies or other well-founded data were available concerning the use or effects of nicotine as a performance enhancing drug even though WADA had placed nicotine on the watch list as a suspected doping agent. Prof. Thevis and his colleagues in Cologne along with a scientist from the National Veterinary Institute of the Department of Chemistry in Uppsala, Sweden set out to develop a "fast and inexpensive" method of analysis that would enable the determination of nicotine and its metabolites while also providing insight on how they had been introduced into the body [1]. During their search to find the most suitable analysis technique for their purposes, Dried Blood Spot (DBS) analysis in combination with online solid phase extraction (SPE) and LC-MS/MS soon emerged as the most promising solution.

World Anti-Doping Agency (WADA)

The World Anti-Doping Agency (WADA) is a foundation initiated by the International Olympic Committee to promote, coordinate and monitor the fight against the use of performance enhancing drugs in sports. The agency's key activities include scientific research, education, development of anti-doping capacities, and monitoring of the World Anti-Doping Code, whose provisions are enforced by the UNESCO International Convention against Doping in Sport. WADA was founded in 1999, it is an international non-governmental organization (NGO) headquartered in Montreal, Canada. Wada organizes world-wide campaigns against the use of doping in sports. These employ urine tests, blood tests and other tests as required by medical indications. Currently around 30 laboratories world-wide are authorized by WADA to analyze the required replicate samples (A and B samples) for traces of prohibited substances and for signs that prohibited methods have been used, such as, for example blood doping. The prohibited list is updated annually and it serves as the international reference for identifying substances and methods prohibited in all sports that fall under the World Anti-Doping Code (WADC). Individual countries have national anti-doping agencies such as the USADA in the US, UKAD in the United Kingdom, AFLD in France and NADA in Germany. *Source: WADA, Wikipedia*

Suggested Reading

OPEN ACCESS ARTICLE!

L. Tretzel, C. Görgens, H. Geyer, A. Thomas, J. Dib, S. Guddat, V. Pop, W. Schänzer, M. Thevis, **Analyses of Meldonium (Mildronate) from Blood, Dried Blood Spots (DBS), and Urine Suggest Drug Incorporation into Erythrocytes**, International Journal of Sports Medicine · DOI10.1055/s-0036-1582317, (https://www.thieme-connect.com/products/ejournals/abstract/10.1055/s-0036-1582317?lang=de)

Cost and speed are the deciding factors

According to the scientists, DBS has proven itself many times over, for example in pre-clinical pharmaceutical research; for monitoring of active therapeutic agents; in forensic toxicology; as well as in studies of metabolic disorders. Meanwhile, several examples were also published on DBS being used in doping analysis. According to Mario Thevis and his colleagues, DBS offers a number of benefits when compared with standard strategies for blood sampling: DBS is minimally invasive – a simple finger prick is enough to withdraw a sufficient sample volume (20 µL) for the analysis. Just a few drops of blood absorbed on a suitable, cellulose based medium is all that is needed for a successful determination of the compounds of inter-

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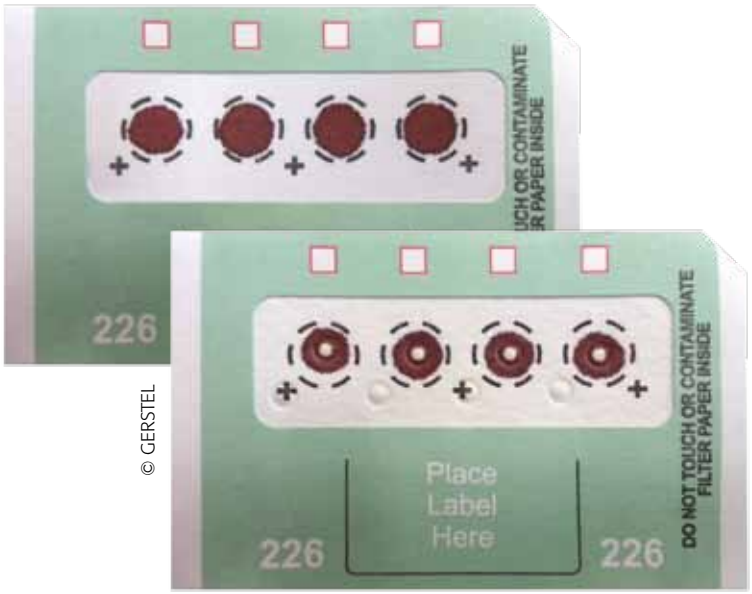
Fully automated DBS system based on the MultiPurpose Sampler (MPS).



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DBS desorption is performed with high accuracy in the user-defined section of the blood spot. Quantitative recovery is achieved resulting in high reproducibility.

est. In addition, blood sampled in this way exhibits good long term stability at room temperature. Samples dry very quickly and the absence of humidity means that enzymes are deactivated, as the scientists point out in their article in the Journal of Pharmaceutical and Biomedical Analysis [1].

To perform DBS analysis, several sample preparation steps are required: "Currently, the pre-analysis workflow includes punching out and dissolving each dried blood spot. Then an extraction is performed with a suitable solvent, occasionally including ultra-sonication. Further clean-up steps involve: Protein precipitation, filtration and transfer of the resulting extract into a sample vial followed by LC-MS/MS analysis", according to Thevis et al.. Automation is an absolute necessity in order to minimize the significant manual workload and to qualify DBS sampling for high throughput analysis in a routine laboratory setting.

Commercially available automation

The scientists set out to determine nicotine, the main metabolites nornicotine, cotinine and trans-3'-hydrocotinine (trans-3'-HCOT), as well as the alkaloids Anabasine and Anatabine using a fully automated system: A MultiPurpose Sampler (MPS) and a Dried Blood Spot Autosampler (DBSA) coupled to an online SPE system (SPE*xos*) all from GERSTEL. This setup was coupled with a high-resolution LC-MS/MS system.

Prof. Thevis explains why this setup is different from previous systems used in the laboratory: "When using an online SPE system, we can extract the DBS sample, clean up the extract, and proceed directly with the analysis". Automation is only one important aspect of the system, according to Prof. Thevis: "Not only does the automated DBS sample preparation reduce the workload, it also improves extraction efficiency and limits of detection". The patented Flow Through Desorption (FTD™) technology enables good concentration factors to be achieved while minimizing the risk of sample to sample carry over. The Online DBS SPE-LC-MS/MS method was developed using standard solutions at different concentration levels, which were spiked into samples from volunteers who had neither smoked nor consumed snuff. The validation was performed following the recommendations of WADA and the European Bioanalysis Forum (EBF). Deuterated analogues were used for quantification of target compounds. In order to investigate potential differences in pharmacokinetics, Thevis et al. used their method on authentic samples, that is, blood samples taken from cigarette- and e-cigarette smokers, as well as snuff users. The project was set up with permission from the local ethics commission, in some countries known as the Institutional Review Board, whose task it is to protect human subjects from harm by overseeing research performed on humans or animals. Written permission was obtained from the volunteers.

Differentiating between normal consumption and doping

When they developed the method, the authors focused on optimizing it for reproducibility and workflow efficiency, according to Thevis and his colleagues [1]. The process steps that held the most promise for improvement was DBS elution, SPE cleanup, as well as Mass Spectrometric Detection. Using the DBS method they developed, the authors succeeded in determining all target analytes with excellent precision and accuracy. The limit of detection for all analytes was 5 ng/mL. The successful analysis of blood samples taken from real smokers as well as e-cigarette and snuff users demonstrated that the method could be implemented for routine doping controls as well.

"All target compounds were found in the real samples", Thevis et al. wrote. Additionally, the statistical evaluation had shown a significant difference in the ratio between nicotine and nornicotine concentrations in the blood depending on whether nicotine was administered via the lungs (inhalational) or via mucous membranes (buccal uptake). This means that based on pharmacokinetic properties, conclusions can be drawn as to the athlete's method of consumption and maybe the longer term pattern of use.

Literature

[1] Laura Tretzel, Andreas Thomas, Thomas Piper, Mikael Hedeland, Hans Geyer, Wilhelm Schänzer, Mario Thevis, Fully automated determination of nicotine and its major metabolites in whole blood by means of a DBS online-SPE LC-HR-MS/MS approach for sports drug testing, Journal of Pharmaceutical and Biomedical Analysis 123 (2016) 132–140

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Consumer Protection

Tattoo ink: A Closer Look

Tattoo removal using laser radiation can carry health risks depending on the breakdown products formed. Scientists from the Federal German Institute for Risk Assessment and Consumer Safety have now shown that pyrolysis GC/MS can be used to simulate the breakdown process and determine the compounds formed from a given ink during laser treatment. Phthalocyanine blue (B15:3), for example, was shown to form a cell poison in the process. Clear as ink? It is hoped that pyrolysis GC/MS can help consumer safety agencies determine whether certain tattoo inks should be approved or banned, in light of possible laser removal treatment.

By Guido Deussing

There can be very good reasons to have a tattoo removed: An allergic reaction to the pigments used; a different motif may be required, commensurate with age and experience; the name embedded in your skin may no longer be the love of your life; older images may have faded or not look as good as they once did due to the aging canvas; or the tattoo may stand in the way of your next career move. In the past, having such a permanent fixture removed required the use of a scalpel or etching or sanding of the skin - an unpleasant process. Fortunately for those suffering from tattoo remorse, techniques have recently become available to remove tattoos relatively gently without leaving visible scars or traces.

Laser treatment is preferred but it is not without risk

It may be a gentler treatment than previous generations of tattooees had to endure, but using a laser could entail certain health risks. At least that is what a joint study by the Federal Institute for Risk Assessment and Consumer Safety and the Laser Department of the Elisabeth Hospital points to. Both are located in Berlin, Germany. The study was published in "Scientific Reports"[1]. In it, Ines Schreiver, Christoph Hutzler, Peter Laux, Hans-Peter Berlien and Andreas Luch report that toxic and even carcinogenic compounds are formed during laser treatment of the copper-containing tattoo pigment phthalocyanine blue (B 15:3). The scientists simulated the fragmentation process using pyrolysis GC/MS and compared the fragments formed with laser breakdown products determined by Dynamic Headspace (DHS) in a separate experiment involving two-dimensional GC coupled with Time-of-Flight Mass Spectrometry (TOF-MS). Among the compounds determined were: 1,2-Benzenedicarbonitrile (BDCN), benzonitrile (BCN), 2-butanone, benzene, and hydrogen cyanide as the main fragmentation products.

Laser radiation meets tattoo pigments

In clinical dermatology, ruby lasers are regularly used to treat pigmented spots, i.e. liver spots and to remove tat-

toos. According to the scientists, radiating the skin with a ruby laser can lead to temperatures of more than 1000 °C in the skin. To break down the relatively stable color pigment phthalocyanine blue (B15:3), temperatures in excess of 800 °C are required. Bleaching of what is apparently the only blue tattoo pigment available to dermal needle workers is assumed to be the result of a thermally induced chemical breakdown process (photo-thermolysis) equivalent to an atomization of the pigment, Schreiver et al. report. To avoid damaging the skin at the high temperatures generated during laser treatment, the energy rich laser light cannot be allowed to emit continuously, but only in discrete, time-limited pulses. The ruby laser has a high pulse energy level making it well suited for medical skin treatment purposes. The efficiency of laser treatment in breaking down tattoo pigments is well proven. It can be observed directly by the ink pigment bleaching effect during treatment. Less clear is the exact identity and quantity of the resulting chemical derivatives and their long-term effect on the human organism. To shine a light on this matter was the stated goal of Schreiver et al. In order to imitate the laser induced, temperature dependent decomposition of the blue pigment copper phthalocyanine blue (B 15:3), pyrolysis - GC/MS was used among other techniques.

Pyrolysis GC/MS shines a light on laser induced breakdown fragments

To pyrolyze the B 15:3 pigment, the scientists relied on a Thermal Desorption Unit (TDU), equipped with a pyrolysis module (PYRO), both from GERSTEL. For the online coupled GC/MS analysis, an instrument setup consisting of a 7890A GC and a 5975C inert XL Mass Selective Detector (MSD) was used, both from Agilent Technologies, Inc., Palo Alto. The pigment sample was placed inside a quartz liner, which was automatically transferred to the PYRO module by the GERSTEL MultiPurpose Sampler (MPS). The pyrolysis step took place within a temperature range from 500 to 1,000 °C lasting 6 sec. A carrier gas flow of 1 mL/min (Helium) transported the pyrolysis fragments via the Cooled Injection System (CIS) PTV type GC inlet, which was kept at a temperature of 260 °C, to the GC column (HP-Plot/Q, 30 m, 0,32 mm x 20 µm ID from Agilent Technologies). Analyte separation was performed using a temperature gradient: Initial temperature 50 °C (2 min); 10 °C/min to 260 °C (10 min); EI ionization; full scan mode detection 10 to 550 m/z. Pyrolysis fragments were determined using the NIST MS library (US-NIST, National Institute of Standards and Technology, 2011 MS Library). Fragments found were: 1,2-Benzenedicarbonitrile (BDCN), benzonitrile (BCN), benzene and Hydrocyanic acid (HCN). Schreiver et al. reported that with increasing pyrolysis temperature the amount of fragmentation products formed also increased.

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Accuracy of the pyrolysis simulation verified

In order to assess whether pyrolysis of pigment B 15:3 produced the same fragments as laser radiation breakdown, the scientists produced different water based dispersions of the pigment and subsequently irradiated these with a pulsed ruby laser. The irradiated samples were then analyzed, first by Dynamic Headspace (DHS)-GC/MS to quantify the volatile compounds HCN and benzene. The previously described MPS-DHS-TDU-GC/MS system was used. D6-benzene was used as internal standard. Secondly, ethyl acetate extracts of the irradiated dispersions were analyzed by two-dimensional GC/Time-of-Flight-MS (Leco-Pegasus 4D GCxGC-ToF-MS) specifically in order to quantify BDCN and BCN. This was successfully achieved using benzyl nitrile and Benzyl alcohol as internal standards. In all cases, Schreiver et al. used the GERSTEL MPS for automated sample preparation and introduction.

The DHS-GC/MS determination was performed by thermostating the samples in the agitator for three minutes at 30 °C. Analytes were purged with a 100 mL volume of nitrogen (N_2) at a flow rate of 50 mL/min and focused in a sorbent trap inside a TDU tube (Carbopack B+X/Carboxen 1000). Analytes were desorbed inside the TDU and re-focused in the CIS at -50 °C. After 12 sec, the

CIS was heated to 40 °C (5.5 min) and then heated within seconds to 240 °C (5 min). The TDU and transfer system temperature were then kept constant at 260 °C for the remainder of the run. Sample introduction to the GC column was performed in splitless mode. The GC oven initial temperature was set to 40 °C (0.5 min) and then ramped at 10 °C/min to 260 °C (10 min). The mass range from 10 to 350 m/z was scanned with parallel Single Ion Monitoring (SIM) of the masses 27, 28, 78, and 84 m/z, each with a dwell time of 40 ms.

The GCxGC-TOF-MS determination of fragments generated during laser treatment was approached as follows: To a 196 µL sample placed in a 2 mL vial, the MPS added an internal standard and subsequently performed a liquid/liquid extraction with ethyl acetate for one hour in the agitator. A 1.5 µL aliquot of the resulting extract was introduced to the GC inlet for two-dimensional separation: The first dimension was based on a Restek Rxi-5Sil MS column (20 m, 0.25 mm, 0.25 µm ID), the second on a Restek Rxi-17Sil MS (1 m, 0.18 mm, 0.18 µm ID) column. The initial oven temperature was set to 70 °C (1 min), followed by a 15 °C/min ramp to 120 °C (0 min), 8 °C/min to 150 °C (0 min) and finally 25 °C/min to 330 °C (4 min). Effluent fractions from the first column were trapped and subsequently released into the second column using thermal modulation based on a cryofocusing temperature of -80 °C. For the second dimension separation, the temperature program was set a few degrees higher than the first dimension program. The ion source temperature was set to 250 °C, the transfer line to the MS to 295 °C. Mass spectra were recorded at a rate of 200 Hz scanning from 35 to 500 m/z. BCN and BDCN were unequivocally identified and quantified.

Assessing toxicity

For Ines Schreiver and her colleagues, a key question in this matter is whether laser induced breakdown of phthalocyanine blue actually generates degradation products in amounts that are unsafe – apart from the fact that hydrocyanic acid and benzene are known to be acutely toxic and a carcinogen, respectively. To find an answer, the scientists used a special experimental design based on human cells, which were exposed to sodium cyanide (NaCN) solutions of different concentrations. DHS-GC/MS was subsequently used to determine the amount of HCN liberated by the cells in order to get a picture of the kinetics of the HCN formation and its distribution in adjacent tissue following exposure to laser radiation. The scientists quote the U.S. Centers for Disease Controls and Prevention (CDC) as source for the fact that the lethal dose of HCN is around 2 mg/kg body weight "in most animal species" and that the "immediately dangerous to life or health concentration (IDLH) in air is 50 ppm (www.cdc.gov/niosh/idlh/74908.html). According to Schreiver and her colleagues, investigations with laser treatment of the tattoo pigment phthalocyanine blue have shown that toxicologically relevant concentrations of HCN are formed and that these have a significant effect on the ability of the cell to survive. In their totality, the experiments indicate that during laser treatment of light resistant phthalocyanine blue B 15:3 in skin, toxic fragments are formed in amounts that could most probably influence both the skin locally and systemically other tissue in the organism. Further studies will be needed using human skin ex vivo to investigate the formation of HCN and benzene during laser treatment as well as the consequences of their presence. Further, the scientists suggest that all this information be taken into account and in future quality assessment and approval processes for tattoo inks.

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It may be a gentler treatment than previous generations of tattooees had to endure, but using a laser may entail certain health risks.

Literature

[1] Ines Schreiver, Christoph Hutzler, Peter Laux, Hans-Peter Berlien & Andreas Luch, Formation of highly toxic hydrogen cyanide upon ruby laser irradiation of the tattoo pigment phthalocyanine blue; Scientific Reports 5, Article number: 12915 (2015) (www.nature.com/articles/srep12915 , 2017/02/15)

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GC/MS system similar to the one used at BfR in Berlin: GERSTEL MPS with TDU 2, PYRO, and DHS mounted on a GC/MS system from Agilent® Technologies.

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Drinking Water Analysis

Efficient monitoring of disinfection byproducts in chlorinated drinking water

Water is chlorinated to eliminate potentially harmful bacteria. In the process, unwanted disinfection byproducts (DBPs) are formed such as halogenated acetic acids (HAAs), which could themselves be harmful, albeit probably to a lesser degree. The US Environmental Protection Agency (EPA) mandates monitoring of HAAs in water using US EPA method 552.3. The procedure in the method is very labor intensive, limiting the number of samples analyzed per day to about 8 or 9 for a seasoned laboratory technician. In this article a system is described, which enables much more efficient monitoring of HAAs. In addition, a method is described for monitoring how polymer materials react with disinfection chemicals.

By Guido Deussing

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A comparable GC/MS system is used by David Benanou and his colleagues to determine chemical compounds leaching from polymer based pipes and pipe systems into drinking water.

The use of chlorinated disinfectants in the production of safe drinking water is aimed at killing or disabling pathogens such as harmful bacteria in the water. The disinfectants of course also react with other dissolved or suspended matter, forming unwanted disinfection byproducts (DBPs) in the process. Concentration levels of some of the approximately 600 DBPs identified to date should be monitored closely since they are suspected of being harmful to human health.

A blessing and a minor curse: Disinfectants

The list of the most unwanted DBPs includes the usual suspects such as trihalomethanes (THMs), with chloroform serving as probably the most prominent representative of this class of compounds. Another set of DBPs, long in the sights of the US Environmental Protection Agency (EPA), are halogenated acetic acids aka haloacetic acids (HAAs): monochloroacetic acid; dichloroacetic acid; trichloroacetic acid; bromoacetic acid; and dibromoacetic acid. The EPA classifies these compounds and compound classes as „probable carcinogens“ [1] and drinking water has to be monitored for residues. The maximum concentration level (MCL) for total THM (TTHM) in drinking water in the US is 0.08 mg/L [2], the same as in the European Union (EU). In Germany, the MCL is set to 0.05 mg/L [3]. The EPA specifies a total of 0.06 mg/L of the previously mentioned five haloacetic acids (HAA 5) as the maximum concentration limit.

According to Dalel Benali, Senior Scientist for chromatography and water analysis expert working for the leading French water supplier Veolia in Paris, the European Union (EU) has been given a recommendation to limit the acceptable total concentration of HAAs in drinking water to 0.08 mg/L. The health risk posed by DBPs may be extremely limited compared with the risk posed by waterborne microbial contaminants [4], says Mr. Benanou, but due to their suspected carcinogenic properties, the routine monitoring of THMs and HAAs in drinking water seems a reasonable and prudent precaution. Equally, swimming pool water should be monitored, since urine of adults and children alike has shown markedly increased HAA levels after swimming in chlorinated water, Mrs. Benali adds [5].

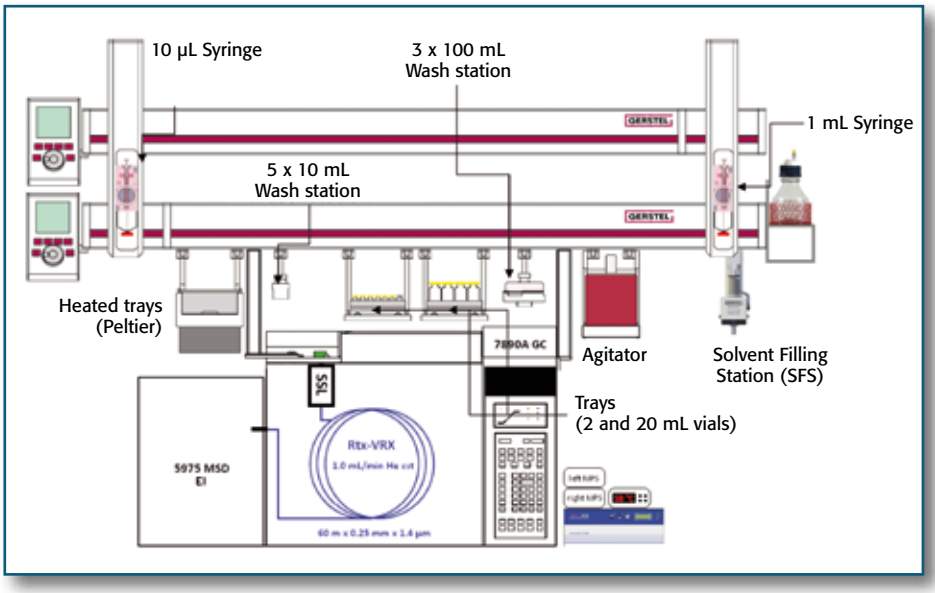
More efficiency and productivity through miniaturization and automation

In the point of view of David Benanou and Dalel Benali, who have both been involved in routine monitoring of drinking water for many years, the determination of HAAs in water needs to be automated. The US EPA method 552.3 specifies the determination of HAAs in water by liquid-liquid extraction using MTBE, followed by derivatization (methylation) and GC-ECD [6]. According to Mr. Benanou, this process is too complex and requires too much organic solvent. Even a seasoned technician can only perform 8-9 analyses per day based on manual sample preparation. By miniaturizing and automating the method using a dual rail version of the GERSTEL MultiPurpose Sampler (MPS) for the extraction and derivatization steps, and by using GC/MS instead of GC-ECD, Mr. Benanou and his scientist colleagues succeeded in dramatically improving both efficiency and throughput for the determination of THM and HAA [7].

Key factors in improving the performance are the analyte concentration and derivatization steps. HAAs are present at very low levels, are by nature polar, and are not easily separated by GC making a derivatization step necessary. The standard 552.3 method specifies the following steps: Adjust the sample pH to 0.5. Extract it with MTBE and derivatize with acidified methanol for two hours at elevated temperature. Separate the phases by add-

GERSTEL Twister

The Twister® is used for Stir Bar Sorptive Extraction (SBSE). The Twister is available in different versions, sorbent volumes, and two different sorbent phases: The polydimethylsiloxane (PDMS) Twister is well suited for extraction and concentration of non-polar to medium polarity compounds from aqueous phase; the ethylene glycol (EG) Silicone Twister is mainly useful for more polar species, especially those capable of forming hydrogen bonds as electron pair donors such as phenols, alcohols, and acids. In order to increase the overall analysis sensitivity, several quite simple approaches can be taken: Several Twisters can be desorbed, either sequentially (sequential desorption) or simultaneously and the combined analytes subsequently focused and introduced to the GC column for a single GC/MS analysis run. Using the GERSTEL Twicester® accessory, multiple Twisters can be used simultaneously to extract a single sample. For example, one Twister can be placed in the headspace of the vial while the other is immersed in and stirs the liquid phase. These Twisters can be the same or different sorbent types. For more information: www.gerstel.com



Graphic rendering of the GC/MS system and MultiPurpose Sampler (MPS) used by Veolia in Paris for automated determination of halogenated acetic acids in water. Key, labor intensive sample preparation steps specified in the EPA method were successfully transferred to the autosampler and sample preparation robot, including liquid-liquid extraction and the required analyte derivatization. The Dual Rail or Dual Head versions of the MPS enable the use of syringes with different volumes without time-consuming syringe changes.

© Veolia / David Benanou / GERSTEL

ing an aqueous sodium sulfate solution and then neutralize by adding sodium bicarbonate ($NaHCO_3$) in solution. A portion of the MTBE phase is finally injected into the GC.

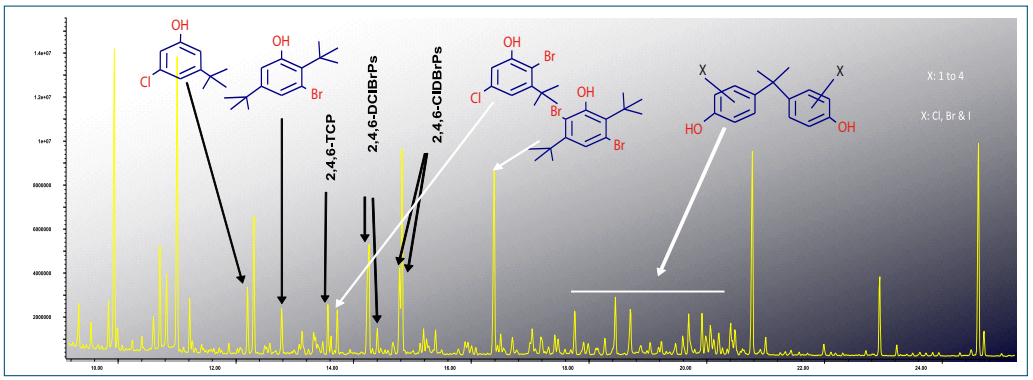
Chlorination furthers the extraction of additives from polymer pipes

When using an autosampler, in this case a GERSTEL MultiPurposeSampler (MPS), only a fraction of the time is needed for sample processing compared with the manual method. In the case of the MPS, the PrepAhead function even provides overlapping, i.e. parallel sample processing and GC analysis, helping to further accelerate matters and improve throughput. In practice, the system can analyze 32 samples per day following the EPA 552.3 method, requiring only 1 hour of technician time for sample loading, preparation and further processing. Another benefit is that much less solvent is consumed saving cost and improving the overall work environment in the lab. Method performance is equally convincing, the limit of determination is 1 ppb; the method was validated for all determined HAAs showing good linearity up to 50 ppb and a median repeatability (RSD) of 3.2 % (n=3 at 1 and 40 ppb) [7].

In practical use, says Mrs Emilie Cocardon, senior scientist at the Veolia Research Center and member of the Analytical Team, the chlorinated disinfectants react with more than just the organic and inorganic matter present in the water: The exposed surfaces of the entire supply system are made up of numerous different polymer materials used in pipes, connectors, gaskets, sieves, filters, or membranes, from which additives can leach into the chlorinated water and/or react with the disinfectant. The experts from Veolia especially focus their attention on additives such as plasticizers and stabilizers, which are used to optimize polymers for their intended use: "It is normally very difficult to predict how a polymer and the additives contained in it react to a chlorinated disinfectant", Mr. Benanou admits, "You really need empirical data". In order to determine DBPs formed as a reaction between disinfectants and polymer materials, scientists developed a special method for Veolia based on the Stir Bar Sorptive Extraction (SBSE) technique using the GERSTEL Twister combined with thermal desorption-GC/MS analysis.

Twister: The ideal Tool for water analysis

SBSE is a powerful extraction and concentration technique, well suited for ultra-trace analysis and determination of organic compounds in aqueous samples. The SBSE technique is very similar to the solid phase micro-extraction (SPME) technique. Both techniques enable the ex-



SBSE of chlorinated water was used to determine the presence of compounds leached from an experimental polymer pipe material in contact with chlorinated water. Three main compound classes were found: Halogenated phenols such as 2,4,6-trichlorophenol, 2,4,6-dichlorobromophenol, and 2,4,6-Dibromochlorophenol; halogenated alkyl-phenols; as well as various isomers of halogenated bisphenol A.

© Veolia

traction of analytes into a polymer sorption phase directly in contact with the sample. The SPME sorption phase is a thin layer applied to a fiber. SBSE uses a glass coated magnetic stir bar known as the GERSTEL Twister, coated with a significantly larger volume of sorbent phase, generally resulting in much higher analyte recovery. Handling the Twister is simple; it is designed for routine use, as Emilie Cocardon and David Benanou explain: "The analyte extraction takes place while the Twister actively stirs the sample, a large number of samples can be extracted in parallel using multi-position stir plates. The Twisters are removed from the samples, dabbed dry on lint-free cloth, transferred to sealed glass tubes and placed in the sample tray for automated thermal desorption using the GERSTEL Thermal Desorption Unit (TDU) or alternatively the Thermal Desorption System (TDS). The Twisters are individually heated in a flow of inert gas and analytes are thermally desorbed and quantitatively transferred to the GC/MS system for determination."

Twister Tap or ARISTOT

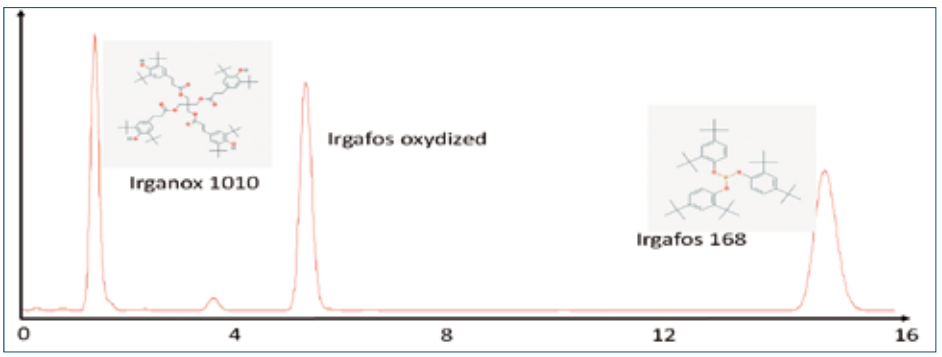
Sometimes drinking water intermittently smells strange, unsettling residents in their home or workplace. When someone finally turns up to take a sample for analysis there may not be a noticeable smell, making trouble shooting and analysis hard to perform. A patented technology is available in the form of an adapter for water faucets that enables time weighted average (TWA) sampling of water. The Twister Tap adapter holds six GERSTEL Twisters which extract odor causing compounds and other contaminants over a period of up to several days for subsequent thermal desorption and GC/MS analysis.

© GERSTEL / Sebastian Widmann

Experimental setup facilitates material testing

To determine the identity and concentration levels of compounds that could potentially leach out of polymer pipes tested for use in water supply systems, Veolia scientists have developed an experimental setup, which is beautiful in its simplicity: A piece of the water pipe to be analyzed is cut off and sealed at one end. The sealed piece of polymer pipe is placed in the upright position on a magnetic stir plate and an aqueous solution containing the disinfectant is added for a specified period of time. The solution is stirred and extracted using a Twister, and any DBPs formed and extracted are subsequently determined by TD-GC/MS. The Twister is used as described above, without the use of toxic solvents, which could dilute the extract and mask peaks of interest in the chromatogram.

Using this method, additives, including stabilizers have been determined in polymer tubing using mineral water as a test solution. Among the DBPs determined in various tested materials are 2,4,6-trichlorophenol, which readily undergoes microbial transformation to the intensely moldy smelling 2,4,6-trichloroanisol (TCA) [8]. Veolia scientists in Paris are routinely using SBSE to test polymer materials before they are accepted for use in the immense drinking water supply systems of Veolia, just in France. The main beneficiary in the end is the consumer, who can be sure that the water that comes out of the tap in his or her home is clean, safe to drink, and free from unpleasant odors.



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Chromatogram of a mineral water showing leached chemical compounds from tested polymer pipe material. The water was kept for a specified period of time inside the pipe and extracted by liquid extraction and LC/MS determination. The eluting compounds were identified as the polymer additives Irganox, Irgafos and their byproducts.

Literature

[1] Controlling Disinfection By-Products and Microbial Contaminants in Drinking Water, US EPA, www.epa.gov/sites/production/files/2015-09/documents/dwstandards2012.pdf
[2] National Primary Drinking Water Regulations, www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants
[3] https://en.wikipedia.org/wiki/Trihalomethane
[4] Disinfections and Disinfection By-Products, www.who.int/water_sanitation_health/dwq/S04.pdf and www.who.int/water_sanitation_health/dwq/fulltext.pdf
[5] M. J. Cardador, M. Gallego, Haloacetic Acids in Swimming Pools: Swimmer and Worker Exposure. Environ. Sci. Technol. 45 (2011) 5783-5790
[6] Determination of haloacetic acids and dalapon in drinking water by liquid-liquid micro extraction, derivatization, and gas chromatography with electron capture detection, https://nepis.epa.gov/Exe/ZyPDF.cgi/901V0400.PDF?Dockey=901V0400.PDF
[7] Poster Presentation, DBP 2014: Efficient Monitoring of Regulated By-Products using automated, miniaturized, green techniques. David Benanou and Dalel Benali-Raclot, Veolia Environnement, R&D Centre for Water, Maisons Laffitte (Paris), France
[8] Poster Presentation, DBP 2014: Characterization of emerging Disinfection By-Products from Polymeric Materials by in situ Stir Bar Sorptive Extraction-GC/MS. David Benanou and Dalel Benali-Raclot, Veolia Environnement, R&D Centre for Water, Maisons Laffitte (Paris), France

MS- and Two-Dimensional Linear Retention Index Database for identification of flavor compounds

The retention time of a compound on a given column phase can be expressed on a scale based on n-alkane retention times. This produces unique retention index values for compounds and serves to standardize gas chromatographic retention data. Both linear retention indices and programmed-temperature retention indices are widely used in the flavor and fragrance field and many published data bases are available. Usually mass spectral information in addition to retention time data is available from a GC run, but either information dimension alone is often insufficient for positive identification – even though modern affordable bench top instrumentation offers highly reproducible retention behavior and information rich mass spectral patterns. Aroma Office ²D, exclusively available from GERSTEL, offers an integrated software approach to automatically process retention index and mass spectral data for improved identification of flavor compounds based on the most comprehensive data base of flavor compounds commercially available. This is a searchable data base with retention index information on >10,000 compounds from greater than 100,000 entries from a wide range of literature references. The program can be integrated into the Agilent ChemStation software and searches are performed using RI values and the CAS No. of a candidate compound. After library searching, a manual cross search for a single or limited number of compounds can be performed or an automated cross search can be performed for multiple compounds. Both use a single RI and a mass spectrum for each compound. When the chromatographic analysis is upgraded to two dimensional with heart cutting the software also offers a cross search using two different retention index values obtained from the orthogonal stationary phases used in the first and second dimension analyses. When GC-O organoleptic evaluation is available from both first and heart cut dimensions these signals can provide complementary RI values. This is often sufficient to propose an identification even if the MS signal is weak or absent. Aroma Office ²D is designed to offer significant additional identification strategies to the practicing flavor analyst.

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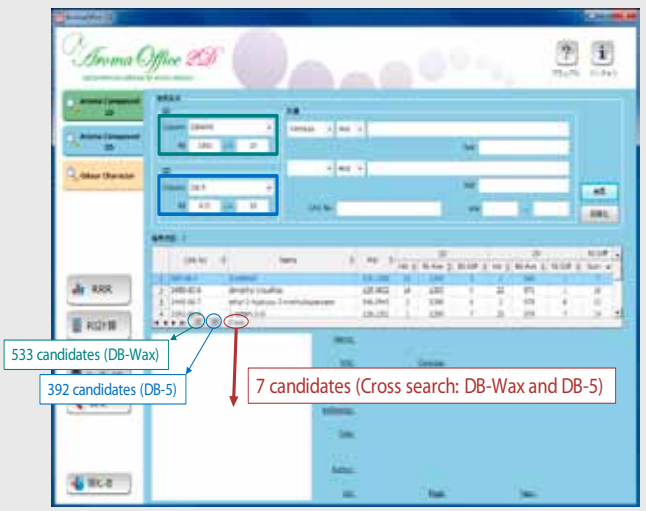
Aroma Office ²D in use: Complex Hop Essential Oil

GERSTEL AppNote 183

Aroma Office ²D (Gerstel K.K.) is an integrated software approach for simultaneous processing of both retention index (RI) and mass spectral (MS) data for rapid and improved identification of flavor compounds. The program can be integrated into Agilent Chemstation Software and searches are performed using CAS numbers of candidate compounds after library searching and corresponding automatically generated RI values. When MS signals are too weak to be used the software allows two RI values from orthogonal columns (after GC-O organoleptic evaluation) to be cross searched in the database. This offers a very useful additional identification procedure for flavor compounds. The searchable database comprises > 10,000 compounds and offers the practicing analyst full results oriented software manipulation of RI and MS data on flavor compounds.

AppNote 183

AromaOffice: Application of a Novel Linear Retention Indices Database to a Complex Hop Essential Oil, www.gerstel.com/pdf/AppNote-183.pdf



RI cross search result (DB-Wax and DB-5).

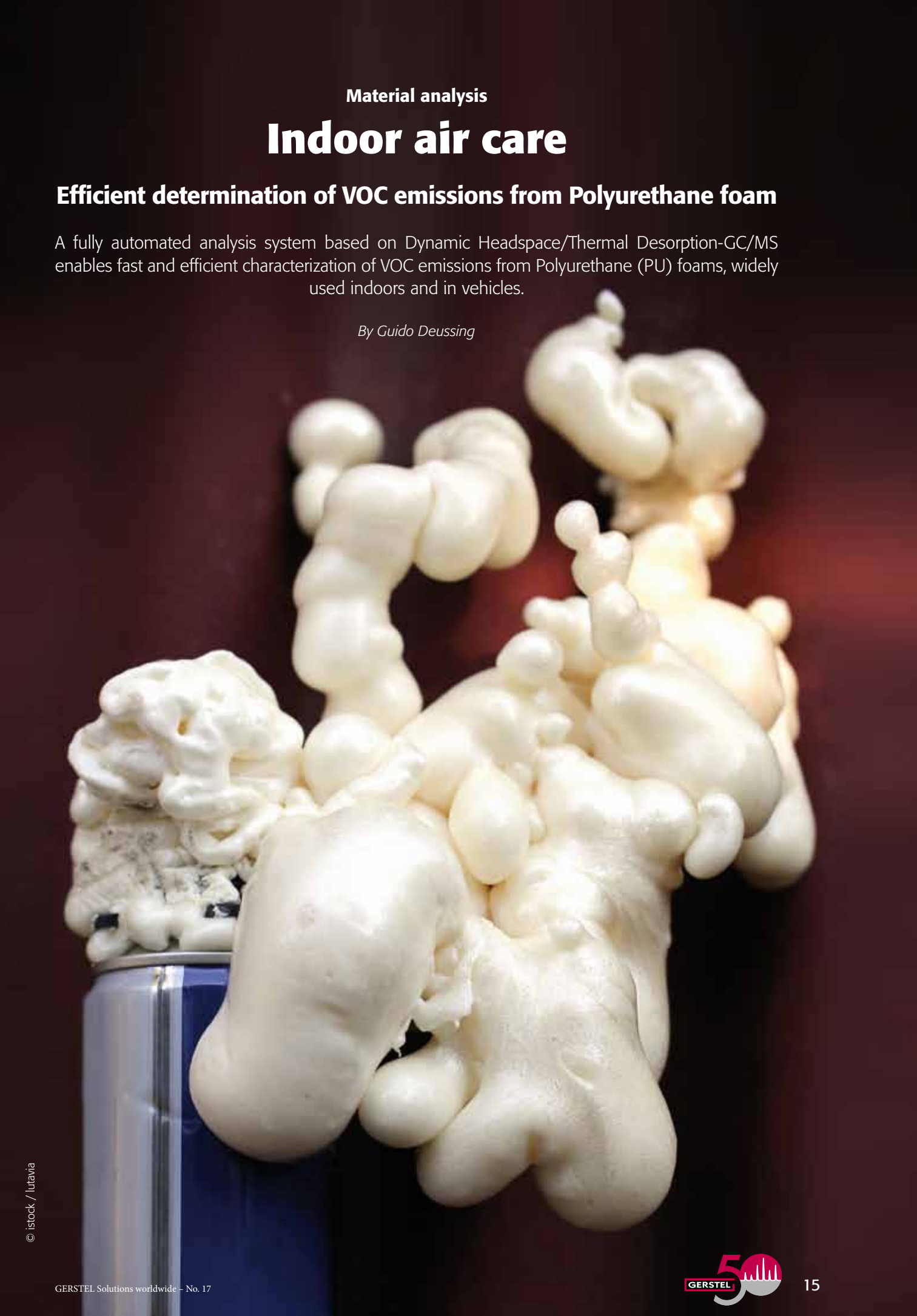
Material analysis

Indoor air care

Efficient determination of VOC emissions from Polyurethane foam

A fully automated analysis system based on Dynamic Headspace/Thermal Desorption-GC/MS enables fast and efficient characterization of VOC emissions from Polyurethane (PU) foams, widely used indoors and in vehicles.

By Guido Deussing



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Polyurethane (PU) is widely used for "indoor" applications in office and residential buildings as well as in vehicles. PU can be made into very versatile foams, well suited for use in furniture, as a sealant for windows and doors, for insulation, in vehicle dashboards and seating, and anywhere else strong and durable foam is required. Depending on the formulation, PU foams contain numerous volatile organic compounds (VOCs), including blowing agent, flame retardants, and amine catalysts. These VOCs can be emitted into indoor air potentially posing a health risk. Because of this, it is important to know just how much of these compounds are present in such materials, in other words what the emission potential is, and just how much is emitted under standardized conditions designed to simulate real world use.

Focusing on PU standard analysis methods

Most existing methods used for the determination of VOCs in PU foams are based on environmental chambers. The chambers are designed to mimic conditions found in an office, residence or vehicle, but they have some drawbacks. Certain VOCs go under-reported, or even disappear due to surface adsorption, also referred to as "sink effects". These are predominantly seen in larger, unheated, environmental chambers, which are also costly, cumbersome, and labor intensive to use. Methods that rely on much smaller micro-scale emission chambers have shown promise, but until now these have only been available as manually operated devices that require manual mounting of sorbent tubes for analyte collection. These are labor intensive to use and do not offer automated and accurate flow, temperature, and timing control, let alone method parameter tracking for validation purposes. Manual handling of micro-scale chambers is not the most efficient and reliable way to operate in the hustle and bustle of modern day laboratories. Automation of sampling parameters and sample collection is the best way to generate meaningful data on emission profiles. Application experts from GERSTEL in the US and in Germany put their heads together to test processes that would satisfy the requirements of the American Society for Testing and Materials (ASTM) for testing of Spray PU foam (SPF) materials [1].

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The PU sample is taken using a special cutting tool, which is also used as sample holder.

"The initial task of the team was to determine the influence of various method parameters on VOC emissions with the goal of assessing, which parameters impact method ruggedness", reports Eike Kleine-Benne, Ph.D., Scientist and Project Manager in the GERSTEL R&D Department. In this context, it was very helpful for the team to be able to use an automated system that allowed unattended operation with fast sampling under

The DHS Large sample containers serve as micro-scale emission chambers enabling the analysis of a wide range of samples without edge effects.

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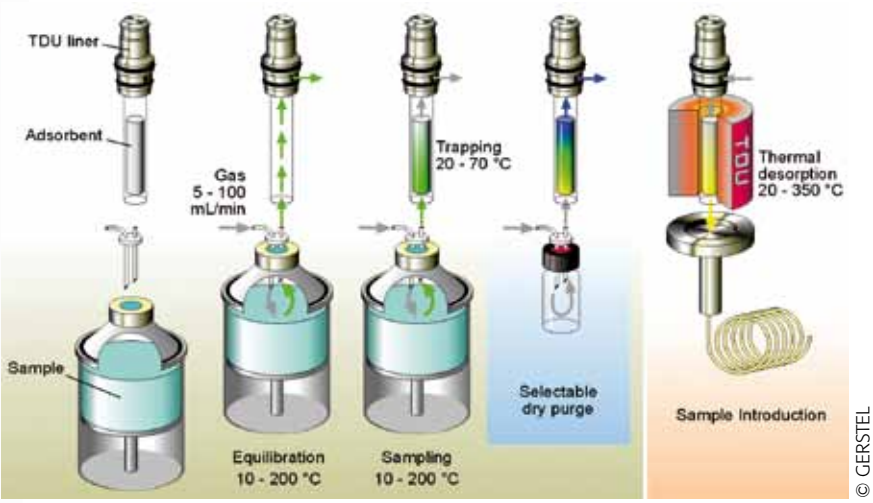

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The DHS Large process from extraction to sample introduction.

controlled and traceable conditions. In order to examine the method's effectiveness for different types of SPF, two different sample types were analyzed: Open cell PU foam and closed cell PU foam. The method parameters were chosen to replicate "real-world" conditions of the materials. Key method parameters investigated were the temperature and air sampling volume as well as GC method parameters. As a further critical item, the influence of the sample shape and size was investigated. Yunyun Nie, GERSTEL application expert explains: "We wanted to miniaturize the whole process as the best starting point to full automation, which would in turn bring us higher efficiency, less risk of errors and full traceability". The GERSTEL Dynamic Headspace (DHS) system was chosen for the project coupled with a Thermal Desorption-GC/MS system for determination of the trapped analytes. The DHS system offers automated control of a wide range of method parameters: Temperature, timing, flow, purge intervals, air volume sampled, and type of (sorbent) trap. The version chosen for the project was the DHS Large (DHS L) capable of processing samples in containers of up to 1 L in volume. The DHS L autosampler holds up to 11 samples, which can be processed automatically overnight or on weekends.

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The cutting tool remains in place and surrounds the sample throughout the analysis, meaning emissions escape and can be measured exclusively via the surface that is typically in contact with the surrounding air.

Yunyun Nie: "The DHS Large sample containers serve as micro-scale emission chambers, enabling us to investigate many different types of samples – edge effects are eliminated by using dedicated sample holders". The edge effect is caused by emission of VOCs from the "edge" of a material that has been freshly cut to fit into a sample chamber. Such emissions can cause high readings, since in typical applications VOCs are emitted only from the surface of the foam. GERSTEL has solved this problem by developing a special cutting/coring tool for taking PU foam samples, which can subsequently be placed in DHS L containers exposing only one surface. Such tools allow the researchers to properly simulate real world conditions with respect to VOC emissions from PU materials.

EVENT
Meet the authors and learn more during the
"19th Conference on Odour and Emissions of Plastic Materials"
from March 21 to 23 at the University of Kassel, Germany.
http://bit.ly/2jXo89u

Comparing Methods

In order to properly assess the results obtained with the DHS L system, the scientists analyzed the same samples in parallel using a standard method from the Association of German Automobile Producers (VDA). Method VDA 278 is widely used in the automotive industry for the determination of VOC and SVOC emissions from materials in contact with vehicle indoor air. Another aim of the comparative work was to determine the performance potential of both methods. Yunyun Nie summarizes the key facts: "Basically the VDA method 278 is quite simple to perform: A small sample is placed in a thermal desorption tube and thermally extracted at elevated temperature. This means you determine the total emission, or emission potential, for a certain sample weight and for two different compound volatility classes." Eike Kleine-Benne adds: "The question remains, however, whether this provides results that relate to real world situations. Using the DHS L, you can more accurately simulate the actual emissions from a material since these mainly depend on the surface emission rates of the various compounds monitored. This is much closer to reality, but obviously the VDA 278 method enables material producers to very quickly determine the emission potential of a material and to make sure that it is suitable for use in a vehicle".

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GC/MS system used for the determination of VOC emissions from Spray PU foam samples; to the right, the DHS Large autosampler.

As expected, the two methods provided different results [1]. The DHS L-TD-GC/MS system enabled fully automated sampling and determination of compounds emitted from the SPF sample surface at a temperature close to ambient temperature. The focus of the DHS L method parameter selection in this project was mainly on flow, temperature, and timing while generating an accurate emission-time profile for SPF with close to zero manual intervention. Such profiles can be highly useful when determining the suitability of a material for indoor use, but normally requires very time-consuming environmental chamber work. Experiments to determine material emission behavior under different material installation conditions were also performed; these were simulated simply by choosing different flow levels.

Comparing Results

As Eike Kleine-Benne reports, blowing agents, amine catalysts, and flame retardants were conclusively determined in both open cell and closed cell PU foams using the DHS L at 23 °C, the temperature specified for standard environmental chamber work in most countries. Unsurprisingly, higher temperatures were found to bring higher emission rates. A 15-hour monitoring program in the DHS L micro-scale chamber yielded unequivocal results about emission behavior and emission factors of the sample. One interesting observation was how sample thickness influenced the results. It was determined that thicker samples resulted in higher emission rates for open cell foams. "This definitely needs to be taken into account in any future standardization work", says Dr. Kleine-Benne, adding: "For open cell foam samples, the volume and thereby the internal analyte transfer plays a key role. For closed cell samples, analyte transfer through the surface is the deciding factor".

Automation brought key insights

Automation of their analysis has brought tangible benefits, the scientists agree: "The analyst is much less tied to the instrument and sample handling process, leaving time for more pressing work such as planning, data handling, and reporting". Additionally, the extensive software control provides full documentation and traceability of method parameters, which in turn helps with future method development and validation. For comparison purposes, direct thermal extraction in the GERSTEL TDS, as described in the VDA 278 method, was successfully used for qualitative evaluation of SPF and other PU foam samples. Using the two methods, the same analytes were found to be present, these were: Bis(2-dimethylaminoethyl) ether (BDMAEE), Bis(2-dimethylaminoethyl) methylamine (PMDTA), Bis(dimethylaminopropyl) methylamine (DAPA), Tris(2-chloroisopropyl) phosphate (TCPP), Tetramethyliminobis-propylamine (TMIBPA) and N,N,N-Trimethylaminoethylethanolamine (TMAEEA). "The automated system," says Eike Kleine-Benne, "helped us gain a better understanding of the emission behavior of Spray Polyurethane Foam (SPF), or rather of the constraints and rate limiting conditions that influence the emission behavior - and the results. This kind of knowledge is important to have when you set out to develop standardized methods."

Literature

[1] Yunyun Nie, Eike Kleine-Benne, Kurt Thaxton, Measurement of Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Using an Automated Micro-Scale Chamber Coupled Directly with the Analysis System, Gerstel Application Note No. 188, 2016. http://www.gerstel.com/pdf/AppNote-188.pdf

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Automated micro-scale chamber

A new fully automated micro-scale chamber analysis system for material emission testing is available from GERSTEL based on standard 3.5" sorbent tubes as specified in regulated methods. In the DHS L 3.5, samples are placed in individual inert chambers with a volume of up to 1 Liter at defined temperature and air exchange. Analytes are automatically collected at user-defined intervals followed by thermal desorption in the new TD 3.5^{+} and GC/MS determination. Emission profiles can be established automatically and automated spiking of standards onto sorbent tubes can be performed for calibration and qualification purposes. GERSTEL tubes with up to **25 % more sorbent** can be used for improved analyte recovery, higher breakthrough volume, and lower limits of detection. For more information, please contact gerstel@gerstel.com.

Improving Method VDA 278 Reproducibility through TDS Temperature Calibration

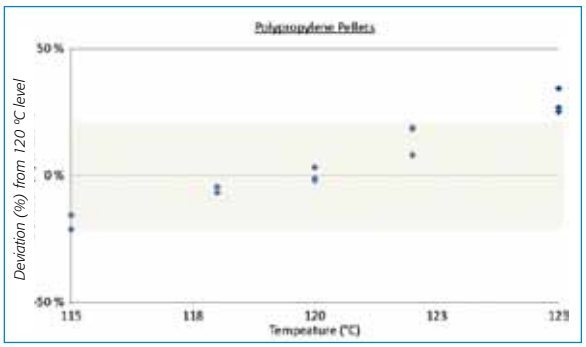
Thermal desorption instruments are widely used for determination of emissions of volatile organic compounds from materials. One technique is direct thermal extraction in which a material sample is placed directly in a thermal desorption tube. An inert gas is supplied under controlled conditions transferring released compounds from the material sample to a GC/MS system.

The widely used VDA 278 method for determination of organic emissions from vehicle interior materials is based on direct thermal extraction. When performing direct thermal extraction, the desorption temperature is the most critical method parameter, with even small changes resulting in large variations.

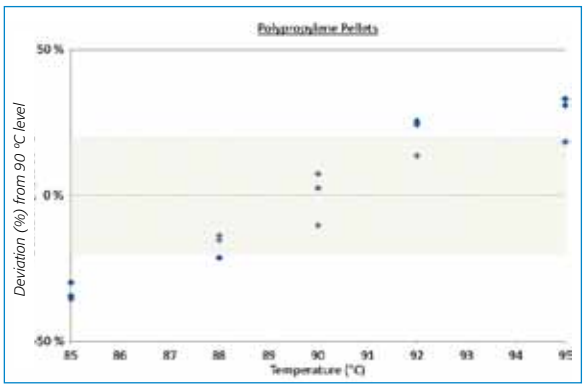
Consequently, temperature precision should be tightly controlled and verified.

The recently developed Temperature Calibration Kit for the Thermal Desorption System (GERSTEL TDS 3) ensures that the user will get the smallest possible desorption tube temperature variation for the set points 90 °C and 120 °C. The calibration is performed through temperature measurements directly in the sample position of the TDS in question on site in the customer laboratory. The procedure is performed using the GERSTEL MAESTRO software feature „VDA 278 calibration“: The TDS sample temperature is calibrated by mouse-click at 90 °C and at 120 °C with a resulting deviation smaller than ± 1.0 °C.

This ensures that reproducible results can be obtained from instrument to instrument and from laboratory to laboratory.



Temperature induced deviation (%) of VOC emission rates from polypropylene pellets compared to the emission rate obtained at 90 °C (marked grey area represents ± 20 % criteria, two or three runs were performed at each temperature).



Temperature induced deviation (%) of FOG emission rates from polypropylene pellets compared to the emission rate obtained at 120 °C (marked grey area represents ± 20 % criteria, two or three runs were performed at each temperature).

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Suggested Reading

GERSTEL Application Note No. 186, 2016 „Improving Thermal Extraction Method Reproducibility through Instrument Temperature Calibration in the Sample Position“ www.gerstel.com/pdf/AppNote-186.pdf

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In the VDA 278 method, the GERSTEL TDS/TDSA-system is listed as standard system.

VDA 278

The VDA 278 method describes Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles. The emissions are classified as VOCs and SVOCs, determined in two different runs. The SVOCs are described as condensable substances (FOG value). To achieve these results, samples are heated and released compounds are trapped and determined by GC/MS.

MPS PrepStation in the LAVES laboratories. Due to its "wing span", the staff refers to it as "Condor". The MPS guarantees uniform results when generating standard solutions even when operated by different users.

LAVES: The first and foremost address in the state of Lower Saxony, Germany, for monitoring food safety including pesticide levels in food.

© Guido Deussing (7)

Laboratory on-site: Visiting LAVES in Oldenburg, Germany

On the Wings of the Condor

The State Office for Consumer Protection and Food Safety (LAVES) in Lower Saxony, Germany, came out on top with the best results in a Europe-wide round robin test of pesticide laboratories for the determination of pesticides residues in cereals. In the words of the President of LAVES, Prof. Eberhard Haunhorst, Ph.D., this achievement is made possible by highly educated, trained, and experienced staff. While obviously true, there is more to the story: In addition to know-how and experience, top notch laboratory performance requires the right laboratory equipment. GERSTEL Solutions Worldwide magazine visited the LAVES pesticide laboratories where we joined the staff at work to gain some insight.

By Guido Deussing

The room has an air of food storage just like you would experience in a large scale kitchen facility. A whiff of ocean is mixed with a tangy earthy smell. Yesterday it was fish, today mushrooms are on the menu. These are delivered straight from the farm to the table: Mushrooms, oyster mushrooms, wood ear / Judas ear, and shiitake in little black and red baskets are lined up across the large table. However, the proof of these foods will not be in their eating – they are here to have their pesticide residue levels determined by a leading European pesticide laboratory.

Among the best laboratories for pesticide analysis in the EU

The Lower Saxony State Office for Consumer Protection and Food Safety (LAVES) has its headquarters in Oldenburg (OL), Germany. Here, the main laboratory is located, part of a network of six laboratories throughout the state. The mission statement makes it clear: "LAVES – we act for the collective good of both humans and animals". Among the bullets in the Mission Statement, may be a hint as to why the laboratories are so successful: "LAVES is committed to continuously improving its processes and achievements". Among its guiding principles is to offer full transparency and to be beyond reproach, always delivering the right results. Harmful food must never be allowed to reach the plate of the consumer. The attitude is sensible, but can it always be ensured? Reality may not always be as clear-cut even though the law is clear: Consumer safety must always be put before business interests. LAVES uses the most modern analytical techniques and equipment to monitor and test food and feed for compliance, forming a key pillar in the consumer safety structure of Lower Saxony, a German State with nearly 8 million inhabitants. The LAVES headquarters are housed in a spacious multi-storied glass covered building and harbors a leading European

GC/TOF-MS for pesticide screening: Thanks to the GERSTEL MPS with Automated Liner Exchange (ALEX), even series of "dirty" samples are easy to analyze.

pesticide laboratory for food and feed analysis. In charge and responsible for its performance is Iris Suckrau, Ph.D., a sprightly food chemist who has learned her trade step by firm step starting with vocational training as a Laboratory Technician followed by a High School Diploma and a Food Chemistry university degree capped with a Ph.D. Talented, hardworking, and ambitious, Dr. Suckrau has radiated her infectious positive energy at LAVES since

Team members: TOF, Casper, Ernie, Bert – every GC/MS System in the LAVES pesticide lab has been given a nickname.

1995, hunting for dioxin in food and feed for fifteen years before joining the pesticide laboratory. Four Scientists and 15 Technicians work in the laboratories. "When I started here, there were only four of us", she reminisces, relaxing at her neatly organized desk in an office that shows no sign of clutter. Dr. Suckrau spends as much time there as in the laboratory, going over analysis protocols, reports, and interpreting results as well as generating expert assessments. "What we generate must be legally flawless and incontrovertible in court", the scientist says, "we do not work for companies or private persons, but solely for the government and public services, our clients are food safety monitoring agencies, counties and towns". The 3,000 food and feed samples received annually by LAVES are generally submitted at the behest of the government.

Food analysis mainly of seasonal produce

In earlier years, says Iris Suckrau, food inspectors were asked to each deliver a specific number of food samples to the laboratory for testing. Some clever inspectors went straight to the nearest supermarket produce department and took samples of every tropical fruit and orange in sight, expecting them to be laden with pesticides and likely to earn the inspector praise. "They of course were able to submit their assigned number of samples in no time at all", says Iris Suckrau, "but from a consumer safety and testing stand point it didn't make much sense. Incidentally, tropical fruits are much better than their reputation".

Times have changed, though, random testing is out. Nowadays, samples are increasingly taken on a risk-assessed basis with sweeping regional controls in our own area, says Iris Suckrau: "A key focus is on seasonal produce such as asparagus and strawberries; we are, so to speak, keeping our own house in order".

Whenever Greenpeace publishes new figures that point to increasing levels of chemical residues in bell peppers, lettuce and similar produce, the workload goes up at LAVES. Sensitized by the news, food inspectors look a little closer

On the same wavelength: Iris Suckrau (left) and GERSTEL have an ongoing collaboration. The first conversation with Sales Manager for the German speaking territories Michael Gröger (right) was about the first Cooled Injection System (CIS) GC inlet, installed at LAVES in 1997.

during unannounced visits to see if hygiene regulations are adhered to and quality standards met. More samples are then taken when visiting bakeries, meat producers, food processors, food merchants, cafes, restaurants, and other large kitchen facilities. If the food quality seems lacking, and if even there is the slightest suspicion of a potential violation of consumer protection laws and food safety regulations, the inspector must take replicate samples. The initial sample is sent to LAVES and the replicate sample is sent to the producer enabling them to request a second opinion from an independent third party certified laboratory in case LAVES confirms that residue levels are indeed too high. Since such tests are costly, typically the case first goes to court and a lawyer gets involved. "The first thing the lawyer defending the company found in violation does is to perform a detailed analysis of whether the sampling was performed in strict accordance with all protocols", says Dr. Suckrau, "and because sampling procedures are both intricate and highly regulated, we train our inspectors on a yearly basis". Many inspectors are trained bakers, cooks, or other food processing professionals that have gone through extra training as food inspectors. Unless the sampling process is performed correctly Dr. Suckrau and her team can never successfully do their job.

A look behind the scenes at the Pesticide laboratory

Hissing and clattering fills the room we enter, shielded from direct sunlight by louvers outside the windows. The interior of the GC/MS lab offers a certain familiarity to anyone who feels at home in gas chromatography. Neat rows of GC/MS systems are lined up on clean lab benches. Behind them, cables and gas lines run to the ceiling to their respective connection points. Exhaust ducts hover above the instruments. But the important thing for laboratory performance is how the instruments are equipped: Most of the GC/MS systems have a GERSTEL MPS mounted on top, outfitted with different options and accessories for comprehensive automated sample preparation and introduction. The introduction techniques range from liquid injection and Large Volume (liquid) Injection (LVI) to Headspace and solid phase micro-extraction (SPME). The QuEChERS extraction method (Quick, Easy, Cheap Effective, Rugged and Safe), is widely used for pesticide analysis, and is part of the daily routine in the LAVES pesticide laboratories. The analyzed QuEChERS extracts often contain a significant amount of matrix residue. Excess matrix residue deposited in the GC inlet liner can lead to changes in analyte recovery and inaccurate results. In order to ensure system stability, QuEChERS extracts are injected using the GERSTEL ALEX option (Automated Liner Exchange), replacing the GC inlet liner at user defined intervals, in this case after every 20 injections. Matrix residue is thereby automatically removed from the analysis system, enabling unattended analysis of large batches of samples in uninterrupted sequences overnight as well as on weekends and holidays. Thanks to ALEX, strawberry extracts and other complex matrices don't pose a problem to system stability.

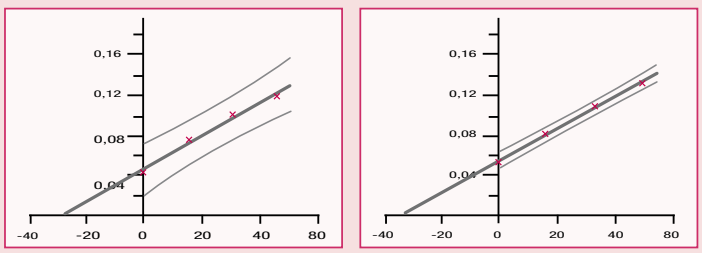
Dr. Suckrau walks over to the GC Time-of-Flight Mass Spectrometer (GC/TOF-MS), which is used to run the first tests on a sample: "Screening with GC/TOF-MS and LC/TOF-MS delivers important clues as to the presence of analytes of interest to us in the sample", she explains, "this information then enables us to find the best way forward in order to determine, for example, the pesticide residue levels as per the EU Regulation 396/2005."

Analyte quantification is then performed using a four point calibration curve. If Maximum Residue Levels (MRLs) are exceeded, the analyst proceeds in well-defined, transparent and traceable steps using standard addition: The pesticides of interest are added to the individual samples in known concentrations. "Speaking of standard addition", Dr. Suckrau suddenly says, "follow me!" The scientist marches towards the window area, takes a sharp right turn at the end of the bench, and stops in front of a GERSTEL

LAVES has a huge arsenal of standard substances at its disposal. These are used to generate dilution series, for quantification and reference purposes.

MPS XL PrepStation in Dual Rail configuration. "Due to its wingspan, we call this MPS stand-alone WorkStation the Condor", explains Katja Kruse, a co-worker of Dr. Suckrau, "it holds a large number of standards and solutions in refrigerated trays for extended storage stability". "The PrepStation", Dr. Suckrau explains, "is extremely important to us". European Union (EU) regulations for method validation and quality control in pesticide analysis require us to validate our results. To this end, LAVES stocks an arsenal of hundreds of reference standards, which can be used to generate standard solutions, mixtures, and associated dilution series. "As has clearly been established", the scientist continues, "the standard addition technique is the best possible method when it comes to confirming and validating analysis results exceeding the specified MRLs. And this applies to both GC/MS and LC/MS". Before "Condor" was given its well-deserved place in the lab, a lot of time was spent on preparing standard solutions, but the quality of these standards was not always sufficient to obtain final results of the highest quality. "Using the MPS PrepStation, we not only work more efficiently, we reliably generate accurate and highly reproducible results", says Iris Suckrau, "and that is extremely important, especially for a public agency that needs to deliver irreproachable evidence for court cases to help enforce consumer safety standards".

For improved quality and productivity leading laboratories like LAVES produce validated standards and automate their sample preparation using the GERSTEL MultiPurpose Samper (MPS). Pictured Katja Kruse (left) and Iris Suckrau.



Manual Standard Addition **Standard Addition using the MPS**

Automating the standard addition process helps on two fronts: Efficiency and performance. Shown to the left: The reproducibility resulting from manually generated standard addition, using pipette and dispenser. Shown to the right: Improved reproducibility resulting from automated standard addition using the GERSTEL MPS.
Source: LAVES, Oldenburg, Germany.

Laboratory robots are only human...

Incidentally, all GC/MS systems in the room have been given nicknames: They are called Casper, Ernie and Bert, and it seems not only out of deference to "Sesame Street": "By giving individual systems clearly recognizable names, it becomes easier to keep an eye on both the instrument and the task assigned to it", according to Dr. Suckrau. Maybe we humans have a propensity for assigning personal traits and identities to robots and machines, as assistants and friends.

Accurate Transfer of Liquids for highest precision using a bench-top Workstation and Accurate Add

AppNote 187

GERSTEL

AppNote 187

Automating the Accurate Transfer of Highly Volatile to Highly Viscous Liquids using a Bench-top Workstation www.gerstel.com/pdf/AppNote-187.pdf

Highly accurate standard addition and generation of standards and dilution series can significantly improve the quality of analysis results. Several useful tools and techniques are presented and evaluated, including thermostating; weighing; Accurate Add function for improved sampler precision; and vial venting to eliminate vial pressure build-up.

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Example: ALEX-GC-MS/MS-System for QuEChERS, Metabolomics, and Liquid Sample Prep

Preview – coming up in the next issue


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Climate change impacts tea quality

Extreme weather with alternating drought and heavy rainfalls can have negative impact on both yield and quality of crops such as tea. These are the conclusions reached by US scientists who have been assessing seasonal tea crops from monsoon areas in China. Multidimensional chromatography and a special data analysis software were important contributors to the success of the project.

Priority Pollutant DDT in sediment

If you are asked to deliver a statement as to the degree of pollution in ocean sediment and to assess the danger to aquatic wildlife, the bio-availability of priority pollutants stored in the sediment will probably need to the investigated. The US scientists Robert P. Eganhouse and Erica L. DiFilippo developed a method based on thermal desorption GC/MS, with which this task could be performed in a "simple, cost-efficient and precise manner".


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Innovative solution for metabolomics

When large sets of blood-, plasma-, or urine samples must be analyzed within an acceptable period of time, under constant conditions, and with reliable reproducible results, manual sample preparation may not be the most sensible approach to the task at hand. Metabolomics studies generally require an automated approach. Laura Yung Wang et al. developed a rugged, fully automated method for the determination of phospholipid fatty acids in human plasma for metabolic phenotyping.

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