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.

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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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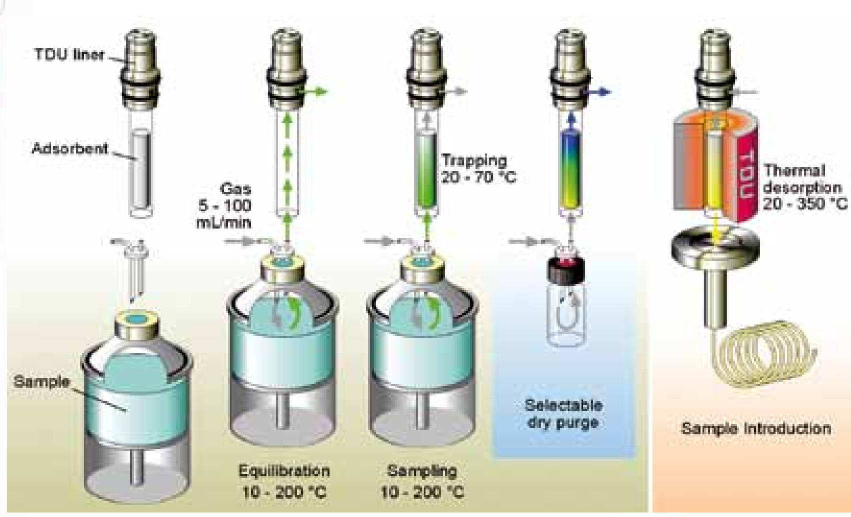

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The DHS Large process from extraction to sample introduction.

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

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.