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50th ANNIVERSARY Shimadzu Europa

Cannabis testing

Customized solutions
meeting latest regulations

Rookie of the Year

New benchtop instrument
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the portfolio

Let's have a party!

50th anniversary celebration
and future perspectives

The quantification of color

Laser toner and nail polish – Study on color pigments with UV-Vis spectroscopy and color analysis software

Inks and pigments make the world colorful. But today, color is not purely ornamental, a signal or symbol, it can also be precious: toner for laser printers is said to be more expensive than its weight in gold.

Figure 1: Shimadzu UV-2600 spectrophotometer

Depending on its characteristics, color generates films for protection against sunlight, heat, corrosion, and many more. To ensure a constant quality, color is prepared following regulations, which describe color scales to make the production of color independent of human subjective judgement.

The material property "color" is linked to the absorption, transmission or reflection of visible light. Pigments absorb light of some wavelengths, appearing in the complementary color to the absorbed light. For this reason, UV-Vis spectroscopy is the tool of choice to measure the color of pigments. While the wavelength of transmission or reflection maxima already gives some implication of the color, the use of color models independent from the measurement method is much more practical. With color software, the transmittance or reflectance values are used for the calculation of color coordinates that describe the color in the context of a given color model.

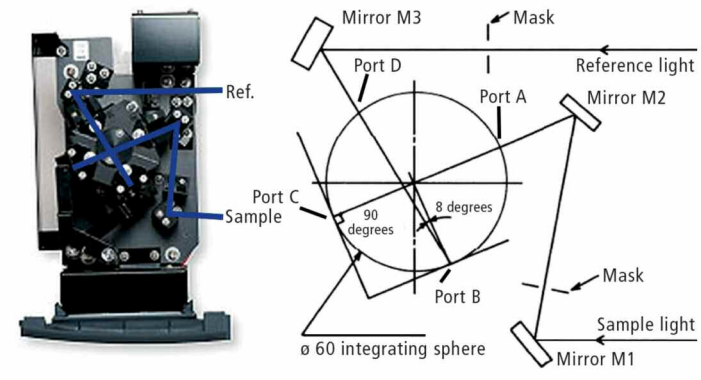


Figure 2: Shimadzu ISR-2600plus integrating sphere with beam diagram

In this application, the Shimadzu UV-2600 spectrophotometer equipped with the ISR-2600plus integrating sphere is used to measure diffuse reflection spectra of laser dye pigments and to calculate color coordinates of these pigments with the LabSolutions UV-Vis color software. Additionally, nail polish samples are measured in direct transmission for the color analysis.

Integrating spheres

The integrating sphere is a hollow ball made of highly reflective material with ports for detectors, samples or white standards. Light entering the sphere through an opaque solid or reflecting into the sphere from a

diffuse reflector will be collected by the reflective inner surface of the sphere and recorded by the detectors.

Figure 2 shows the schematic of the ISR-2600plus. The detectors are mounted on top and bottom of the sphere and are excluded from the diagram on the right side.

Sample and reference beam can be switched depending on the target measurement. To measure the diffuse only reflectance from a sample, the sample is placed at port C and the sample beam enters through port A. Specular reflected

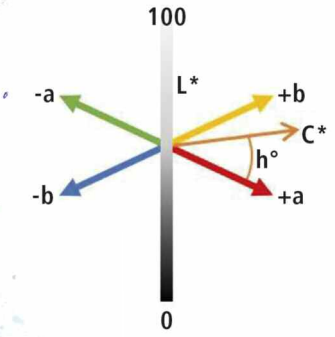


Figure 3: CIELab color scheme illustrated as vectors

light is excluded, as it exits the sphere through port A. To include specular reflectance, the sample is mounted on port B and the sample beam enters through port D. The incident angle of light to sample surface in that case is 8 degrees and a mixture of specular and diffuse reflected light is included in the measurement. For transmittance measurements, the sample is placed at port A. White standards are used to close ports B and C if no sample is placed there.

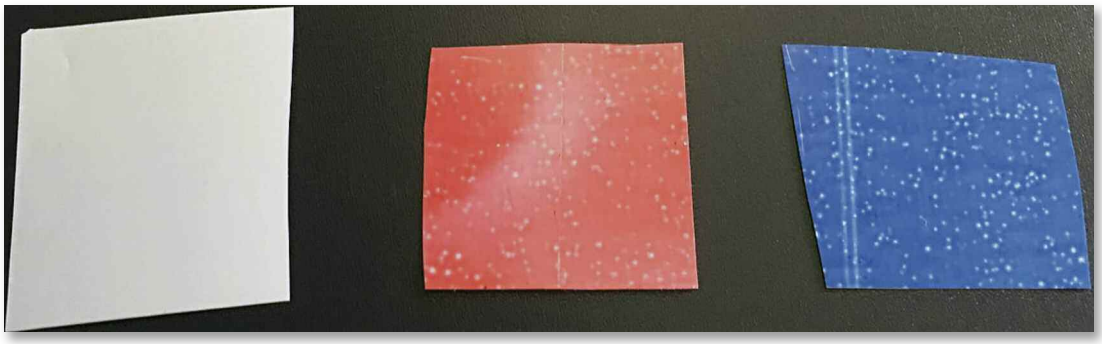


Figure 4: Laser dye film samples. From left to right: White, red and blue.

Figure 5: Nail polish film samples. From left to right: Gel blue, blue, turquoise, yellow, orange, pink, red.

Color models

Two popular color models are used in this application. The color values are calculated from the reflectance spectra by different equations, that are not described in detail here.

One color model is the tristimulus model [1], which describes color as combination of three (abstract) color stimuli X, Y and Z. This model is based on the three kinds of color receptors in human eyes and how the mixture of stimuli is interpreted as color by our brain.

A graphical representation plots color coordinates x and y in a representation similar to the color circle ("color horseshoe"), as shown on the left side of figure 8 (page 4).

The CIELab [2] model is based on a three-dimensional color space and was developed to represent color in a manner that is consistent with human perception of color. The axes of the three-dimensional coordinate system are based on the three stimuli bright – dark, red – green and blue – yellow.

Any point in the CIELab color space can be described by its lightness index L* and either in cartesian color coordinates a* and b* or in polar coordinates hue angle h° and chroma C*. Hue is the color as in the color circle and chroma is the intensity of that color. A graphical representation uses a two-dimensional plot for the color coordinates at one fixed L* (right side of figure 8) or a three-dimensional color sphere.

Just as our perception of colors depends on the lighting conditions, the color values in each model differ with the chosen reference light source and observation angle. This choice depends on the purpose of the color measurement, e.g. color fastness of products that are presented to customers under defined lighting conditions. Here, the standard illuminant D65, ▸

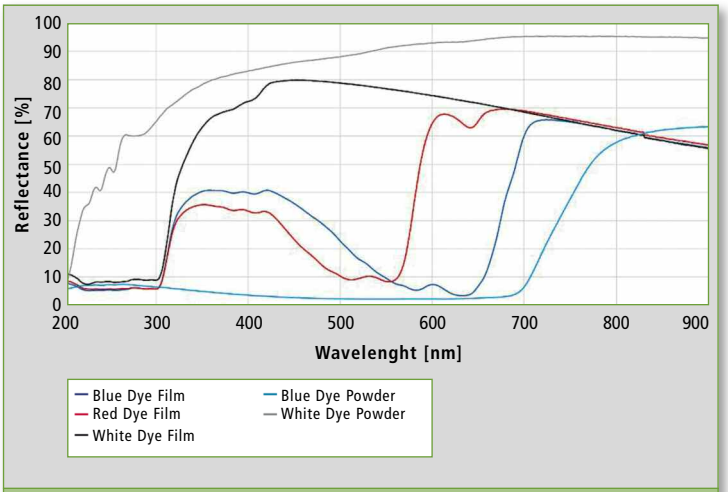


Figure 6: Diffuse reflectance spectra of the laser dye samples

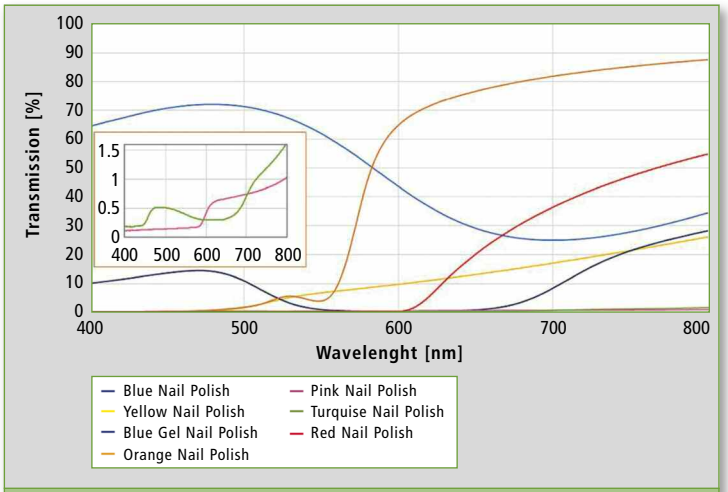


Figure 7: Spectra of the nail polish samples. Inset: zoom into the spectra of the turquoise and pink nail polish.

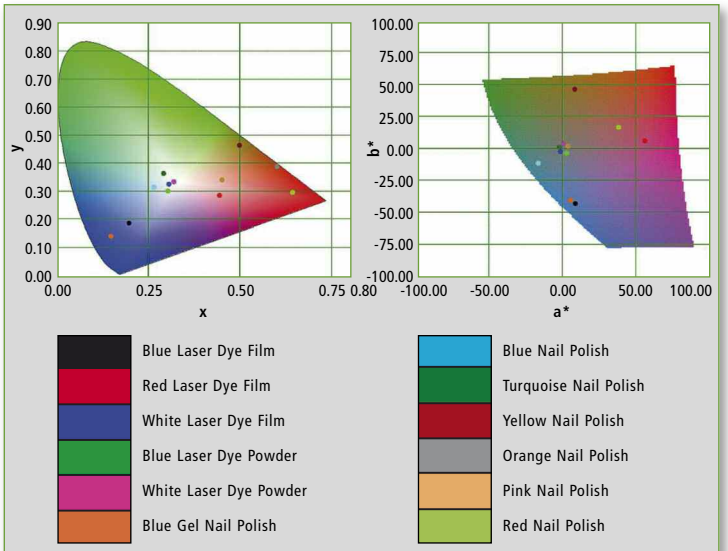


Figure 8: x-y-plot (left side) and a*-b*-plot (right side) of the color coordinates from table 1. Mind that brightness L* is not plotted, but it is different for all samples.

that simulates sunlight, and an observation angle of 10° were used for all calculations.

Samples

Three powder samples and three film samples from ink and pigments were analyzed. The powders were coarse and would be difficult to measure by pressing into the surface of Barium Sulphate (the preferred method of sample preparation), so instead were measured in a special powder cell. Each of the laser dye samples was mounted at the diffuse reflectance port (port C in figure 2, page 2) of the integrating sphere. The reference material was uncovered Barium Sulphate, the surface material of the integrating sphere.

Seven different nail polishes were applied to glass substrates and measured with a film holder in direct transmission mode without integrating sphere. A clean glass plate was used as reference.

Spectra

The diffuse reflectance spectra in the range of 200 - 900 nm are shown in figure 4 (page 3). The dark and light blue traces are from the blue dye film and powder measurements, the black and grey lines are from the white dye film and powder measurements and the red trace is from the red dye film measurements.

All film spectra show peak structures in the range around 400 nm. These may be characteristic for the film material or the base coat of the treatment. The spectra of the white samples show a more or less flat line over the visible range, as expected. The spectrum of the red sample shows a reflectance maximum at 600 nm and general high reflectance in the red spectral region. The blue color is not reflected by specific peaks: both film and powder sample of the blue dye show the highest reflectance in the region of 700 nm and above and a small maximum at 600 nm. Blue is a mixed color in this case and a more detailed analysis is needed to discern it from the spectrum.

The spectra of the nail polish samples are shown in figure 7 (page 3). Most of the colors are already indicated by the transmission maxima. The spectra of the blue nail polishes show a transmission maximum below 500 nm, at the edge of the blue and green spectral region. Blue is again a mixed color here. The spectrum of the turquoise nail polish shows a transmission maximum around 500 nm, in the green spectral region. This transmission maximum is shifted to longer wavelengths for the orange nail polish. The spectra of the yellow and red nail polishes don't show a sharp peak, but a general rise of the transmission value that starts in the yellow and red spectral region, while the pink line shows a steep rise of the transmission value at 600 nm. All spectra show a rise of transmission towards the red end of the wavelength scale.

Color analysis

The five diffuse reflection spectra from figure 6 (page 3) and the seven transmission spectra from figure 7 (page 3) were evaluated with the LabSolutions UV-Vis color module [3]. The evaluation table is shown in table 1. Evaluation items are: peak wavelength, color coordinates x, y, a* and b* and lightness index L*. For all color coordinates and the lightning index, standard illuminant D65 [4] was used as colorimetric illuminant and 2° as viewing angle.

Sample Name	Peak [nm]	x	y	L*	a*	b*
Blue Laser Dye Film	421	0.2	0.2	40.0	8.7	-43.2
Red Laser Dye Film	600	0.4	0.3	57.6	56.1	5.9
White Laser Dye Film	451	0.3	0.3	90.0	-1.7	-2.3
Blue Laser Dye Powder	400	0.3	0.3	16.0	2.7	-3.5
White Laser Dye Powder	599	0.3	0.3	96.5	0.5	3.5
Blue Gel Nail Polish	470	0.1	0.1	19.4	5.3	-40.7
Blue Nail Polish	478	0.3	0.3	80.5	-16.6	-11.6
Turquoise Nail Polish	480	0.3	0.4	3.5	-2.4	0.8
Yellow Nail Polish	600	0.5	0.5	31.6	8.4	46.5
Orange Nail Polish	600	0.6	0.4	57.0	55.3	88.4
Pink Nail Polish	600	0.5	0.3	2.1	3.6	1.6
Red Nail Polish	600	0.6	0.3	11.9	38.0	16.4

Table 1: Evaluation results for the dye UV-Vis measurements and the LabSolutions UV-Vis color analysis.

Figure 8 shows the plot of the x and y color coordinates in the left graph and the plot of the a* and b* color coordinates in the right graph. This analysis shows, that all expected colors are indeed reflected in the color graphs, even though they might not be visible at the first glance of the spectra. The white samples are placed in the green region in the a*-b*-plot by their color coordinates, but they show very high lightness indices L*, near 100 %. All three values are important, when judging a color. In the x-y-plot they are at the white center, as expected.

Conclusion

UV-Vis spectroscopy is a valuable tool for color analysis and quality control. Even though human individual perception of colors might be different, the use of color models with defined illuminants and observation angles allows to define testable color coordinates. This analysis works well both for transmission and reflection spectra. With the LabSolutions UV-Vis color software, the color analysis is easily done without the need to export data and it can even be automated.

Special thanks to:

Dr. Robert Keighley, Shimadzu UK for the results of the laser dye measurements.

Literature

[1] https://en.wikipedia.org/wiki/CIE_1931_color_space
[2] https://en.wikipedia.org/wiki/CIELAB_color_space
[3] ISO 11664-2:2007(E)/CIE S 014-2/E: 2006 colorimetric illuminants
[4] LabSolutions UV-Vis Brochure

Rookie of the Year

MALDI-8020: new benchtop instrument in the MALDI portfolio

The new MALDI-8020 complements Shimadzu's MALDI family. The linear benchtop time-of-flight mass spectrometer serves various applications in the positive ion mode, such as analysis of proteins, peptides or polymers. It is ideal for researchers developing MALDI-based diagnostic methods, and for routine labs carrying out quality control and fast analysis of intact samples.

The MALDI-8020 is fast and accurate, has a high resolution and its compact size makes it fit in any laboratory. The robust design promises reliable analysis and low maintenance. The MALDI-8020's features make it the 'Rookie of the Year.'

Rookie of the year: the new compact MALDI-8020

Impressive performance

With a mass range of 1-500,000 Da, a mass resolution of more than 5,000 (for ACTH 18-39, *m/z* 2,465), a mass accuracy of < 20 ppm after internal calibration and a sensitivity of 250 amol (Glu-Fib, *m/z* 1,570), the MALDI-8020 achieves the same specifications as the more advanced version, the Axima Assurance for high throughput screening.

Compact size – quiet pumps

Thanks to its small dimensions of 450 x 745 x 1,055 mm and weight of 86 kg, the new MALDI-8020 fits on any lab workbench. The oil-free diaphragm pump and a turbo pump ensure reliable and low-noise operation (< 55 dB).

Optimized ion source for a faster analysis

Extra-fast motors drive the high-speed stage. Motor installation outside the vacuum reduces the volume to be evacuated, so pumping time after changing of sample is the fastest on the market: around 90 seconds. The 200 Hz solid-state laser allows further optimization of the analysis time. The typical Shimadzu wide-bore ion optics increase ion transmission and reduce the likelihood of contamination. If the source is nevertheless contaminated, it can be cleaned within ten minutes using the UV laser-based TrueClean.

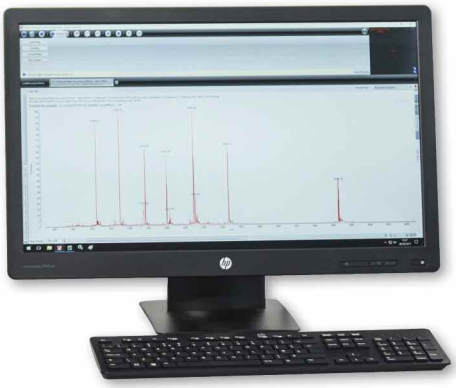
Various fields of application

The MALDI Solutions software provides intuitive and easy operation, and includes interfaces for evaluating polymer, protein and oligonucleotide spectra.

SampleStation, AuraSolution and QC Reporter offer various options for automated lab routines. During sample preparation, data can be collected with the SampleStation software.

The barcode reader integrated into the mass spectrometer enables automated measurement using AuraSolution. The QC Reporter software allows specification of different criteria that can be used for automatic evaluation of the analyses.

Data is stored in a Microsoft® SQL database with automatic backup. Personalized user logins can be used to document quality control, and different levels can be assigned to individual users. In this way the user is prepared for potential audits.



Conclusion

The MALDI-8020 has a compact and robust design and offers a low-cost solution for broad fields of application, including research and teaching as well as quality control.

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Counting down the days

RoHS II – screening of phthalates in electrical and electronic equipment

On 22nd of July 2019, the EU RoHS II directive will come into effect. The transition period will then be over and limit values for four phthalic acid esters in electrical and electronic equipment must be adhered to.

Some phthalic acid esters, known as phthalates, have been banned in Europe since years due to their potential health risks. Since 2009, limit values have been applied to the content of certain phthalates in toys and baby products which can be hazardous when put into children's mouths. The list of products for which phthalate concentration is regulated by law is expanding constantly. It covers cosmetics, plastics for food packaging and soon also electrical and electronic equipment.

Time and again, some phthalates make headline news as substances hazardous to health. Low molecular phthalates such as di-(2-ethylhexyl)-phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DIBP) are especially suspected of having an endocrinological (hormone-like) effect. Endocrine disruptors affect hormonal balance and can cause health disorders in sufficiently high concentrations. The effect of substances that interfere with the sex hormone system and impair reproductive ability is currently the subject of heated debate.

DEHP, BBP, DBP and DIBP in the RoHS II Directive

The compounds listed above (DEHP, BBP, DBP and DIBP) have therefore been included in the EU REACH chemicals regulation. Since February 21 2015, they may only be produced and used with a special exemption that is difficult to obtain. Additionally, the European Commission has decided to restrict the four phthalates with the RoHS II Directive (Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment).

Figure 1: Pyrolysis-GCMS

The RoHS II Directive specifies a maximum permissible concentration of 0.1 mass percent (i.e. a maximum of 1,000 mg/kg) per substance. The planned transition period expires for most device groups on 07/22/2019. Medical devices as well as control and measuring instruments have a longer period until 2021.

Phthalates are still used worldwide as plasticizers, especially in plastics such as PVC, nitrocellulose or synthetic rubber. According to current EU legislation, manufacturers of electrical and electronic equipment are now obliged to ensure that their equipment complies with RoHS. The manufacturers must therefore ensure that the content of the four regulated phthalates is lower than the limit of 1,000 mg/kg. In particular, companies that process supplied products must rely on the supplier or check for themselves.

Special screening method for phthalates in polymers

The IEC 62321 international test standards provide methods enabling the electrical industry to determine the concentration of certain regulated substances in electrical products on a globally uniform basis. Part 8 of this standard (IEC 62321-8:2017) describes the method for determination of "phthalates in polymers by gas chromatography mass spectrometry (GC-MS) and gas chromatography mass spectrometry using the addition of pyrolysis/thermal desorption (Py/TD-GC-MS)." The Py-Screener described here was specially developed as a screening method to determine phthalates in polymers and is fully compliant with Part 8 of the IEC 62321 standard.

Figure 2: Sample preparation tool kit

A major advantage of this screening method: it needs very little sample preparation, and the complete method package allows polymer samples to be analyzed quickly without the necessity for extra method development. Classical methods of analyzing and quantifying phthalates are based on complex sample preparation. In this case, extraction of the samples occurs using a solvent over several hours, with subsequent GC-MS analysis.

The Py-Screener is based on a coupled pyrolysis GC-MS. For measurement, a small piece of the polymer sample (approx. 0.5 mg) is placed in a stainless steel cup and entered in the preheated pyrolysis furnace using an autosampler. The semi-volatile phthalates are extracted from the polymer using a special temperature program. Gaseous phthalates are transported with a helium carrier gas stream into the gas chromatograph, separated on the analytical column and then identified and quantified with the mass spectrometer.

Pyrolysis GC-MS method package

The method package of the Py-Screener supports users right from the beginning with a detailed manual describing each step. Sample preparation of standards and polymer samples can even be followed via a video tutorial. Depending on the shape, the sample is punched out or cut with the tools from the toolkit (figure 2) and then weighed

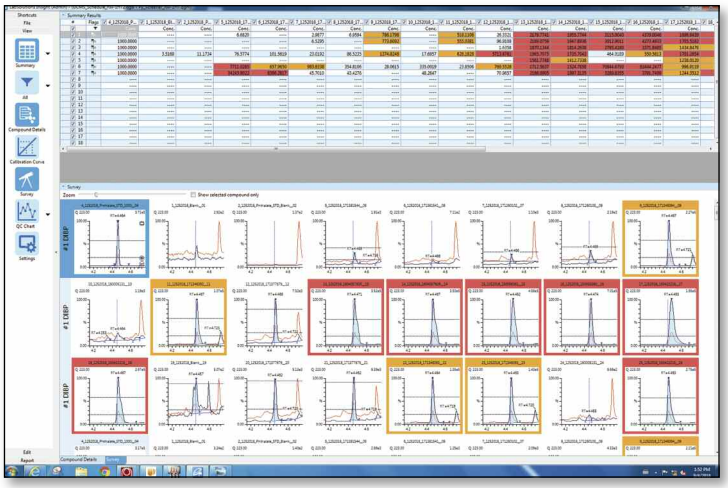
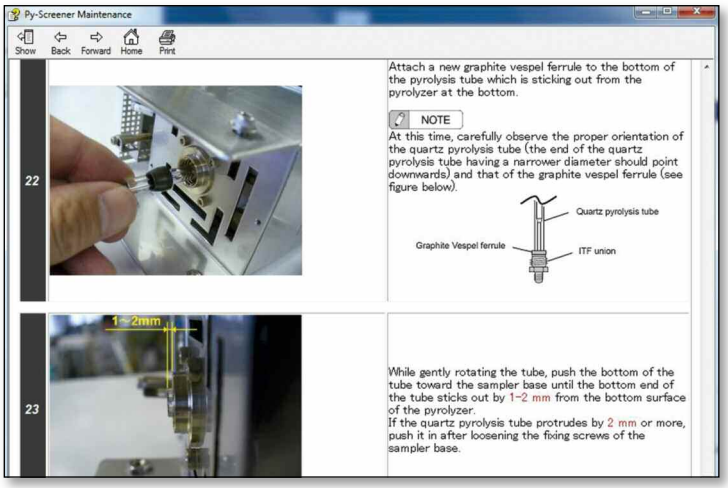


Figure 3: Special evaluation software: For faster optical identification, different concentrations of indicator substances are highlighted in color.



Figures 4a and 4b: Examples from the Maintenance Navigator

for quantification. Method and instrument parameters are already optimized for the analysis of phthalates; batch tables for sampler and instrument software only have to be filled in.

Calibration and quantification parameters are already part of the method, including QA/QC controls to check sensitivity of the system and column performance. With the unique AART function (Automatic Adjustment of Retention Time) of the GCMSsolution software and a simple alkane standard, retention times of the quantification table can be adapted easily and quickly to a new column or, after maintenance work, to the shortened column.

Measurements are evaluated in the LabSolution Insight software, which was developed specially for processing large sample quantities. Data is presented clearly in tabular and graphical form, and the quantification results are color-coded with so-called flags (figure 3). This allows users to see with a glance whether the concentration of a polymer sample is harmless or far above the limit value. In both cases, the sample requires no further analysis.

Screening and exact quantification without modification using GC-MS

However, if the phthalate concentration determined by the screening method is within the range of the limit value (500 -1,500 mg/kg), a second, more precise quantification should be carried out to determine the exact concentration. One possibility is the classical GC-MS method with prior extraction of the sample and subsequent liquid injection.

Shimadzu's Twin Line MS System is an ideal solution. It is equipped with an additional liquid injector, an autosampler (AOC-20i) and a second capillary column. With a special kit, both columns can be installed simultaneously in the mass spectrometer as the powerful turbomolecular pump of the GCMS-QP2020NX allows a column flow of up to 15 mL/sec. With this system, either polymer samples can be screened or extracted liquid samples can be quantified exactly without further modification of the GC-MS.

The all-round package also includes a "Maintenance Navigator" which supports users with detailed descriptions and clear step-by-step illustrations for regular maintenance work, such as replacing the pyrolysis or injector liner. If a leak occurs in the system, the "Maintenance Navigator" provides valuable information for systematic troubleshooting (figures 4a and 4b).

Analysis of polybrominated flame retardants

In addition to limit values for some heavy metals, the RoHS I Directive already prescribes a maximum concentration for the organic compounds PBB (polybrominated biphenyls) and PBDE (polybrominated diphenyl ethers) used as flame retardants. These compounds are also GC-MS compatible and can be analyzed with the Py-Screener system. The optimized methods are already part of the package and can be used directly if required.

Conclusion

The "Py-Screener" screening system is a comprehensive package for the analysis of phthalic acid esters in electrical products and is compliant with Part 8 of the IEC 62321 standard. The package contains optimized method and instrument parameters, ready-made sequences for pyrolyzer and GC-MS software, a toolkit for sample preparation and special evaluation software. This makes quantification of phthalates easy to learn, even for new users. As a screening method, the Py-Screener saves both solvent consumption when compared to classical methods, and time, since many polymer samples can already be excluded from further analysis after the first measurement.

Literature

[1] Official Journal of the European Union 6/4/2015.

[2] Commission Delegated Directive (EU) 2015/836 of 31st of March, 2015, directive of the European Parliament and of the Council amending Annex II to Directive 2011/65/EU as regards the list of substances subject to restrictions.

Further information on this article:

- Brochure: C146-E285 Py-Screener
- Application: Analysis of Phthalate Esters using the Py-Screener (1) (LAAN-J-MS-E110); Analysis of Phthalate Esters using the Py-Screener (2) (LAAN-J-MS-E111)
- Technical Report: Comparison of Screening Method (Py-GCMS) and Quantitative Method (Solvent Extraction-GCMS) for Phthalate Ester Analysis

Customized solutions for cannabis testing

Analytical solutions meeting latest regulations

As of July 2018, over 20 European countries have legalized cannabis for medical use, and more are expected to follow in the coming years. Possession of cannabis is still illegal by federal statute; however there is an ongoing debate concerning legalization of medical and recreational cannabis. The demand for cannabis testing and analytical tools is therefore growing.

Numerous health benefits have been reported for cannabis, including general pain reduction, antinausea and reduction of seizures and autism. QC testing for cannabinoids is essential for the accurate labeling of cannabis products in both medical and recreational cannabis markets. Cannabinoids are the primary active components of cannabis; these are target compounds for potency testing. Terpenes influence the homeopathic effect, and contaminants such as pesticide residues and mycotoxine in cannabis products also need to be controlled to ensure consumer safety.

Shimadzu offers a wide range of analytical equipment and provides customized solutions, appropriate configurations and application support for cannabis analysis, including sample preparation.

Potency testing for cannabis products by HPLC

While the reason for controversy of cannabis as a legal medicine is the psychoactive effect of only one of the cannabinoids contained, namely Δ9-tetrahydrocannabinol (d9-THC), therapeutic benefits such as pain relief and reduced severity of nausea and seizures were also reported with use of a combination of other phytocannabinoids [1, 2]. Additionally, a number of studies showed high safety with regard to a wide array of side effects and no tolerance to cannabidiol (CBD), another major component of cannabis, has so far been demonstrated [3, 4]. CBD-rich products with no or neglectable d9-THC content are therefore becoming increasingly popular, as they can

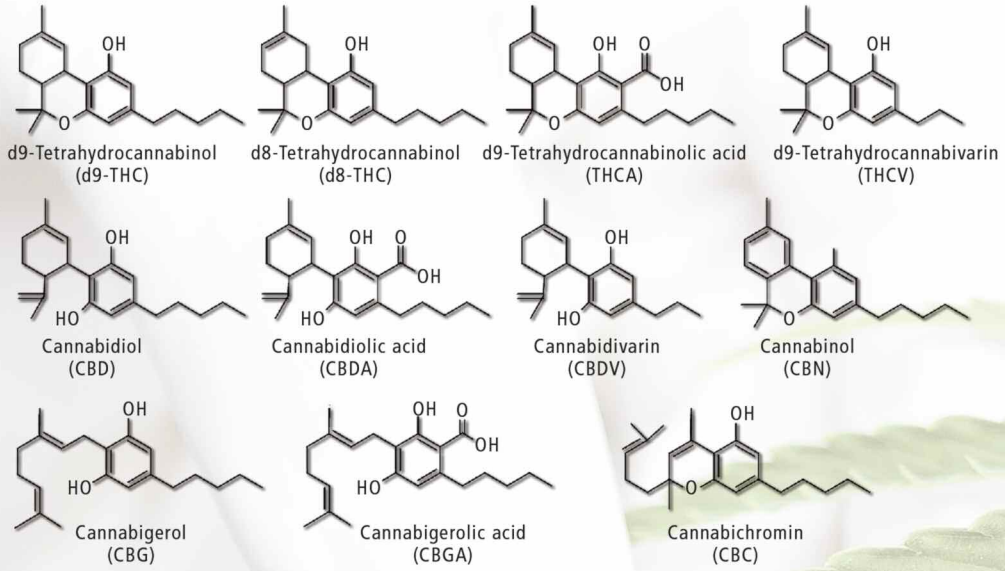


Figure 1: Cannabinoids determined in potency testing

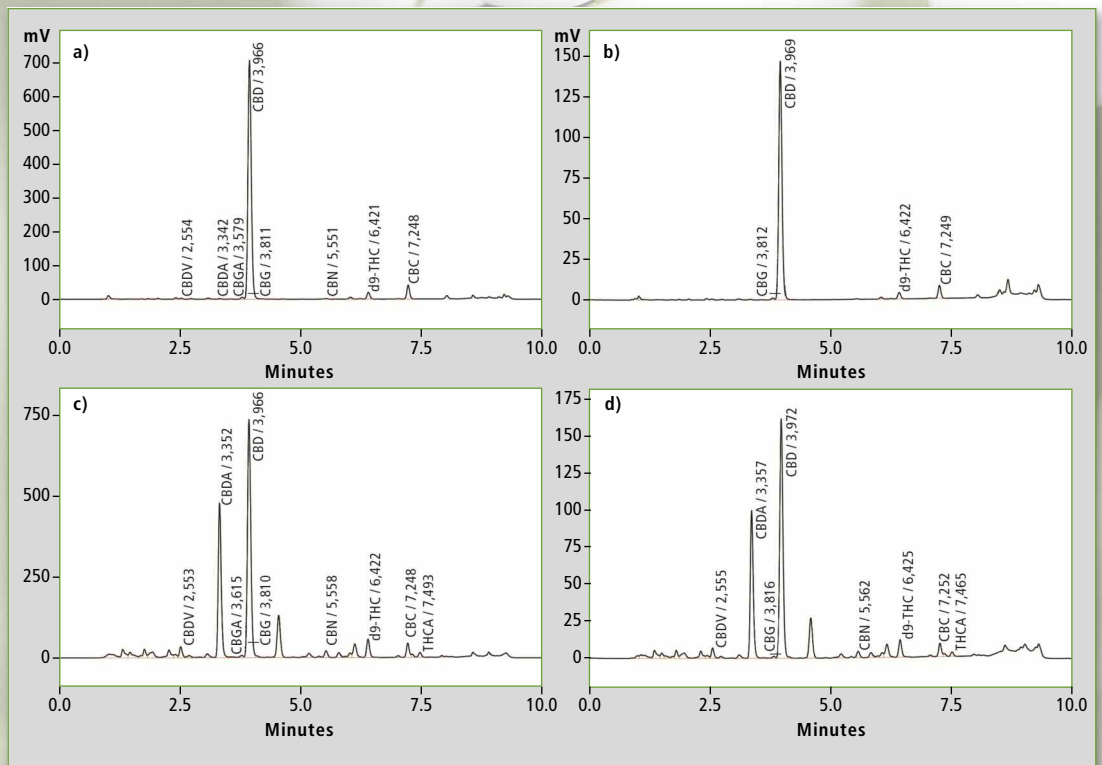


Figure 2: Representative chromatograms for total cannabinoid content (a + c) and CBD content (b + d) in two different hemp oils

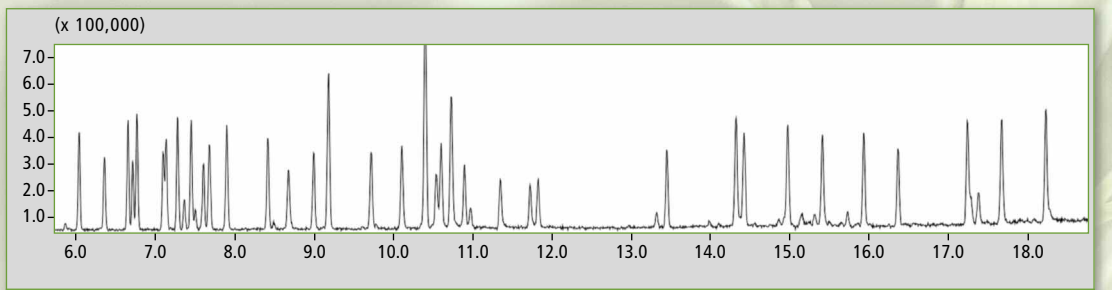


Figure 3: TIC chromatogram of terpene standard

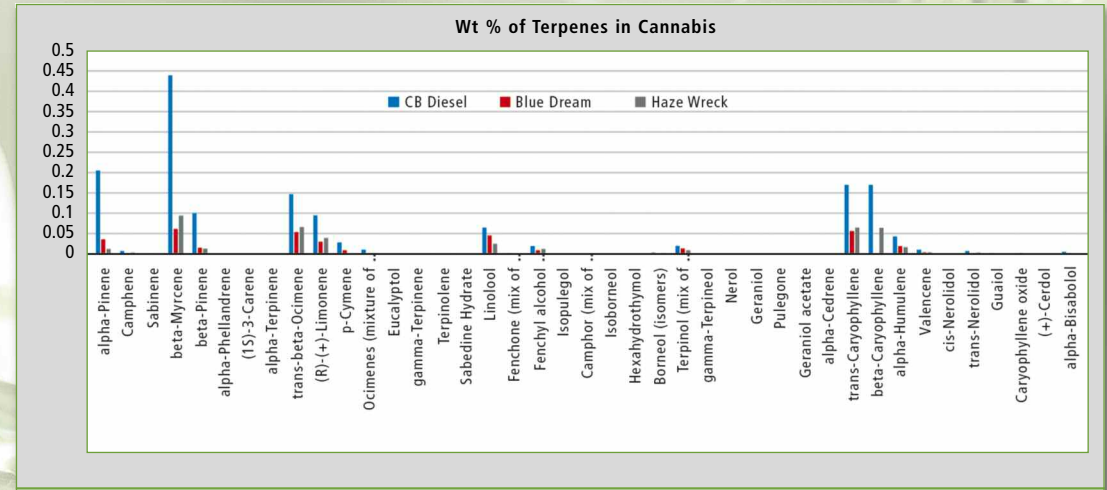


Figure 4: Terpene distribution in three different strains of cannabis: CB Diesel, Blue Dream and Haze Wreck

be obtained legally without the prescription necessary for d9-THC containing medication.

Regulatory demands regarding d9-THC make it the primary focus of potency testing. Cannabis plant material contains d9-tetrahydrocannabinolic acid (THCA), the non-psychoactive, carboxylic acid form of d9-THC which is the precursor and is converted to THC upon heating. High performance liquid chromatography (HPLC) is the method of choice for quantification of cannabinoids in the presence of their acid form, as the high temperatures in gas chromatography (GC) only allow determination of total THC.

Cannabis "potency" is normally determined by quantitation of the major cannabinoids, including THCA, THC, CBD and CBN. The i-series HPLC analyzer for potency testing of cannabis products enables reliable quantification of eleven important cannabinoids (figure 1) using a fast and simple HPLC-UV assay. In the example described it was used for quality control in hemp oil with regards to the label claim of CBD as well as THC content.

Five hemp oil samples from various mail-order vendors were dissolved in isopropyl alcohol, diluted with methanol and filtered prior to HPLC analysis. Figure 2 shows chromatograms obtained from analysis of two different hemp oil samples for determination of total cannabinoid content (81 x diluted) as well as CBD content only (405 x dilution).

Two of the five oils tested were clear with a weak yellow/green coloration and showed high ratios of CBD to total cannabinoid content (92 %). Both samples also tested close to label claim at 95 % and 92 % respectively. This led to the assumption that each of these oils was a product of multi-step purification after extraction.

A third sample on the other hand was not transparent, and brown/green and gritty in appearance. It also exhibited a distinctly "earthy" odor and revealed the highest content of CBD and total cannabinoids, with the lowest ratio of CBD to total cannabinoids (59 %). It was most likely the result of crude extraction only, with no further refinement. Although its CBD % of label claim tested the lowest (81 %), this sample contained the highest level of CDB compared to all other oils tested.

The two remaining hemp oils tested higher than label claim at 122 % and 200 % respectively, calling into question the type and accuracy of testing used to justify label claim.

All samples contained less than 0.3 % d9-THC, as expected from hemp products. This study showed that in three out of five randomly selected samples the actual concentration of CBD did not comply with the stated content, and provides a simple and fast assay for CBD and total cannabinoid content for improved quality control of cannabis products.

Terpene profiling by GC-MS

Terpenes and terpenoid compounds are produced in trichromes (where THC is generated) and give cannabis its unique flavor and fragrance. Aside from their aromatic properties, terpenes also have advantageous health benefits. They act as essential, medicinal hydrocarbon building blocks and have a synergistic relationship with cannabinoids, influencing the overall homeopathic effect.

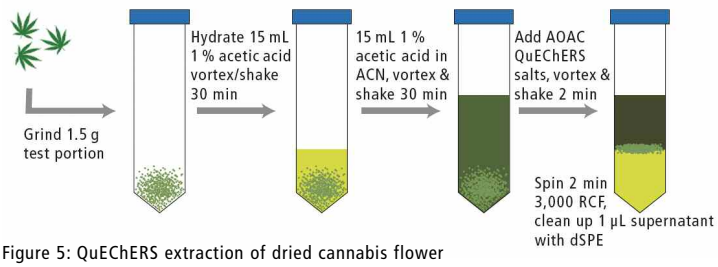


Figure 5: QuEChERS extraction of dried cannabis flower for pesticide analysis

From the pine odor of pinene to the citrus-like smell of limonene, characterization of terpenes is achieved easily using gas chromatography. With the Shimadzu GCMS-QP2020, HS-20 head space sampler and NIST spectral library more than 3,000 flavor and fragrance compounds can be identified for most efficient terpene profiling.

Cannabis has over 140 terpene components, many of which are of medicinal interest [5]. Predominant terpenes in cannabis include

- β-myrcene, which has antibiotic properties and enhances the THC muscle relaxant effect,
- α-pinene, which improves the THC bronchodilator effect and exhibits anti-inflammatory properties and
- β-caryophyllene, which also acts as an anti-inflammatory agent and increases the THC gastric cytoprotective effect, amongst other health benefits [6, 7].

The concentration of individual terpenes varies by strain, can be anywhere from 0.1 to 1.5 % of its total dry weight and can vary depending on harvest time, drying and storage conditions. Terpene levels can decrease over time and can, after three months of storage, be reduced by more than half [8].

The decrease in terpene amount over time varies for different terpenes. Due to the uniqueness of terpene profiles, they can be used by cultivators as a "fingerprint" to partially ID the specific strain in question. As an example, the analysis of several strains of cannabis for 41 terpenes using GC-MS with headspace injection is described here.

A five-point calibration curve was created with concentrations ranging from 12.5 - 100 µg/mL. A part of the flower weighing 1.0 gram was frozen, followed by grinding to ensure a representative sample. Ten to 30 mg of the flower were then weighed into a headspace vial and capped. The final result was calculated to give wt %.

The first sample of cannabis, CB Diesel, was analyzed shortly after harvest. The resulting wt % of terpenes was similar to that in current literature [5]. The two other samples, Blue Dream and Haze Wreck, were stored at ambient temperature and exposed to light for one month prior to analysis. It has been demonstrated that different storage conditions can change terpene results over time, which should be taken into consideration when analyzing cannabis samples (figure 4, page 9).

Pesticide screening by LC-MS-MS

Pesticides are used in commercial cannabis grow operations to kill insects and spiders that thrive on cannabis plants. Above certain levels pesticides may be carcinogenic and mutagenic, causing serious harm to consumers, especially immuno-compromised medicinal cannabis users. Sensitive and selective detection of chemical residue contamination is necessary for consumer protection. QuEChERS extraction and LC-MS analysis offer effective and efficient detection of pesticides commonly employed during cannabis cultivation.

Pesticide-free organically-grown cannabis was used for spiking studies and calibration curves. A variety of cannabis samples offered for retail sale, including cannabis concentrates, were then analyzed for pesticides.

Samples were prepared according to the QuEChERS extraction protocol (figure 5) and analyzed using a Shimadzu Prominence HPLC with LCMS-8050 triple quadrupole mass spectrometer. Electrospray ionization in continuous polarity switching mode was used for detection.

Optimized MRM settings were used for each compound and at least one quantifier and one qualifier transition were selected. The retention times were determined and used to program the MRM segments for optimum duty cycle. Figure 6 shows a representative chromatogram of pesticide mix spiked in cannabis matrix at an intermediate level (31 ppb).

The calibration curve was prepared in spiked matrix over the range of 20 to 2,000 ng/g dried flower weight. Limits of quantitation were determined by measuring samples in triplicate at various levels. Signal-to-noise of at least ten to one and RSD of 20 % or better were required at the limit of quantitation. In addition, reproducibility of three QC replicates in three different cannabis strains was also required to be within 20 % RSD.

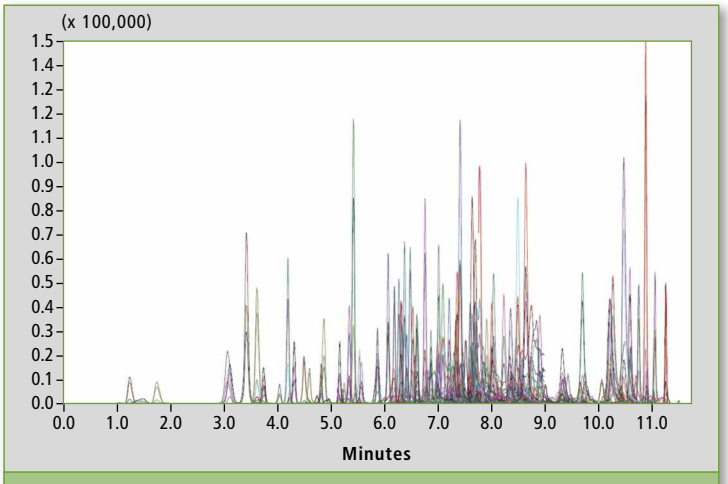


Figure 6: Representative chromatogram of pesticide mix spiked in cannabis matrix

The most commonly detected pesticide was piperonyl butoxide which finds wide use in pesticide formulations to enhance activity of the main ingredient. It was detected over a wide range of concentrations. Myclobutanil, an antifungal known to be used in cannabis cultivation, was detected in a number of samples as well. Among the cannabis concentrates, a high percentage tested positive for one or more pesticides.

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Shimadzu does not support or promote the use of its products or services in connection with illegal use, cultivation or trade of cannabis products. Shimadzu is not condoning the use of recreational nor medical marijuana, we are merely providing a market summary of the cannabis testing industry.

https://www.shimadzu.eu/cannabis-testing-solutions

Carbon content in ultrapure water

Risk assessment, experiments, measurements

Many industry sectors such as pharmaceutical production or semiconductor manufacturing require ultrapure water. Regular controls of the organic carbon content are necessary to make sure the water quality complies with specifications.

The definition of the purity of ultrapure water for production is based on various physical, chemical and microbiological parameters. A central sum parameter is the content of total organic carbon (TOC). It comprises the largest of all substance groups.

To determine TOC, the ultrapure water sample is mixed with an acid which converts the inorganic carbon compounds, carbonates and hydrogen carbonates, into carbon dioxide. A purge gas, usually synthetic air, expels the resulting CO_2. An aliquot of the sample is then oxidized to convert the dissolved organic substances to carbon dioxide, which is detected by a non-dispersive infrared (NDIR) detector.

Regular inspection

No matter how ultrapure water is produced, it is never completely free of foreign substances such as organic compounds. Over time, carbon content in the water increases. Materials in contact with water release organic substances, and organic and inorganic substances are dissolved from the ambient air into the ultrapure water. It is therefore challenging to store and handle ultrapure water, and it must be checked before use. In TOC analysis, ultrapure water is both sample and operating material; it is contained in the rinsing solutions of the analyzers and used to prepare calibration solutions.

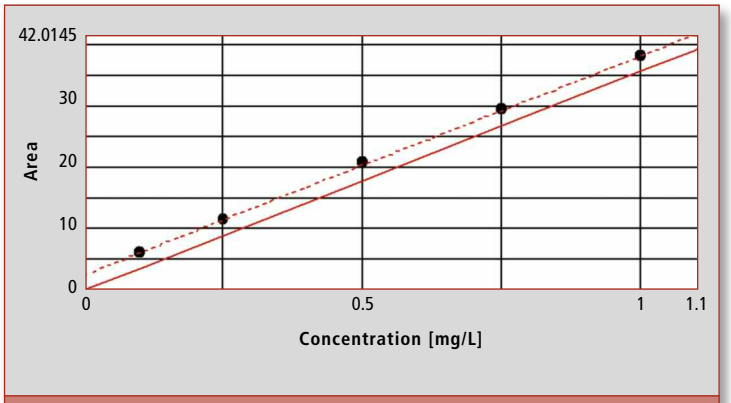

Figure 1: Calibration function with zero offset at TOC-L_{CPH}

Due to the blank value or residual concentrations of the ultrapure water used in standard solutions, the results shift to higher measured values, and the calibration curve therefore gets a positive Y-axis section. The smaller the measuring range, the greater the influence of the blank value on the calibration.

For TOC measurement of ultrapure water samples and samples in the trace range, a positive Y-axis section is not desirable, since such samples do not have residual concentrations. Using the calibration curve for quantification with the formula: TOC content = (measured area value minus axis intercept) divided by the slope, the TOC content would be changed unintentionally. To avoid this, a zero offset, the parallel shift of the calibration line through the zero point is necessary. It needs to be performed ahead of evaluation in order to subtract the blank value from the preparation of the standard solutions with TOC content (figure 1).

Impurities from the environment

In addition to blank values from the ultrapure water and the reagents used, impurities from the environment can also be present in the TOC measurement. These are often random, and in many cases neither reproducible nor clearly determinable. For example, they originate from residues in sample bottles, measuring vessels and chemicals, or from the laboratory environment.

To illustrate this contamination process, ultrapure water from a bottle (HPLC ultrapure water) was analyzed. TOC specification of the water was below 5 µg/L. An aliquot of the sample was taken, analyzed, and the bottle closed tightly. Even the first analysis value did not meet the specifications as it showed a higher TOC content of 25 µg/L. This examination was repeated several times within three hours. During this period, the TOC content increased to over three times the initial value (table 1, page 12).

The type and number of sources of contamination, their influence and effect on trace analysis depends among other things on the structure, equipment and analytical parameters of a laboratory. It is therefore necessary for every lab doing ultrapure water measurements to identify sources of contamination and to evaluate them through tests and examinations of the lab processes. On the basis of a risk assessment, measures must be taken to limit the carbon input to an acceptable level.

Identifying contamination sources

A simple experiment shows how large the TOC input from the laboratory air can be. Four beakers, 100 mL each, remained open to the environment of the TOC laboratory. The ultrapure water from a fifth beaker was filled directly and acidified for the measurement. Every two hours, one of the four open beakers was filled and acidified for analysis. In the end, all five samples (0 h, 2 h, 4 h, 6 h and 8 h) were tested for TOC.

In addition to laboratory space, it may be useful to examine adjacent areas or the outside air to find contamination paths. This test setup works analogously without acidification for conductive inorganic and organic compounds.

Another useful test, even if all laboratory processes work well, is to check the glassware set for TOC entry. At random, at least two of each of the glassware from the laboratory cabinet would be removed for TOC analysis. One from each pair is then prewashed according to the working instructions. The other glassware is used without further preparation. For the actual test, the glass vessels are filled with ultrapure water with known TOC content (blank value measurement) and left to sit for at least two hours before samples are taken. In case of small glassware such as 10 mL volumetric flasks, several can be flushed.

For sample vessels or storage containers for acids, standards or rinsing solutions, it makes sense to extend the time span usually used for sampling or analysis. The use of plastic vessels is not recommended for TOC trace analysis. But if they are already in use, glass and plastic should then be compared.

Conclusion

It is easy to carry out tests to see how far organic substances contaminate ultrapure water. The tests indicate the extent to which the environment affects the contamination of ultrapure water. Hence, it is possible to observe and reduce the carbon input.

This article was written in cooperation with Mr. Arno Bayerl, Divisional Head cleaning validation and hygiene, TECHPharm GmbH.

Read for you in Nachrichten aus der Chemie 5/18

Withdrawal	Time	NPOC in µg/L	Injections per sample
1	12:08	25.21	4
2	13:01	34.08	4
3	13:25	35.77	4
4	14:14	55.88	4
5	14:40	75.08	4
6	15:10	79.25	4

Table 1: Table of test results

APPLICATION

Connecting wine to headaches

Determining higher alcohols and ethyl acetate in wine

The taste and aroma of wines relate to the amount of different alcohols and solvents like methanol, butanol and ethyl acetate. These are said to be the main reasons for causing headaches, next to dehydration, histamines (see Shimadzu-NEWS 3/2005), sulfites and tannin.

While ethyl acetate as an ester brings a fruity taste, the alcohols give a solvent-like taste. During fermentation, yeast makes acetic acid and ethanol react to form the pleasantly tasting ethyl acetate, but also generates the uncomfortable alcohols isobutanol, isoamyl alcohol and methanol [1, 2].

Winemakers are therefore interested in a quantification of these substances. Controlling fermentation

for better taste, and even more importantly reducing damage to health by alcohols other than drinking alcohol, are main concerns.

Higher alcohols in wine with GC-FID

Determining higher alcohols with the GC-2030 gas chromatograph and a flame ionisation detector (FID) is a fast and efficient way to measure the amount of ethyl acetate, isoamyl alcohol, n-propanol, isobutanol and even methanol. In a test row, the newest Shimadzu white wine „Science Selection – Pinot gris late harvest dry“(figure 1), a pinot gris wine, was compared with a dry red wine.

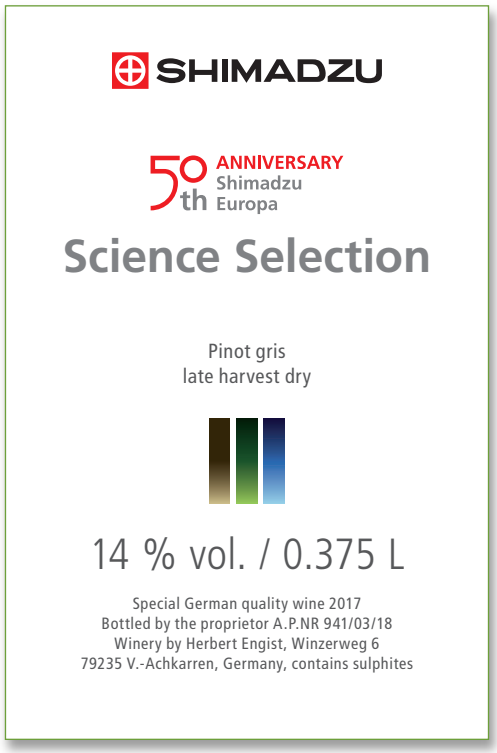

Figure 1: Shimadzu wine »Science Selection – Pinot gris late harvest dry«

Sample preparation was done by liquid extraction with organic solvent in a milliliter scale. It needs only 5 mL sample volume and 2 mL solvent to give reliable results. In a first step, the alcohols were identified in the chromatogram. A calibration mixture of a standard solution and an internal standard solution, created in a wine matrix with pH = 3.5, was used. 2-Butanol was applied as an internal standard (ISTD) and the concentrations of the compounds in the calibration mixture were in the range of 50 to 200 mg/L.

Table 1 shows the parameters of the GC method. Analysis time was optimized at 25 min. As column, a SH-Rxi-624Sil MS of 30 m length, 0.25 mm ID and 1.4 µm df was used.

In the second step, the cold wine sample, added with internal standard solution, was vortexed with NaCl and dichloromethane; phase separation was done at room temperature followed by centrifugation. The dried organic phase is ready for injection.

Quantification of target compounds was done via response factors, calculated from the areas and concentrations of the calibration mixture. With these response factors, concentrations of alcohols in the sample were calculated.

Results

Table 2 summarizes the results for both wines measured, and figure 2 shows a chromatogram of the Shimadzu wine analyzed.

Both wines tested showed similar values for n-propanol and ethyl acetate. The main differences were found for methanol, isobutanol and isoamyl alcohol, showing much higher amounts in the red wine. These results correlate to average concentrations of methanol in red and white wines as stated in the literature. According to [3], about 60 to 230 mg/L methanol in red wines and 17 to 100 mg/L in white wines are present. Furthermore, a common method from the OIV (International Organization of Vine and Wine) for methanol analysis provided similar results in their validation tests of the methanol analytic method for GC.

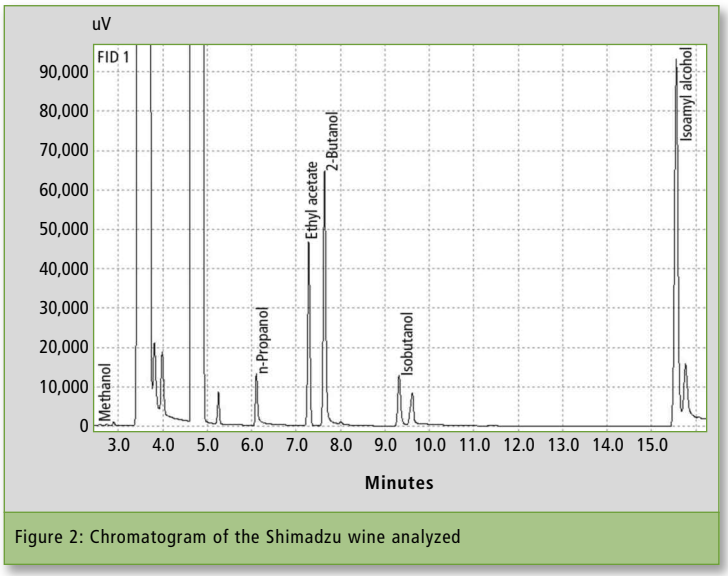

Figure 2: Chromatogram of the Shimadzu wine analyzed

Conclusion

With identification of alcohols and other organic compounds, it is possible to support aroma profiling of wines and to monitor their quality. GC-2030 with FID detection offers an efficient way to reliably analyze these without the need for advanced equipment and complicated sample preparation. For winemakers, a helpful method to elevate the enjoyment of their wines ...

Literature

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[2] https://glossar.wein-plus.eu/methanol
[3] https://glossar.wein-plus.eu/essigsaeure-ethylester

Parameter	Value
Injection volume	1 µL, Split 1:10
Injector temperature	220 °C
Carrier gas	He
Carrier gas speed	30 cm/s, linear velocity mode
Column oven program	40 °C, 3 min, 5 °C/min, 50 °C, 4 min, 5 °C/min, 70 °C, 3 min, 45 °C/min, 240 °C, 5 min
FID temperature	260 °C

Table 1: Method parameters for alcohols and ethyl acetate in wine

Compound	Red wine [mg/L]	Shimadzu wine [mg/L]
Methanol	170	28
n-Propanol	34	39
Ethyl acetate	68	58
2-Butanol (ISTD)	100	100
Isobutanol	41	24
Isoamylalcohol	241	120

Table 2: Concentration in mg/L of alcohols and ethyl acetate in both wines analyzed

Multimodal imaging by elemental and molecular mass spectrometry

European Innovation Center – Interview with Prof. Uwe Karst, University of Münster (Germany)

Shimadzu's European Innovation Center (EUIC) merges cutting-edge analytical technologies of Shimadzu with game-changing topics and expertise from leading scientists. This innovation-oriented cooperation focuses on creating new solutions for tomorrow.

The European Innovation Center applies a decentralized structure all over Europe to be in close local proximity to scientists and related markets.

With their leading-edge research expertise, highly-reputed scientists from well-known European universities cover the academic part of the EUIC. Their scientific focus areas include clinical applications, imaging technology, food and composites, with an emphasis on new methods, tools, techniques, diagnostics and solutions.

This issue of Shimadzu NEWS covers an interview with Professor Uwe Karst, University of Münster, Germany. With a focus on imaging technology within the EUIC, he gives insights on his current research projects.

To start, can you outline the research you conduct in general? What is currently state-of-the-art?

Our group specializes in the development and application of analytical methods and instrumentation to address complex analytical problems, originating mainly from the biomedical area.

One of our major research areas is speciation analysis. The need for speciation analysis is caused by the fact that the physiological properties (uptake, distribution, metabolism and excretion) of metal-containing compounds are strongly dependent on the individual metal species rather than on the heteroatom in general. This is easily proven using the example of hexavalent chromium, which is considered to be toxic and carcinogenic, while trivalent chromium is regarded as a possible essential trace metal species.

A second major research area of our group is chemical imaging – analysis of the distribution and spatially resolved quantification of low molecular weight analytes in biological matrices.

How much are speciation analysis and chemical imaging linked to each other?

Speciation analysis and chemical imaging complement each other perfectly regarding the analysis of metal species in the organisms of humans, animals and plants.

Speciation analysis mostly uses liquid phase separations to separate the metal or metalloid species prior to identification by electrospray mass spectrometry (ESI-MS) and quantification by inductively coupled plasma-mass spectrometry (ICP-MS).

Chemical imaging, on the other hand, is carried out by matrix-assisted laser desorption/ionization-mass spectrometry (MALDI-MS) and related techniques to obtain distribution information about intact molecules, while distribution and quantification of the elements is accessible by laser ablation (LA) coupled to ICP-MS and micro-X-ray fluorescence (μXRF). As an example, investigation of side effects of Cisplatin-based tumor therapy requires speciation analysis to detect and quantify the individual platinum species formed in body fluids and tissues, while imaging by LA-ICP-MS provides quantitative distribution information on platinum in human or animal tissues.

Uwe Karst holds the Chair of Analytical Chemistry at the University of Münster in Germany. After diploma and Ph.D. studies in Münster, which he finished in 1993, he joined the University of Colorado in Boulder as postdoctoral associate. He returned to Münster to obtain his habilitation and was appointed as Full Professor of Chemical Analysis at the University of Twente in the Netherlands from 2001 to 2005, after which he assumed his current position.

He is author of more than 250 publications in peer-review journals and 18 patents. Together with his research group, Prof. Karst has organized several international and national conferences including the International Symposium on Chromatography in 2008, the Metallomics Conference in 2011 and the European Winter Conference on Plasma Spectrochemistry in 2015.

Can you describe the research you are doing at the European Innovation Center with Shimadzu?

We have been collaborating with the EUIC on imaging for more than a year, and a major topic at this moment is further improvement of the combination of laser ablation and ICP-MS for chemical imaging purposes. As in other previous and current cooperations with various instrument manufacturers, we see our role not only in developing applications, but also in contributing to the further development of the actual and future instrument generations. This also includes suggestions for improved hardware, software for instrument control, data evaluation and integration of the instrument´s data with data of other imaging methods. Within our current project, the focus is directed on LA-ICP-MS and its combination with MALDI-MS and

MALDI-MS/MS, as many of our current analytical challenges require the combined use of complementary imaging techniques.

Why are you interested in this research? What is the goal? Why is it important?

The analysis of low molecular weight compounds with physiological effects is currently (and probably always will be) an area of high complexity and individual analytical solutions. In contrast to Omics techniques, the potential for automation of procedures for high-throughput analysis is limited due to the strongly varying chemistry behind each analytical problem we are facing.

However, this chemical variability and the need to address challenges with a combination of technology and chemistry is exactly what I like in this field of research. For each question, there is a plethora of possible approaches to be checked, and interdisciplinary teams with colleagues from Medicine and Biology have to cooperate well to be successful. Even during my postdoctoral times, I would never have expected to be able to contribute to investigations on the side effects of platinum cancer chemotherapy, on the deposition of gadolinium from magnetic resonance imaging (MRI) contrast agents in the human brain or on fibrosis caused by certain types of nanoparticles in the lung.

Even more exciting, the combination of chemical and medical imaging opens up completely new routes for research. MRI, computed tomography (CT) or positron emission tomography (PET) are highly complementary regarding in vivo/in vitro situation, spatial resolution, limits of detection and capabilities for quantification.

How do Shimadzu instruments support your research?

As stated, combined imaging techniques are particular intriguing. Cooperation with manufacturers active in the fields of chemical imaging are therefore particularly attractive to us (and hopefully for the manufacturers as well). I just came back from a large Radiology congress which Shimadzu also attended, presenting equipment for medical imaging at their booth. While we have been using chromatography (LC, GC) and spectroscopy (UV/vis, fluorescence, AAS) instrumentation from Shimadzu for more than 20 years for research and education, our cooperation in the imaging field was established only three years ago, and is currently centered around LA-ICP-MS and complementary MALDI-MS work.

What are Shimadzu's strengths compared to other vendors (not limited to the instruments)?

Cooperation is always based on trust and on personal relations, and a major reason for us to work with Shimadzu equipment at a larger scale during my habilitation phase, in which I had very limited equipment, was an excellent relation with the local sales agent. He was always helpful to a much larger extent than we could expect, and he was just an outstanding ambassador for the company.

Of course, well-performing and robust instrumentation helps as well, but the more complex the analytical challenges become, the more important is excellent communication and cooperation between individuals on both sides. Additionally, in our current situation, a broad spectrum of imaging instrumentation from any manufacturer is particularly attractive to us due to the complexity of our analytical problems and the increased chances to tackle the most difficult challenges.

Could you share any requests that you have with respect to analytical and measuring instrument vendors?

Let me start with a very general statement that is not addressed to any particular vendor: While the world of analytical challenges is converging more and more, even including a vanishing "wall" between "organic" and "inorganic" analysis, there are often business decisions of instrument vendors that lead to fragmentation of product lines and separation of business units that are hard to understand in the light of the increasing complexity of analytical challenges. Sometimes I wish that scientists were more involved in business decisions of instrument vendors, as this is not just a matter of rapid sales but also of long-term business relations and business development in a complex market situation. It may be naive to think that sometimes, wise long-term decisions should overrule rapidly profitable decisions, but it would accelerate technical progress so much …

Back down to earth again, my wish would be that manufacturers improve integration of their major product lines to a larger extent, which would be beneficial especially in our research areas of speciation analysis and chemical imaging. This is one of the major factors we are trying to contribute to in our cooperation with the Shimadzu European Innovation Center on imaging.

Take a look into the future: What will happen in the imaging field and how will the change influence the instruments/procedures in ten years?

In my opinion, this goes very much in line with my reply to your earlier question: I am aware that your major markets of today are not the research areas which we are currently working on and that your sales will go mostly to the mass markets in routine labs. However, we are facing an increasing degree of complexity, and being prepared to address this situation will become even more important in the future. While the medical imaging area will continue to expand due to its immediate and obvious benefit for the patient/customer, the chemical imaging area is harder to predict, as the immediate necessity for the paying customer is not as clear, thus hampering large investments in this field.

Regarding scientific content, there will be massive progress in chemical imaging, leading to strong optimism regarding future development. However, reaching the mass markets in routine labs (medical, environmental, food) will require a significant reduction in cost per analysis and for the need for highly qualified personnel. This can only be achieved by strong improvements in speed of analysis (more spots per second in imaging mode), improved hard- and software integration and possibly even strategic alliances between vendors of complementary instrumentation or between different divisions of one vendor.

Let me conclude with the statement that there is an increasing amount of light on the horizon, but that the full sunrise has to be earned by hard work and smart decisions in academia and industry. We will do our best to contribute!

From fatberg to fuel

Controlling the quality of biofuels with gas chromatography

Biodiesel refinery of Argent Energy in the UK

Argent Energy is the UK's leading supplier of biodiesel, taking waste fats, such as used cooking oils, tallow and sewer grease, and turning them into high quality biofuel for the freight and transport industries. Despite the huge inherent variability in the starting materials, the company must reliably and consistently meet strict quality standards relating to the ester and glyceride content of the biofuels it produces. Argent Energy's laboratory in Stanlow near Liverpool relies on a trio of gas chromatographs from Shimadzu to analyze its biodiesel, the latest addition being a Nexis GC-2030 that was installed to increase testing capacity and optimize production methods.

When travelling on a London bus, the journey may just have been fueled by Argent Energy biodiesel, perhaps even refined from the city's own infamous fatberg, a monstrous blockage that was removed and some of it sent to the company for processing.

From fatberg to fuel

To get from fatberg to fuel, Argent Energy must undertake several rounds of laboratory testing – screening of raw materials arriving at the refineries, in-process testing and analysis of the end product – all overseen by scientists working in Stanlow's production, QC and R&D laboratories.

While the production lab typically uses basic titration methods to monitor the raw starting materials, both the QC and R&D labs depend heavily on gas chromatography (GC) for process optimization and end product testing to ensure that the legal maximum allowable amount of total glycerides in biodiesel (0.2 %) is not exceeded.

Steve Lindley, QC Laboratory Manager at Stanlow, explained: "During the refinery process, we need to convert all the glyc-

Truck with biofuel for passenger and freight transport

Argent Energy is the UK's leading provider of renewable transport fuel, supplying biodiesel to the commercial freight and passenger transport industries.

The company produces biodiesel at sites in Motherwell near Glasgow, Scotland and Stanlow near Liverpool, England by refining waste oil streams from plants, factories and the food and restaurant industries.

erides into an end product that is close to 100 % esters. To ensure that we have achieved this, we use GC to screen for trace amounts of any remaining glycerides and to determine the ester content of the biofuel. We are looking for really low levels of triglycerides, and the Shimadzu instruments are great for this type of work, not least because they support a temperature program of between 270 and 400 °C – a real challenge of glyceride screening that not many GCs can handle."

Leave no trace

Although until recently the QC and research labs at Stanlow have shared two Shimadzu GC-2010 instruments, they have very different analytical needs, which has presented some operational hurdles. Whereas the QC lab performs trace analysis, the research lab's main remit is method development and process design, involving regular handling of samples of vastly differing composition to those of the QC team, and there was a clear need to separate the workflows.

Lee Knight, Process Development Chemist in the R&D lab, explained: "The composition of the feedstocks we receive varies tremendously. We never get the same raw material twice, and so we have to work on a case-by-case basis and vary our processes accordingly. Today's raw materials vary widely in glyceride content and composition. We now need to look for anything between 10 and 70 % triglyceride in our mid-process samples – it really can be that high. This was overloading the columns we had, and detection wasn't optimal."

Steve Lindley added: "Combining trace and high concentration analyses on the same instrument presents a challenge for the QC lab. With the glycerides, we're looking at very, very low levels. If we then put samples with a high concentration of analyte through the same system, it can contaminate the column and yield weird results. There was a real need to separate the two types of testing, and so we got in touch with Shimadzu to see what solutions the company could offer."

Laboratory work: testing in the production process and analysis of the final product

Expansion to Nexis GC-2030

Shimadzu's GC application specialists evaluated several potential solutions for Argent Energy before recommending the recently launched Nexis GC-2030 dual column instrument with FID detectors. For convenience and ease of use, the system includes two autosamplers – one for each column – enabling overnight analysis of non-urgent samples with instantly-accessible results ready and waiting in the morning. Lee Knight observed: "Column installation is much easier with Shimadzu's ClickTek connectors than with conventional screw thread fittings, and the inclusion of a light inside the oven means that you can actually see what you are doing. The system's touch-screen operation is straightforward, and so users, whether they are new to GC or already familiar with Shimadzu software, can learn how to use the instrument with little more than a day's training."

Steve Lindley said: "The support we receive from Shimadzu is quite hands-on; its technical specialists did a lot of behind-the-scenes work to identify suitable starting configurations and set-ups, and will always speak to us on the phone, via email, or even drop in to the lab. The Nexis is Shimadzu's latest GC system, offering even better detection capability and greater sensitivity for our work. Having a third GC will relieve the burden on the other instruments and allow us to separate trace and high concentration analyses."

An early adopter

The Nexis GC-2030 is still a relatively new addition to the Argent Energy lab bench, having been installed just a few months ago, and the company is exploring its capabilities for existing and potential applications. Steve Lindley commented: "We were one of the first companies in the UK to take delivery of a Nexis GC-2030, and we're experimenting with how we will use the system in the long term. At the moment, we're running two different columns to see which one gives us the best results; it may be that we find one type is best for samples with high analyte concentrations and another for low concentrations."

Future plans

Moving forward, the plan is to continue to perform trace glyceride and ester content analysis on the two GC-2010 and use the Nexis to support in-process testing, method development and process development to optimize the plant operating conditions. Lee Knight: "We're now looking at the next stepping stones in method and process development, which is where the main gains are at present, for example to understand how the processing method can be refined to save on reagent costs, increase throughput and improve quality and consistency, moving towards a better, more effective steady state. It's a work in progress, but if we can perform fewer treatments of the in-process samples, we would benefit from even greater reliability of our results. To support all that, we need to perform more detailed in-process and feedstock analysis, which is where the Nexis GC-2030 will be a big advantage in helping us to achieve our objectives."

Run time cut, possibilities enhanced

Nexis GC-2030 quantifies contaminants in oil and gas for recycling

Celtic Recycling, based in Wales and running two facilities close to the country's capital of Cardiff, specializes in the recovery, management and recycling of redundant heavy electrical equipment. The company is one of a small number of specialist contractors that work with National Grid, which owns and manages grids for electricity and gas supply in the UK, and other major electricity industry companies to safely remove, dismantle and recycle end of life, oil-and gas-insulated electrical equipment.

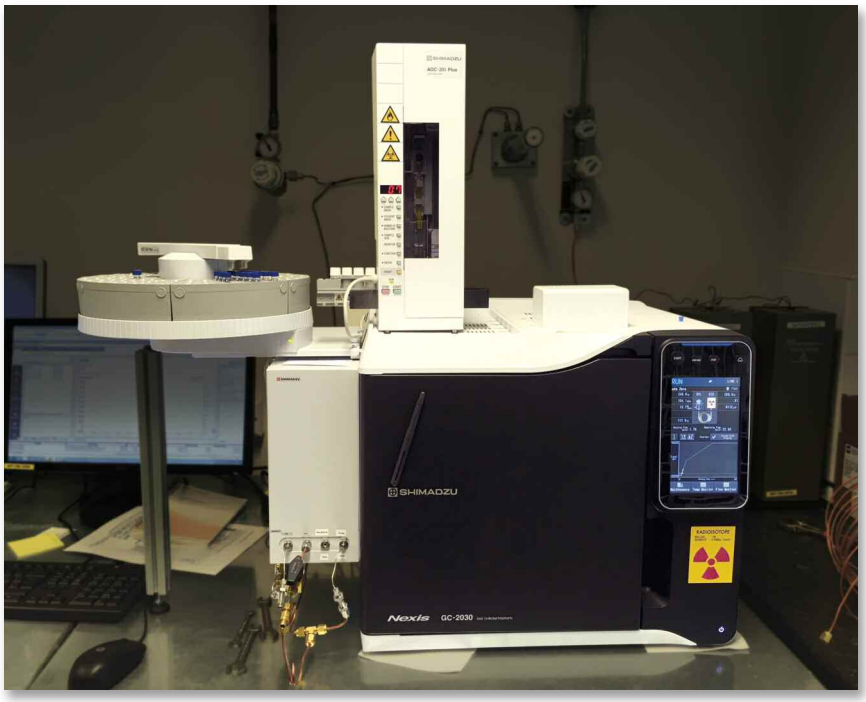

Figure 1: Shimadzu custom gas chromatograph Nexis GC-2030

Both the oil and the gas recovered from high voltage electrical equipment can be recycled after testing to ensure that the levels of any contaminants are within the specified limits. Celtic Recycling's laboratory in Newport, Gwent, has long used gas chromatography (GC) to analyze polychlorinated biphenyls (PCBs) in insulating oils but lacked the capability to screen sulfur hexafluoride (SF_6) from gas-filled equipment. With legislative changes set to make it more difficult to import virgin SF_6, and to increase the demand for recycled SF_6 in the UK, the company invested in a dual column Nexis GC-2030 gas chromatograph to broaden its GC capabilities to include gas analysis and to enhance PCB testing capabilities.

Why test for PCBs?

In the past, PCBs were used as dielectric insulating fluids in transformers and other high voltage electrical equipment. At the time they were thought of as the 'wonder substance' because they have superb insulating properties and don't break down. Their use was banned in the 1980s after it became clear that they were hazardous to humans and the environment, however, insulating oil containing PCBs is still occasionally found as electrical equipment has a long life span.

While samples that are high in PCBs are very rare, trace level contamination may still occur. Typically, this is attributed to PCB-fluids being pumped out and replaced with an alternative oil to comply with legislation; any residual PCBs not cleaned out of the equipment, however, cause trace contamination of the fresh insulating oil. For this reason, all samples received by Celtic Recycling undergo quantitative GC analysis for PCBs over the range of 5 to 100 ppm, with higher concentrations also quantifiable. Samples below the legal limit of 50 ppm can be reused and recycled, while any oils containing PCBs above this level are treated as hazardous waste and are destroyed.

The SF_6 challenge

Changes made to EU legislation since 2015 will make it increasingly difficult to produce or import new supplies of SF_6, an inert gas with a global warming potential many thousands of times greater than carbon dioxide, making it extremely harmful to the environment. SF_6-filled equipment can be emptied and the gas recovered and stored, but great care must be taken in case arcing has occurred within the equipment, resulting in the formation of highly toxic contaminants.

Portable analyzers give a broad indication of any contaminants that are present, such as hydrogen fluoride, sulfur dioxide and moisture, most of which can be removed using molecular sieves.

One of the biggest contaminants is air, and Celtic Recycling has invested in an air separation plant, enabling it to produce recycled SF_6 in 'good as new' quality.

Once the cleaned gas has been analyzed and its quality certified by quantitative GC analysis, it can be resold. Currently, no other company in the UK is able to offer this service.

A bespoke GC system

Celtic Recycling wanted to increase capacity for PCB analysis and, at the same time, introduce GC screening of SF_6 which could not be done using the laboratory's existing instrument. While PCB testing can be performed using a standard GC set-up with an electron capture detector (ECD), SF_6 requires a system tailored to gas analysis. This led the company to choose a twin column Nexis GC-2030, taking advantage of Shimadzu's state-of-the-art technology and expertise in gas sampling and custom-build instrumentation.

Shimadzu worked with the laboratory to customize the system so that it samples SF_6 directly from a gas cylinder, using a barrier discharge ionization detector (BID) to determine whether any contaminants are present. Shimadzu's patented BID is a universal detector that can detect all organic compounds except Helium and Neon.

It offers significantly enhanced sensitivity compared to thermal conductivity and flame ionization detectors – enabling the detection of all types of trace components at the 0.1 ppm level – and incorpo-

rates unique electrode-preserving plasma generation technology that ensures long-term stability. To avoid saturating the detector, the design incorporates a 'dump valve', allowing SF_6 to be diverted once the substances of interest have eluted. PCB samples are introduced via a split/splitless injector, and analyzed using an ECD.

Reaping the benefits

The Nexis GC-2030 was installed at the end of 2017, and the laboratory is already seeing the benefits. Not only has it extended the laboratory's GC capabilities to include SF_6 analysis, it also provides additional flexibility as the SF_6 and PCB set-ups are installed alongside each other in a single instrument. This avoids the need to switch out columns and change detectors, or to install two separate instruments, one for each type of analysis. The inclusion of a BID helps to future-proof the system, as this detector is suitable for many other applications should business needs change in the future.

Previously, GC analysis was performed using nitrogen carrier gas, but the laboratory opted to use helium with the new set-up. This has reduced the PCB run time from 45 to 22 minutes, significantly improving turnaround times and allowing more samples to be run in the same time period as before. The system's powerful LabSolutions software enhances integration, making it easier to detect small peaks and discern them from background noise, and resulting in increased PCB sensitivity compared to the laboratory's older instrument.

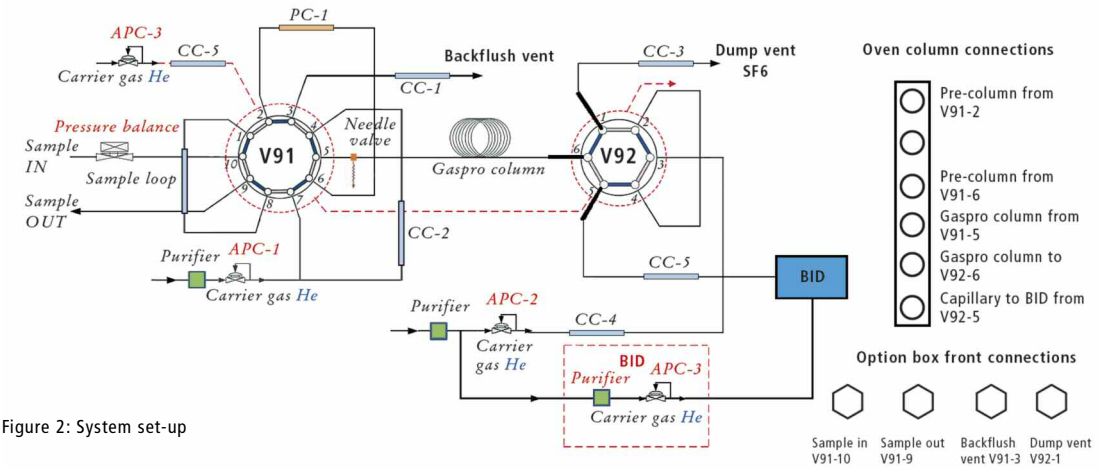

Figure 2: System set-up

The laboratory has now established a quantitative assay to determine the level of any contaminants in the SF_6 gas, improving accuracy for most compounds from around 1,000 ppm using the portable analyzers to single figure ppm with the Nexis GC-2030. To date, the implementation of the new GC assay has allowed Celtic Recycling to recover and certify over 3,000 kg of SF_6 gas for sale and reuse in new equipment.

Celtic Recycling's laboratory chemist, Jennifer Rapp, commented: "I am really pleased with the new system and enjoy working with it. It is easy to use, and I can generate customized reports that look very professional with just a few clicks. Maintenance is quite straightforward and it is very easy to change columns; having a light inside the oven is a definite advantage – I hadn't realized how dark the oven is until now! The product specialists at Shimadzu have been great, providing training and helping me to set up the methods. It's good to know that I can rely on their support."

Acidic? Basic? Chelating? No problem for inert columns!

For reactive substances, inert LC columns are essential for a symmetrical peak shape

In any chromatographic separation, symmetrical peaks with an ideal Gaussian shape are preferable. Under standard conditions, this can usually be accomplished in case of neutral substances. However, the examination of strongly acidic, basic or chelating compounds often leads to so-called "peak tailing" and thus to a clearly asymmetric peak shape. In these cases, the right choice of column is crucial: it should be as inert as possible for ionizable analytes in order to avoid undesired secondary interactions with the stationary phase.

The inertness of a column

What exactly is meant by "inertness" of a column? Generally speaking, inertness means that as few undesirable interactions as possible take place between the column and the analyte.

When the three substance properties, acidic, basic and chelating have an asymmetric peak form (i.e. with undesirable interactions), it suggests that acidic substances show an insufficiently chemically bound phase or impurities that are contained in the phase and react with acidic substances. An insufficiently chemically bound phase contains free silanol groups. Unprotonated acids can compete with protons of protonated silanol groups. This generates asymmetrical peaks.

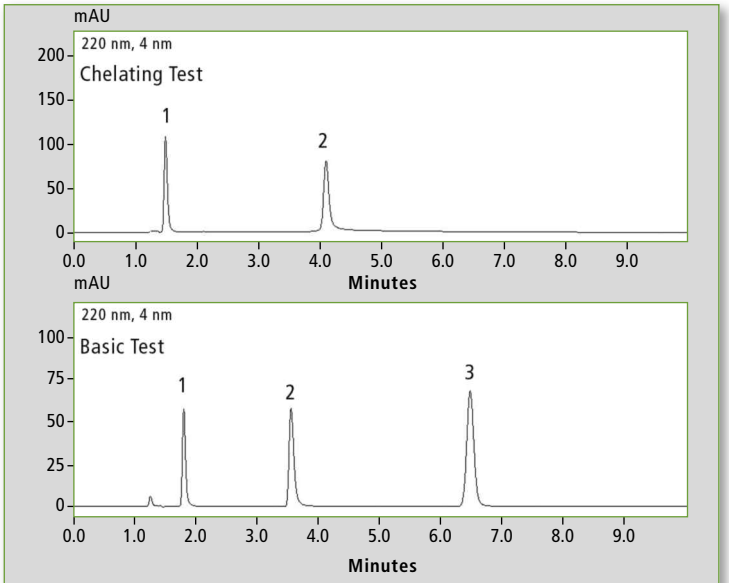

Figure 1: Chelating test (1 caffeine, 2 hinokitiol) and basic test (1 pyridine, 2 dextromethorphan, 3 propyl paraben), measured on the Shim-Pack GISS C_{18}

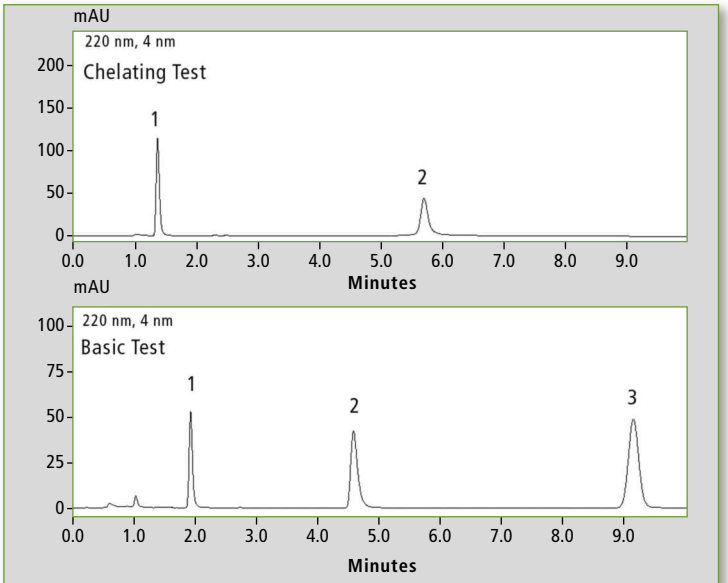

Figure 2: Chelating test (1 caffeine, 2 hinokitiol) and basic test (1 pyridine, 2 dextromethorphan, 3 propyl paraben), measured on the Shim-Pack GIST C_{18}

Contaminants in the stationary phase that can trigger hydrogen bonds, or are basic, can interact with acidic analytes and lead to asymmetric peaks.

Positively charged basic analytes may interact with remaining slightly acidic silanol groups on the stationary phase if they have a negative charge. "Endcapping", i.e. the blocking of accessible silanol groups by trimethylsilyl ligands, is carried out to reduce this interaction as much as possible.

Asymmetric peaks of chelating analytes indicate that metal is present on the phase which chelating groups can approach and potentially irreversibly bind. With the undesirable interactions described, strong tailing of the peak occurs which in the worst case can also lead to a decrease of the peak area.

Most importantly, a column with little inertness is not the same as a bad column! Whether or not inertness is desired is always specific to the application. For some analytes, particular polar interactions or metal interactions are advantageous to achieve stronger retention.

This article deals exclusively with analytes for which inert columns are important. Different column types were investigated with regard to their inertness and their interactions.

Measurement parameters and methods

Instrument:
LC-2040C 3D (Shimadzu)

Column:

Shim-pack GISS C_{18}; (100 mm x 2.1 mm I.D., 1.9 µm);
Shim-pack GIST C_{18}; (100 mm x 2.1 mm I.D., 2 µm)
C_{18} (Competitor column 1);
100 mm x 2.1 mm I.D., 2,7 µm)
C_{18} (Competitor column 2);
100 mm x 2.1 mm I.D., 2.6 µm)
Shim-pack GIS RP-Shield;
(150 mm x 4.6 mm I.D., 5 µm)
Shim-pack GIST C_{18}-AQ;
(100 mm x 2.1 mm I.D., 1.9 µm)
Shim-pack GIST Phenyl;
(100 mm x 2.1 mm I.D., 3 µm)

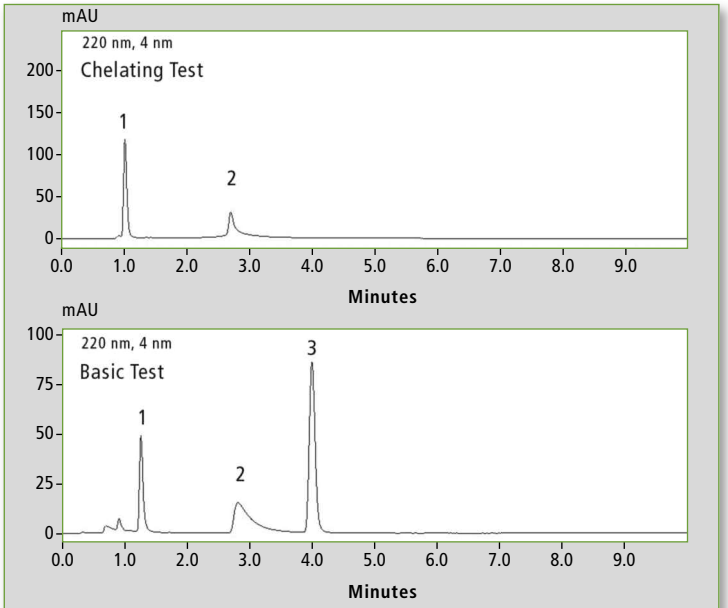

Figure 3: Chelating test (1 caffeine, 2 hinokitiol) and basic test (1 pyridine, 2 dextromethorphan, 3 propyl paraben), measured on the C_{18} competitor column 1

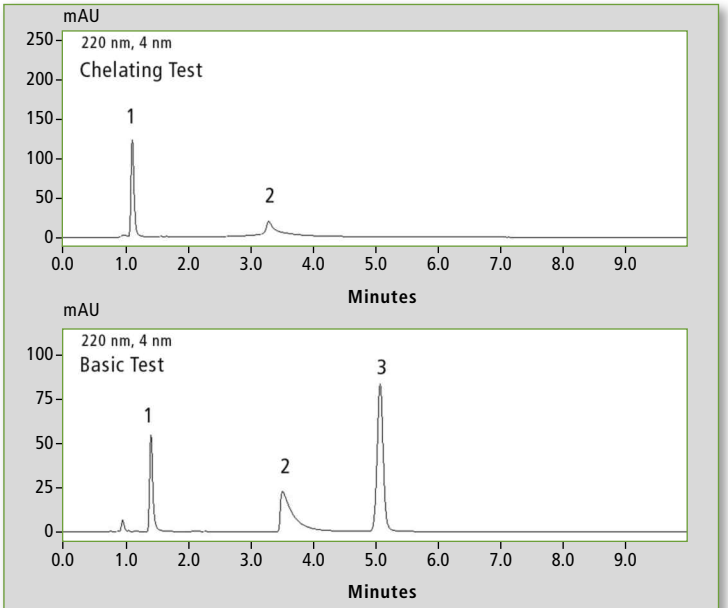

Figure 4: Chelating test (1 caffeine, 2 hinokitiol) and basic test (1 pyridine, 2 dextromethorphan, 3 propyl paraben), measured on the C_{18} competitor column 2.

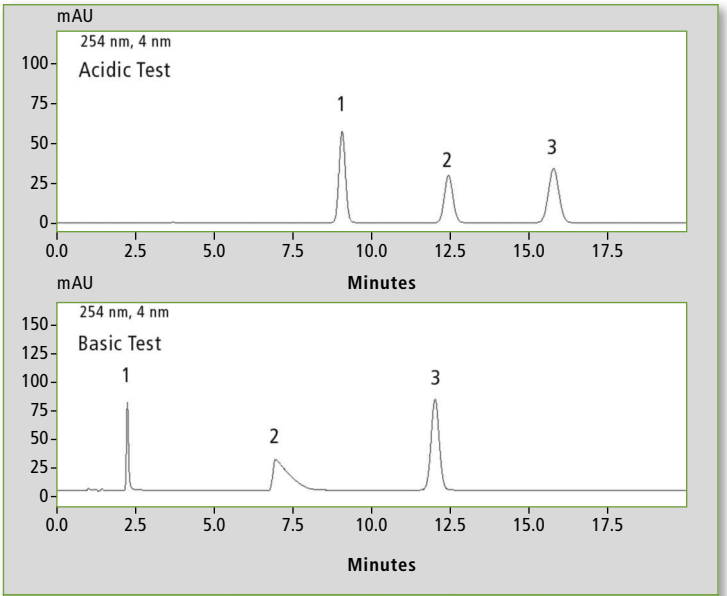

Figure 5: Acidic test (1 Salicylic acid, 2 Methyl parabene, 3 Cinnamic acid) and basic test (1 pyridine, 2 dextro-metorphan, 3 propyl paraben), measured on the Shim-Pack GIS RP-Shield

Shim-pack GIST Phenyl-Hexyl; (100 mm x 2.1 mm I.D., 3 µm)

Mobile Phase:

Acid Test: 75 % 0.1 % H_3PO_4; 25 % ACN
Chelation test: 60 % 0.1 % H_3PO_4, 40 % ACN
Basic test: 65 % 20 mmol KH_2PO_4, pH 6,9, 35 % ACN
Furnace temperature: 40 °C

Flow rate and injection volume were adapted to the column dimensions.

Results

Differences in the measurement results of the column tests with regard to inertness were observed. The highest inertness was shown by the Shim-pack GISS C_{18} and the Shim-pack GIST C_{18}. Inertness is one of their greatest advantages. The chromatograms in figures 1 and 2 demonstrate that all peaks are symmetrical and have a high intensity.

This illustrates an extraordinary inertness in the analysis of reactive substances, e.g. strongly acidic, basic or chelating analytes. Figures 3 and 4 illustrate comparative measurements on two different competitor C_{18} columns. Compared with figures 1 and 2, the chelating agent hinokitiol and the basic substance dextrometorphan show clear peak tailing and a lower intensity.

The GIS RP-Shield column has a polar functional group embedded between the silica surface and the C_{18} groups. This allows stability even under 100 % aqueous conditions.

In the column test, this property is clearly visible in the chromatogram in the basic test, since the peaks, especially the dextrometorphan peak, are misshapen and asymmetrical (figure 5). On the other hand, for acidic analytes which can be measured ideally with this column, symmetrical peak forms are obtained.

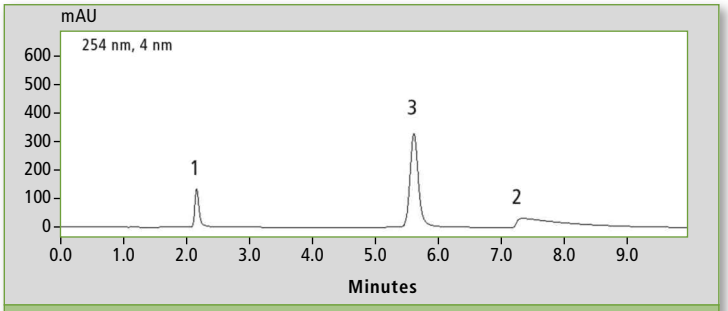

Figure 6: Basic test (1 pyridine, 2 dextrometorphan, 3 propylparaben), measured on the Shim-pack GIST Phenyl

Compared with the phenyl-hexyl column, the phenyl column has no endcapping and therefore offers more polar interactions. This can be seen in the chromatograms in figures 6 and 7 when comparing the analyses of the basic substances on both columns.

Dextrometorphan shows strong tailing on the phenyl column compared to the phenyl-hexyl column; the elution order is even reversed. This reversal is caused partly by the different functional groups of the phenyl and phenyl-hexyl columns.

Compared to conventional C_{18} columns, the GIST C_{18} AQ column shows very good retention to hydrophilic polar analytes. It can also be used with a 100 % aqueous mobile phase without loss of retention. The C_{18} AQ column is very inert. It shows tailing of basic substances due to the free silanol group present on more polar phases such as C_{18} AQ (figure 8).

Conclusion

For the analysis of strongly acidic, chelating or basic substances, an inert column must be used. In the Shimadzu range, GIST C_{18} and GISS C_{18} show particularly inert properties. Substances can be measured accurately with these two inert columns and show symmetrical peaks with a high intensity.

If polar interactions are desired in order to obtain an alternative selectivity for analytes, the choice should fall on one of the different columns with polar interactions in the Shim-pack range.

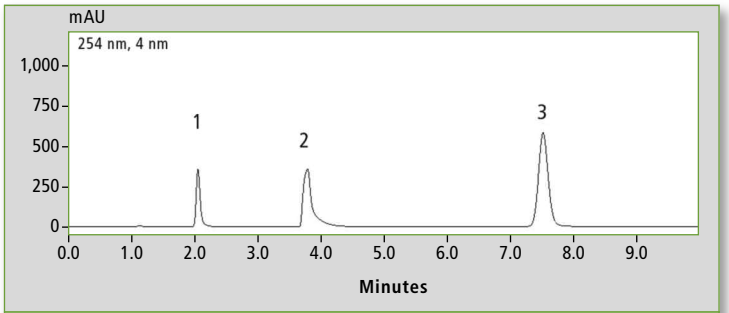

Figure 7: Basic test (1 pyridine, 2 dextrometorphan, 3 propyl paraben), measured on the Shim-pack GIST phenyl-hexyl

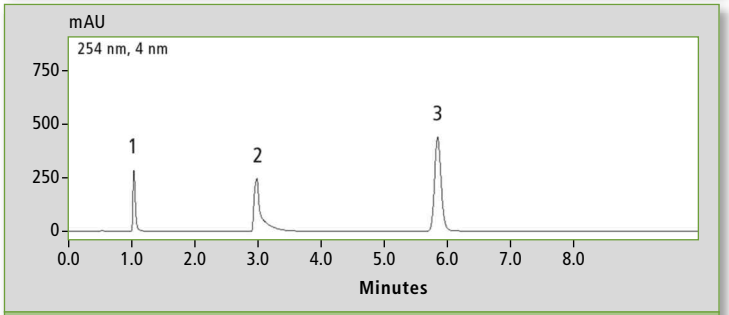

Figure 8: Basic test (1 pyridine, 2 dextrometorphan, 3 propyl paraben), measured on the Shim-pack GIST C_{18}-AQ

Let's have a party!

50th anniversary celebration and future perspectives

#Cheers

Over 300 guests from all over Europe celebrated the 50th anniversary of Shimadzu Europa on September 11, 2018. The fully booked Mercator Hall in Duisburg, Germany hosted the 'Magic Moments Night', an event featuring music, show acts, dinner, speeches, greeting notes and a 'Walk of History.' The Supervisory Board and Executive Board came from Japan to party together with the European Shimadzu family, management of the Shimadzu subsidiaries and distributors from all over Europe. The program was hosted by Asli Sevindim, a TV journalist born in Duisburg, the hometown of the Shimadzu Europa headquarters.

The musical part of the evening was covered by members of the Duisburg Philharmonic Orches-

50 years

tra. The show act performed by 'Physikanten & Co' combined entertainment and science. Using physical phenomena, the group made the 300 guests laugh, smile and wonder. Giant vortex rings flew 20 - 30 m, and showed in a rapid sequence of experiments the fascinating aspects of carbon dioxide, other than its threat of being a greenhouse gas.

Scientific edutainment ideally combines the worlds of physics and chemistry, both a part of Shimadzu's technological homebase.

For the 'Walk of History', Shimadzu collected historic advertisements, brochures and photographs from exhibitions covering 50 years of corporate history ➧

in Europe. These items bridged the gap between then and now. A corporate chronicle of 100 pages put the development of Shimadzu Europa in the context of technological, economic, political and social change in Europe.

Akiro Nakamoto, Chairman of the Board of Shimadzu Corporation, emphasized in his welcoming speech the importance of the European market where Shimadzu is represented in all countries and employs about 750 people. The President and CEO of Shimadzu Corporation, Teruhisa Ueda, sent his best wishes to the workforce and described Shimadzu Europa as a strong and creative voice in the global organization, employing over 11,000 people worldwide. Jürgen Kwass, Managing Director of Shimadzu Europa, mentioned that an anniversary is a time to party, as well as an opportunity to review and recap what has been accomplished in the past, in order to draw the right conclusions for future goals and developments. He stated: Shimadzu has the best skilled people, innovative products and an excellent distribution network supporting the future plan to soon offer 1,000 jobs in Europe.

Shimadzu live

EBF
Barcelona, Spain
November 21 - 23, 2018
bcn.europeanbioanalysisforum.eu

Ministerial Conference on Nuclear Science and Technology
Vienna, Austria
November 28, 2018
www.iaea.org/events

EMEC19
Royat, France
December 3 - 6, 2018
https://emec19.sciencesconf.org/

MS-Tage 2018
Munich, Germany
December 4 - 5, 2018
www.shimadzu.de/ms-tage

Klinische Dag
Deventer, Netherlands
December 12, 2018
https://www.dz.nl/Paginas/Default.aspx

Material and Objects in direct contact with food
Milan, Italy
December 13, 2018
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