

**New family member LCMS-8060**

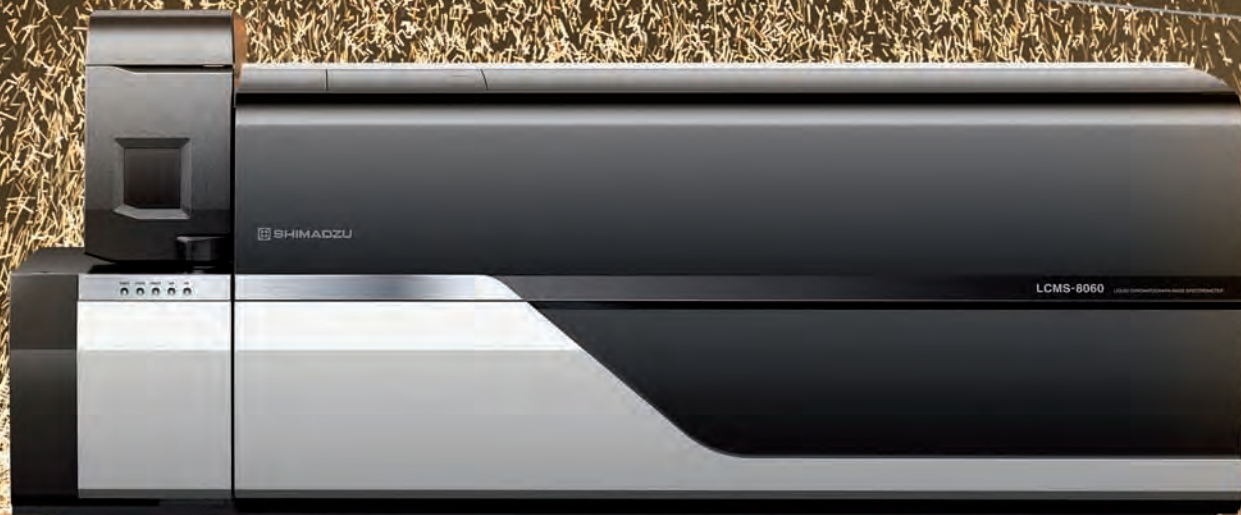
The fastest triple-quadrupole system  
extends LCMS product portfolio

Determination of organic pollution  
of wastewater

A comparison between COD and TOC

For liquid and solid substances

RF-6000 spectrofluorophotometer



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# New instrument with extended application areas

For liquid and solid substances: RF-6000 spectro-  
fluorophotometer



The new RF-6000 spectrofluoro-  
photometer

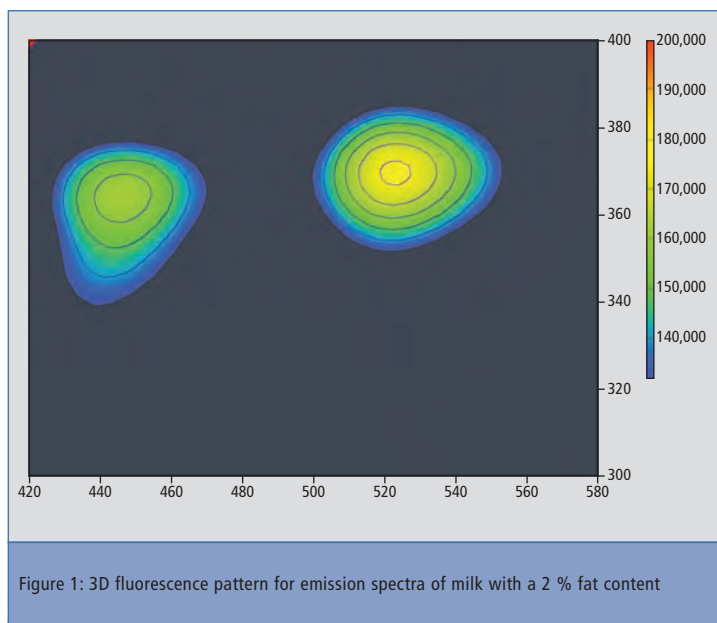
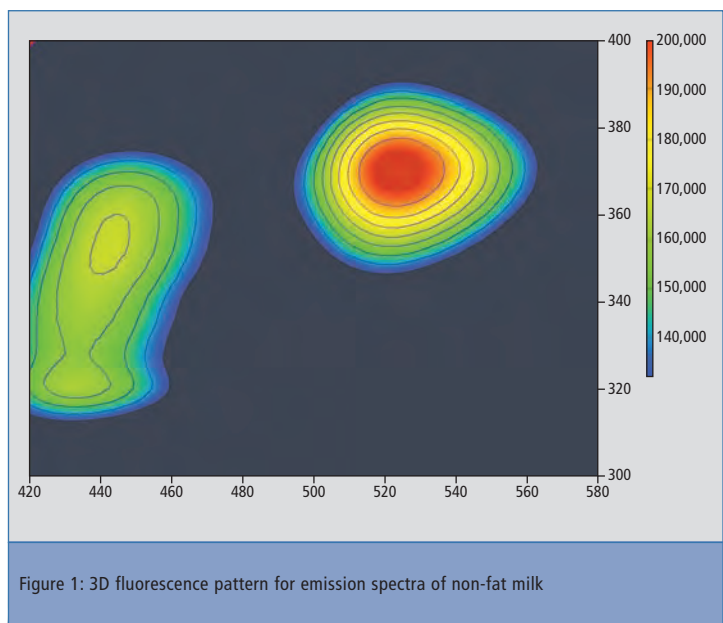
**W**ith RF-6000 instrument  
Shimadzu continues its  
successful fluorescence  
spectroscopy product line and  
replaces the well-known  
RF-5301PC. The new generation  
RF-6000 system is universally  
applicable. It combines a broad  
measuring range with high sensi-  
tivity using a broadband photo-  
multiplier. Together, this results  
in a measuring range of 200 to  
900 nm for emission as well as  
excitation measurements.



The RF-6000 is a double mono-  
chromator system. A high-ener-  
gy xenon lamp is used for excita-  
tion measurements. Designed as

a continuous light source, the  
associated physical effect of  
flickering is compensated via  
an additional detector system.





### Larger sample compartment extends applications

New components and instrument controls in combination with the broadband detector, result in a signal-to-noise ratio S/N of 350. This is more than twice the S/N value of the predecessor model. An additional innovation with respect to the predecessor model is the larger sample compartment, which allows for mounting larger and bulkier accessories. As a result, the accessible application range extends from the use of a simple cuvette with four polished sides, to the use of sippers and all the way to the use of integrating spheres.

The multitude of accessories enables the processing and analysis of liquid as well as solid substances. Application areas are food and environmental analysis as well as biological and chemical applications. The system is designed for straightforward quality control but also for training and research.

### Software with preprogrammed applications

The RF-6000 is supported via new software. The LabSolutions RF software was developed based on Shimadzu's LabSolutions platform, and not only offers instrument control but also preprogrammed applications for fluorescence spectroscopy. The software can calculate quantum yield and

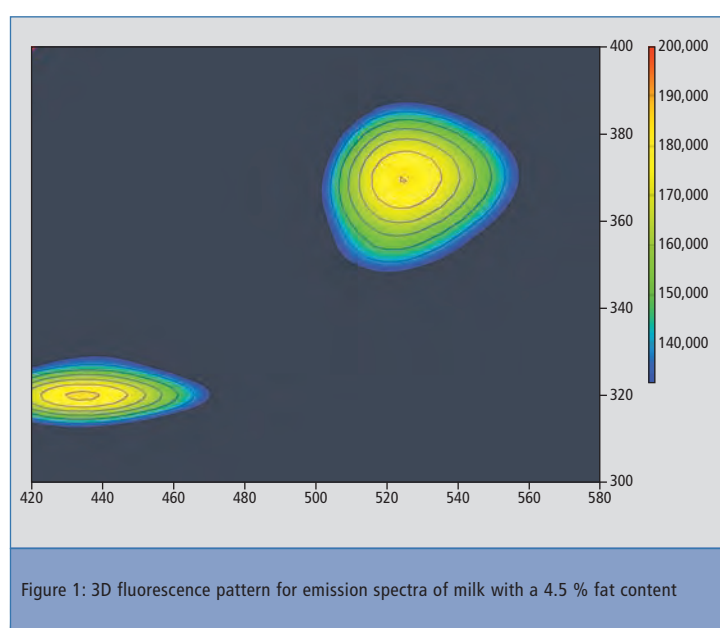
quantum efficiency and can also carry out spectral correction. For validation there is a separate module enabling to test instrument specifications according to specified industry standards.

### Application example: analysis of milk fat

Stability, sensitivity and the extended measuring range allow the use of the RF-6000 for various application areas in which fluorescence as well as chemiluminescence, bioluminescence and electroluminescence play a role, such as in pharmaceuticals, chemistry, foods, electronics, environment and life sciences. Also, 3D mea-

surements are possible using high recording speeds.

As an example of a high-speed 3D measurement, the analysis of various types of milk is presented here. The focus of the analysis was the recovery of milk fat. Samples without fat, 2 % fat and 4.5 % fat were examined. In figures 1, 2 and 3 the measurements are represented in a contour plot. The fluorescence intensities at excitation wavelengths (300 – 400 nm) were plotted against the emission wavelengths (420 – 580 nm). The presented views show the difference in fat content.



# Farewell to sample preparation...

The alternative for synthetic organic chemists – fast and direct ionization using the DART-LCMS-2020

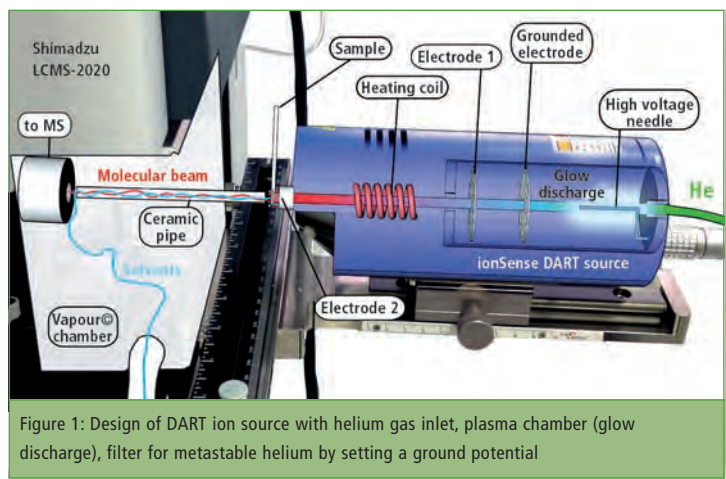


Figure 1: Design of DART ion source with helium gas inlet, plasma chamber (glow discharge), filter for metastable helium by setting a ground potential

Organic synthesis of complex molecular structures often involves several synthesis steps and requires extensive purification of the intermediates and products. Some intermediates can only be detected with conventional analytical methods after time-consuming method development. For such a complex analysis of the intermediates and byproducts there is, however, insufficient time. Simple, universal and fast analytical methods can therefore bring enormous time savings, also in synthetic organic chemistry.

At the Institute of Organic Chemistry of the University of Basel, Switzerland, synthesis of new structures with unknown characteristics is a daily routine for the scientific assistants. Various mass spectrometric methods are used for synthesis control and structure determination. This is why the selection of a suitable analytical method (GCMS, LCMS with various ionization technologies such as ESI, APCI, APPI, MALDI) for each newly synthesized molecule is a great challenge.

Due to the many different molecular structures, a universal method is not available at present. Low molecular weight, non-polar (hydrophobic) compounds are prefer-

ably analyzed using GCMS. The LCMS with an ESI and APCI ion source serves either for the detection of more polar, often charged (ESI) or thermally stable, weakly polar compounds (APCI). In addition, many of the structures to be investigated are often thermally unstable. The MALDI technique is especially suitable for the analy-

sis of high molecular weight compounds.

## DART: fast analysis of synthesis products directly out of the reaction mixture

The DART (Direct Analysis in Real Time) ionization technology offers a highly promising alternative and allows for direct ionization of gases, liquids and solids under atmospheric pressure. In combination with a Shimadzu LCMS-2020 single-quadrupole mass spectrometer, rapid analysis of synthesis products directly from the reaction mixture without any sample preparation becomes possible.

In the DART source, a stream of helium is excited under atmospheric pressure by applying an electric potential to a helium plasma (see figure 1). This metastable helium plasma ionizes water molecules, which then transfer protons to the sample molecules.

the  $[M-H]^-$  ion in the negative mode. Depending on the structure of the analytes,  $M^+$  ions (such as for polycyclic aromatic hydrocarbons) or fragments can be formed. Multiple charged ions or adducts with alkali metal cations are not observed.

The DART source is easily installed and can be used directly 'out of the box' without parameter optimization. The He stream transports the ionized sample molecules into the mass spectrometer through a ceramic capillary, which can be cleaned easily whenever necessary (see figure 2).

Small volatile molecules, such as solvents or water, are removed via the rotary vacuum pump.

Figure 3 shows the qualitative analysis of a reaction mixture from a flask without further sample preparation. The sample can be removed easily from the reaction flask using a capillary and held in the gas stream of the DART source. An application example shows the use and benefit of the DART source.



LCMS-2020

## Various ionization modes

In addition to charge transfer via water molecules, the analytes can also be ionized directly. In the negative mode, ionization takes place via oxygen anions. This 'indirect' ionization results in simple mass spectra, mainly through the formation of the protonated  $[M+H]^+$  molecular ion or

## Control of a synthetic route

The analysis of multi-stage synthetic routes is particularly challenging. Because of the continuously changing parent molecules, the mass as well as polarity and stability of the compounds and, consequently, also the appropriate mass spectrometric methods vary strongly. As an example, figure 4 shows the structure of a cyclic compound with six aromatic rings over twelve synthesis steps.

Each individual stage must be characterized, by which only the first eight synthesis products could be determined via GCMS. In the figure, the corresponding  $M^+$  molecular ion is shown in

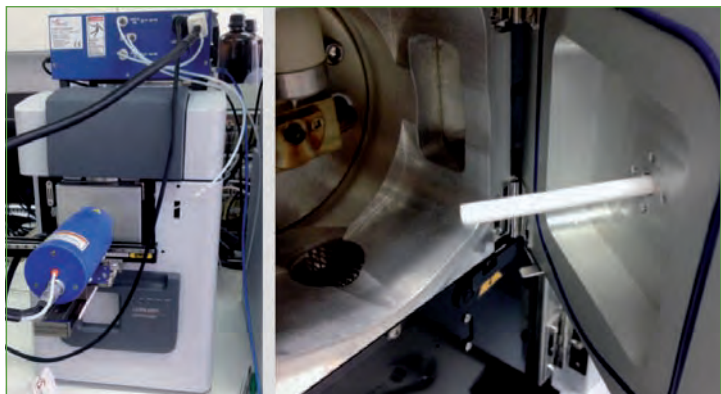


Figure 2: DART ion source from IonSense coupled to Shimadzu's single-quadrupole LCMS-2020 (left). The chamber in front of the inlet to the high vacuum (image on right) is under slight vacuum in operation.

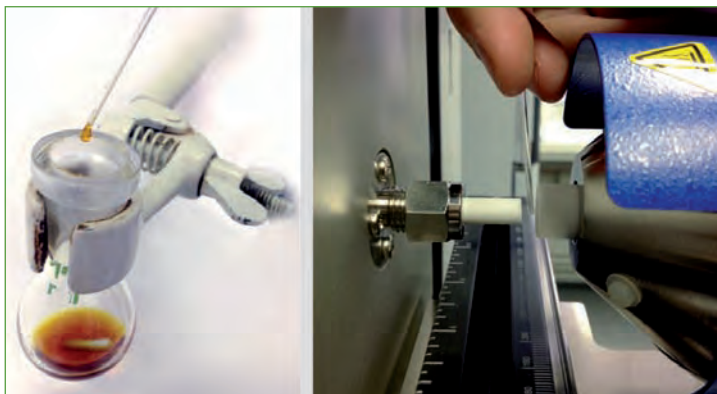


Figure 3: Sampling out of a reaction mixture of unknown concentration using a glass capillary and sample measurement by briefly holding the capillary in the ionization gas stream between the DART ion source and the LCMS-2020

blue. The intermediate stages shown in pink were difficult to determine via GCMS due to their thermal instability or their high molecular weight.

As of synthesis stage nine, the molecules reach a mass range critical for GCMS.

Analysis via LCMS with an ESI or APCI ion source is also not easy, due to the low polarity of the compounds. In this case, the DART ion source with which all molecules labeled in green can be analyzed without much effort proves to be the method of choice. The high polarity switching speed (15 ms) of the LCMS-2020 en-

abling simultaneous measurement of positively and negatively charged molecules is an additional advantage.

### Summary

Combining the LCMS-2020 with the DART ionization technique enables the analysis of chemically very different polyaromatic compounds directly out of the reaction mixture. For qualitative measurement, a test capillary with a small amount of sample is held in the DART ion source in order to obtain a mass spectrum. Even large hydrophobic compounds are ionized in the helium stream and can be identified reliably.

The simple operation and robustness of this analytical method make the DART-LCMS-2020 ideal for daily routine use in organic chemical synthesis at the University of Basel.

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### IMPRINT

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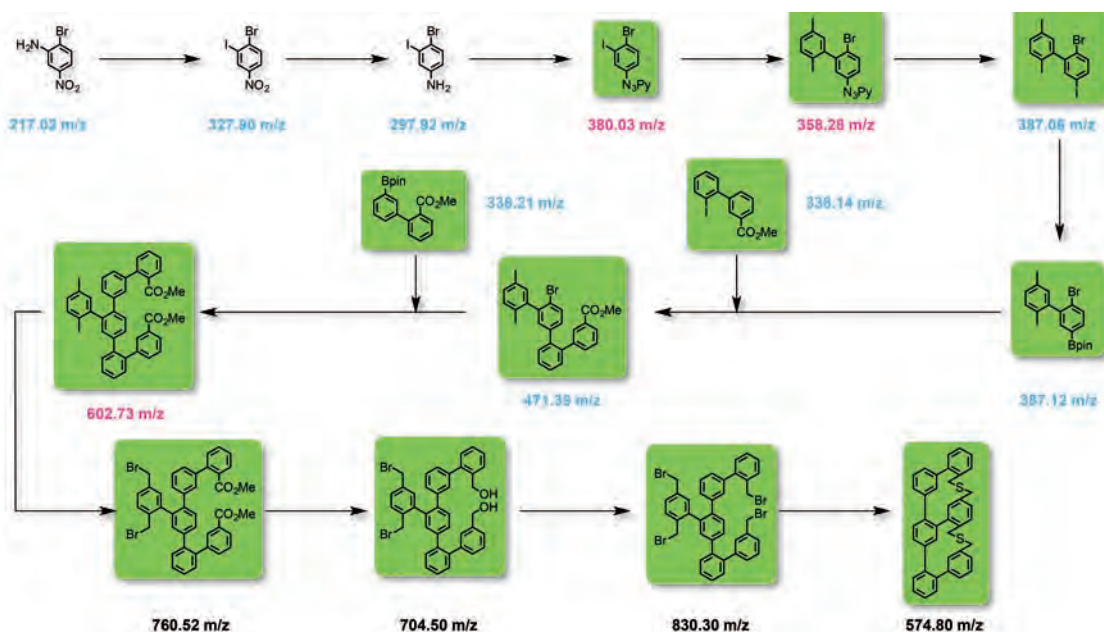


Figure 4: Synthesis route of the target molecule m/z 574.8 in twelve synthesis steps. Blue: analysis using GCMS, pink: analysis using GCMS (only possible to a limited extent); green: analysis using DART-MS.

Further information on this article

• App Note  
» Farewell to sample preparation ...«





# Straightforward identification of high performance polymers

## Reactive and conventional pyrolysis GC-MS using the GCMS-QP2010 Plus

Several newer classes of thermosets and high performance polymers are developing quickly, motivated by ever-changing requirements combined with growing industrial interest and commercial demand. As an example, newer polymers based on phenolic resins, even a century after their introduction, are still expected to be applicable in the high-tech aerospace industry. This is due to good to excellent thermostructural heat and flame resistance, desirable chemical resistance, excellent electrical insulating properties, improved ablative properties

and, last but not least, due to the relatively low production cost. For similar specific key properties, newer polyimides and epoxy resins are also in demand in many engineering areas.

As new products and applications continue to emerge, analytical science needs to be prepared to characterize such polymers with up-to-date instrumentation. Reactive pyrolysis and conventional pyrolysis can be applied as solutions.

Pyrolysis techniques in combination with GC-MS have become

important tools for the characterization of polymers and polymer additives. Reactive pyrolysis can be seen as the smaller brother of fundamental analytical pyrolysis with the difference that a reagent is added to the polymer in order to selectively cut the target molecules and identify the remaining reaction products.

### In comparison: conventional and reactive pyrolysis

The main difference between conventional and reactive pyrolysis is the information density obtained from the pyrogram. While conventional pyrolysis produces a broad range of pyrolysis products, reactive pyrolysis gives a limited number of peaks, but identification is more precise and puzzling back the initial mixture of monomers is easier and more exact. While conventional pyrolysis applies a higher temperature (e.g. 650 °C) to statistically cleave the carbon covalent bonds, reactive pyrolysis requires a lower temperature (e.g. 440 °C) in order to suppress the formation of pyrolysis products and enables efficient selective thermo-chemolysis reaction on desired chemical bonds to form methanol adducts (e.g. methyl esters, methyl ethers, etc...).

Tetramethylammonium hydroxide (TMAH) at a concentration of 25 weight % in methanol is the most abundantly used reagent for reactive pyrolysis, being a very strong base and therefore finding its application in selective hydrolytic cleavage of the sample. As a benefit, the same hardware configuration can be used for reactive py-

rolysis as well as conventional pyrolysis.

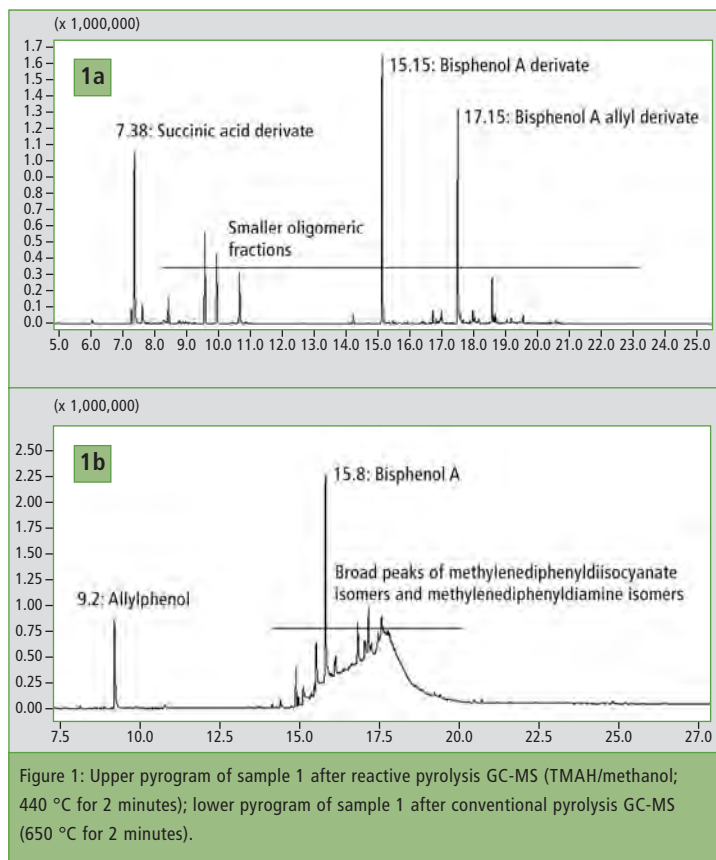
### Equipment and application

For these measurements, the PY-2020iD thermal desorption unit from Frontier Laboratories Ltd. was used equipped with a 48 position auto sampler connected to a GCMS-QP2010 Plus from Shimadzu. A special metal capillary separation column (Ultra ALLOY-5; 0.25 mm inner diameter x 30 m, Frontier Laboratories Ltd., Japan) coated with a thin (0.25 µm) film of diphenyl-dimethylpolysiloxane was used to separate the pyrolysis products.

This pyrolysis improves analytical reproducibility through quick heat transfer towards the sample by a free-fall injection in the furnace of a deactivated stainless steel sample-cup containing a few mg of sample. The hardware combination of the autosampler with the programmable furnace enables optimizing of pyrolysis instrumental parameters while reducing memory effects by using a system conditioning program. However, to avoid carry-over problems, it is essential to check the cleanliness of the sample path between 2 samples by injecting a sample blank. The initial procedure (pyrolysis or reactive pyrolysis) is then followed by GC-MS analysis to separate and identify released chemicals.

### The results

Figure 1 shows reactive and conventional pyrograms of a 2-component maleimide-allylphenol formulation, an addition-cure phenolic resin. These resins cure by double bond Alder-ene reactions and have the advantage that they cure at moderate low temperatures without the production of volatiles, thereby creating void-free products. In the reactive pyrogram (figure 1, upper picture), the most intense emissions are the dimethylether and allyl derivatives from bisphenol A, smaller oligomeric fractions and succinic acid dimethylester. The main emissions in the conventional pyrogram (figure 1, lower picture) are allylphenol, bisphenol A, methyl-



enediphenyldiisocyanate isomers and methylenediphenyldiamine isomers (broad peak). After combining results, this resin was identified as a reactive blend of 4,4'-bismaleimido diphenyl methane with 2,2'-diallyl bisphenol A (figure 2). This phenolic resin formulation cures in addition by

Reactive pyrolysis and conventional pyrolysis can be used for defect analysis by comparing a defective polymer with a reference polymer. Using this comparative analysis, differences appearing in the pyrograms may relate to the reason for the targeted defect. In the reactive pyrograms in figure 4,

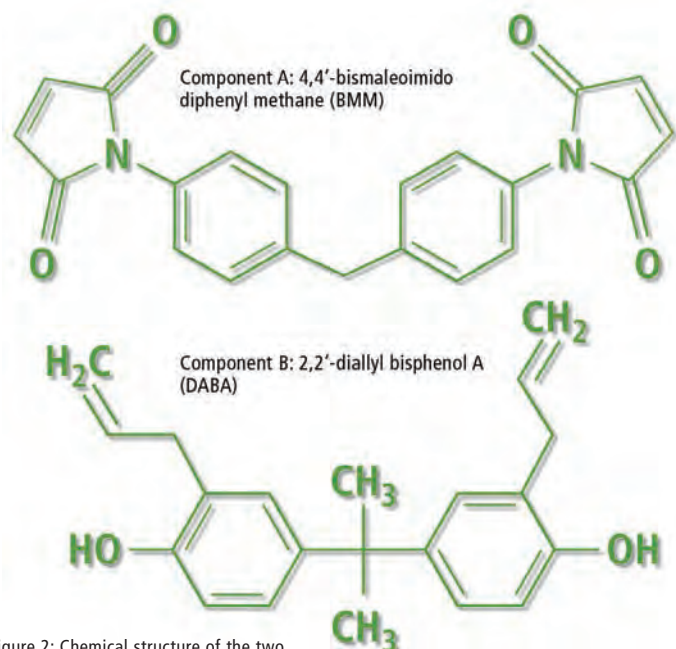


Figure 2: Chemical structure of the two monomers before curing

copolymerization of maleimide and alkyl groups as the major reaction.

Figure 3 shows the conventional pyrogram of a polyetherimide sample with main emissions coming from phthalimide based substances, bisphenol A and alkylated phenols. Polyetherimide has similar characteristics to polyether ether ketone (PEEK). While cheaper, its application temperature and impact strength are lower.

two polyurethane samples were compared with different flame resistance properties.

Dimethylether of tetrabromobisphenol A was detected in the polyurethane with higher flame resistance using reactive pyrolysis. Tetrabromobisphenol A is a commonly used flame retardant in many polymer applications and can be reactively bounded into the polymer chain. In addition, reactive pyrolysis performs well when considering reproducibility of

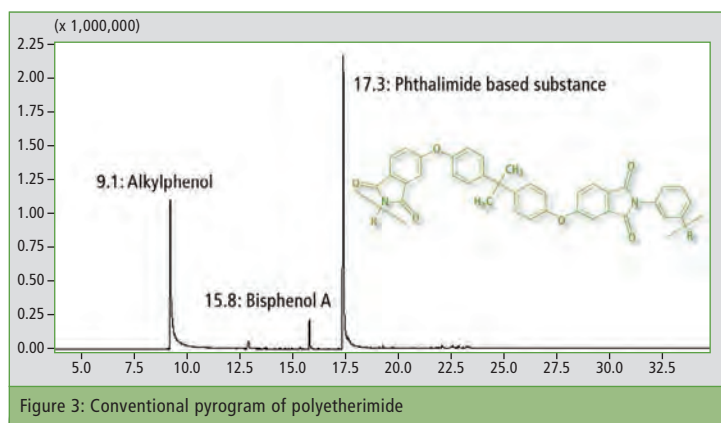


Figure 3: Conventional pyrogram of polyetherimide

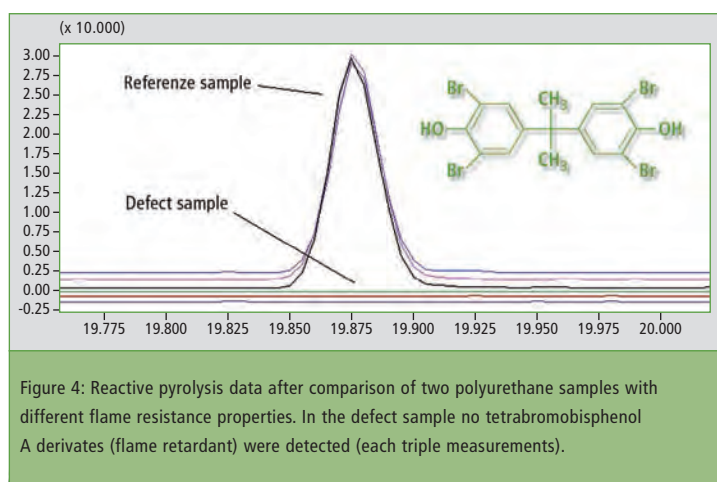


Figure 4: Reactive pyrolysis data after comparison of two polyurethane samples with different flame resistance properties. In the defect sample no tetrabromobisphenol A derivatives (flame retardant) were detected (each triple measurements).

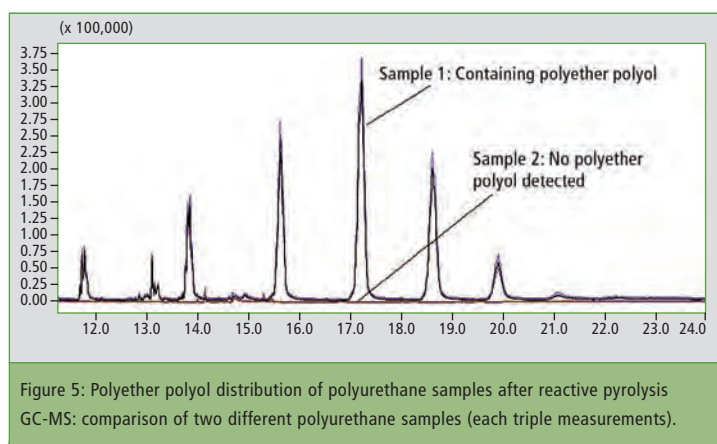


Figure 5: Polyether polyol distribution of polyurethane samples after reactive pyrolysis GC-MS: comparison of two different polyurethane samples (each triple measurements).

results as shown in figure 5, where a polyether polyol distribution of a polyurethane sample is shown after triple measurement compared to a polyurethane sample without a polyether polyol in the polymer backbone.

Chemical analysis of thermosets is an ambitious task using conventional spectral techniques. As an example, Fourier transformed infrared spectroscopy (FTIR) gives poor information about the sample, since a variety of possible chemical structures can make typical resonance frequencies of target structures. Reactive and non-reactive pyrolysis can be more applicable as these techniques selectively cut certain bonds and the chemicals obtained can give the analyst an image of initial substances used.

## Conclusions

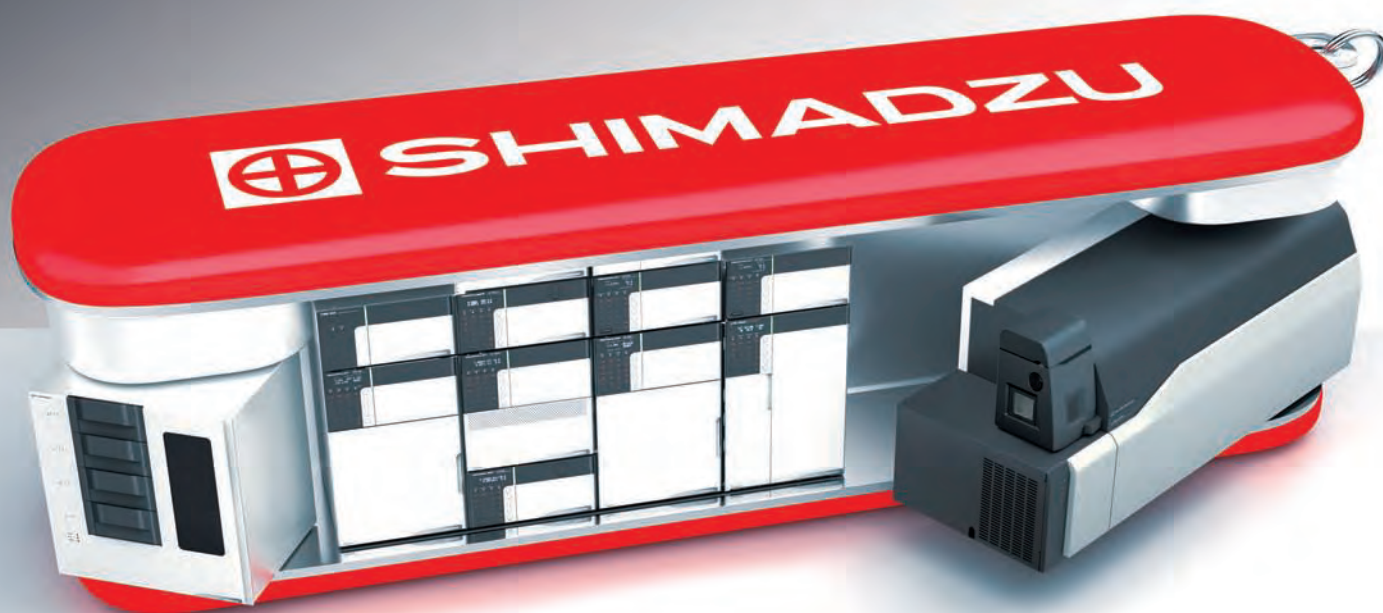
The combination of reactive and conventional pyrolysis seems to be a very powerful tool for the characterization of thermosetting

polymers with a complex cross-linking system.

In addition, reactive pyrolysis can re-order or simplify data obtained from thermosets very close to the initial monomers. In some cases pyrolysis can be used as a tool for defect analysis where the problem with the material is based on composition of the polymer.

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# The Swiss Knife of analytics

## Unified Chromatography applying the new Nexera UC SFE-SFC-MS System

The new Nexera UC SFE-SFC-MS platform unifies quick and easy on-line sample extraction with state-of-the-art chromatographic separation and high sensitivity detection. This 'unified chromatography' system showcases complete automation of SFE sample preparation

so-called 'supercritical' carbon dioxide is used as extraction medium and mobile phase respectively. Supercritical CO<sub>2</sub> is a fluid state of carbon dioxide where it is held at or above its critical temperature (31.1 °C) and critical pressure (73.8 bar). In this supercritical state, fluid density is strongly

Use of 'supercritical' CO<sub>2</sub> for extraction as well as chromatographic separation is therefore faster, more efficient, cheaper and more environmentally friendly than use of toxic organic solvents such as hexane, acetonitrile or chloroform.

### Reduced risk of human error

The Nexera UC unified chromatography system combines SFE and SFC in a single flow path. Target compounds are extracted from solid samples such as a dried blood spot, food sample or polymer, and then transferred auto-

matically to LC or SFC/MS analysis. The automated workflow reduces the risk of human error considerably during sample preparation as well as overall time of the experiment (see figure 1).

Supercritical CO<sub>2</sub> is introduced into the extraction vessel, where static and/or dynamic extraction conditions can be adjusted in pressure and temperature according to the sample requirements. As all samples are extracted under light-shielding, anaerobic conditions, decomposition even of labile compounds, that are easily oxidized, photo- or heat-labile can be avoided. Extraction selectivity

Conventional sample preparation method (QuEChERS) – approx. 35 min.



SFE sample preparation – 5 min.



Figure 1: Reduction in sample preparation time using the Nexera UC system

ration and analysis by liquid or supercritical fluid chromatography.

### Faster, more efficient, cheaper and more environmentally friendly extraction

In supercritical fluid extraction (SFE) and chromatography (SFC)

affected by temperature and pressure, and its physical and thermal properties are between those of the liquid and the gaseous phase. Compressibility and diffusion coefficient of the supercritical solvent are much higher, while viscosity is decreased compared to a pure liquid, so it is far better suited to permeate penetrable solids.

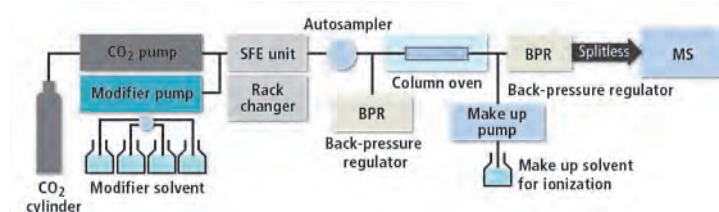


Figure 2: System configuration of Nexera UC SFE-SFC-MS System



can be carefully controlled by adjusting the solvating power of the CO<sub>2</sub> through changes in pressure and temperature. After extraction in the SFE unit, the sample-containing CO<sub>2</sub> is introduced into the SFC flow line for chromatographic analysis by LC or SFC (see figure 2).

The fact that properties of supercritical CO<sub>2</sub> near the critical point change drastically with only small variations in temperature or pressure is advantageous in SFE, as extraction selectivity and efficiency can be easily adjusted. However, it also renders supercritical conditions a non-robust area to work in, in super-critical-fluid chromatography, where changes in fluid density (hence selectivity) with column length and diameter,

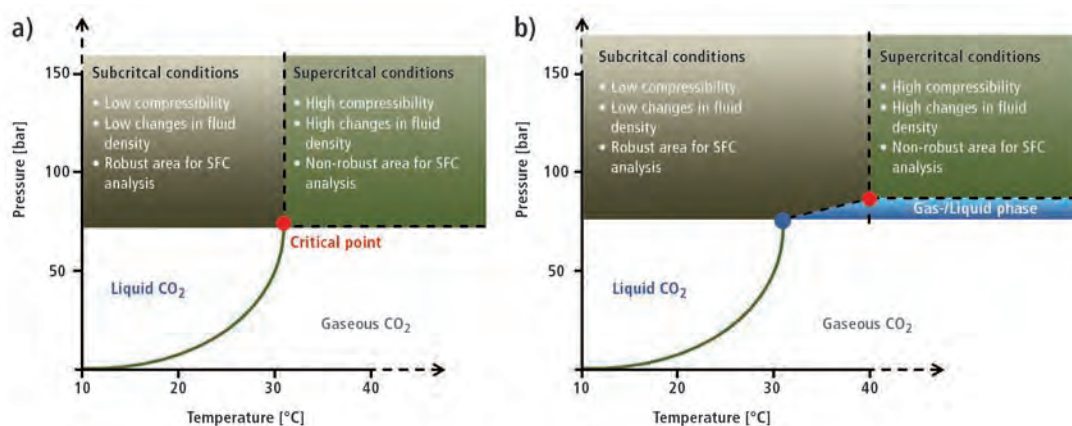


Figure 3: Phase diagram for a) pure CO<sub>2</sub> (critical point at 73.8 bar, 31.1 °C) and b) 96.5 % CO<sub>2</sub> / 3.5 % MeOH (critical point at 83 bar, 40 °C) [Eric Lesellier ICOA, UMR 7311, SFC 2014]

Many solvents are miscible with CO<sub>2</sub> (e.g. MeOH, EtOH (H-bonding), ACN (dipole)) and offer additional interactions. They therefore induce controlled

LC/MS is achieved by evaporation of the CO<sub>2</sub> leaving a more concentrated sample. In addition, the Nexera UC features an ultra-low volume back-pressure regulator that can remain in the flow path when running the sample to the detector, enabling splitless sample

transfer into the mass spectrometer. Back pressure regulators with larger dead volume cause peak dispersion, and have to be bypassed. With the Nexera UC, the total eluate can be transferred directly into the detector for extra high sensitivity (figure 5).

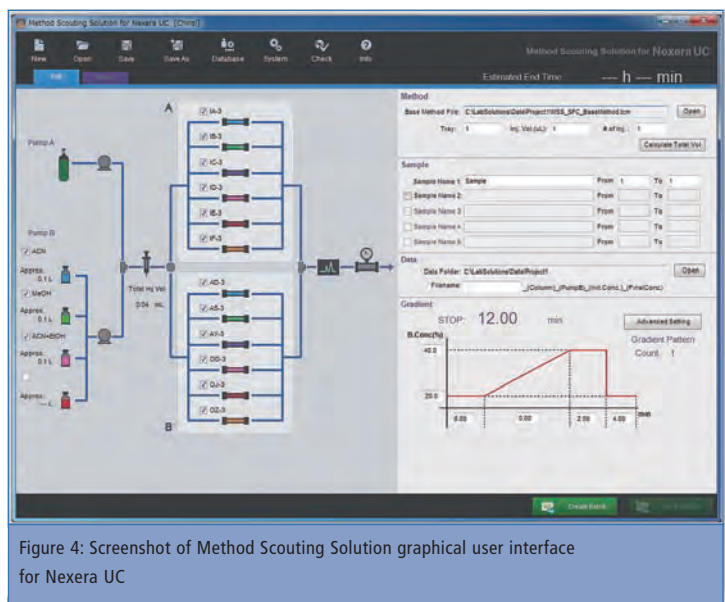


Figure 4: Screenshot of Method Scouting Solution graphical user interface for Nexera UC

particle size and flow rate are unwanted.

## Robust area to work in

CO<sub>2</sub> at its critical point is non-polar, and solvent strength is often increased using a polar co-solvent. As soon as such an organic modifier is introduced, the mobile phase is no longer truly supercritical, although the terminology continues to be used. These now 'sub-critical' conditions imply much lower changes in fluid density with small variation in pressure or temperature and are therefore a better, more robust area to work in for a reproducible SFC separation (see figure 3).

changes in retention and provide a valuable tool in improving the selectivity of a separation.

## Simplified method development

Method development using the Nexera UC system is simplified by the method scouting option. It offers fast screening of up to twelve columns and four mobile phase modifiers with the dedicated method scouting solution platform that generates scouting methods automatically according to initial input parameters (figure 4).

An increase in sensitivity of a SFC/MS separation compared to

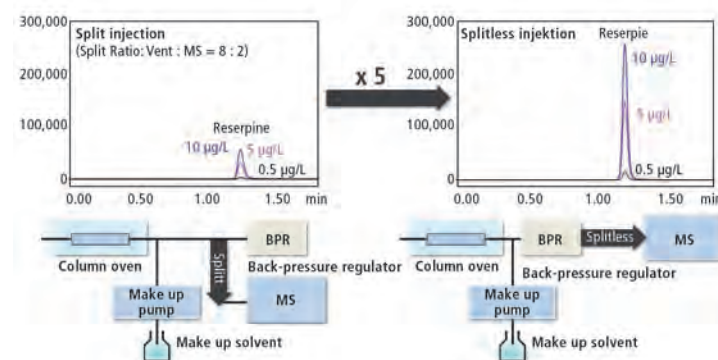
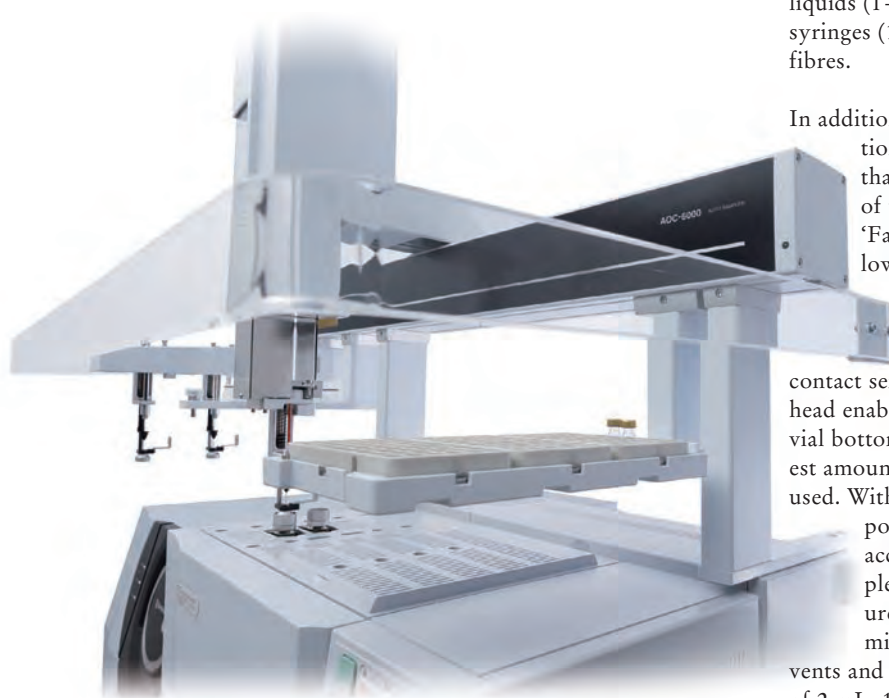


Figure 5: Improved sensitivity due to low dead volume BPR

# Next level sample pre- paration

## The new AOC-6000 autosampler



The new AOC-6000 autosampler

For more than a decade, the AOC-5000 autosampler has been state-of-the-art for various injection techniques and is still today a reliable sampler for daily laboratory routine. However, in recent years the specifications of many laboratories have increased significantly – from simple sample preparation with subsequent injection to complex automated processes. Automated systems make sample preparation and analysis results more reliable as they eliminate the influence of ‘human error’. At the same time, efficiency is increased and costs are minimized.

With the AOC-6000, an autosampler is now available that not only meets these needs, but also sets standards in integrated sample preparation.

### New developments

The development of the AOC-6000 focused on extension of its

application range. The automated syringe exchanger unit (figure 1) plays a central role here. While the AOC-5000 was limited to the use of one syringe during operation, the AOC-6000 can handle up to six different syringes during ongoing operation – syringes for

liquids (1 – 10,000  $\mu\text{L}$ ), headspace syringes (1 – 5 mL) or SPME fibres.

In addition, other minor modifications were implemented that extend the possibilities of the AOC-6000. The ‘Fast Injection Mode’ allows for non-discriminating injection of hydrocarbons up to a chain length of C40. A small contact sensor in the injection head enables the detection of the vial bottom so that even the smallest amounts of sample can be used. With 5  $\mu\text{L}$  of sample, it is possible to inject  $3 \times 1 \mu\text{L}$  accurately from this sample. A vortex mixer (figure 2) enables thorough mixing of different solvents and reagents. Vials in sizes of 2 mL, 10 mL or 20 mL can be agitated at up to 2,000 rpm.

### New possibilities

One of the new application areas results from combination of the AOC-6000 with the high-end GCMS-TQ8040 or GCMS-QP2010 Ultra instruments (figure 3). Through the patented design of the high-vacuum range



Figure 1: Syringe exchanger unit



Figure 2: Vortex mixer

of these systems, two chromatographic separation columns can be operated simultaneously without any loss in sensitivity and with no cross contamination. This creates the possibility for fully automated injection of various types of samples onto the most suitable chromatographic separation column with subsequent ultra-high sensitivity analysis. In this way, for example, a liquid sample can first be injected onto a non-polar separation column while the headspace sample is being prepared simultaneously in the incubator. When the sample preparation is completed, a portion of the headspace can be injected directly onto the second polar column in the next step.

### Complex sample preparation made easy

The AOC-6000 reaches its greatest potential in complex sample preparation. This usually involves the combination of very different steps, the use of strongly differing volumes and the mixing of highly reactive compounds. Some examples of complex preparations are the addition of an internal standard, the creation of a calibration curve or the derivatization of substances that are difficult to analyze using gas chromatography without chemical conversion. For these basic tasks, the AOC-6000 offers ready to use methods that can be implemented easily in the daily laboratory routine, enabling easy access to automated sample preparation.

A very time-intensive and error-prone routine task in the laboratory is the creation of a dilution series. When using the AOC-6000, it is sufficient to load the autosampler with chemicals and vials





Figure 3: Combination of the GCMS-TQ8040 and the AOC-6000

as well as to parametrize the pre-configured basic method. Fully automated preparation as well as subsequent injection into the GCMS then takes place. Figure 4 shows a calibration curve created with the aid of the AOC-6000, while figure 5 shows the corresponding stepwise approach.

The possibilities of the autosampler are, however, not limited to these basic tasks. Every analytical laboratory has its own specific know-how and requirements, which must be taken into account during automation of sample preparation. To integrate this unique knowledge into the sample preparation process in an optimum way, it is possible to develop customized methods in close cooperation with experienced Shimadzu engineers and to integrate these methods in daily laboratory practice.

#### Smart software control

Especially important for a simple and efficient use of an autosampler is the way the control soft-

ware is integrated in the chromatographic data acquisition system. Typically, autosamplers are controlled via a second software, which can lead to synchronization problems between autosampler and chromatograph. This is not the case with the AOC-6000, which is fully integrated in the tried and tested GCMSsolution software. All parameters needed for sample preparation and measurement are entered into the software and can be viewed very easily and afterwards verified.

Figure 6 shows a screenshot of the GCMSsolution software. Each of a total of six preconfigured methods is divided into three parameter groups. In this way, the user can easily select the basic parameters (setup + analysis) of a method. If special parameters requiring an increased level of knowledge on the injection technique need to be adapted, this can be carried out via the advanced section.

With this high degree of flexibility and easy handling, the AOC-6000

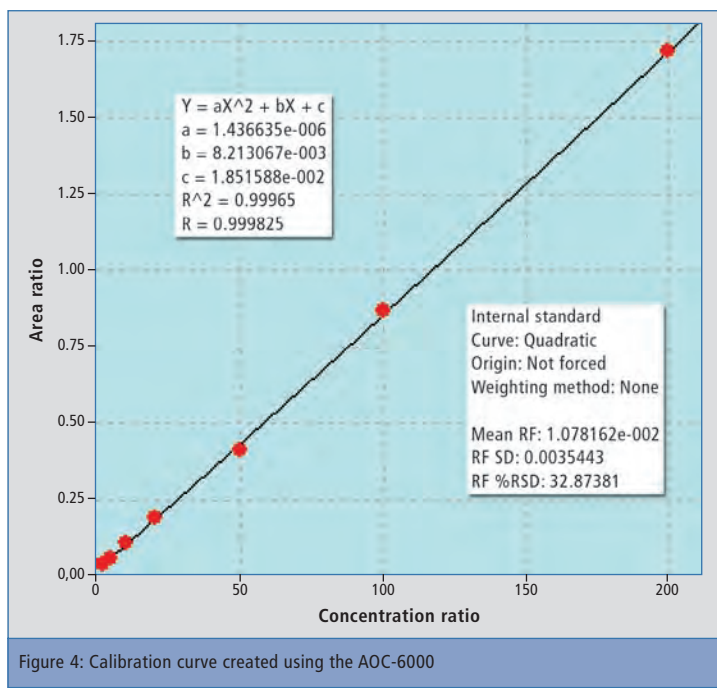


Figure 4: Calibration curve created using the AOC-6000

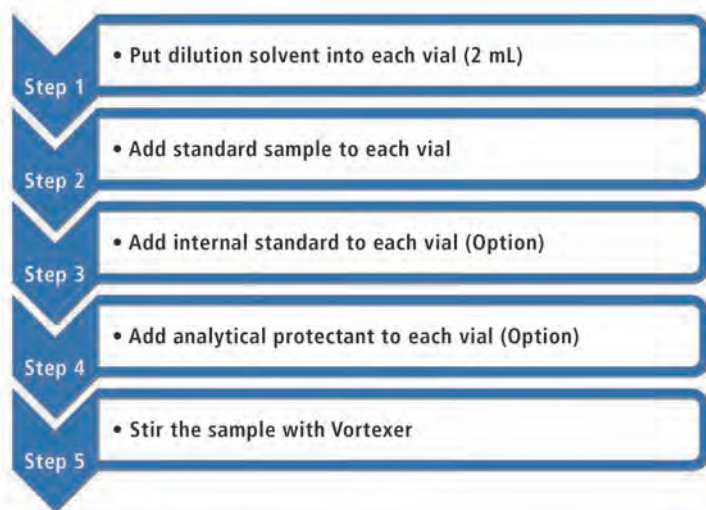


Figure 5: The stepwise process for the creation of a calibration curve using the AOC-6000

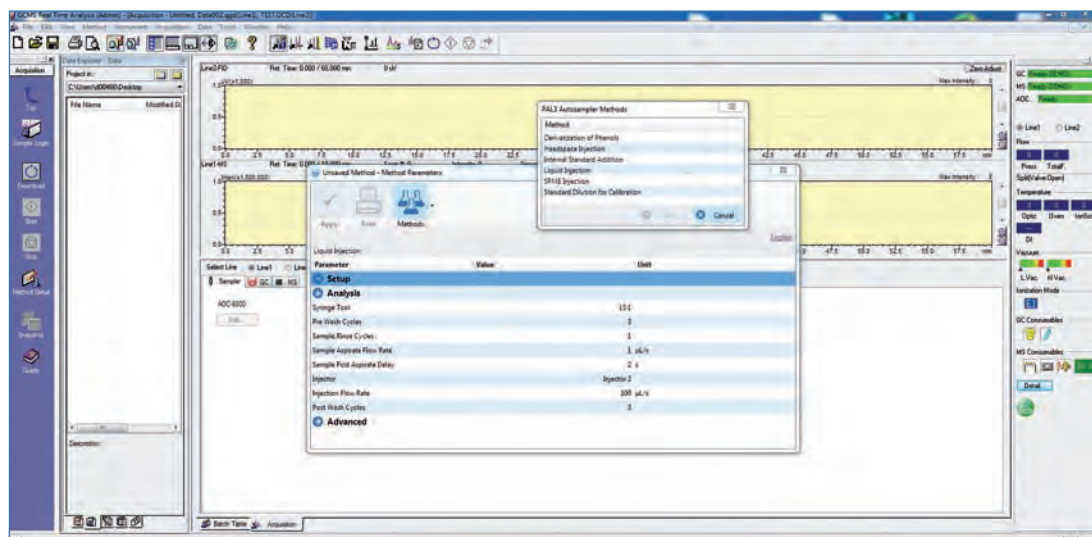


Figure 6: The control software GCMSsolution for sample preparation and injection

sets new standards for integrated sample preparation, and offers both routine and advanced users a broad application spectrum.

# LED's – little helpers in everyday life

## Emission measurement using the emission fiber optics probe of the UV-2600

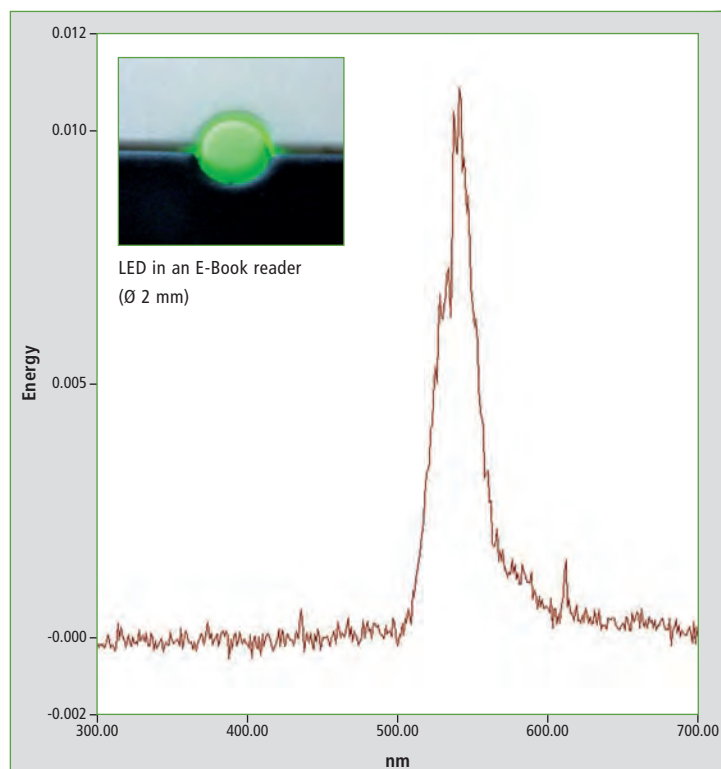


Figure 1: LED with a diameter of 2 mm in an e-book reader and its visible spectrum from 300 to 700 nm

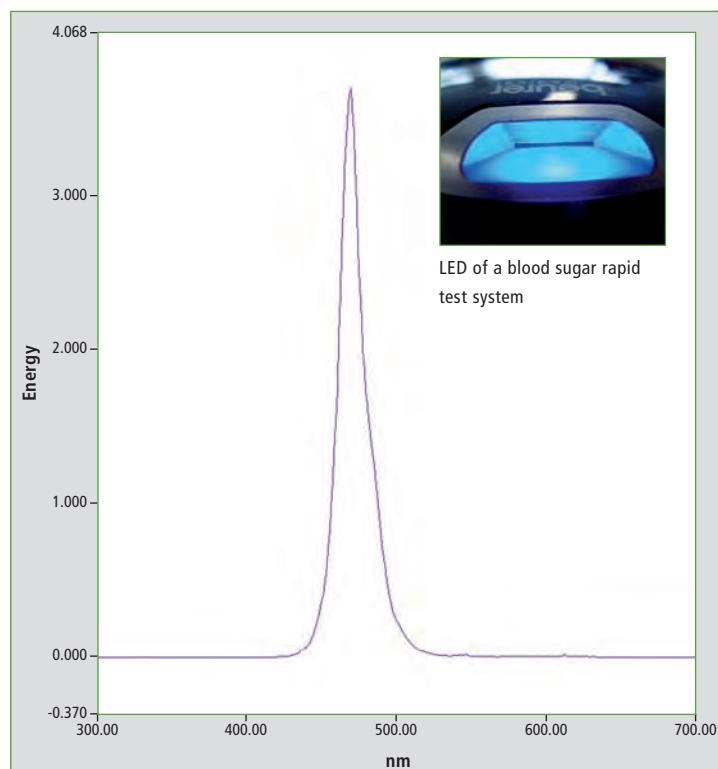


Figure 2: LED of a blood sugar rapid test system used to illuminate the shaft (approx. 1.3 cm) in which the test stick is inserted. The LED is placed under a plastic plate, which is used as a diffuser. The visible spectrum of 300 to 700 nm is shown on the right.

Working while we are sleeping – according to a German legend, this is what the house gnomes named 'Heinzelmännchen' are known for. Gyro Gearloose, a Disney character, also had an assistant called little helper, who supported him in his projects. In everyday life, a modern variation thereof is the LED that, for instance, can indicate the status of an electrical appliance. These LEDs can be found everywhere and are vividly noticeable in the darkness of the night.

With their red, blue, green or orange colors, they are used in

offices, in transportation and in households. In the newest generation of traffic lights, they save many municipalities money due to their intense luminosity and low energy consumption.

Depending on the lighting objective, the light emission of LEDs can be dosed. The radiant power of a traffic light must draw the attention of road users, while an

LED on an e-reader should only indicate that it is switched on. An intense green LED glowing from an e-book could lead to short-term red-green vision impairment when reading for a prolonged time.

### What is an LED?

LED stands for light-emitting diode. The diode consists of a semi-

conductor material that, depending on its composition, can emit light in different colors. This light is attributable to the phenomenon of luminescence. The luminescence colors are dependent on doping of the semiconductor material with mixtures of inorganic salts, including those of rare earths. Based on doping, a so-called specific light color can be set to a fixed analytical wavelength [1].

Source	LED color	Detector amplification*	Analytical wavelength	Energy intensity
E-book reader	Green	4	542 nm	0.011
Blood sugar measuring device	Blue	2	469 nm	3.698
UV-2700 power-on indicator	Green	4	500 nm	0.019
Monitor power switch	Blue	4	461 nm	1.2

Table 1: LED sources, their color and their characterization as determined via emission measurement in the UV-VIS measuring range.

\*Maximum amplification level 6 is used for utilization of the photomultiplier.

In the following application, the luminosity and color emission of various commonly used LEDs are investigated. The LEDs were not removed from



their devices but were investigated in their built-in state. Depending on their intended use, LEDs are directly visible or are installed behind diffuser plates where they are used to illuminate a specific area instead of a selective point.

### Which spectrum is to be expected?

Due to the characteristics of single-color LEDs, bandwidth spectra with an analytically meaningful bandwidth reflecting the inorganic substances are to be expected.

intensity, color, signal half-width or the dominant wavelength.

The literature shows that doping with rare earth salts results in a colorful LED world. It has been demonstrated that for the colors green and blue, gallium, indium or mixtures of both can be applied [1], [2].

### The measurements

To carry out an emission measurement, the light source of the analytical measuring instrument is blocked. Instead of the instru-

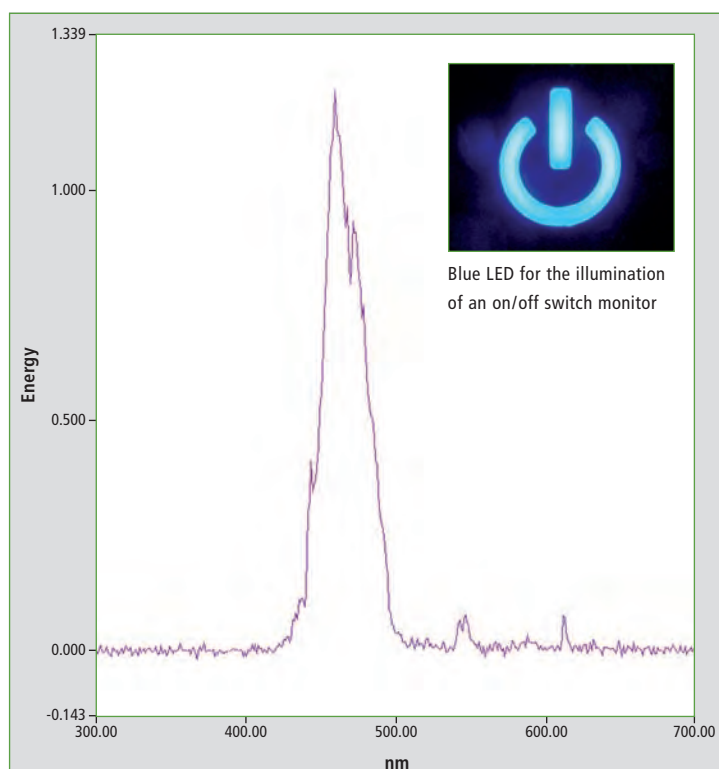


Figure 3: Blue LED for the illumination of an on/off switch monitor and its visible spectrum from 300 to 700 nm

LEDs are thus monochromatic. The situation is different with LEDs that emulate white light. Here, the combination of, for instance, a blue LED with a luminescent dye that, excited by the 'blue', will emit a broad band and thus covers the visible range, which includes the primary colors green, red and blue.

As luminescence is an emission phenomenon, its light intensity can be characterized via emission measurement. Emission measurement using UV-VIS spectroscopy enables the determination of

ment's standard light sources (D2 lamp and halogen lamp), the light of an external light source is guided into the optical path of the UV-VIS instrument with the aid of a fiber optics probe. The fiber optics probe is a light path extension and makes it possible to place the head of the fiber optics probe directly onto the light source.

To classify the intensity, the detection sensitivity can be adjusted via the detector. In this application, measurements were carried out using Shimadzu's UV-2600, equipped with an emission fiber

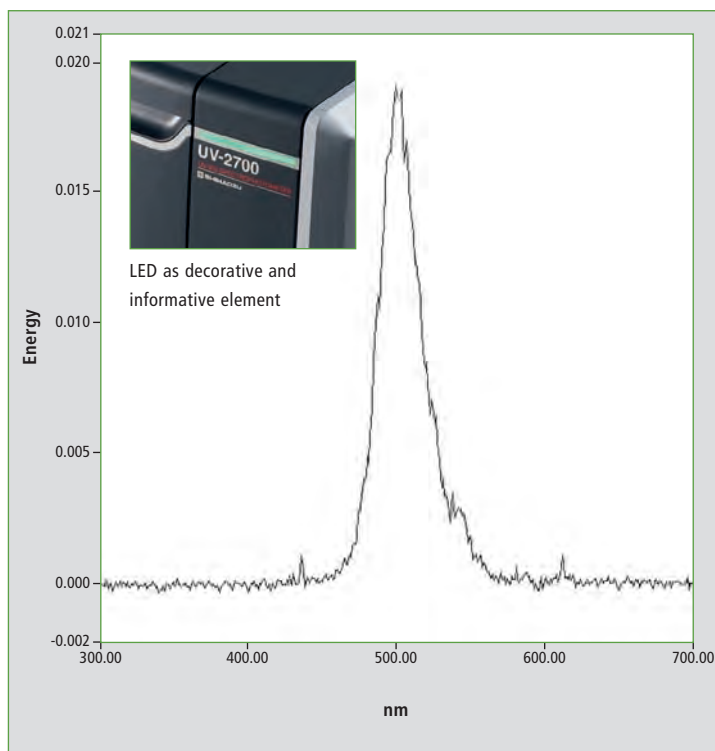


Figure 4: LED as decorative and informative element on a Shimadzu UV-VIS UV-2700 spectrophotometer and its visible spectrum from 300 to 700 nm

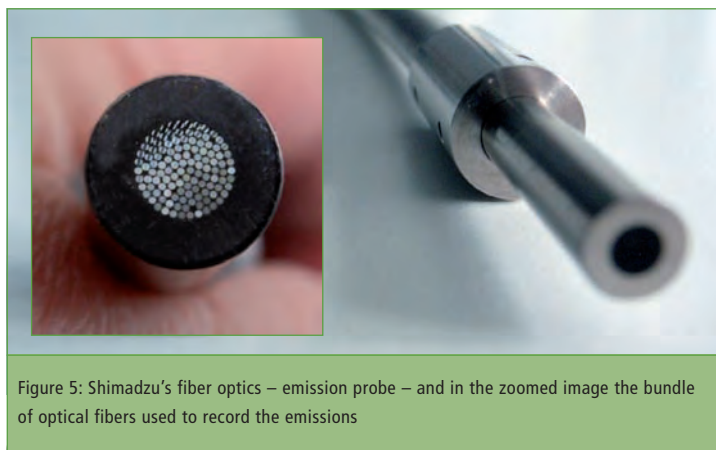


Figure 5: Shimadzu's fiber optics – emission probe – and in the zoomed image the bundle of optical fibers used to record the emissions

optics probe (figure 5). LEDs from everyday life were used as samples (figures 1 to 4).

The emission fiber optics probe is placed directly over the light source on the instruments. The surrounding area was not obscured. Influences by fluorescent lamps of the room lighting system cannot be excluded but are considered to be minimal. The results are summarized in table 1. The analytical wavelength of the single-color LEDs is determined by the chemical doping agents used.

With the help of the emission optics accessory, LEDs can be checked easily and quickly, and

qualified in their built-in state. Other light sources can be tested directly using this accessory.

### Literatur:

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- [2] Characterization of Light Emitting Diodes (LEDs) by UV-Visible Spectrophotometry, C. Mark Talbott, Robert H. Clifford, SSI-JAIMA-UV001

# Antimony in breakfast tea?

Consequences going hand in hand with today's materials



In recent times, design, shape and sensation of tea bags on the shelves of retail stores has changed. It seems that some of them may be made of plastics.

In the food industry, the polymer PET (polyethylene terephthalate) is used widely for packaging materials and antimony (Sb) is applied in its production. From harmless to harmful, the effects of antimony and its compounds on human and environmental health differ widely. Can Sb contaminate the food product?

Non-destructive testing using FTIR (Shimadzu IRAffinity-1S equipped with a Specac Quest single reflection ATR) and EDX (Shimadzu EDX-8000) gives clues about the material a tea bag is

made of and the amount of Sb present in the tea bag. In addition, the highly sensitive ICP-OES technique (Shimadzu's ICPE-9820; hydride vapour technique is ESI Elemental Scientific) is applied for elemental analysis of the brewed tea and tea bag. It was found that paper may be disrupted and lose its functionality after long immersion in hot water. The newer generation of tea bags is therefore made of plastics. Of course, tea bags are also still made of cellulose, but which other materials are in use? To find a solution for such questions diverse tea bags from different suppliers of tea were analyzed.

## IR spectroscopy

These materials are easy to investigate using nondestructive infrared analysis. For sample preparation, the material is simply placed on the window of a single reflection ATR-accessory. The material is pressed with an anvil onto the diamond window, and measurement of the infrared spectrum for identification can then be performed. Diverse tea bags were analyzed and the result was astonishing. Different classes of tea bag material were found among a small selection of various tea suppliers. According to the spectra, the tea bags were made of pure PET, cellulose plus PET and almost 100 % cellulose (without PET, nylon or PP (figure 1). PET is applied either in part as a surface material for cellulose or as the major part. It was surprising to find that even bags with an apparent cellulosic structure were made of PET. PET is probably the most common plastic used in the production of soft drink bottles. During manufacture of PET, antimony is commonly applied as a catalyst. Recent studies indicate that the antimony is subsequently found in the liquids stored in these bottles. Antimony is under strong control of Council Directive 98/83/EC on the quality of

water intended for human consumption. The limit of 5 µg/L in drinking water should not be exceeded. For soft drinks filled in bottles, this rule is not applicable. With a focus on these studies, it was checked whether or not antimony (in the chemical form of antimony trioxide) has been used as a catalyst in the production of PET fibers for tea bags.

## Non-destructive element analysis

For a fast screening of tea bags with focus on antimony, the energy dispersive X-Ray fluorescence (XRF) spectroscopy technique was used. Both FTIR and EDX are non-destructive and surface sensitive. Depending on the sample, both techniques measure just one millimeter deep into the material, and sometimes only the first micrometers are measured. FTIR delivers molecular information (types of material/molecule) whereas EDX delivers elemental information on the ppm level in units of mg/kg (elements and concentrations). EDX analysis revealed that PET tea bags contained antimony.

For the measurement, the tea was removed from the bag. Eight bag layers were placed on top of each other to increase the signal intensity. More sample atoms in the same volume produce a larger signal. Before the analysis process started, the folded tea bag was fixed with tape in the instrument. After only three minutes measurement time, the elemental composition of the sample was identified. Besides Ti (titanium), a small amount (231 ppm) of Sb (antimony) could be found (figure 2). A cellulose tea bag does not usually contain Sb; however, plastic bags do so as they are produced using Sb as a catalyst. For energy dispersive XRF spectrometers, it is a challenge to differentiate between similar organic substances, if the elemental composition is the



same. But using the combined results of FTIR and EDX, it can be clearly stated that the tea bag is made of PET (FTIR) and contains about 200 ppm Sb (EDX). EDX can perform quantitative measurements with and without standards up to the single ppm range. But in comparison, LLD and accuracy of methods such as AAS and ICP are still superior. The higher accuracy is usually connected with more advanced sample preparation. Suitability of the method depends on user requirements.

### The analytical masterpiece

Indication of antimony found with EDX led to the next step: the analysis of brewed tea. Water-based liquids need a more sensitive analysis technique, which is provided by the inductively coupled plasma optical emission spectroscopy (ICP-OES). The detection limit is in the low ppb range [ $\mu\text{g/L}$ ] and lower. For antimony analysis, the hydride vapor technique is the right method of choice. Using this technique, some elements of the sample such as mercury, arsenic, selenium and antimony, come into contact with a  $\text{NaBH}_4$  solution and form gaseous compounds (pre-reaction). In the next step, the formed gas phase is separated from the remaining liquid, so only the hy-

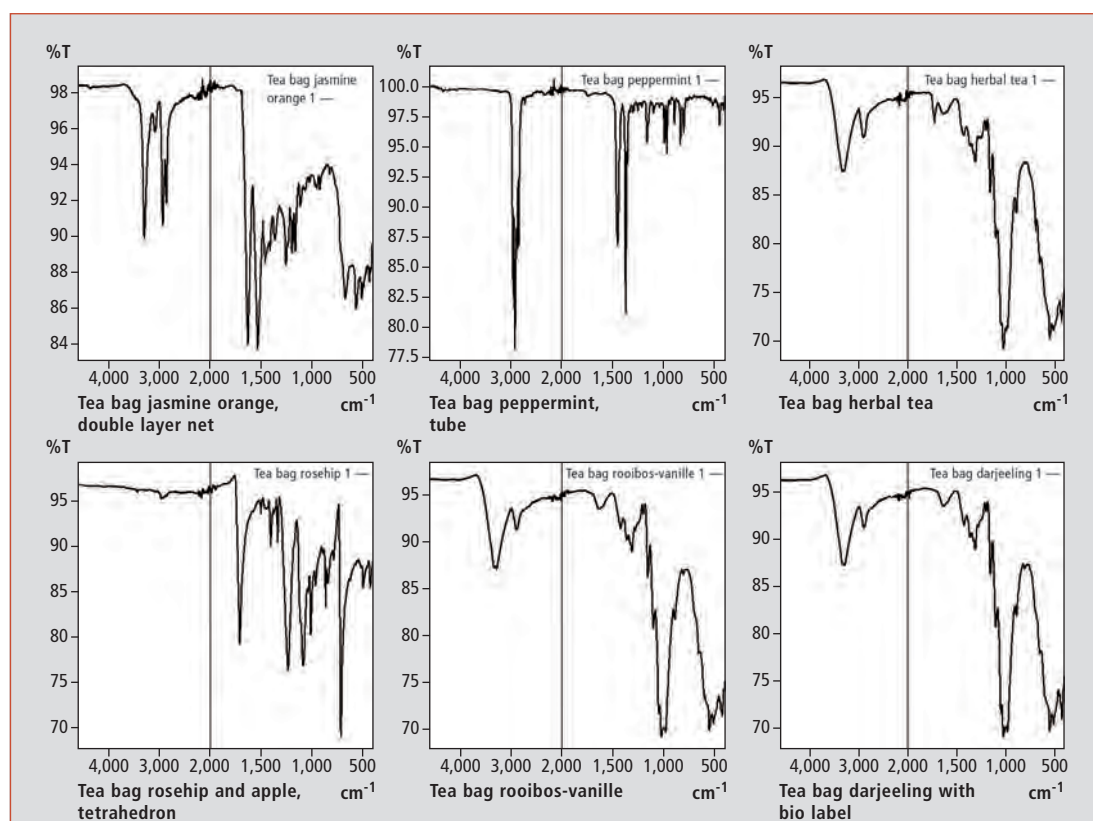
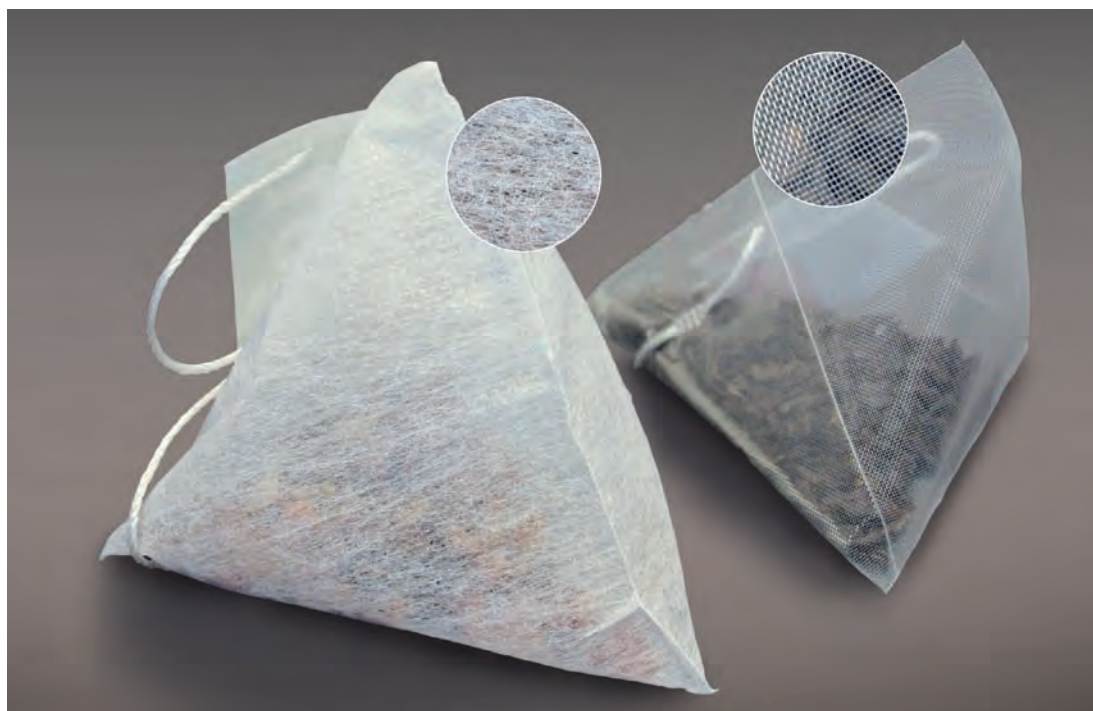


Figure 1: IR spectra from tea bags measured with diamond based ATR from top (1 - 3, left to right) and to bottom (4 - 6, left to right): (1: Jasmine orange) Nylon, (2: Peppermint) Polypropylene PP, (3: Herbal tea) cellulose plus PET, (4: Rosehip apple) PET and (5: Rooibos vanillin + 6 bio Darjeeling) cellulose spectrum.

dride elements (gas phase) are analyzed. Unlike common direct nebulization of samples (with only 2 – 4 % of generated sample aerosol), utilizing the hydride vapor tech-

nique analyses almost 100 % of the elements (gas phase after pre-reaction). This aspect brings higher sensitivity, and additionally the elements are separated from



Tea bags in comparison – cellulose without PET, nylon or PP besides cellulose plus PET (Polyethylene terephthalate)

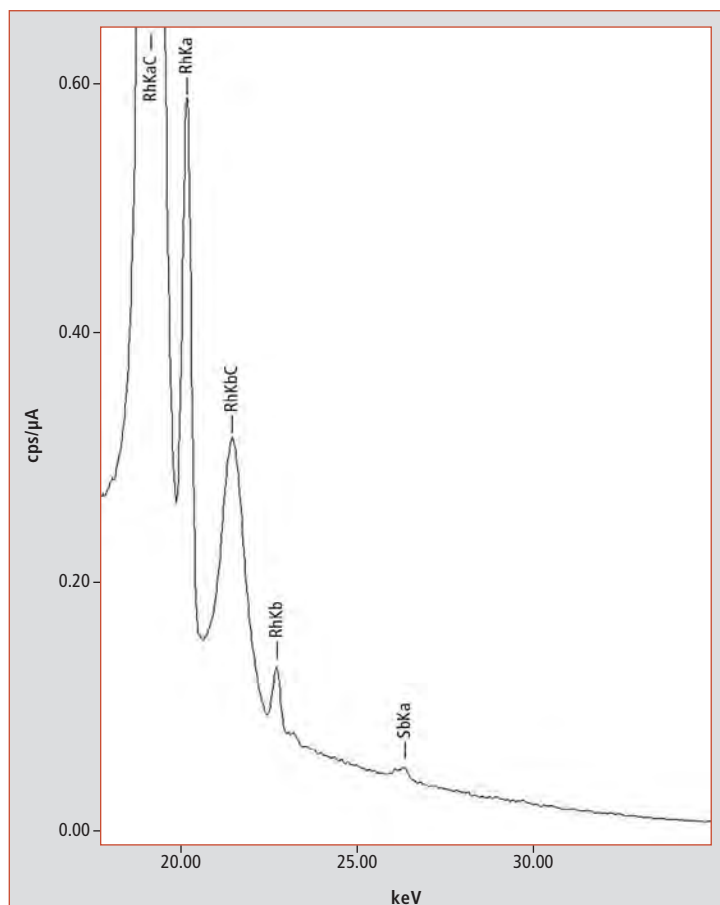


Figure 2: Extract from an EDX spectrum showing Rh and Sb lines. The Rh lines are created by the X-Ray tube; the tube contains a Rh target. Sb is used in the production of PET but not in the production of cellulose tea bags.

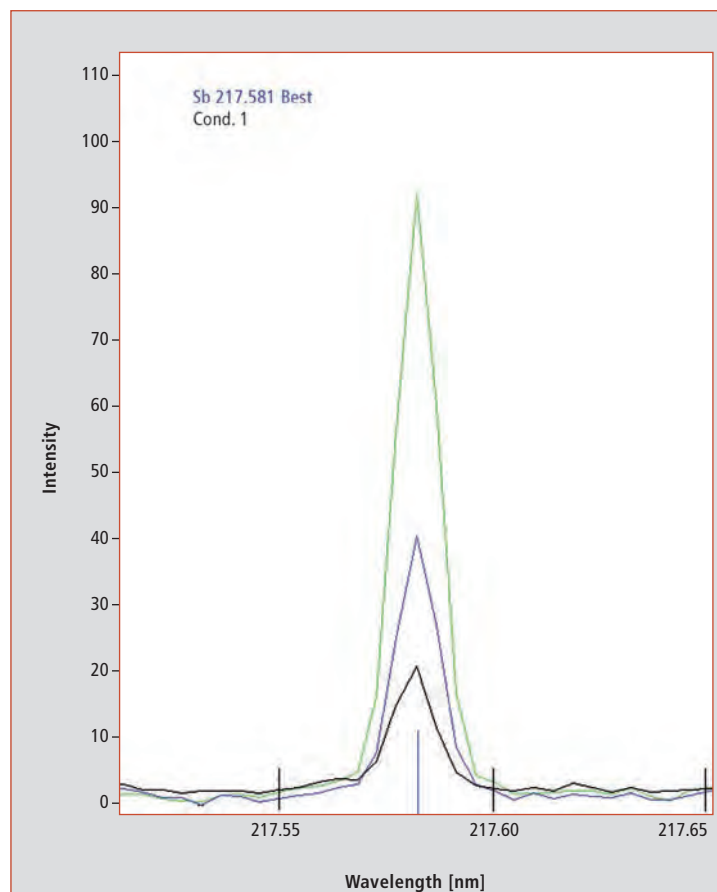


Figure 3: Emission profile of antimony generated by ICP-OES technique. 5  $\mu\text{g/L}$  Sb (blue), 10  $\mu\text{g/L}$  Sb (green) and a five-fold dilution of tea prepared with the fine structured PET bag (black).

the sample matrix (waste). Bag, Tea Bag and Loose Tea. Three tea bags made of different kinds of material were selected. First, the tea was removed from the bags so as to evaluate which material would release the biggest amount of antimony. For each sample, 200 mL of tap water was boiled and the samples were brewed for 5 minutes. Tap water boiled with a cellulose tea bag (layered with PET) was found to contain  $1.8 \pm 0.5 \mu\text{g/L}$  antimony. The tap water in contact with a different tea bag (coarse-meshed PET structure) resulted in  $2.8 \pm 0.3 \mu\text{g/L}$  antimony. Both results are within an acceptable range, which is not increased, as typical tap water contains up to  $3 \mu\text{g/L}$  antimony and up to  $5 \mu\text{g/L}$  are allowed for drinking water. A 100 % cellulose bag has not been regarded. As last sample, a bag made of very fine structured PET was examined. This sample released the highest amount of antimony and the water contained  $8.4 \pm 0.8 \mu\text{g/L}$

after the five minute brew process, which means a significantly increased concentration above the level defined by Council directive 98/83/EC. The reason for this significantly higher concentration seems to be given by the classification of this sample as “fine structured” PET. The surface area of this material is much larger than the coarse-meshed PET bag, for example. As a consequence, contact area with the liquids is increased enormously by the fine structure. The cellulose bag layered with PET also has a large surface area, but the amount of PET in this material is quite low, so the ability to release antimony is limited. As the fine structured PET tea bag seems to be most critical, further experiments focus on the real application. Using same conditions, this tea bag was prepared including tea (rosehip apple), and the final product contained  $15.4 \pm 0.5 \mu\text{g/L}$ . The different compounds in the tea appear to place the surface under more

stress, and the antimony releasing properties are increased by the different contents of the tea.

#### Antimony in raw material?

Analysis determined that the same tea brewed without the bag had a concentration of antimony of only  $2.3 \pm 0.1 \mu\text{g/L}$ . So, the tea is safe to use. In addition, other elements were monitored, since ICP-OES analyses the whole wavelength range at the same time. The absence of arsenic, mercury and selenium, for example, could be confirmed. The detected signal increased only for antimony (figure 3).

#### Conclusion

It is demonstrated that the consequences which go hand in hand with today's materials are not always obvious. The tea bag material with the highest amount of antimony and also the highest ability to release this element dur-

ing brewing ( $15.4 \pm 0.5 \mu\text{g/L}$ ), looks more like cellulose (lead image) than plastics. It is apparent that the structure of the cellulose bags used traditionally has been imitated in the use of this plastic material. Using FTIR, EDX and ICP-OES techniques, such a hidden story can be investigated and revealed.

#### Acknowledgements

Special thanks to Albert van Oyen (Carat) for insights into this fascinating research project.

#### Read for you

In G.I.T. Laboratory Journal 1-2/2015 and FOOD LAB 1/15



# Genzo Shimadzu's trip around the world



Genzo in Duisburg, Germany ...

Founded in 1875 in the Japanese city of Kyoto, Shimadzu has evolved from a 'local workshop' to a global player. 140 years later, it has become one of the worldwide leading manufacturers of analytical instrumentation and diagnostic imaging systems. Shimadzu currently operates production facilities and distribution centers in 76 countries and employs more than 10,000 people.

Founder Genzo Shimadzu would certainly be very proud to see how, today, his company has grown dynamically since its early days. Symbolic is the first balloon flight in Japan in which Shimadzu flew over the Imperial Palace in Kyoto in a hot-air balloon that he designed himself. The balloon flight and conquest of the skies in the following years also stand for the transition of the age of the industrial revolution to the age of science.

On the occasion of its 140<sup>th</sup> anniversary, Shimadzu has created an event involving all of its employees worldwide. The company



... and at the Hofbräuhaus in Munich, Germany.

founder, in the form of a traditional Japanese doll, is travelling to Shimadzu's locations on five continents. The goal is to have every employee sign a book of traditional Japanese rice paper as a sign of their affiliation with the Shimadzu family. Without its valuable employees, Shimadzu could not have written its history. All events in which colleagues get together will be presented as a lasting memory on a digital map of the world. In this way, every employee can take part virtually

in the journey. Special impressions from cities or from well-known landmarks like the Hofbräuhaus in Munich are also included on the map. The Genzo Shimadzu doll has been travelling all over Europe since February and will visit a total of twelve countries before starting the return journey from Russia to Japan in July.

## Europe tour

### February

- Munich, Germany
- Darmstadt, Germany
- Jena, Germany

### March

- Berlin, Germany
- Hannover, Germany
- Langenfeld, Germany
- Duisburg, Germany
- Basel, Switzerland
- Zagreb, Croatia
- Sarajevo, Bosnia-Herzegovina

### April

- Beograd, Serbia
- Vienna, Austria
- Praha, Czech Republic
- Bratislava, Slovakia
- Milano, Italy
- Paris, France
- Lyon, France



Inventors by themselves – Genzo and Nikola Tesla in Belgrad

### May

- s'Hertogenbosch, Netherlands
- Milton Keynes, UK
- Scotland, UK
- Manchester, UK

### Juni

- Moscow, Russia
- St. Petersburg, Russia
- Vladivostok, Russia

### July

- Kyoto, Japan



With its previous LCMS-8030, LCMS-8040 and LCMS-8050 triple-quadrupole systems, Shimadzu has set leading standards in terms of speed, sensitivity and functional design. With the introduction of the new LCMS-8060 (figure 1),

# New family member

»Changes Everything ...« The fastest triple-quadrupole LCMS-8060 system extends LCMS product portfolio

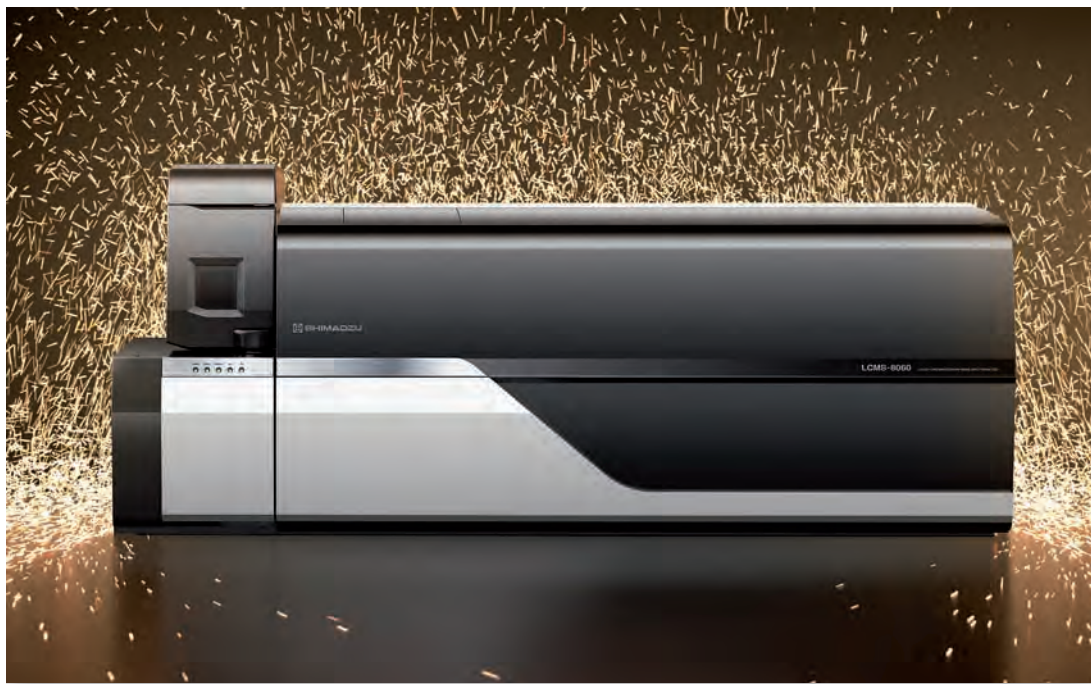


Figure 1: The LCMS-8060 combines the highest speed with the world's best sensitivity

the success story of the LCMS-triple-quadrupole family reaches another milestone.

In addition to its heated ESI source, the youngest member of the UFMS (ultra fast mass spectrometry) family combines all UF technologies. These include the UFsweeper III, a collision cell filled with argon gas that, due to its high-speed technology, enables dwell times of 0.8 ms per MRM. Furthermore,

the UF scan rate of 30,000 Da/s and the UF polarity switching time of 5 ms is maintained. These properties were already outstanding in the LCMS-8050. Sensitivity was also increased through the new UF Qarray (figure 2).

With the powerful vacuum system of the LCMS-8060 and the optimized ion inlet consisting of a desolvation line (DL) and orifice, it has been possible to introduce

an increased number of ions into the mass spectrometer.

## World's best sensitivity meets highest speed

Using electrical fields, the new UF Qarray, based on quadrupole technology, minimizes ion scattering that occurs during transfer from the DL into the first vacuum chamber. The design of the advanced UF Qarray is similar to that of its predecessor and also retains the low susceptibility to contamination. Due to the novel design of the UF Qarray, ion focusing and entry of ions into the next ion chamber is optimized, ensuring an efficient ion beam. This effective ion focusing, together with an improved background noise reduction, leads to a significantly improved signal-to-noise ratio and thus to higher sensitivity (figure 3).

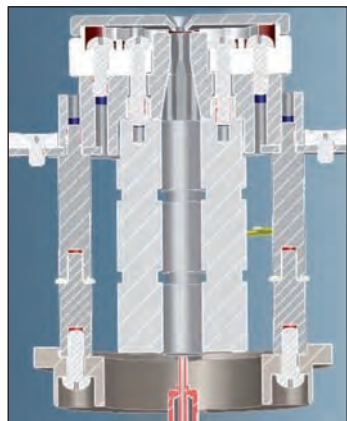
With the new UF Qarray, Shimadzu has achieved a technological breakthrough that com-

bines high, apparently contradictory, demands such as increased sensitivity and robustness of LCMS systems. New applications become conceivable and feasible when the world's best sensitivity is combined with high-speed parameters in the LCMS-8060.

The smallest sample amounts in complex matrices – or any low sample concentrations that need to be further diluted to decrease matrix effects – are now detectable. As an example, (d6-)norepinephrine is discussed here, of



Figure 2: The Qarray is the key to higher sensitivity



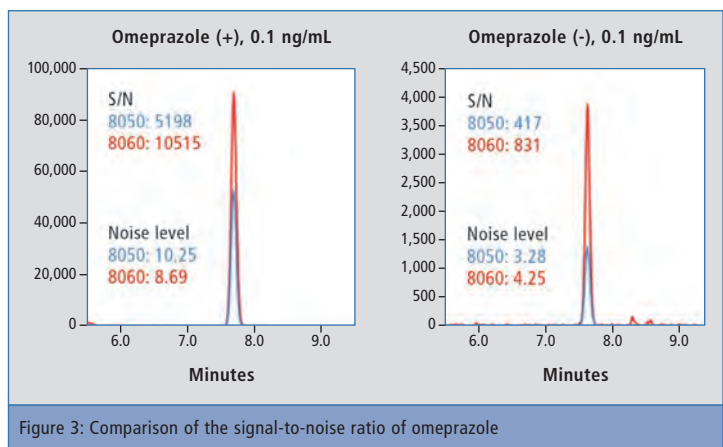
2015	<b>LCMS-8060</b>	A new vision in sensitivity. It simply changes everything.
2013	<b>LCMS-8050</b>	First mass spectrometry company to achieve a scan speed of 30,000 u/sec and 5 m/sec polarity switching time. Increased sensitivity by 30 times.
2012	<b>LCMS-8040</b>	Increased sensitivity by a factor of five compared to the LCMS-8030.
2010	<b>GLOBAL LAUNCH LCMS-8030</b>	First mass spectrometry company to achieve a scan speed of 15,000 u/sec and polarity switching time of 15 m/sec.

which just 5 ppt can be extracted from plasma and still be detected (figure 4).

## Uniform software for all triple-quadrupole models

The increasing demands for quantification at trace levels in clinical





research, food analysis and in other market segments place high demands on instrument technology as well as on users.

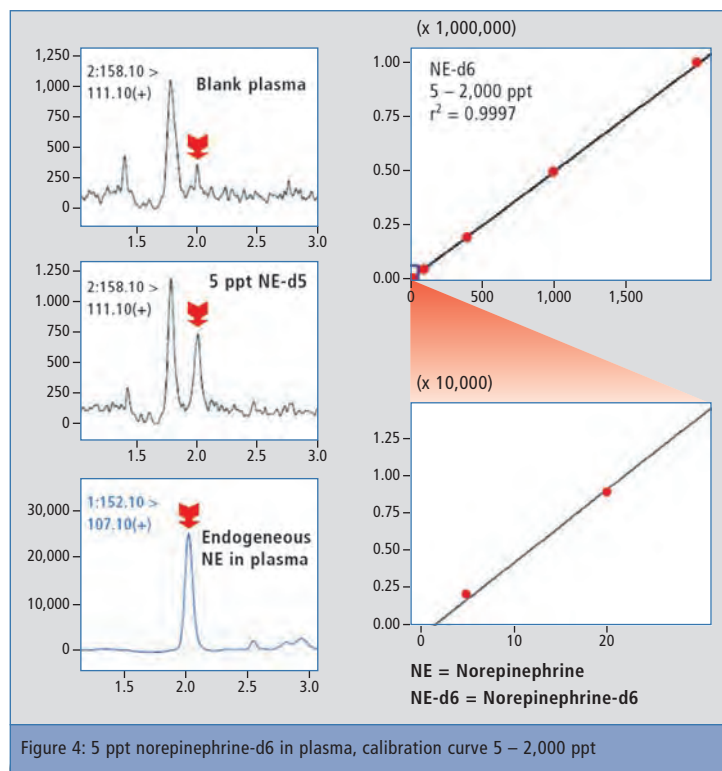
The LCMS-8060 offers not only technological advancements at the highest level, but also continuous adaption of the instrument software to changing user needs.

The LCMS-8060, as well as all other triple-quadrupole models and Shimadzu's HPLC/UHPLC systems, is controlled using the LabSolutions LCMS software. A uniform user interface enables overview and control of the hardware as well as simultaneous processing of initial analysis results.

### Additional functions

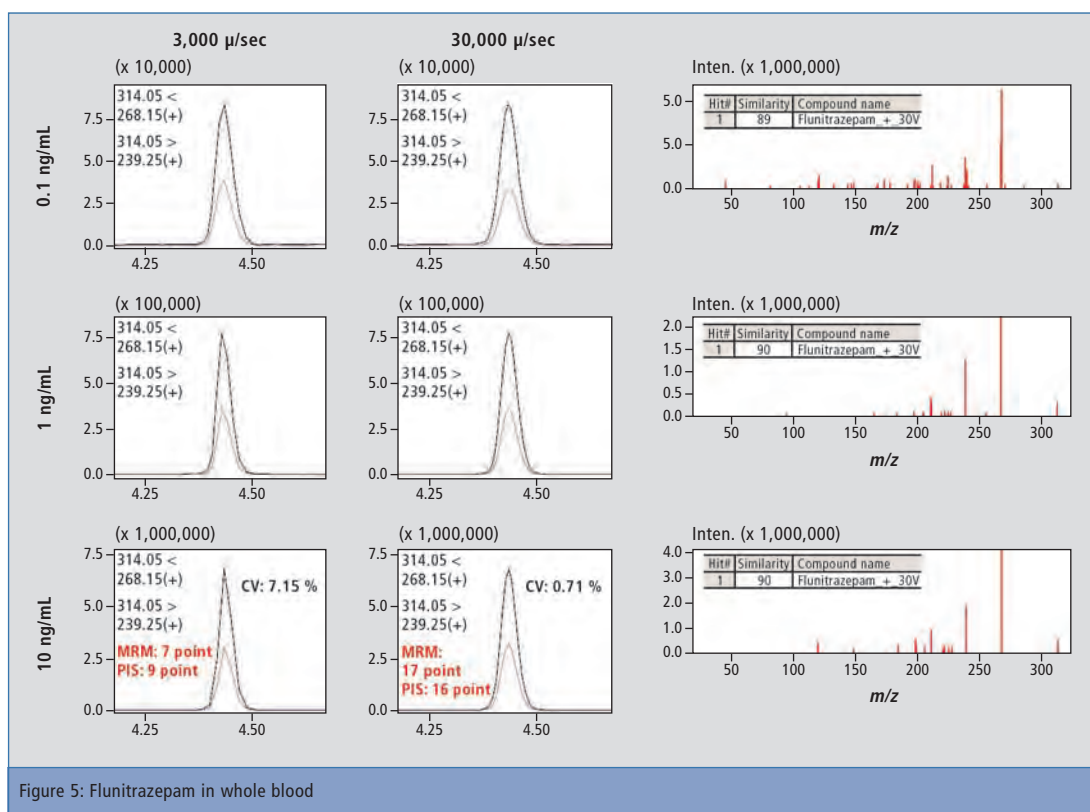
The excellent speed parameters of the LCMS systems and the advanced software enable implementation of helpful additional functions such as the so-called Synchronized Survey Scan (SSS).

This additional MS/MS experiment is triggered when a predefined intensity in the associated experiment is exceeded. As an example, it is possible with this function to carry out an MRM and the corresponding qualitative product-ion scan almost simultaneously within one analysis run, without compromising accuracy of the quantitative analysis.



For example, extracted whole blood samples spiked with flunitrazepam (figure 5) demonstrate impressively that, despite the simultaneously measured SSS, the peak reproducibility attained is very good. This is only possible with the help of high UF scan speeds that assure generation of a

sufficient number of data points, necessary to describe the peak accurately. In addition to the quantitative results, high-quality mass spectra are obtained that correlate well with library spectra, even at low concentration. This enables unequivocal peak characterization.



### Workload reduction due to fully automated MRM optimization

The improved, fully automated MRM optimization enables a real reduction in workload. While it was still necessary with earlier versions to determine and enter the parent ion manually, it is now sufficient to indicate the molecular weight. The software then calculates the protonated or deprotonated ions as well as all possible adducts and takes these into consideration during optimization.

With the LCMS-8060, Shimadzu has further advanced the MS technologies of its predecessor models. Particular attention has been paid to robustness and straightforward operation. Outstanding performance of the instrument is thus guaranteed over a long period of time.

# Innovative analytical solutions for the automotive industry

## CAR Symposium in Bochum, Germany

Opportunities and challenges for future mobility – this was the topic of discussion for approximately 1,000 managers and decision-makers in February 2015 during the annual international CAR symposium in Bochum, Germany. This high-ranking industry meeting brings automobile manufacturers and automotive industry suppliers together.

symposium as a partner company and was represented in the exhibition and the lecture program.

Environmental compliance and recycling, higher costs of raw materials and increasingly sophisticated customer requirements on the quality of the finished product and the materials used are major challenges for the automotive and supplier industry. With its spec-

cles. Accordingly, substance bans apply to heavy metals such as mercury, cadmium and lead. These elements can be quantified easily and quickly using an energy-dispersive X-ray fluorescence spectrometer such as the EDX-7000.

- Quality control of fuels, lubricants, motor oils and additives is carried out using the ICPE-9820 ICP-OES spectrometer according to international standards such as ASTM 5185 for the elements calcium, magnesium, phosphorus, sulfur and zinc.
- Unequivocal identification of materials like plastics, polymers and rubber can be carried out applying molecular spectroscopy with FTIR spectrometers such as the IR-Affinity-1S for the mid-infrared range.
- For failure analysis of polymer materials and components in motor vehicles, pyrolysis GC-MS is the method of choice.

### High-performance materials on the test bench

Another application area is materials testing. Material properties are very diverse and, depending on the forces exerted and environmental conditions, exhibit different behaviors. For the development of high-performance materials, R&D departments of automotive manufacturers need very precise and reliable data for production and quality control. Shimadzu's testing machines are state-of-the-art in terms of control technology, sensor technology or information processing and thus reliably support developers and users.

Using the AG-Xplus series of testing machines, it is even possible to compare unknown materials reliably without pre-testing. The autotuning function enables

strain-controlled experiments compliant with ISO 6892-2009 for steel samples as well as for synthetic materials and ceramics.

### High-speed camera for material testing and fuel injection

In a variety of scientific applications, the most interesting phenomena occur within fractions of a second. Ultra-high-speed cameras like the HPV-X enable the observation of these instants in material testing or during optimization of fuel injection. With its completely newly developed CMOS sensor, the HPV-X achieves continuous recording at a speed of up to 10 million frames per second (10 Mfps).

### New: fiber-optic probe for combustion processes

For the optimization of combustion properties in engines, Shimadzu offers the new ExDop fiber-optic probe, which can detect the efficiency of the combustion process based on transmittance measurements (typically 60 %) in the wavelength range of approximately 200 to 600 nm. This method is suitable for replacing the conventional pressure sensors.



Figure 1: Professor Ferdinand Dudenhöffer, University of Duisburg-Essen, Department of Business Administration and Automotive Economics, discussing the ExDop fiber-optics probe at the Shimadzu stand

As an important business and employment factor and raw materials processor, the automotive industry with its growing sales figures is also expected to take care of environmental and consumer protection. In recent years, considerable emphasis has been placed on more environmentally friendly materials and stricter disposal guidelines. Shimadzu, a supplier of advanced solutions and technologies, joined the CAR

troscopy, chromatography, mass spectrometry and environmental analysis systems as well as its testing machines, Shimadzu offers a comprehensive product portfolio to meet these challenges.

- Typical application examples are the quantitative determination of hazardous substances in motor vehicles in compliance with the Directive of the European Parliament on end-of-life vehi-

Further information on this article

• [www.shimadzu.eu/car-symposium-2015](http://www.shimadzu.eu/car-symposium-2015)



# Rapid and highly informative analysis

## TOC Process Analysis Day in Duisburg – 25 experts exchange information on the latest applications

The “TOC Process Analysis Day” at Shimadzu in Duisburg, Germany in March this year showed how process analysis is becoming increasingly important. More and more process analyzers are being applied where, until recently, time-consuming laboratory analysis had been used. The total organic carbon (TOC) is an important parameter in a wide range of water monitoring applications and can be determined easily online.

25 users, planners and engineers from various process analysis sectors attended the Shimadzu event. Several speakers from academia as well as from the chemical, pharmaceutical and paper industries presented application-related lectures to the participants.

### TOC assures product quality while protecting plant and equipment

The topic ‘ultrapure water monitoring’ presented by Ulrich Richter, infraLeuna GmbH, focused not only on water as a solvent but also as an energy source. At a large chemistry park in Germany, the on-site service provider supplies water for a wide range of applications. To meet demand, up to 350 m<sup>3</sup>/h of steam are generated – in various pressure ranges. The greater part flows into various chemical processes as an energy source.

High purity water is essential to prevent damage to processes and products. Organic impurities in water can have negative effects on quality during the production and processing of high-purity chemicals. TOC represents as an indicator the level of organic impurities. In ultrapure water, the limit value allows a maximum TOC concentration of 0.1 mg/L.

The ultrapure water used is also led back into the system and evaluated using the TOC. Especially in the chemical industry, large amounts of hydrocarbons can get into the condensate due to leaks, for instance in heat exchangers. In order to protect the equipment from high levels of pollution, the

return condensate is monitored for TOC and disposed of whenever limit values are exceeded.

### Challenge for wastewater treatment plants

Another lecture (‘TOC as key parameter for monitoring trace substance elimination? A field test’ by Peter Maurer, University of Stuttgart, Germany, Civil and Environmental Engineering Sciences) clearly demonstrated the major challenges that municipal wastewater treatment plants are facing. Industrial wastewater treatment plants purify wastewaters to a certain agreed discharge value. At first, the ‘easily’ degradable substances are converted during the biological purification stage. However, many substance classes are present that are very difficult or impossible to degrade via the biological processes in a wastewater treatment plant. These substances ultimately enter the municipal treatment plants, which are having increasing difficulty in removing these substances from the water.

Since microbiological degradation is incomplete or is not taking place at all, filters with different absorption media such as activated carbon or sand are often used to purify the water. Different filtration and absorption methods are being developed and optimized.

Also in this application area, TOC represents a valuable and meaningful parameter. Even though the

individual compounds are usually present in the low µg/L range in wastewater, the sum of all compounds is detectable via the TOC sum parameter and is therefore relevant. Determination of the individual parameters requires too much time for an effective process optimization.

In this context, it also became clear that although COD (chemical oxygen demand) was a commonly used parameter for such sum determination, the detection sensitivity is too poor. The detection limit for the COD method (in accordance with DIN 38409) is 15 mg/L, which is not sufficient for such studies.

### Paper industry: rapid information via TOC

The TOC sum parameter is also used in the paper industry. Hans-Thomas Armbruster of the August Koehler AG paper factory explained that 35 different types of paper were manufactured by one machine with up to 20 paper type changes every month.

For each type of paper, specific starting materials and chemicals are used. As a result, the wastewater composition changes. The short analysis time offered by TOC measurement is, compared to COD, a much-appreciated advantage since the wastewater composition entering the treatment plant changes as soon as the paper type is changed. Using TOC measurement, treatment plant

employees can obtain information very rapidly on the incoming wastewater.

Information on TOC content is also forwarded to the papermaker since the composition of the wastewater also provides information on dosage of the starting materials and chemicals used. In this way TOC, in addition to other parameters such as pH value and conductivity, can help to refine the addition of starting compounds.

### TOC systems are site-specific configurations

TOC application areas in the chemical industry are just as versatile as the requirements on the analytical system. For instance, the water at a measurement site for cosmetics raw materials contains high levels of fats and fat-like substances. For this application, the focus was on sampling, because the fats accumulated over time onto the sampling system and started to clog it. To prevent this, a hot water rinse was constructed for the system.

Sampling and integration in a process requires a tailor-made solution for each measurement site. The system must be adapted to the process – and not vice versa.

The role of process analysis technology (PAT) was discussed by two practitioners – Dr. Martin Gerlach of Bayer Technology Services and Thomas Pützer of BASF. The importance of online measurements for process control, optimization and product quality control is increasing steadily. Also with regard to environmental protection, the importance of process analysis technology continues to increase. For this purpose, many different analytical methods and parameters are used. As one of many parameters, the TOC sum parameter is, however, very important.



# Determination of organic pollution of wastewater

## A comparison between COD and TOC

The European Union continues to limit the use of toxic chemicals. Chromium VI (CrVI) for instance is a highly toxic substance and is used in electroplating or in wood preservatives. In Annex XIV of the European Chemicals Regulation REACH, it is listed as a 'Substance of Very High Concern.' Chromium VI is, however, also one of the most important reagents for COD analysis (chemical oxygen demand), which is used as a sum parameter to quantify the pollution of wastewaters with organic compounds.

### COD determination

The COD value indicates the amount of oxygen that is needed to chemically oxidize organic compounds in wastewater. For this purpose, an oxidizing agent (chromate ions) is added to the sample. The Cr(VI) ions are reduced to Cr(III) and thereby oxidize all oxidizable substances. During COD determination, the consumption of Cr(VI) ions is measured and is converted to the amount of O<sub>2</sub> used. In addition to the organic compounds, other compounds (nitrites, bromides, iodides, metal ions and sulfur compounds) can also be oxidized and therefore have an influence on the measuring value.

### TOC determination (Total Organic Carbon)

In contrast to COD determination, TOC determination is free from environmentally harmful chemicals. The TOC parameter measures the total amount of carbon in organic substances. The TOC content is a measure of the concentration of organically bound carbon and therefore directly reflects the pollution levels by organic compounds in wastewater.

For TOC determination, the sample is typically first acidified in order to convert the inorganic carbon as carbonate and hydrogen carbonate compounds into carbon dioxide. The CO<sub>2</sub> is subsequently removed from the sample via sparging with a stream of air. The remaining organic carbon compounds are then reconverted to CO<sub>2</sub> with the aid of high-temperature (catalyst) or wet-chemical oxidation. The carbon dioxide

### Correlation between COD and TOC

In recent years, the COD parameter has increasingly been replaced by the TOC parameter. However, as the limit values for organic pollution levels in wastewater have usually been described in terms of COD values, efforts are made to find a correlation between the two parameters. This can only be an empirically determined correlation.

TOC = 621 mg/L  
Correlation COD/TOC = 3.55

**Example 3: Ethanol (C<sub>2</sub>H<sub>6</sub>O)**  
1,000 mg/L  
COD = 2,087 mg/L  
TOC = 522 mg/L  
Correlation COD/TOC = 4.00

The examples show the bandwidth of the correlation factors. Moreover, during COD determination, inorganic compounds like nitrites, bromides, iodides, metal ions and sulfur compounds are also detected. This is why correlation factors in wastewater may lie between 2.5 and 4 and can also vary when the wastewater composition changes.

### Conclusions

Compared with COD determination, TOC determination is free from environmentally harmful reagents. The determination of a correlation factor between COD

and TOC is dependent on various factors and may therefore vary. Therefore, it would make more sense to directly determine TOC limit values instead of establishing a factor that is the same for all wastewaters.



ASI-L and TOC-L

obtained is determined via NDIR detection, which is a specific detection mode that renders TOC determination free from the effects as described for other parameters. Based on this fact, the TOC parameter is specified in many environmental regulations. An additional advantage of this method is the relatively simple conversion into a continuous monitoring procedure.

tion, as the factor for the individual components vary.

**Example 1: Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)**  
1,000 mg/L  
COD = 1,067 mg/L  
TOC = 400 mg/L  
Correlation COD/ TOC = 2.66

**Example 2: Acetone (C<sub>3</sub>H<sub>6</sub>O)**  
1,000 mg/L  
COD = 207 mg/L

# Free choice

## Alternatives to switching software

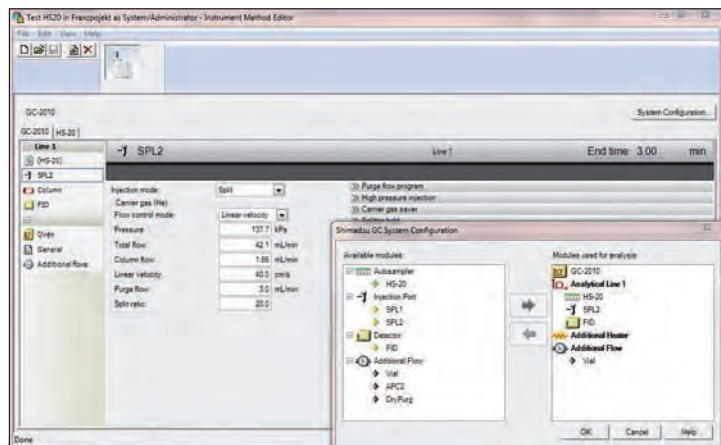


Figure 1: Screenshot of a Shimadzu GC-2010 Plus configuration and 'Method Development' window in Empower 3. Available modules of an analytical line are configured in the 'System Configuration' window. Suitable for the selected modules, the 'Method Development' window offers all parameter settings for temperatures, gas flows and gas pressures.

Instrumental solution for an analytical problem has been found, but the existing software does not fit! What is to do – implement new software in the laboratory or do without the benefits of the improved hardware?

Good software solutions, together with accessories such as autosamplers, injectors and detectors, have become indispensable for the operation of chromatographic systems. They automate the entire analysis and support method development as well as subsequent evaluation and presentation of the results. In terms of functionality, chromatographic data systems (CDS) have grown significantly in scope, which is why switching to new software requires a significant learning phase. To upgrade the existing software to the required hardware would thus make life much easier.

For this reason, Shimadzu is paving the way to implement, whenever possible, newly developed hardware solutions in the most commonly used CDS systems using device drivers. Two representatives of these CDS solutions are Empower (Waters Corporation) and OpenLAB (Agilent Technologies).

### Compatible with Empower version 2 and 3

Empower is currently available in version 3. A large number of users, however, are still working with version 2. Shimadzu's GC driver for Empower is compatible with both versions and is available since January 2015 in the upgraded version 2.0. In addition to the GC-2010 Plus, GC-2010 and GC-2014 gas chromatographs, the AOC-20i autosampler for liquid as well as the HS-20 for headspace injection are all integrated in the GC driver.

A driver for the AOC-5000 and AOC-5000 Plus is also optionally available, when in addition to liquid and headspace injection, other injection techniques such as solid-phase micro-extraction (SPME) and in-tube extraction (ITEX) are of interest.

### Simple and efficient

With the aid of Shimadzu's 'Configuration Wizard', it is very easy to implement a Shimadzu GC system – optionally including the AOC-20i or the HS-20 autosamplers – in Empower. Within the software, individual GC modules can be configured to any of the

analytical lines. For the new driver, system configuration layout and method development layout were further simplified. Modules of an analytical line are clearly recognizable via distinctive icons. These icons, when clicked, open to the parameter input window for the corresponding module.

### Typical design and functionality

Also in the new design, and functionally identical in both CDS packages, is the status indicator or instrument monitor (figure 2). All modules in an analytical line are clearly displayed with their associated parameters – beginning with the autosampler, injector, column oven, and finally the detectors. The windows of the individual modules are expandable for a detailed overview on the current states. In the stand-by mode, set values can also be changed. For the HS-20, another window with vial information is available. When equilibration time of the samples is longer than GC analysis time, the HS-20 prepares the samples in such a way that the GC can measure continuously, if possible. If several headspace samples are equilibrated simultaneously, the respective equilibration times are listed in the window and one can monitor, at a glance, the progress of the analysis sequence, also in case of overlapping headspace sample preparation.

### New – Shimadzu GC control in OpenLAB EZChrom Edition

With the driver development for OpenLAB EZChrom Edition,

Shimadzu's GC-2010, GC-2010 Plus and GC-2014 systems can be controlled using the most common CDS software packages. OpenLAB also supports dual-line operation of the GC-2010 (Plus), including the AOC-20i Dual Tower configuration – i.e. one AOC-20i autosampler for each analytical line. To achieve the highest sample throughput, simultaneous injection in two analytical lines is possible in this way.

This is not possible in Empower because the software can only operate one analytical line actively. A second line can be configured, but is not simultaneously available for measurements.

### Flexible and efficient

Figure 3 shows an example of dual-line operation under OpenLAB. Two chromatograms are measured during one GC run. Consequently, more results are available within the same time. The instrument monitor shows the current status of the GC and provides detailed information on the current states of all modules in an analytical line. It is possible to switch between both analytical lines via a switching button in the monitor window.

The analytical lines can be configured for various applications. All method parameters are set individually, with the exception of the temperature program of the GC column oven. The AOC-20i Dual Tower offers free choice between injection of two samples simultaneously or, alternatively, individual use of the analytical lines. ♦

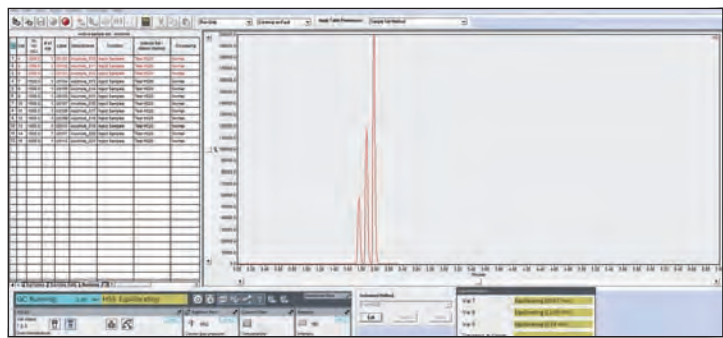


Figure 2: Screenshot from Empower version 3 during a headspace analysis sequence. The sequence table on the left shows the ongoing as well as the already completed analyses in red. Below left, the instrument monitor shows the current status of the GC and the HS-20 headspace autosampler. Another window of the instrument monitor provides an insight into the progress of the headspace sample preparation (equilibration).

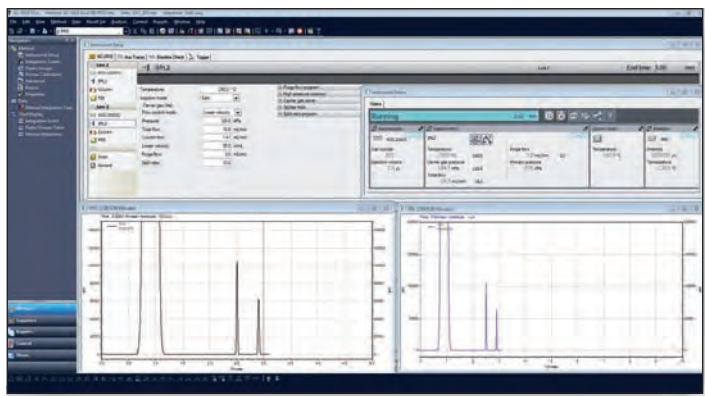


Figure 3: Screenshot from OpenLAB during an analytical run of a GC-2010 Plus dual-line configuration with the AOC-20i Dual Tower. The 'Method Development' window shows both analytical lines, each equipped with an AOC-20i, split-injector, column and detector. The 'real time' chromatograms for both detectors are shown below. Above the chromatogram on the right, the instrument monitor shows the GC status and an overview of all modules in an analytical line. Via a switching button, the view can be switched to the other analytical line at any time.

Simultaneous injection always means 'at the same time.' A new injection can only take place when the measurement on both analytical lines has been completed. If one of the two AOC-20i towers is faster than the other, due to different rinsing cycles, it will wait until simultaneous injection is again possible.

In addition to efficiency, dual-line operation also offers more flexibility. OpenLAB is available as 'standalone' and as 'client server' solution. For client server installation, a network is used that enables access to any number of instruments. Measured results and methods are stored

centrally on a server and, just like the instruments, are available from any PC in the network. With the required access rights, it is possible to control any instrument from any location within an organization. This is where the key advantages of a dual-line system become evident. Without needing to be present in the laboratory, one can decide how any particular sample can be measured on which analytical line.

### Conclusions

The development of high-performance CDS software solutions offers new possibilities for automation of chromatographic

analyses and remote monitoring. Continuous advances in software and hardware have contributed to an enormous increase in efficiency of analytical processes in recent years. To make good hardware solutions accessible only for a single software solution does not meet the demand offering always the best solution. In this

respect, Shimadzu has begun to integrate chromatographic systems of other manufacturers (for instance Agilent GC and LC) in its LabSolutions software, as well as to continue to pave the way for making Shimadzu instruments accessible for the most commonly used software packages.

## Looking for clever minds!

### »lab4you« program for young scientists



With the »lab4you« program, Shimadzu offers young scientists from all over Europe the opportunity to win laboratory bench space in the ultra-modern 'Shimadzu Laboratory World' in Duisburg, Germany. There, they will have access to the latest analytical HPLC/UHPLC and mass spectrometry instruments to achieve the best analytical results for their research. They will be supported by product specialists from the Shimadzu Europa GmbH. Preconditions for participation are an undergraduate degree in

the domain of science, an interesting research topic and previous knowledge of HPLC/UHPLC and/or mass spectrometry. Master students, PhD students and post-docs from all scientific disciplines where chromatography and mass spectrometry are used can apply.

#### Applications

in English language may be submitted via [www.shimadzu.eu/lab4you](http://www.shimadzu.eu/lab4you) with a short abstract of the research project.

## Shimadzu live

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August 30 - Sept. 4, 2015  
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[www.tiaft.org](http://www.tiaft.org)

### CSI

August 30 - Sept. 3, 2015  
Figueira da Foz, Portugal  
[csi2015.fis.uc.pt](http://csi2015.fis.uc.pt)

### Euroanalysis

September 6 - 9, 2015  
Bordeaux, France  
[www.euroanalysis2015.com](http://www.euroanalysis2015.com)

### MSACL

September 8 - 11, 2015  
Salzburg, Austria  
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