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Soil pollution

Analysis of pesticide residues

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The LCMS-8045 workhorse system with key features of UFMS

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Pesticides: killers of bee colonies

Ultra-sensitive and rapid assay of neonicotinoids, fipronil and some metabolites in honey by UHPLC-MS/MS

Neonicotinoids are a class of insecticides widely used to protect crop areas such as corn, canola and soybean as well as fruit and vegetables. These substances have an influence on the central nervous system of insects, causing paralysis and death. The first neonicotinoid, imidacloprid, was discovered by Shinzo Kagabu (Bayer CropScience, Japan). Their systemic distribution with high efficiency against sucking insects and long residual activity has made them very popular within the global pesticide market. Nowadays, there are roughly ten molecules classified as neonicotinoids (please see table 1).

Use of these compounds has recently become controversial as they are believed to be a cause of honeybees Colony Collapse Disorder (CCD). Since pollination is essential for agriculture, extensive studies have been conducted to evaluate the impact of neonicotinoids on bee health.

The European Food Safety Authority (EFSA) has identified risks to bees in the use of neonicotinoids. Three types of insecticides are involved: clothianidin, imidacloprid and thiamethoxam. They may have acute and chronic effects on survival and development of bee colonies, their behavior and larvae.

Following this, the European Food Safety Authority (EFSA) limited the use of thiamethoxam, clothianidin and imidacloprid. Some European countries have banned or restricted the use of neonicotinoids.

In order to better understand the effect of these compounds on bees and their contamination in pollen and honey, a highly sensitive assay method was necessary. For this purpose, an UHPLC-MS/MS analysis was developed including the controversial and well-known fipronil compound. Fipronil is a broad-spectrum insecticide of the phenylpyrazole chemical family and disrupts the insect central nervous system in the same manner as other neonicotinoids.

Figure 1: Overview of the UHPLC-MS/MS system

Acetamiprid	Commercialized by Scotts & Bayer Cropsciences
Clothianidin	Commercialized by Bayer Cropsciences
Imidacloprid	Commercialized by Bayer
Thiacloprid	Commercialized by Bayer
Thiamtehoxam	Commercialized by Syngenta
Dinotefuran	Commercialized by Mitsui Chemicals
Nitempyram	Commercialized by Jiangsu Sword Agrochemicals

Table 1: List of commercial neonicotinoids

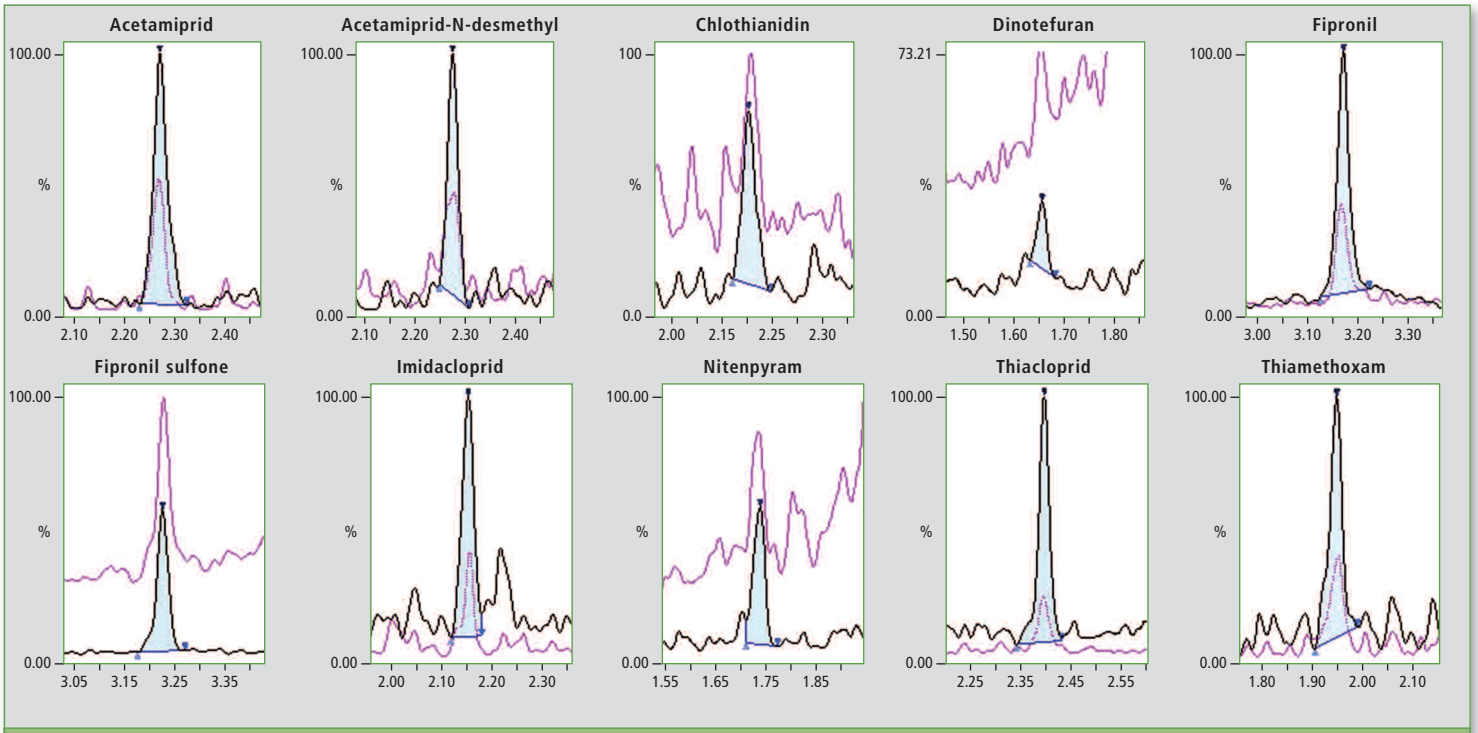

Figure 2: Chromatogram of the target compounds at their lower limit of quantification

Materials and Methods

Standards and Reagents

All of the analytical standards were provided by Sigma-Aldrich. The Internal standards thiamethoxam-d3, imidacloprid-d4 and chlothinidin-d3 were purchased from Sigma-Aldrich. The solvents used, including water and mobile phase additive, were of UHPLC/MS quality (Biosolve).

Sample Preparation

Compound extraction was performed using a QuEChERS method (Quick, Easy, Cheap, Effective, Rugged and Safe) with an additional dispersive Solid Phase Extraction (dSPE) step. 5 g of honey (± 1 %) were weighed in a 50 mL polypropylene tube. 5 µL of internal standard solution at 5 µg/mL of each compound in acetonitrile was added to the honey and dried for ten minutes. 10 mL of ultra-pure water were subjoined, and the samples were homogenized by vortex mixing for one minute. 10 mL of acetonitrile were then added followed by vortex mixing for one minute.

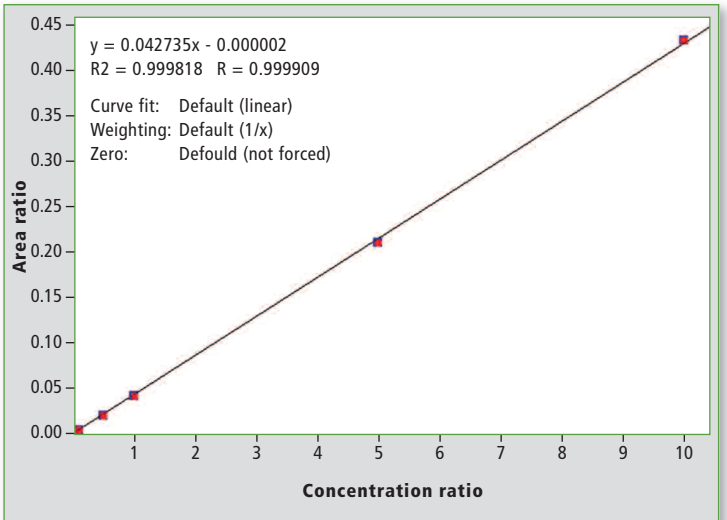

Figure 3: Calibration curve of clothianidin

Parameter	Value
System	Nexera X2
Column	ACE Super C18 100 x 2.1 mm 2 µm
Column temperature	30 °C
Mobile phases	A: Water + 0.05 % ammonia B: Methanol + 0.05 % ammonia
Flow rate	0.6 mL/min
Gradient	5 % B to 100 % B in 3 min. 100 % B to 5 % in 0.1 min. Total run time 6 min.
Injection volume	1 µL (POISe mode with 10 µL of water)

Table 2: UHPLC parameters

Salts mix (4 g $MgSO_4$, 1 g Sodium Citrate, 0.5 g Sodium Citrate sesquihydrate, 1 g NaCl; Biotage Q0020-15V) were added to the samples. After manual shaking, samples were centrifuged at 3,000 g for five minutes at 10 °C.

The supernatant (6 mL) was transferred into a 15 mL tube containing 1,200 mg $MgSO_4$, 400 mg PSA and 400 mg C18 (Biotage Q0050-15V). After centrifuging at 3,000 g and 10 °C for five minutes, the supernatant was transferred into inert glass vial for analysis (Shimadzu LabTotal 227-34001-01).

UHPLC-MS/MS Conditions

Analysis was performed using a Nexera X2 UHPLC system coupled with LCMS-8060 triple quadrupole mass spectrometer with Heated ESI in positive and negative ionization (figure 1). Mobile phase composition was optimized to generate the highest sensitivity. Ion source parameters (gas flows, temperatures) were also optimized using the Interface Setting Support Software (Shimadzu Corp.)

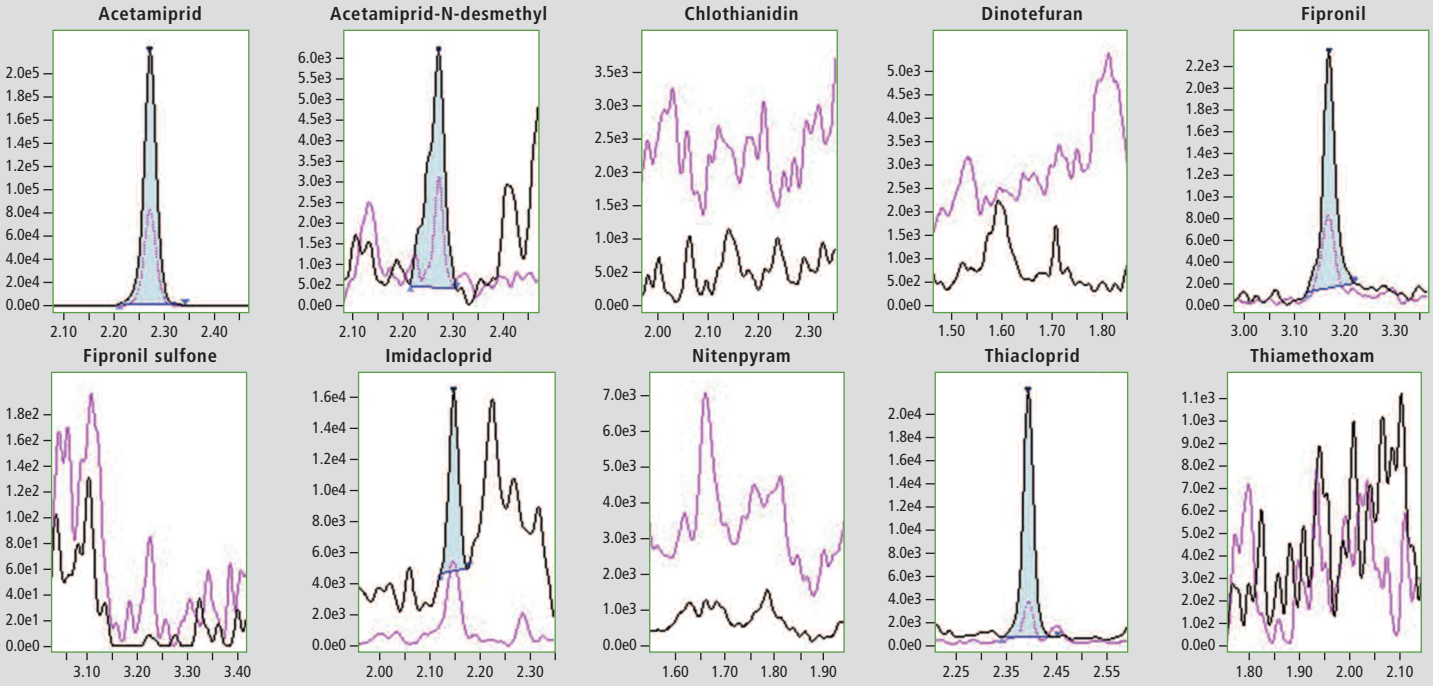

Figure 4: Chromatogram of a sample honey (pyrenees)

Parameter	Value				
System	LCMS-8060				
Ionization mode	Positive HESI				
Acquisition mode	MRM				
MRM transitions	Name	MRM quan.	MRM qual.	ISTD group	Polarity
	Acetamiprid	223.1 > 126.0	223.1 > 56.1	2	+
	Acetamiprid-N-desmethyl	209.1 > 126.0	211.1 > 128.0	2	+
	Clothianidin	250.1 > 169.1	250.1 > 132	3	+
	Dinotefuran	203 .0 > 114.0	203.0 > 87.0	1	+
	Fipronil	435.0 > 330.0	435.0 > 250.0	3	–
	Fipronil sulfone	451.0 > 415.0	451.0 > 282.0	3	–
	Imidacloprid	256.1 > 175.1	258.1 > 211.1	2	+
	Nitenpyram	271.0 > 126.0	271.0 > 225.0	3	+
	Thiacloprid	253.1 > 126.0	253.1 > 90.1	1	+
	Thiamtehoxam	292.1 > 211.1	292.1 > 181.1	1	+
	Thiamethoxam-D3	295.1 > 214.05	—	1	+
	Imidacloprid-D4	260.1 > 179.1	—	2	+
	Clothianidin-D3	253.1 > 132.05	—	3	+
Dwell time	7 to 16 msec depending upon the number of concomitant transitions to ensure to have at least 30 points per peak (max total loop time 115 msec).				
Pause time	1 msec.				
Quadrupole resolution	Q1: Unit	Q3: Unit			
Temperature	HESI: 400 °C	DL: 200 °C	Heater block: 400 °C		
Gaz flow	Interface: 10 L/min	Nebulizer: 3 L/min	Drying: 5 L/min		

Table 3: MS parameters

Results

Calibration

The calibration curves were prepared in acetonitrile in order to obtain final concentrations ranging from 2.5 pg/mL (2.5 fg on column) to 5 ng/mL. These concentrations correspond to 5 ppt and 10 ppb in honey respectively. A typical calibration curve is shown in figure 3 (page 3).

Recovery

An "all-flowers" honey from the local supermarket was extracted with or without spike at 50 ppt. A blank extract (no honey) was prepared to evaluate losses or non-specific interactions. Results are presented in table 5.

All calculated recoveries were within acceptance values of 70 - 120 % from EU SANTE/11945/ 2015.

Real Samples Analysis

Nine honey samples purchased at the local supermarket or used as raw materials in cosmetics (orange tree honey) were assayed as unknowns. All honeys tested showed concentrations far below the maximum allowable residue limit. But thanks to the very high sensitivity reached, even low concentrations of neonicotinoids were quantified. Results are presented in table 7.

Stability

The thyme honey sample with no detectable target compound was spiked at 50 ng/kg with all compounds prior to extraction. The extract obtained was then consecutively injected 150 times in the system.

The results presented in figure 5 show excellent stability of the signal even at these low concentra-

Standard (ng/g)	Accuracy (%)
0.005	110
0.010	96.0
0.050	100
0.100	98.4
0.500	97.0
1.000	99.0
5.000	98.4
10.000	101

Table 4: Concentration for calibration and accuracy

tions. This demonstrates that excellent sensitivity can be maintained over a long series of real sample analysis thanks to the ion source ruggedness.

Conclusion

A method for ultra-sensitive assay, covering most neonicotinoids of interest including fipronil in honey was set up. Sample preparation was simple but provided excellent recoveries, whatever the honey type. The injection mode used prevented the use of tedious evaporation/reconstitution or dilution steps.

The sensitivity obtained enabled assay in real samples at very low levels far below the regulated residue levels. This method can be a very efficient support tool for better understanding of the impact of neonicotinoids on honey bee colonies.

Literature

Application note C140: Ultra-Sensitive and Rapid Assay of Neonicotinoids, Fipronil and Some Metabolites in Honey by UHPLC-MS/MS [LCMS-8060]

EU SANTE/11945/2015: Guidance document on analytical quality control and method validation procedures for pesticide residue analysis in food and feed. https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrk-doc_11945.pdf

Compound	Recovery	Compound	Recovery
Acetamiprid	78.8 %	Fipronil sulfone	74.2 %
Acetamiprid-N-desmethyl	93.4 %	Imidaclorpid	83.2 %
Chlothianidin	70.6 %	Nitenpyram	87.0 %
Dinotefuran	76.5 %	Thiacloprid	82.2 %
Fipronil	78.1 %	Thiamethoxam	75.6 %

Table 5: Measured recoveries in honey

Compound	LOQ (µg/kg)	Compound	LOQ (µg/kg)
Acetamiprid	0.005	Fipronil sulfone	0.001
Acetamiprid-N-desmethyl	0.005	Imidaclorpid	0.020
Chlothianidin	0.020	Nitenpyram	0.020
Dinotefuran	0.010	Thiacloprid	0.005
Fipronil	0.001	Thiamethoxam	0.005

Table 6: Limits of quantification in honey

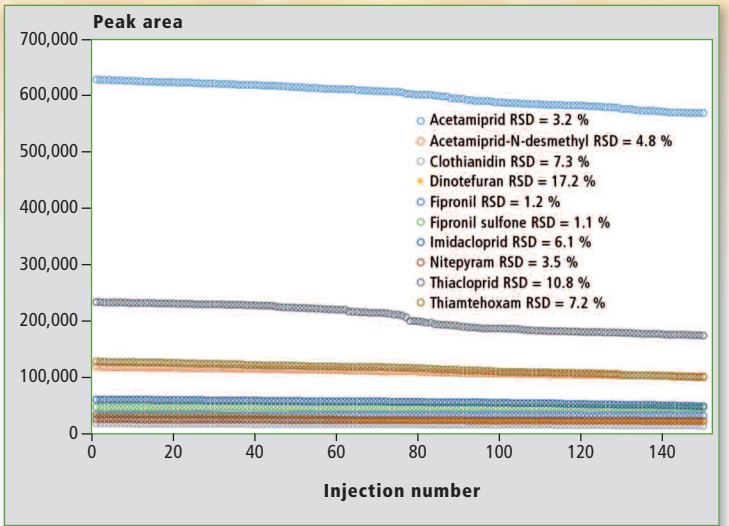

Figure 5: Stability of peak areas in real honey samples

Further information on this article:

- Application: Ultra-Sensitive and Rapid Assay of Neonicotinoids Fipronil and Some Metabolites in Honey by UHPLC-MSMS

Honey	Acetamiprid	Clothianidin	Imidacloprid	Thiacloprid	Thiamethoxam
Provence creamy	—	—	0.20	—	0.010
Italy creamy	0.15	—	0.17	—	—
Pyrenees liquid	0.38	—	0.043	0.020	—
French-Spanish creamy	0.27	—	0.047	0.020	—
Thyme liquid	—	—	—	—	—
Lemon tree creamy	1.7	—	0.15	0.033	—
Orange tree liquid	1.2	—	0.62	—	—
Flowers creamy	0.14	—	0.055	0.39	—
Flowers liquid	0.34	—	0.11	0.010	—

Honey	Dinotefuran	Nitenpyram	Acetamiprid-N-desmethyl	Fipronil	Fipronil sulfone
Provence creamy	—	0.052	0.005	—	—
Italy creamy	—	0.040	—	—	—
Pyrenees liquid	—	—	0.015	0.004	—
French-Spanish creamy	—	0.032	-—	—	—
Thyme liquid	—	—	—	—	—
Lemon tree creamy	—	—	0.020	—	—
Orange tree liquid	—	0.024	0.018	—	—
Flowers creamy	—	—	0.016	—	—
Flowers liquid	—	—	0.006	—	—

Table 7: Honey samples results (concentrations in µg/kg)

Investigating soil pollution

Analysis of pesticide residues in soils using supercritical fluids

Intensive agriculture and its associated use of pesticides have resulted in the presence of pesticide residues in our entire ecosystem. In 2006 and 2007, about 2.4 megatons of pesticides were used worldwide to protect fruits and vegetables from insect infestation. However, not all crop protection agents act only on targeted pests. Often, beneficial insects are also non-selectively affected.

When resistant insecticides and fungicides get into human and animal foods via water and air, additional health risks arise. These range from simple skin and eye irritation to nervous system damage, hormone-like effects or possibly even certain kinds of cancer.

Mix soil sample with drying agent

Transfer to extraction vessel

Loading the rack-changer

Figure 1: Sample preparation for SFE

The ecological footprint of the ideal pesticide

This is why, in the development and regulatory approval of new pesticides, their ecological footprints are essential in terms of stability and decomposition studies. The ideal pesticide should be as selective as possible and target only specific pests. In addition, it should be quickly biodegradable without leaving any residues. As the group of pesticides include many different compound classes, they differ strongly in terms of their chemical structure and characteristics, which makes the analysis of these types of compounds rather complex.

For the determination of pesticide residues in soils, an initial extraction step is required. Typically, this step is carried out using liquid-liquid extraction. This is, however, time-consuming – also due to the use of special reagents and laboratory equipment.

The analysis is often complicated by contamination due to the presence of metal ions or other ionic compounds. Also challenging is the sensitivity of certain pesticides to external influences such as oxidation, exothermic reactions or other effects that result in partial decomposition of the analytes during liquid-liquid extraction.

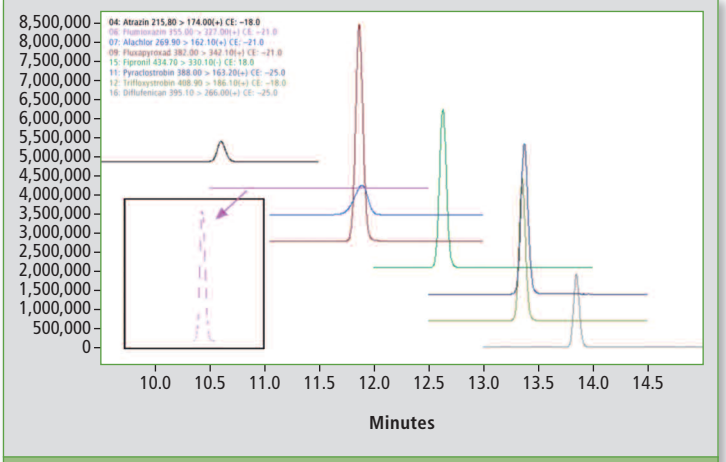

Figure 2: MRM-chromatograms of the pesticides

Supercritical fluids for automated extraction of pesticides from soils

To avoid these problems, extraction using supercritical carbon dioxide (CO_2) offers a gentle alternative to the conventional liquid-liquid extraction. Supercritical fluids combine the properties of gases and liquids: They have a low viscosity while exhibiting high diffusivities – just like gases.

However, they also possess a high solubility, just like liquids. CO_2 (at or above its critical temperature and critical pressure) is the most commonly used supercritical fluid for chromatographic purposes because it is highly inert, non-toxic and inexpensive, in addition to having suitable physico-chemical properties and being easily available.

Supercritical fluid extraction (SFE) using supercritical CO_2 therefore combines the good solubility properties of liquid-liquid extraction with the excellent diffusion properties of gases, so that the sample to be extracted is optimally permeated and the analytes can be extracted efficiently. By using carbon dioxide, the need for large amounts of organic solvents is eliminated, thereby reducing solvent waste.

Extraction of pesticides without the need for sample pretreatment

Shimadzu's Nexera UC SFE system was used for the extraction of pesticides. The analytical conditions are presented in table 1. In contrast to the traditional liquid-liquid extraction, no complex sample preparation is necessary, except for the addition of a drying agent to bind residual moisture. A typical sample preparation workflow is shown in figure 1.

By expanding the autosampler with a rack changer, automated preparation and processing of up to 48 samples is possible. In this way, the analysis is not only much more time-efficient and possible overnight or during the weekend but, in addition, human errors during sample preparation are also minimized.

System	Nexera UC SFE System
Extraction solvent	A: CO_2
	B: Methanol
Flow rate	5 mL/min
Extraction programm	4 min (static → dynamic)
Extraction temperature	40 °C
Back pressure	150 bar
Trapping column	Shim-pack VP-ODS (50 mm x 4.6 mm, 5 µm)
Column temperature	40 °C
Eluent	Acetonitrile / Hexane 50/50
	2 mL/min, for 2 min

Table 1: Analytical conditions of the extraction

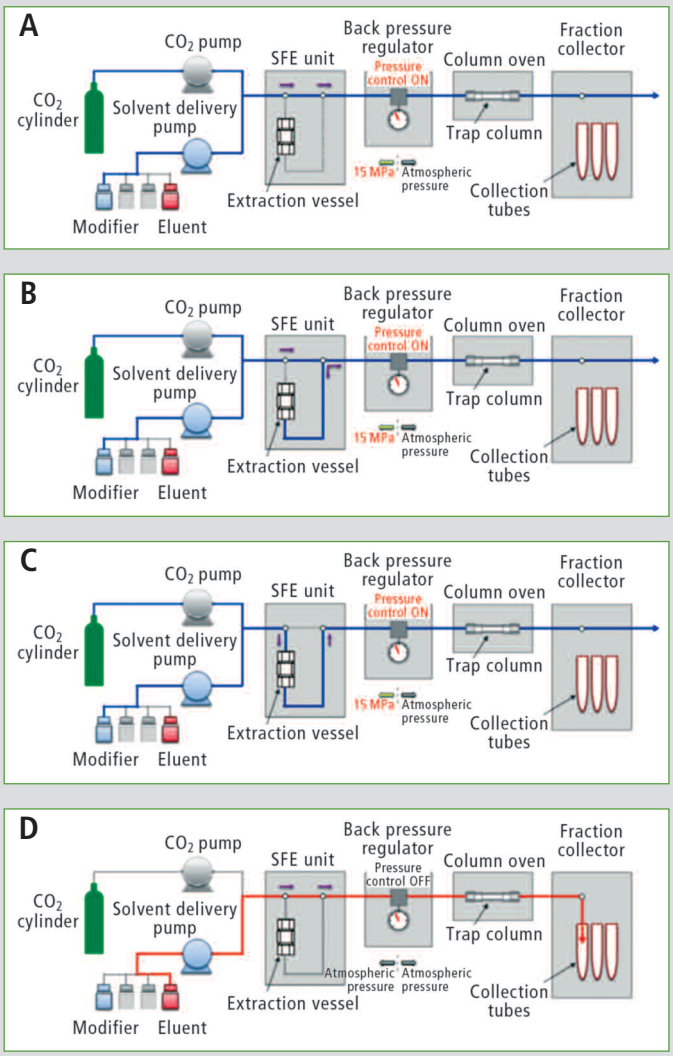

Figure 3: Exemplary scheme of the extraction process

For the actual extraction, the extraction vessels can be heated up to 80 °C. Meanwhile, the trapping column can be rinsed and equilibrated (see figure 3A).

Using supercritical carbon dioxide and optionally additional organic modifiers, the analytes are extracted from the sample and retained on a trapping column (B).

If necessary, further rinsing steps for the purification of the extract on the column can be implemented (C).

The extract is then released from the column by an eluent and collected in the fraction collector (D).

By using the trapping column, multiple extraction steps are possible without diluting the sample unnecessarily, as the release only takes place after addition of the eluent.

Conclusion

Extraction using the Nexera UC demonstrates that the complex sample preparation usually needed for the analysis of pesticides in soil samples can be avoided. The use of supercritical carbon dioxide ensures an efficient extraction and also minimizes the amount of organic solvents used. Autosampler and rack-changer automate the analysis. Their use precludes the influence of human error. In this way, the Nexera UC offers a simple and fast method for sample preparation prior to residue analysis and provides a reliable investigation of pesticide pollution in soil samples.

New formaldehyde determination method

Fully automated analysis with the barrier ionization discharge detector

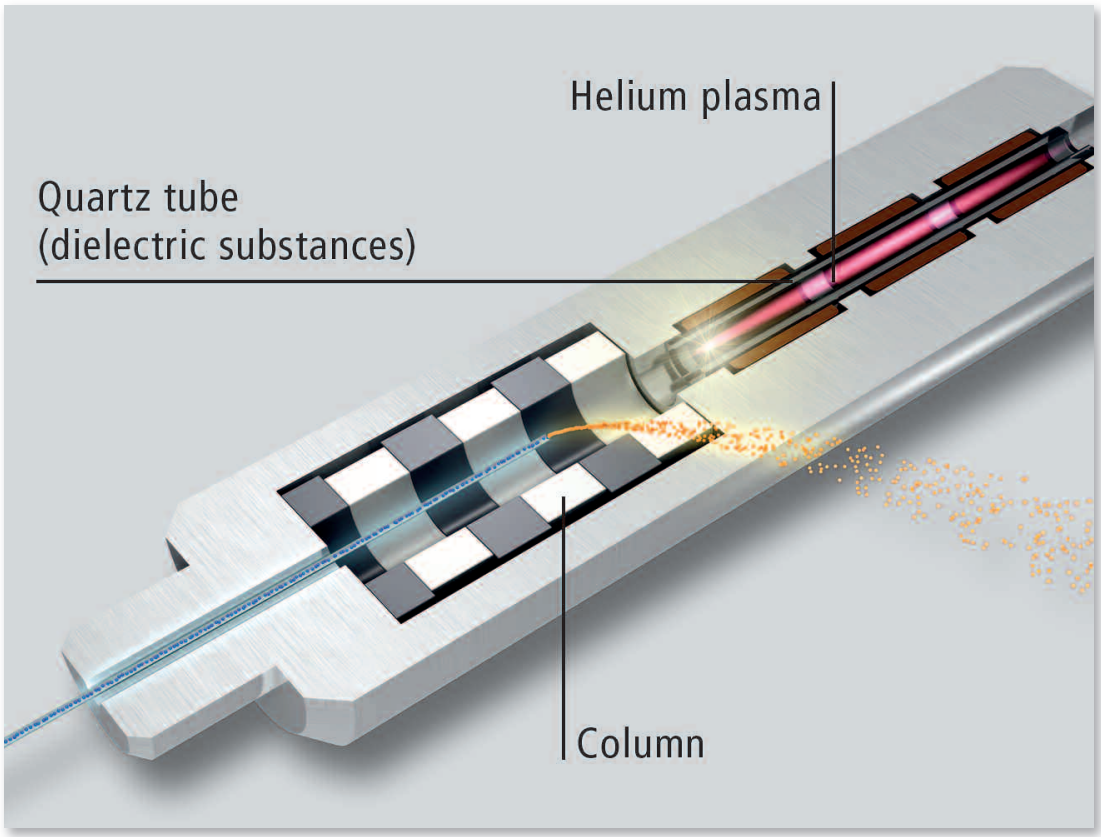

Figure 1: Schematic representation of the BID detector. A helium plasma is generated in the upper zone (shown in red). The emitted photons ionize the sample (lower zone). The sample cannot reach or contaminate the plasma zone due to the inner flow architecture and flows sideways.

The fully automated process presented in this article is based on headspace sampling with subsequent gas chromatographic separation of the components. A helium plasma is used for detection, achieving a detection limit of less than 0.2 mg/L.

Formaldehyde (systemic chemical name according to IUPAC: methanal) has the shortest chain length of all aldehydes. With a molar mass of 30.03 g/mol and a boiling point of -19 °C, this gas is highly soluble in water. Originally, formaldehyde was used mainly as a preserving agent. The use of formaldehyde as a component in wood adhesives increased significantly, for instance in furniture making and interior construction.

Formaldehyde has been classified as category 1B according to the CLP regulation as of June 2014. The potential hazard is therefore classified as 'probably carcinogenic to humans' [1]. Today, formaldehyde is a widely used chemical. It is used as starting material for various polymers, to treat clothing, and it serves as a preserving agent in various products.

New method without derivatization

Due to formaldehyde's toxicity, there are defined limit values for all application areas that should not be exceeded. Various methods have been established to control these limit values. The method presented here does not include the otherwise typical derivatization step. The sample is simply transferred to a headspace vial and hermetically sealed. In the subsequent step, the sample is incubated at 80 °C for 20 minutes.

An equilibrium is reached between the aldehyde concentration in the liquid and gas phase according to the partition coefficient. The autosampler withdraws 1 mL of the gas phase and transfers the volume onto the gas-chromatographic separation column.

A complete separation of the air and water peaks is critical for quantification of the formaldehyde. In addition to formaldehyde, this method is also suitable for measuring other analytes within one step, such as longer-chain aldehydes (shown here up to butyraldehyde).

Detection is carried out using a barrier ionization discharge detector (BID) from Shimadzu (figure 1). The BID operates with a helium plasma that ionizes the sample. The ionization energy is so high (17,7 eV) that virtually all substances are detected and the detector , can therefore be considered to be universal (with the exception of helium and neon).

Robust, maintenance-free detector

Two new designs make this detector extremely robust and maintenance-free. On the one hand, the helium plasma is shielded from the electrodes by a dielectric barrier, preventing them from being attacked by the plasma. On the other hand, the flow architecture separates the plasma generation zone from the ionization zone (figure 1).

This prevents possible contamination of the plasma by the sample. To check the suitability of the detector for formaldehyde detection, a concentration range of 0.5 to 50 ppm of the aldehyde in water was calibrated. A 30 mm Shimadzu Rt-U-Bond PLOT column with an internal diameter of 0.53 mm and film thickness of 20 µm was used as a separation column. Details of the measuring method are summarized in table 1.

Result

The result of these measurements is presented as a chromatogram (figure 2). Measurement took about 15 minutes. Formaldehyde was separated sufficiently from the air and water peaks – a prerequisite for accurate quantification.

Formaldehyde eluted after about 1.5 minutes. The detection limit of this method was 170 µg/L (ppb) for formaldehyde. Longer-chain aldehydes can be detected at a significantly higher sensitivity due to the increased detector response. Details of the statistical evaluation (correlation coefficient, rel. standard deviation and method detection limit (MDL)) for the individual components can be found in table 2. The relative standard deviation is, with 6.6 % at a concentration of 0.5 ppm for formaldehyde, somewhat higher than for the other components. This is due to the fact that because of the constant background, it is a challenge to create a formaldehyde-free sample. Moreover, formaldehyde is so volatile that sample preparation is a critical step in which analyte can easily be lost. Lastly, the chromatographic separation also plays a role. As can be seen in figure 2 (below), the formaldehyde peak sits on the shoulder of the air peak, which somewhat deteriorates the precision of the peak area calculation.

Conclusion

The method is highly suitable for determination of formaldehyde as well as other short-chain aldehydes, without requiring any further sample preparation steps. By combining the HS-20 headspace autosampler with the BID detector, all steps are fully automated, making the analysis robust and simple. Reproducibility is very good, while the detection limit is outstanding.

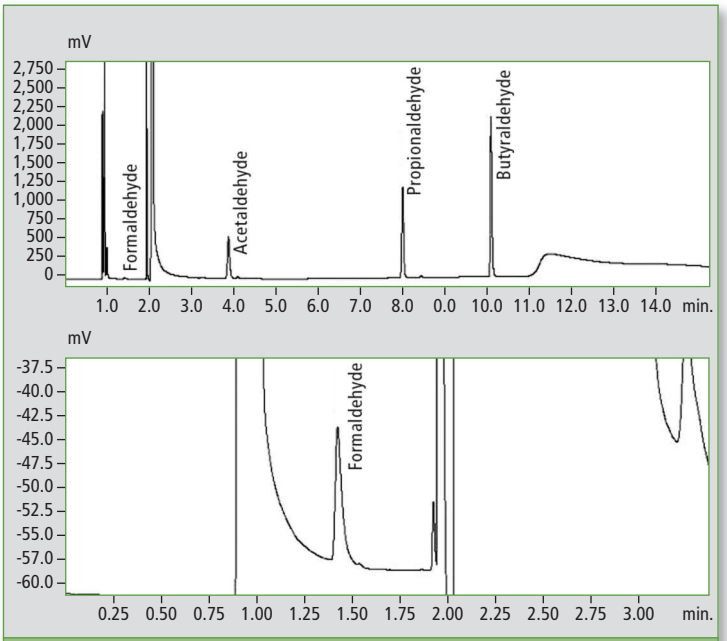

Figure 2: Chromatogram of the standard solution with 10 ppm (above). Below is a section of the same chromatogram for the formaldehyde peak at about 1.5 minutes.

Instruments	Tracera and HS-20
Incubation temperature	80 oC
Incubation time	20 minutes
Agitation strength	3 (of 5)
Pressure in sample vial	90 kPa (relative)
Sample temperature	150 °C
Sample volume	1 mL
Injector temperature	150 °C
Partition coefficient	1:3
Gas and flow rate	Helium 60 cm/sec
Oven program time	15.25 min
Detection	Helium ionization (BID)
Detector temperature	180 °C

Table 1: Details of the instrument and method parameters

Components	R^2	RSD (at 0.5 ppm)	MDL (ppm)
Formaldehyde	0.9992	6.6 %	0.17
Acetaldehyde	0.9998	1.5 %	0.02
Propionaldehyde	0.9997	1.3 %	0.03
Butyraldehyde	0.9988	2.3 %	0.05

Table 2: Statistical data of the method. Correlation coefficient of the calibration, relative standard deviation at a concentration of 0.5 ppm, as well as the calculated detection limit of the investigated components

Literature

[1] Umweltbundesamt, https://www.umweltbundesamt.de/themen/gesundheit/umwelteinfluesse-auf-den-menschen/chemische-stoffe/formaldehyd

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How reliable are additively manufactured alloys under very high cycle fatigue (VHCF) loading?

Ultrasonic fatigue testing systems USF-2000 and USF-2000A

Figure 1: Shimadzu's USF-2000 ultrasonic fatigue testing system (in standard configuration)

Selective laser melting (SLM) technology for additive manufacturing has advanced in recent years. Since the additive manufacturing process offers a high level of design freedom, it is used to create lightweight structures. It is possible to optimize their topology and in this way to create new designs with significantly lighter components.

However, prior to using SLM components in the automotive and aerospace industry and for the sake of safety and cost-effectiveness, the required fatigue strength must be guaranteed.

Process- and microstructure-based assessment of performance

Although the performance of SLM components is given under static loads, their fatigue strength is greatly reduced due to process-induced porosity. Even a (residual) porosity of less than 0.4 % seriously affects reliability under fatigue loading [1,2].

In order to prevent fatigue failure of SLM-manufactured structures, a microstructure-based process-specific characterization of the performance has to be carried out. Using new test methods based on ultrasonic fatigue, failures with very high cycle fatigue (VHCF) for loads below the so-called 'fatigue limit' were determined [3,4]. Moreover, in the HCF to VHCF range, some alloys with body-centered cubic (BCC) and face-centered cubic (FCC) lattice systems show a shift in crack initiation from the surface to the inner volume of the material [5].

Production and HCF fatigue properties of SLM-AlSi12

Using a commercial SLM system, samples of the aluminum alloy AlSi12 were manufactured in an inert argon gas environment. Quasi-static tensile strength tests were performed in accordance with ISO 6892-1: 2009. Evaluation of the HCF fatigue behavior was performed under load increase and constant amplitude tests with a frequency of 20 Hz.

The process optimization results, tensile and HCF fatigue characteristics as well as the measurement and test methodology used to evaluate process-induced damage and its effect on the characteristics have been described in literature [1, 2, 6]. These studies serve as the basis for determining the effects of process-induced defects on the VHCF fatigue behavior until 1E9 cycles.

New experimental methodology with ultrasonic fatigue – testing system USF-2000

Tests to determine fatigue strength in the VHCF range were performed using Shimadzu's USF-2000 ultrasonic fatigue testing system at a frequency of 20 kHz and a load ratio of -1, i.e. fully-reversed (without mean load). Figure 1 shows an overview of the USF-2000 testing system.

Samples with the geometry shown in figure 2 were clamped at the threaded end of the testing system and were free to move at the bottom end. In the testing system, a piezoelectric crystal is used as an actuator and oscillates at 20 kHz.

The design is such that maximum stress is experienced at the middle of the sample and maximum dis-

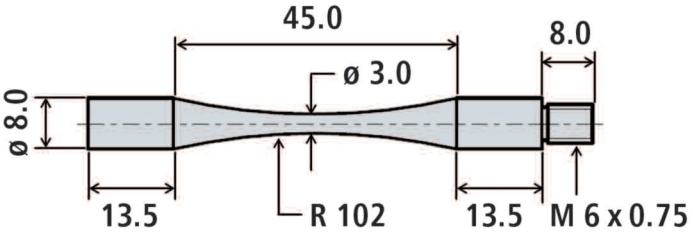

Figure 2: Sample geometry in mm for AlSi12 aluminum alloy

placement occurs at the free end of the sample.

To eliminate temperature increases induced by deformation at high test frequency, the samples were tested at a suitable pulse-pause ratio and were in addition cooled using compressed air. To determine the fatigue strength at 1E9 cycles, the staircase method was used. If a sample fails, the stress in the following test will be lowered; if the limited number of cycles is attained, the load will be increased in the following test. Sample failure in the testing system is detected by means of the change in the resonance frequency and the test is terminated automatically.

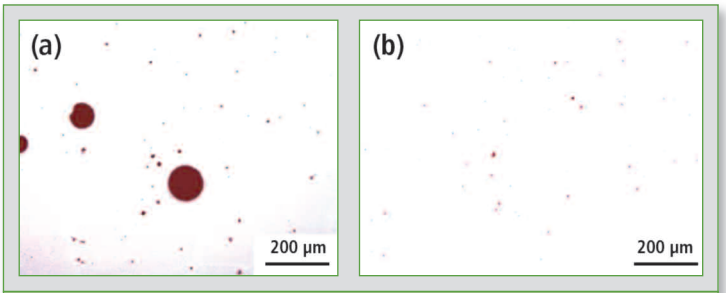

Figure 3: Microstructural images for AlSi12 samples of batch I without base plate heating (BPH) (a) and batch II with BPH (b)

Microstructure and VHCF fatigue properties of SLM-AlSi12

Two batches of AlSi12 alloy were tested: for batch I, base plate heating (BPH) was omitted in the SLM system; whereas batch II samples were manufactured using a heated base plate at 200 °C. Figure 3 shows microstructural images of the two batches.

There is a clear difference in the pore fraction of the samples without and with BPH, i.e. samples with BPH do not exhibit large-size, fatigue-critical gas pores. The reduction of large pores is attributed to the degassing process in the manufacturing chamber due to preheating. Figure 4 shows exemplary Woehler (S,N) curves for both AlSi12 batches in the range of high to very high cycle fatigue. The test results illustrate that a fatigue fracture in the VHCF range can occur for both batches and that the fatigue strength of samples with BPH is about 45 % higher than that of samples without BPH.

New experimental methodology with ultrasonic fatigue and mean load application – testing system USF-2000A

To determine the fatigue strength in the VHCF range under concurrently applied mean stress, Shimadzu's USF-2000A ultrasonic fatigue testing system is used (figure 5). In addition to the above results under fully-reversed loading, i.e. at a load ratio of -1, the influence of static mean stress on the VHCF fatigue strength can be characterized for different load ratios.

Summary and outlook

Developments in ultrasonic vibration testing systems significantly advance the state of the art. This allows detailed testing under realistic operational conditions and lifetime in the context of safety and cost-effectiveness. Very powerful tools are now available for reliable determination of the effect of SLM processing parameters on the resulting functional performance in a wide range.

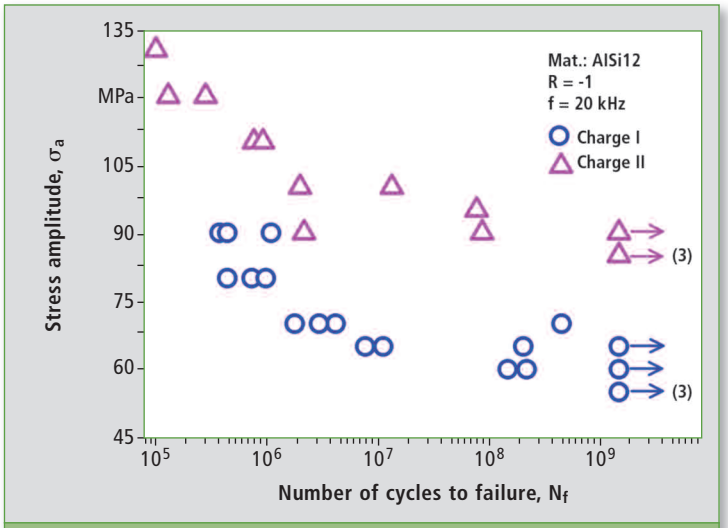

Figure 4: Woehler (S,N) curves for AlSi12 samples of batch I without BPH and batch II with BPH

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Figure 5: Shimadzu's ultrasonic fatigue testing system USF-2000A (with mean load application)

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Colorful packaging – with big know how

Risks from printed food packaging

Plastic packaging is used for all types of food, although not all packaging materials are the same. Food packaging must meet many requirements specified by producers and consumers. The main purpose of food packaging is to protect foods from harmful environmental influences such as light, oxygen and microbial decay to ensure a long shelf life. Safety, transport properties and recyclability play an important role as well. Apart from this, however, packaging also serves as an advertising space and should be both appealing to the consumer and easy to handle.

In order to meet these various requirements, food packaging materials are increasingly complex in structure [1].

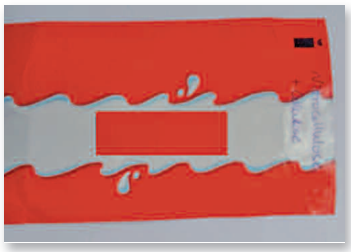

Figure 1: Image of sample no. 01

Identification of printed films using FTIR spectroscopy

The analysis of transparent, colorless plastic packaging materials used in the food industry was discussed in the Shimadzu News 3/2016 (page 6 - 9). This study focused on the analysis of 32 different packagings of different origin using FTIR spectroscopy. The measuring technology applied allowed a non-destructive analysis of surfaces of up to 2 µm layer thickness.

The present article focuses on the investigation of food packagings and their printed information including for instance, company logos, product information and marketing-relevant designs.

A total of 50 samples were analyzed, among which were two different categories of packagings, each revealing different types of printed information:

1. surface prints
2. under-surface prints

Analysis performed in two steps

The surface print group includes 15 of the 50 samples collected (30 %). They are characterized by the printed information which has been applied to the top polymer layer. The group of under-surface prints dominates with 35 out of 50 samples (70 %) and includes packagings where the printed information is protected from the outside by an additional polymer layer.

In the first step, the plastic composition of all samples was determined using FTIR spectroscopy. The absorption was measured using Shimadzu's IRTracer-100 equipped with a diamond ATR unit. This method is based on the fact that the IR beam penetrating into the sample leads to attenuation of the intensity of the reflected light compared to that of the incident light.

Selected colored areas larger than 1 cm were subsequently analyzed using the EDX-8000P specifically for the presence of inorganic components, which are frequently used in pigments and fillers. Energy-dispersive X-ray fluorescence analysis makes it possible to determine elements from carbon to uranium while also accurately detecting concentrations in the lower ppm range. The analysis is non-destructive and, just like FTIR spectroscopy, requires no sample preparation.

A total of 199 IR spectra and 60 EDX spectra were recorded in the course of these analyses. As an example, the analysis results for ten selected samples are presented

in table 1. Samples for which the main components could not be unequivocally identified are designated as 'unknown'.

No.	Sample	Internal surface	External surface	Imprint	Recycling symbol	EDX (>10 ppm)
01	Chocolate bar	Cellulose, Acrylate	Nitrocellulose / Cellulose	Surface print	—	Si, Ti, S, Al, Fe
02	Fruit jellies	PP	PP	Under-surface print	symbol	Ti, Al, Si, P
03	Fruit	PP	PP, PA	Surface print	—	Ti, Al, Si, P
04	Nuts	PE	PET	Under-surface print	07 PET, Alu, PE	Al, Ti, Fe, S, Si
05	Rusks	PP	PP	Under-surface print	—	Ca, Ti, Si, Al
06	Coffee	PP	PP	Under-surface print	—	Ti, Al, Si, P, S
07	Coffee	PP	PP	Under-surface print	—	Ti, Al, Si, P, S
08	Carrots	unknown	unknown	Under-surface print	compostable	Ti, Si, Al
09	Croissants	PE	PET	Under-surface print	07	Ti, Si, Al, S
10	Snickers	PP	PA	Under-surface print	—	Ti, Si, Al, P, S, K

Table 1: Identified main polymers of ten printed food packagings and their inorganic components

A detailed look at a sample

As an example, sample no. 01 will be further discussed below. It is a film imprinted with three colors of ink, serving as the outer packaging of a chocolate bar. Spectra of the colored areas on the outer surface of the film were measured using the IRTracer-100.

The spectra in figures 2 and 3 suggest that the outer surface of the film contains imprinted cellulose fibers. In addition to the cellulose fibers, the spectrum of the red imprinted area also points to the presence of cellulose nitrate. This compound is often applied as a binder for liquid printing inks that are used for imprinting packaging materials. Therefore, the red color is a surface print.

In the second step, EDX analysis is used to draw conclusions on the element composition. The red area on the film was examined first, followed by the back side of the film. As can be seen in figure 4 (page 14), the film does not contain any significant amounts of metals, meaning that the red ink is an organic compound.

Subsequently, the metal film on the inner surface of sample no. 01 was examined. The film was separated from the glued-on cellulose fiber layer and analyzed separately. Since the metal film consists of the light element aluminum, the spectrum was recorded in the vacuum with an excitation energy of 15 kV. This prevents absorption of X-ray fluorescence radiation by air and increases the intensity of the aluminum signal.

In addition to aluminum, there are, however, also large amounts of iron that could be detected at an excitation energy of 50 kV.

To prevent contamination of the chocolate, the aluminum film is additionally coated with a polymer layer as apparent from the IR spectrum of the separated aluminum film, that prevents contact of the aluminum with the chocolate bar and subsequent contamination of the chocolate.

It is important to ensure that foods are not contaminated with aluminum as this poses a health risk (see paragraph: Health risks resulting from aluminum?).

Printing inks and packaging materials

Among the 15 samples with surface prints, nine samples contain cellulose nitrate. The other printing inks contain, in some cases, acrylate, polystyrene or other not yet identified components. Figure 6 (page 14) presents an overview of the imprinted packagings of the 50 samples investigated. The non-identified components are not shown.

Polypropylene (PP) is the most frequently used imprinted packaging material. More than 50 % of the samples contain PP, while polyethylene (PE) and polyethylene terephthalate (PET) occur in only 20% of the samples. Interestingly, only one imprinted packaging appears to be made of polystyrene (PS).

Of the 50 packagings investigated, 17 are composed of two or more main components. It should be noted that only surfaces with a layer thickness of 2 µm were being investigated. It cannot be ruled out that further components may be identified upon investigating cross sections of packaging films. Conversely, this means that recycling of polymers represents a real challenge because of the complexity of packaging materials.

Risks from printing inks in food packagings

Inks used for imprinting cardboard and plastic food packagings have long been the focus of analytical control labs because harmful substances in printing inks can migrate into packaged food products.

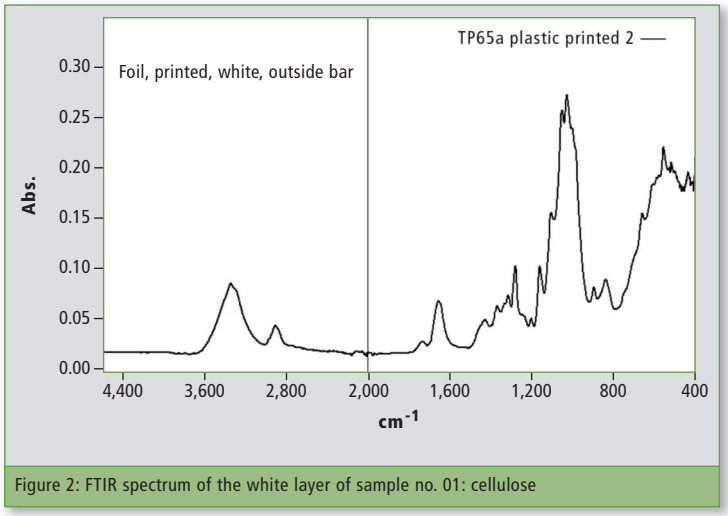

Figure 2: FTIR spectrum of the white layer of sample no. 01: cellulose

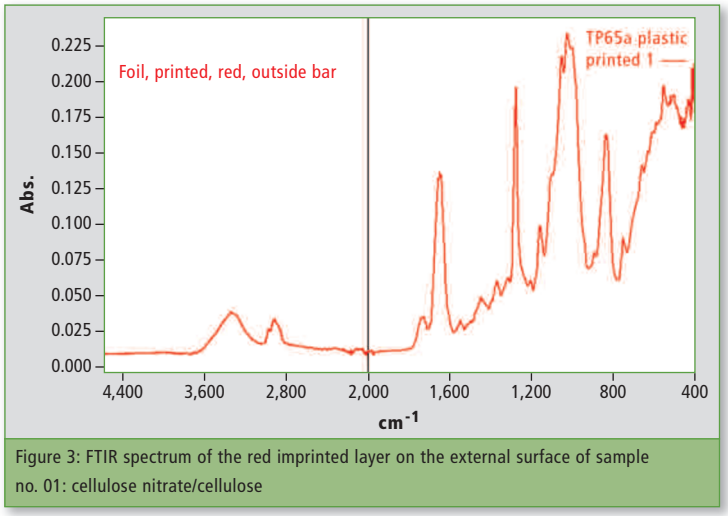

Figure 3: FTIR spectrum of the red imprinted layer on the external surface of sample no. 01: cellulose nitrate/cellulose

In accordance with the relevant regulations, materials that come into contact with foods may not contain any substances or components that can migrate into foods in harmful quantities. Packaging materials must also not lead to any unacceptable changes in the food or cause any odor or taste impairment.

Food contact materials must, therefore, be produced according to good manufacturing practice [3].

Harmful substances in foods

Today, harmful substances are found in a multitude of foods that can be introduced into the foods along the entire production and retail chain. Possible sources are primarily packaging materials, but also fuels, exhaust gases, lubricating oils, dust-binders, anti-sticking agents and many more.

The multitude of contamination sources present great challenges for the analysis and quantification of harmful substances in foods.

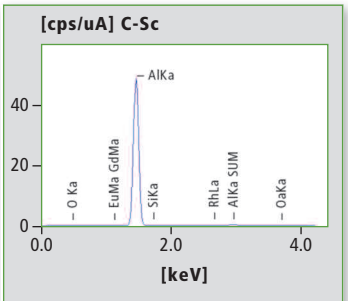

Figure 5: EDX spectrum of the separated aluminum film of sample no. 01 (excitation energy 15 kV)

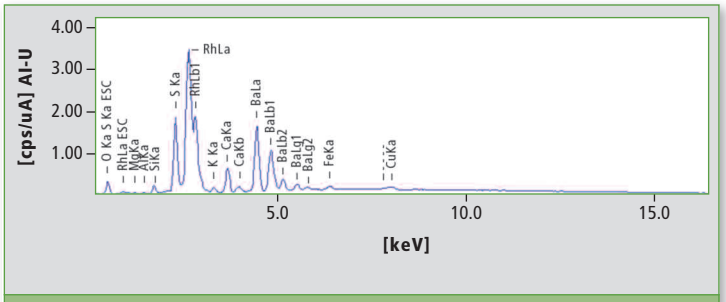

Figure 4: EDX spectrum of the red imprinted layer of sample no. 01 (excitation energy 50 kV)

According to the Switzerland-based health website ("German: Zentrum der Gesundheit") about 100,000 substances migrate from packaging to foods [4].

Health risks resulting from aluminum?

Aluminum can enter the human body via drinking water as well as via foods and their packagings. Aluminum, distinguished by its light weight, is used in beverage cans and canned foods, caps for glass bottles, Tetra Paks, packagings for ready-made meals and foils to protect foods from environmental influences. A disadvantage is, however, that under the influence of acidic beverages such as fruit juices and caffeine-containing soft drinks, but also salt, aluminum is soluble and can migrate into foods and beverages.

Aluminum is suspected of causing kidney damage, having a negative impact on bone development and is associated with cancer and Alzheimer's disease. Qualitative and quantitative analysis of aluminum in food packagings can be carried out using Shimadzu's EDX-8000P energy-dispersive X-ray fluorescence spectrometer.

Summary and outlook

FTIR enables surface analysis of all types of packaging materials. EDX complements FTIR identification and is suitable for detection of critical substances, for instance RoHS elements. Both FTIR analysis and EDX spectroscopy allow non-destructive and fast analysis of the plastic materials.

The present studies have focused on transparent, colorless and imprinted food packagings. Non-transparent, colored packagings will be addressed in following investigations, in which harmful substances such as heavy metals and organic substances like mineral oils are analyzed. Mineral oils residues can be differentiated into mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH), which are suspected of causing organ damage or cancer.

Mineral oils can migrate directly into foods from freshly ink-printed paper and plastic packagings, especially when the packagings are imprinted.

The analysis of MOSH/MOAH contamination in foods and food packagings is performed using chromatographic methods like the HPLC-GC-FID method described in the draft version of DIN EN 16995:2016-05 [4].

This method will be discussed in a subsequent article in the Shimadzu News 2/2017.

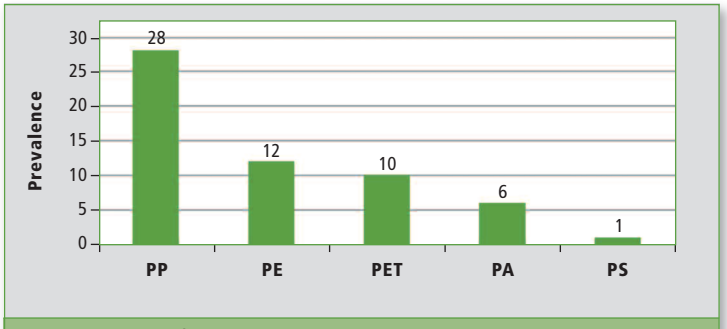

Figure 6: Prevalence of various polymers in the tested samples

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[3] Fachgruppe Druckfarben im Verband der deutschen Lack- und Druckfarbenindustrie e.V.: „Merkblatt: Flüssige Druckfarben" http://www.lackindustrie.de/druckfarben/allgemeine-informationen/Seiten/Uebersichtsseite.aspx (20.12.16)

[4] DIN EN 16995:2016-05 – Entwurf: Titel (deutsch): Lebensmittel- Pflanzliche Öle und Lebensmittel auf Basis pflanzlicher Öle – Bestimmung von Mineralölen aus gesättigten Kohlenwasserstoffen (MOSH) und aus aromatischen Kohlenwasserstoffen (MOAH) mit on-line HPLC-GC-FID; Deutsche und Englische Fassung prEN 16995:2016

TOC determination of a PFOS solution

Comparing wet-chemical oxidation with the combustion method

Perfluorooctane sulfonate (PFOS) is a man-made organic straight-chain compound consisting of an 8-carbon chain with fluorine atoms bonded to each carbon and a sulfonic acid terminal group. The specific characteristic of PFOS is that the perfluorinated group is non-polar, whereas the polar anionic group is hydrophilic. It is a surfactant that dissolves readily in both oil and water.

Sample	TOC (theoretical)	TC-measurement result	IC-measurement result	TOC calculated (TC-IC	Recovery
10 mg/L PFOS	1.921 mg/L	1.898 mg/L	0.058 mg/L	1.840 mg/L	95.8 %
5 mg/L PFOS	0.961 mg/L	0.959 mg/L	0.038 mg/L	0.921 mg/L	95.8 %

Table 1: TOC determination results using the difference method

Sample	TOC (theoretical)	TC-measurement result	IC-measurement result	TOC calculated (TC-IC	Recovery
10 mg/L PFOS	1.921 mg/L	0.085 mg/L	0.077 mg/L	0.008 mg/L	0.4 %
5 mg/L PFOS	0.961 mg/L	0.079 mg/L	0.064 mg/L	0.014 mg/L	1.5 %

Table 2: TOC determination results of PFOS using the TOC-V_{WS}

Figure 1: TOC-L

PFOS is an extremely stable compound due to its strong carbon-fluorine bonds and is therefore persistent in the environment, bio-accumulative and toxic to mammalian species. In October 2006, the European Parliament restricted use of PFOS to a limited number of application areas.

Due to its structure, PFOS is a good example for highlighting the differences in oxidizing power between the wet-chemical oxidation method and the combustion method used in TOC determination. For this application, the TOC content of a PFOS solution was determined using Shimadzu's TOC-L_{CPH} and TOC-V_{WS} analyzers.

Two methods for TOC determination

Shimadzu offers two TOC systems featuring different oxidation methods. While the TOC-$V_{WP/WS}$ uses wet-chemical oxidation, the TOC- L_{CPH} applies the catalytic combustion method at 680 °C. With their wide measuring ranges from 0.5 µg/L up to 30,000 mg/L, they support many applications, from ultrapure water to heavily contaminated waters (for instance in cleaning validation, extraction solutions or wastewater).

TOC determination of PFOS using the TOC-L_{CPH}

For sample preparation, PFOS was dissolved in ultrapure water and subsequently diluted to obtain a solution of 5 mg/L PFOS (equivalent to 0.961 mgC/L) and 10 mg/L PFOS (equivalent to 1.921 mgC/L). Surfactants like PFOS are prone to foaming, so the difference method was used for TOC determination.

Measurement system:
TOC-L_{CPH} with standard catalyst
Measurement method: Difference method (TOC = TC-IC)
Calibration curve: TC: 0 - 3 mg/L (2 points)
IC: 0 - 3 mg/L (2 points)

TOC determination of PFOS using the TOC-V_{WS}

Measurement system: TOC-V_{WS}
Measurement method: Difference method (TOC = TC-IC)
Calibration curve: TC: 0 - 3 mg/L (2 points)
IC: 0 - 3 mg/L (2 points)

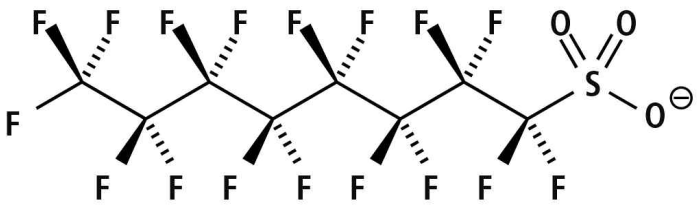

Figure 2: Perfluorooctane sulfonate

Summary

The results clearly show that wet-chemical oxidation is not sufficient to break down highly stable compounds such as PFOS. Such compounds require the strong oxidizing power of catalytic combustion at 680 °C offered by the TOC-L series.

This underlines the different application areas of both analyzers. The strengths of the TOC-V series (wet-chemical oxidation) lie in the extremely low detection limit and excellent reproducibility in the lower ppb range. For this reason, the TOC-$V_{WP/WS}$ is particularly suitable for determination in the ultra-trace range.

The advantage of the combustion method is its high oxidizing power, particularly when highly stable compounds and/or particles are present in the sample. In addition, simultaneous TOC/TN_b measurements can be performed.

The application range of the TOC-L series is therefore more versatile and encompasses all TOC regions (except for the ultra-trace region < 20 µg/L TOC).

Complete solution for mycotoxin analysis

Mycotoxin Screening System analyzes ten different mycotoxins in only 14 minutes

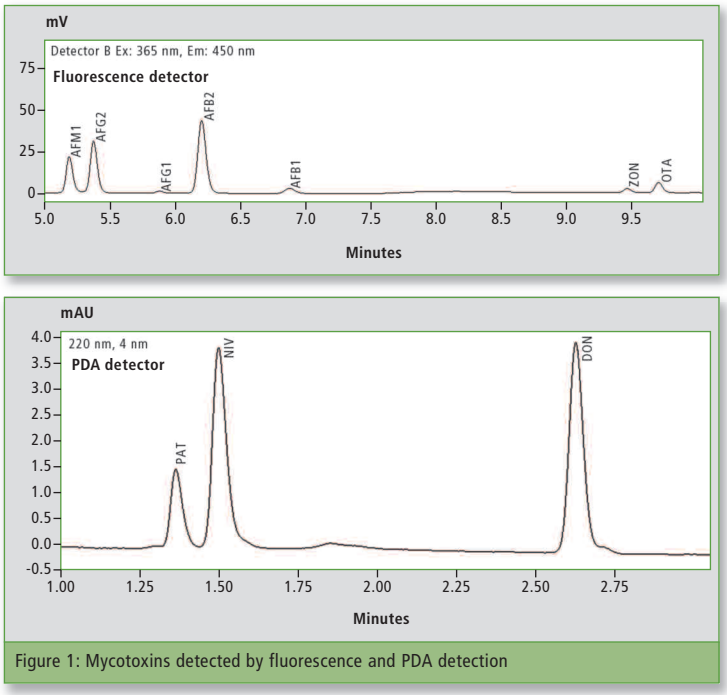

Figure 1: Mycotoxins detected by fluorescence and PDA detection

It is hazardous to health, it is genotoxic and carcinogenic. It is one of the most dangerous substances in food: Aflatoxin B1. Of all types of aflatoxins, Aflatoxin B1 is the most common one present in food products [1]. It is part of mycotoxins, which are secondary metabolites produced by fungi [2]. Analysis of mycotoxins in food is therefore essential in order to assure healthy nutrition for humans and animals.

Aflatoxins are produced by fungal molds of the *Aspergillus* species, which prefer a warm and damp climate. They are often associated with commodities produced in the subtropics and tropics, like peanuts, cotton, spices or pistachios. Furthermore, they can be produced by fungal infestation during or after harvest of grain and can end up in processed products such as beer, brewed from malt.

Ochratoxin is produced by *Penicillium* and *Aspergillus* species. It is a contaminant in beverages such as beer and wine. Patulin, produced by P. *expansum, Aspergillus, Penicillium* and *Paecilomyces fungal* species, is often found in moldy fruits and vegetables. Zearalenone is produced by *Fusarium* species and may be present in crops; AFM_1 is often found in milk products.

Mycotoxins are not destroyed by temperature treatment, and are barely influenced by cooking, freezing or digestion. These properties make the investigation in food crucially important as consumers need to be protected from these toxic substances. Sensitive methods for the analysis of mycotoxins are required.

	NIV	DON	AFB_1	ZON	OTA	PAT	AFM_1
EU residue [µg/kg]	not determined	500 - 1,750	2 - 12	20 - 400	2 - 10	25 - 50	0.05

Table 1: EU residue limits for mycotoxins

Complete solution

The Shimadzu „Mycotoxin Screening System i-Series Solution Package“ is a one package single solution. The system simultaneously investigates ten different mycotoxins in only 14 minutes. This i-series instrument specializes in identification of mycotoxins in grain, such as wheat flour and rice flour, as well as in apples and milk. Sample preparation, analysis and evaluation are easy comprehensible, explained progressively, and represent an easy-to-use solution for users.

Neither in-depth analytical nor chromatographic knowhow are necessary to operate the system. An additional benefit is the combination of a fluorescence detector with a PDA detector (Photo Diode Array). This prevents a complex derivatization, and the mycotoxins can be identified easily and efficiently.

AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, ZON, DON, NIV and PAT were investigated. For this approach, the five analytes most commonly tested in malt products were extracted and analyzed in spiked and non-spiked beer samples from different batches, as well as PAT in apple juice and grape juice. EU limit values are: Aflatoxins (B1, B2, G1 and G2: total: 4 to 15 µg/kg; AFB_1: 2 to 12 µg/kg); AFM_1: 0.05 µg/kg; OTA: 2 to 10 µg/kg; PAT: 25 to 50 µg/kg; DON: 500 to 1,750 µg/kg; NIV: not specified; ZON: 20 to 400 µg/kg.

Detection of the mycotoxins was conducted using a combination of fluorescence and photodiode array (PDA) detection.

Investigation of mycotoxins in juice and beer

This method was applied to different non-spiked and spiked beverage samples. In all spiked beverage samples, the mycotoxins were successfully identified despite the complexity of the matrices. All ten mycotoxins were successfully separated from each other and detected by fluorescence detection and PDA

Analytical conditions

Instrument:	LC-2040C 3D (Shimadzu)
Column:	Shim-pack GIST C18 (3.0 mm x 75 mm I.D., 2 µm); Shimadzu
Mobile phase:	
A:	20 mmol/L sodium phosphate buffer pH 2.5 (10 mmol NaH_2PO_4 and 10 mmol H_3PO_4)
B:	Acetonitrile
C:	Methanol
Flow rate:	1.0 mL/min
Injection vol.:	10 µL
Ofen temp.:	55 °C

t [min]	B [%]	C [%]
0	5	0
2.3	9	0
2.31	15	15
6.5	15	20
6.51	35	15
10.0	35	15
10.01	5	0

Table 2: LC gradient program

Detection:

Fluorescence:	RF-20AXS:
Ex:	365 nm and 320 nm
Em:	450 nm and 465 nm
PDA:	D2 at 190 - 500 nm, Reference at 350 nm

Sample preparation

Two batches of beer, apple juice and grape juice were the object of this investigation. The samples were prepared as non-spiked or spiked with mycotoxins. 4 g of the beverages were mixed with 21 mL acetonitrile. The mixtures were

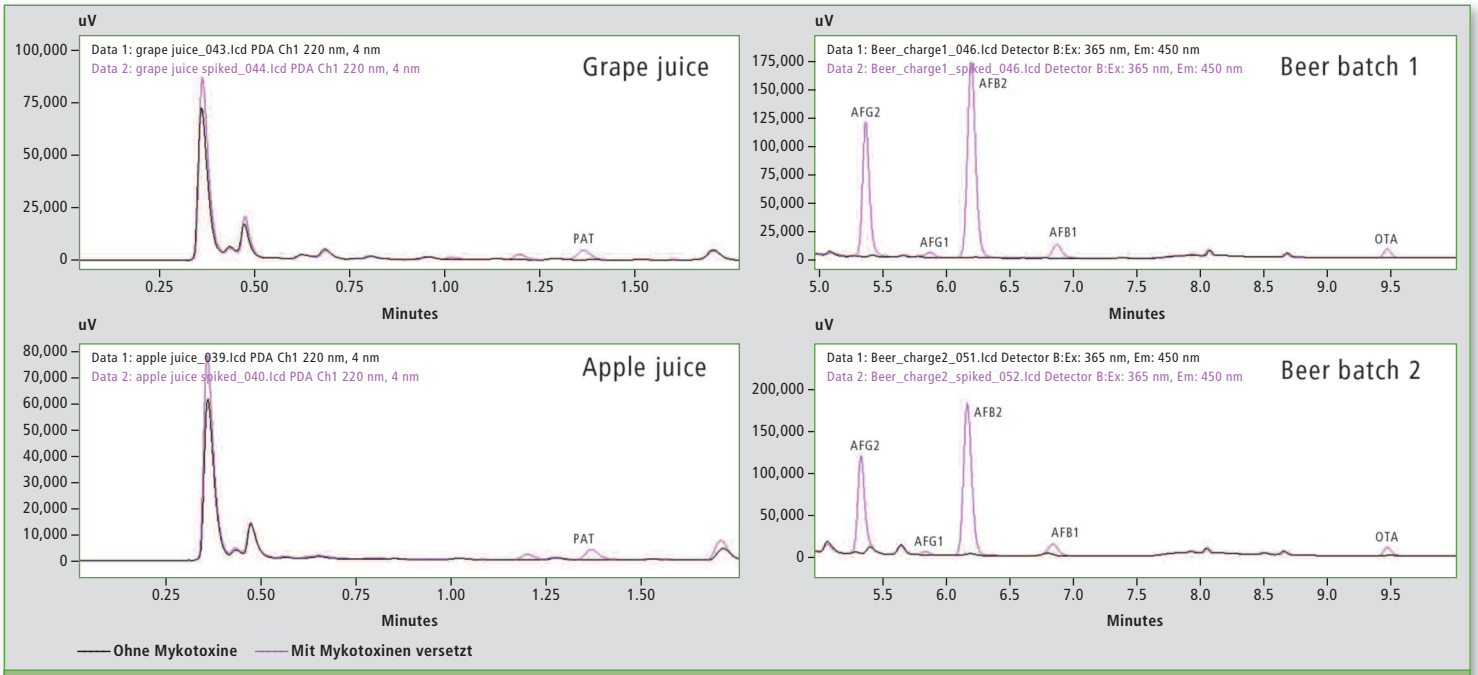

Figure 2: Comparison of pure and spiked beverage samples: apple juice, grape juice and two different batches of beer

cleaned with a multifunctional column (MultiSep 228, cartridge type). 4 mL of the elution were collected and evaporated to dryness with nitrogen gas. The samples were then re-dissolved in a 400 µL water/acetonitrile (95/5, v/v) solution and used directly for analysis. A standard mixture containing ten different mycotoxins (AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, ZON, DON, NIV and PAT) was prepared.

EU maximum residue limits, LODs and LOQs

The EU maximum residue limits for mycotoxins as specified by EU standards are the strictest in the world [3-5]. To check whether the food samples investigated contain mycotoxins within the EU maximum residue limits, standards with the mycotoxins were prepared using the same concentration as that of the EU control criteria. A simple and fast one point calibration was enough to assess compliance with the criteria.
A batch was created with the calibration standard and the food samples, and the results show if the peaks of the mycotoxins in the food samples were below or above the criteria.

In this study, all measured samples (apple juice, grape juice and two batches of beer) either contained no mycotoxins or were in a range far below the EU criteria. The same, spiked samples showed mycotoxin concentrations above the EU criteria.

For all mycotoxin standards, LODs and LOQs were determined as shown in table 2. Limit of Detection (LOD) and Limit of Quantitation (LOQ) were low and at least half of the EU maximum residue limits.

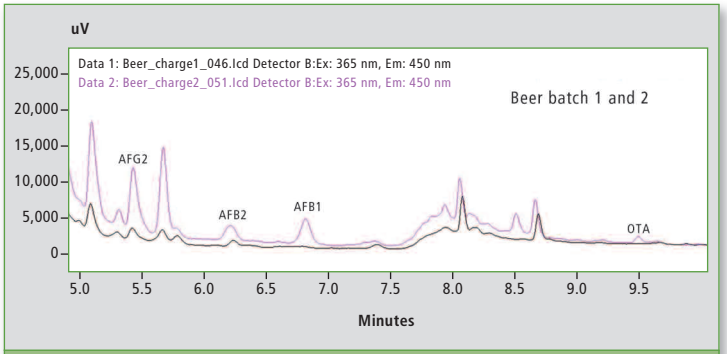

Figure 3: Comparison of non-spiked beer batch 1 and non-spiked beer batch 2

	NIV	DON	AFG_2	AFG_1	AFB_2	AFB_1	ZON	OTA	PAT	AFM_1
LOD [pg]	80	10	0.025	4	0.0002	0.0025	25	0.1	13	0.25
LOQ [pg]	200	20	0.075	12	0.0005	0.0075	75	0.3	50	0.75

Table 3: Absolute LODs and LOQs of the mycotoxins, determined using fluorescence and PDA detection. Error for the LOQs was below 10 % for all analytes.

Figure 3 compares the different beer batches. The beer sample of batch 2 showed small peaks for AFG_2, AFB_2, AFB_1 and OTA. Even though the concentration of the mycotoxins is far below the EU maximum residue limits, this is a clear indication of the presence of mycotoxins in the beer of batch 2.

The limits of detection (LOD) as well as the limits of quantification of each mycotoxin have been defined and are listed in table 3. According to the regulations of sample preparation, LOD and LOQ are below the EU maximum residue limits.

Conclusion

The level of these mycotoxins was below the European regulation. The results show that different batches of the same beer show differences in mycotoxin content. Within this study, a fast, safe and easy method was shown for the analysis of mycotoxins in beverages. A further advantage, especially for food quality control analysis, is the simultaneous separation of all ten mycotoxins in just 14 minutes.

Literature

[1] European Food Safety Authority (http://www.efsa.europa.eu/de/topics/topic/aflatoxins)
[2] Richard JL, J. Food Microbiol. 119 (1-2): 3-10 (2007).
[3] EU: Commission Regulation (EC) No 1881/2006 of 19 December 2006 (consolidated version 2010-07-01). Setting maximum levels for certain contaminants in foodstuffs.
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[5] EU: Commission Regulation (EC) No 105/2010 of 5 February 2010 amending Regulation (EC) No 1881/2006. Setting maximum levels for certain contaminants in foodstuffs as regards ochratoxin A.

E-cigarettes – Heavy metals in e-liquids and e-vapors

ICP-OES technology meets Tobacco Products Directive (TPD) regulations

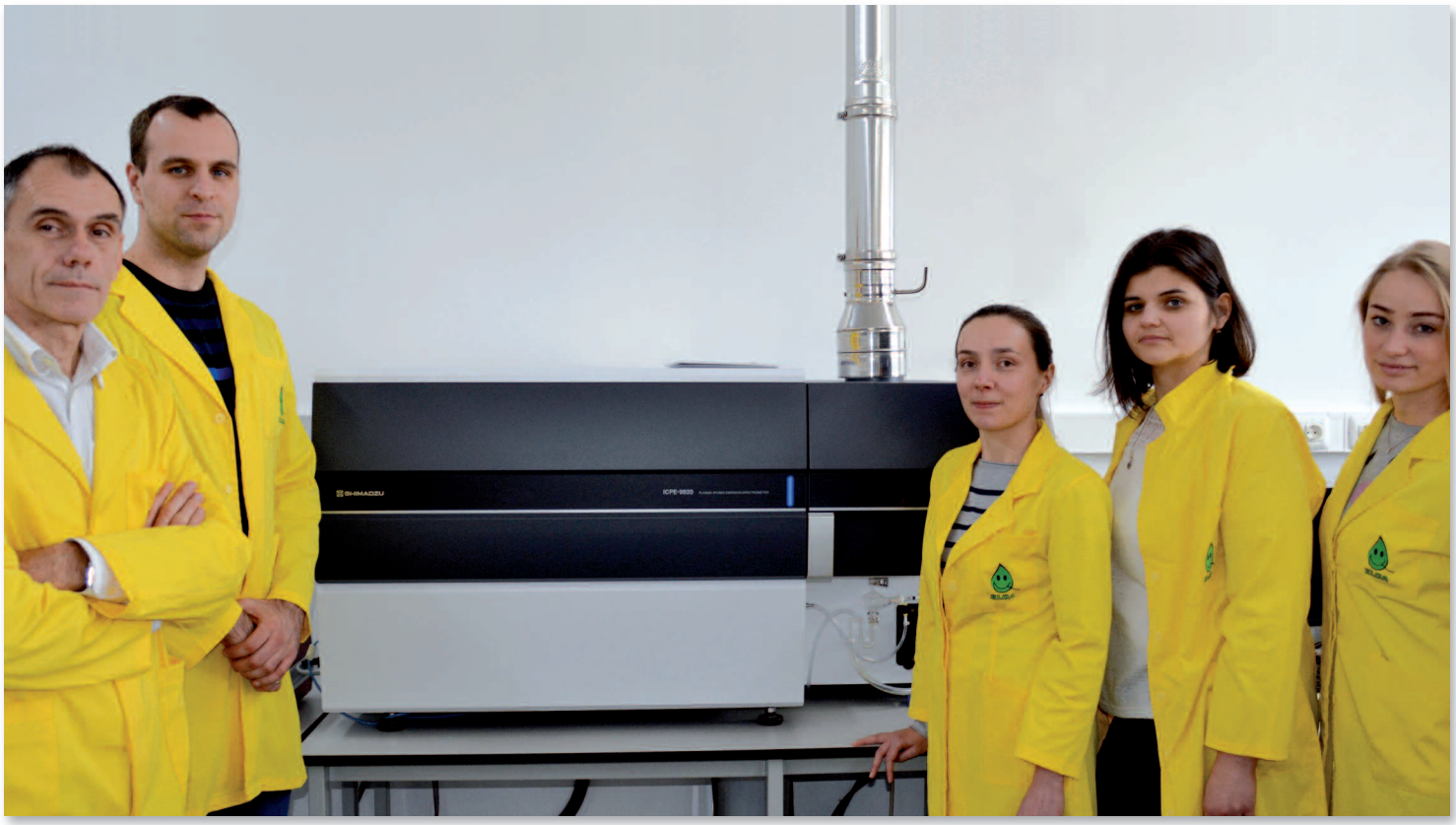

Figure 1: ELDA staff next to the ICPE-9820

The manufacture of e-liquids is growing rapidly and exponentially in Europe, especially in UK, France and Germany. Unlike conventional cigarettes, E-cigarettes do not burn tobacco to deliver flavor. Instead, they contain a liquid-based flavorant (e-liquid) that is thermally vaporized by an electric element and inhaled by the smokers.

E-liquids are usually made of nicotine, propylene glycol, glycerine and flavorings. Their compositions vary between and within manufacturers all over the world, so there is a need for quality control in order to avoid unexpected harm or toxic effects.

Besides possible organic degradation products, the presence of trace elemental impurities in some e-liquids or e-vapor aerosol has been previously reported. Each e-liquid component can contain elemental impurities and be a source of contamination. E-cigarettes have several metal components in direct contact with the e-liquid, e.g. clearomizer, the tank attached

	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	Y
Wavelenhgt/nm	396.153	193.759	226.502	267.716	224.700	259.940	184.950	231.604	220.353	271.581	371.030
View mode	Axial										
Torch	Mini torch										
Radio frequency power	1.20 kW										
Plasma gas	10 L/min										
Auxiliary gas	0.60 L/min										
Carrier gas	0.70 L/min										
Exposure time	30 sec										
Condition	Wide range										

Table 1: Measurement conditions

to the e-cigarette battery to hold e-liquid. So potential toxins can also leach out of device materials depending on the composition.

Tobacco Products Directive (TPD)

In May 2016, the Tobacco Products Directive 2014/40/EU (TPD) came into force defining regulations covering e-cigarettes (Article 20). Article 20 of the TPD places an obligation on the manufacturers and importers of electronic cigarettes and refill containers to submit a notification to the competent authorities of the Member States of such products they intend to market. The notification must list ingredients and emissions which result from the use of the products.

Depending on the material composition of the e-cigarettes, information on aluminum, chromium, iron, nickel and tin emissions should be provided. If other metals such as lead and mercury are present in the e-cigarette components, information on these metals should be included as well.

By May 2017, all products sold to customers must be fully compliant with TPD.

Each EU Member state can place further restrictions, but they all have to comply with the central rules of Article 20 of the TPD. Norm XP D90-300-2 AFNOR (France) defines maximum concentration of heavy metals in e-liquid as follows: lead (Pb) 10 mg/L, arsenic (As) 3 mg/L, cadmium (Cd) 1 mg/L, mercury (Hg) 1 mg/L, antimony (Sb) 5 mg/L.

Simultaneous determination of heavy metals

For simultaneous quantitative determination of heavy metals in e-liquids and e-vapor, ICP-OES (inductively coupled plasma – optical emission spectrometry) is the method of choice. Shimadzu's ICPE-9820 achieves a broad dynamic range from ppb to percent order due to axial and radial plasma observation capabilities, ➧

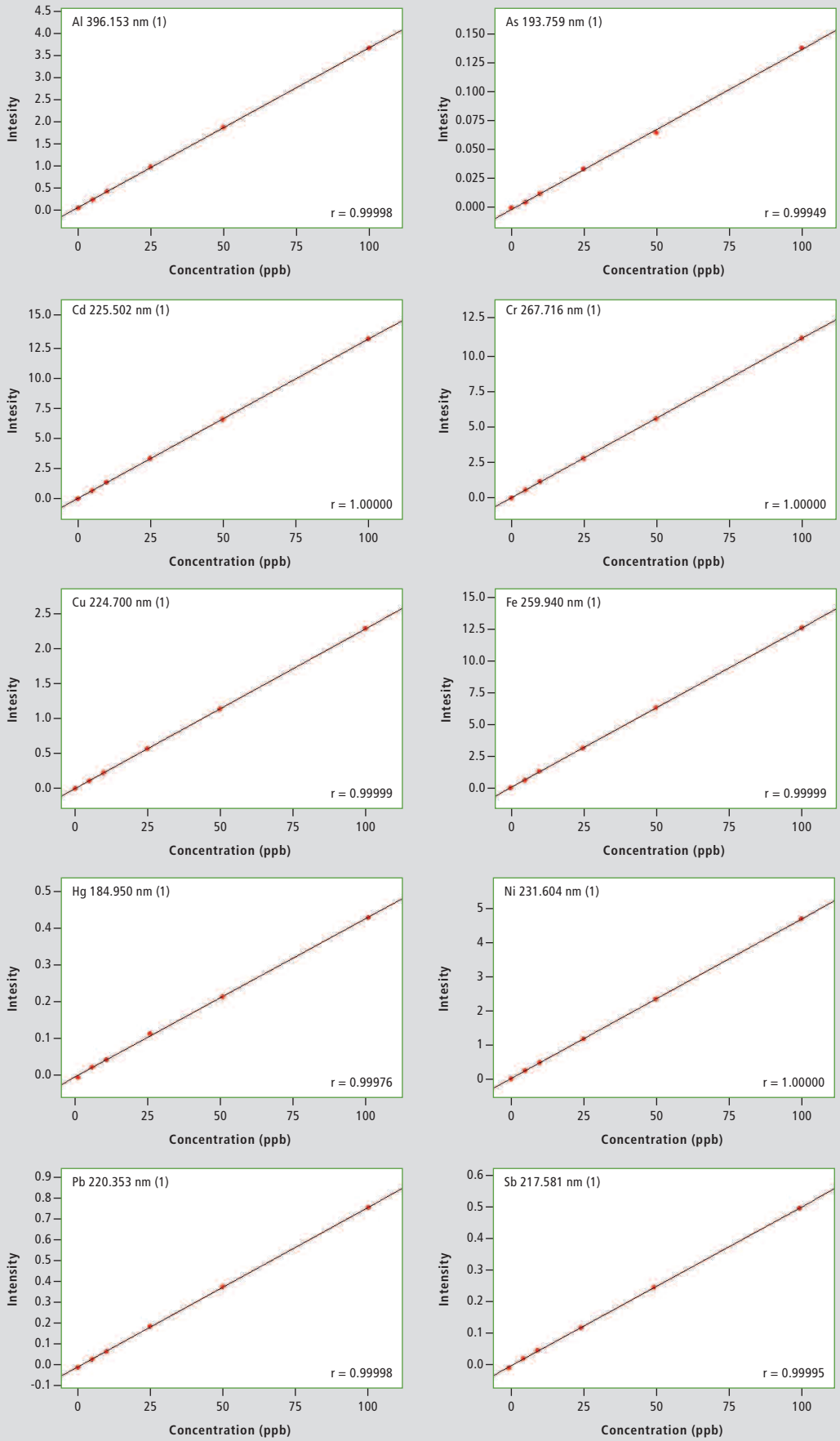

Figure 2: Calibration curves of metals obtained by ICPE-9820

Sample	E-liquid, nicotine content 18 mg/mL	E-vapor, nicotine content 18 mg/mL
Element	Metal quantity (µg/L)	Metal quantity (µg/10 puff)
Al	142.00	0.015
As	ND	ND
Cd	24.05	0.003
Cr	16.55	0.001
Cu	77.00	0.008
Fe	162.50	0.053
Hg	ND	ND
Ni	51.00	0.004
Pb	ND	0.002
Sb	ND	ND

Table 2: Selection of results for metals quantitation by ICPE-9820;
ND (not detected)

high sensitivity and high sample throughput.

ICPE-9820 is equipped with vacuum high performance optics and uses a 1024 x 1024 pixel CCD (Charge Coupled Device) detector.

This system allows simultaneous acquisition of spectral data over the entire wavelength range from 167 nm to 800 nm; all element information and wavelengths are available to users without the need for any additional measurement. Because of the ICPE-9820's sophisticated vacuum technology, purging is no longer required, thus completely eliminating any additional operating cost such as argon consumption.

Sample Preparation

Because of the high viscosity and the organic matrix, e-liquids samples were diluted and measurement was conducted using the calibration curve method with an internal standard.

0.5 g of e-liquid sample is weighed and filled up to 25 mL with 2 % nitric acid, with addition of 50 µL of 50 ppm yttrium as an internal standard. The aliquot is analyzed by ICPE-9820 with low-flow mini-torch, reducing plasma gas consumption to 10 L/min and less.

For metal emission analysis of e-cigarettes, the resulting aerosol is collected by an LM4E smoking machine with electrostatic precipitation, customized for e-cigarettes, which models human puffing behavior.

E-cigarettes were puffed based on the CORESTA recommended method N° 81 with the following puffing regime: 55 mL puff volume, three second puff duration, 30 seconds puff interval and a rectangular wave puff profile.

Electrostatic precipitate is washed twice with 2 % nitric acid to obtain a total volume of 25 mL. Internal standard is added as well. The aliquot is analyzed by ICPE-9820 under the measurement conditions listed in table 1 (page 19).

Results

After building calibration curves over six concentration levels, analytical quantitative determination is performed for aluminum, arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead and antimony. This approach targets all metals likely to be found in e-liquids and in the aerosols of most e-cigarettes.

Figure 1 shows all calibration curves using multi-element standards from 5 µg/L to 100 µg/L, which yielded excellent linearity for simultaneous ICP-OES. Many e-liquids were tested with different nicotine strengths.

Table 2 shows selected results for metal quantity in e-liquid and e-vapor at high nicotine strength (18 mg/mL). Metal quantities for a given e-liquid are all within previous reported data and the maximum concentration defined by the AFNOR standard.

Conclusion

The ICPE-9820 is ideally suited to implementation of the TPD, providing users with a simple and reliable metal analysis in a single run in just a few minutes.

Also, the mini-torch and vacuum optics ensure that operating costs remain at a minimum level. E-liquids manufacturers need to improve quality control of the products in order to protect consumers from potential adverse effects. Further investigations using this analytical technique should provide more information on emissions tests related to material composition of the e-cigarettes.

ELDA Ltd. is the leading manufacturer of e-liquids for electronic cigarettes in Europe. Together with his co-owner, Dario Marenić, President of the Managing Board of the company, started his vision by finding the highest quality and rich aromas, and designing and creating formulas that have become the best recipes in the world.

In 2016, ELDA won numerous awards: At the VaporFair exhibition in Frankfurt, Germany, ELDA was the proud bearer of awards for the best vapor product; at the Expovape fair in Madrid, Spain, they were also awarded for the most innovative product of the entire e-liquid industry; the Vape Expo in Moscow, Russia awarded them for the best European e-liquid. With these awards, recognition has been granted for the best e-liquid manufacturer in the entire industry. Also in 2016, the company opened a new production facility and laboratory for complete analysis of e-liquid and electronic cigarettes on the basis of which they ensure, in cooperation with Shimadzu, fulfillment of the high criteria of the new TPD legislation.

According to ELDA, there has been no legislation of e-cigarettes for a long time. "It is good that this market is becoming more regulated. Because we have an ICPE-9820 among other Shimadzu instruments, we are happy that we can use reliable instruments to gather information on elemental impurities in the e-liquids and emissions tests for the purpose of quality control, with the desire to protect our end users."

Boosts productivity

The LCMS-8045 workhorse system with key features of UFMS to improve throughput

Figure 1: Combination of Shimadzu Nexera with LCMS-8045

The LCMS-8045 triple quadrupole mass spectrometer is the new member of the well renowned UFMS (Ultra-Fast Mass Spectrometry) range. It is based on the UFMS platform with Heated ESI, fast polarity switching and fast scanning speed. The LCMS-8045 addresses laboratories performing demanding routine quantitative analyses, e.g. in food safety, environmental testing and analytes in clinical samples. The system offers an optimum balance in sensitivity, robustness and cost-effectiveness.

The LCMS-8045 features a modified ion sampling device and collision cell technology, resulting in greater efficiency and high quantitative accuracy and reliability. In addition, the ion source features a cable-less, tubeless housing, and the desolvation capillary can be replaced without breaking vacuum. This leads to increased durability, easier maintenance and a lower total cost of ownership.

Higher throughput even for the most demanding matrices

As part of the Shimadzu Ultra-Fast Mass Spectrometer series, the LCMS-8045 features an array of ultra-fast technologies.

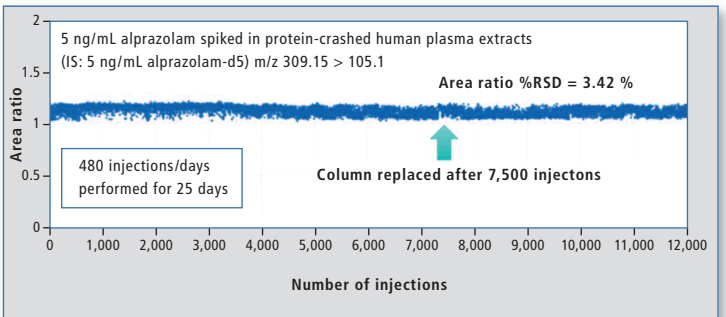

Figure 2: LCMS-8045 instrument stability test

These include a unique scan speed of 30,000 u/sec without the loss of mass accuracy, and a polarity switching time of 5 msec, which ensures higher throughput and highly reproducible data even for the most demanding matrices.

The LCMS-8045 is operated using Shimadzu's LabSolutions software platform, either in standalone mode or in a client/server environment. It is an intuitive package that enables simplified instrument control, diverse data handling and integration with regulatory compliance requirements like FDA 21 CFR part 11.

Numerous options are available to address specific customer requirements, for example application-specific method packages (lipids mediators, pesticides, veterinary products ...), libraries and open-access quantitative analysis software.

In case new challenges or applications requiring higher sensitivity arise, the LCMS-8045 can be upgraded to the high-sensitivity LCMS-8060.

Analyses around the clock

The new LCMS-8045 constitutes the heart of the successful UFMS range and provides a very cost-effective solution for all routine applications laboratories.

The LCMS-8045 is the workhorse instrument in the Shimadzu LC-MS/MS lineup, designed to analyze samples around the clock. The heated ESI probe, high-temperature heating block, heated desolvation line, drying gas and focusing optics all act to maximize sensitivity while minimizing contamination.

This means continuous operation in the laboratory with reliable data collection, even for complex matrices like biological fluids or foods.

Further information on this article:

- www.shimadzu.eu/lcms-8045

Arsenic in Beer?

Determination of heavy metals in beer using ICP-MS spectrometry

Figure 1: ICPMS-2030

Beer is probably one of the oldest alcoholic drinks in the world. In fact, Chinese and Egyptians already made beer in 4000 years BC. In Europe, beer was the Celts' famous beverage throughout the ancient times.

In order to assure standards regarding quality, freshness, appearance and flavor, much regulation exists in Europe since the early XVIth century ("Reinheitsgebot" in 1516 in Germany; royal decree of 1495 in France ...). Louis Pasteur, one of the most famous 19th century scientist, started his career by researching beer process improvement. Nowadays, with wide interest in the diversity and variety of beers, more than 6,500 breweries exist in Europe.

The quality standards for beer analysis are defined by the Central European Commission for Brewing Analysis (MEBAK) and the European Brewery Convention (EBC), representing technical and scientific interests of the brewing sector in European countries. These regulations include the determination of numerous elements (e.g. Arsenic (As), Calcium (Ca), Copper (Cu), Sodium (Na), Potassium (K) ...), anions (such as nitrate and sulfite) as well as organic components (ethanol, glycerine) and others (pesticide residues) [1]. In order to maintain the highest level of quality, some chemical investigations have to be performed, using different analytical techniques to quantify all the potential contaminants.

Constant control of beer

Nowadays, the health effects of trace elements and the maximum concentration of trace elements in beers are controlled continuously. Determination of trace metals in beers is relevant as they may be essential or toxic in the human body, and also have an influence on the brewing process. The element distribution, however, shows significant differences based on the natural sources of soil, water, cereal, hops and yeast as well as anthropogenic sources such as environmental pollution and agricultural treatment by fertilizers, pesticides and fungicides.

Metal content in beer

Last but not least, the metal content in beer can be influenced dur-

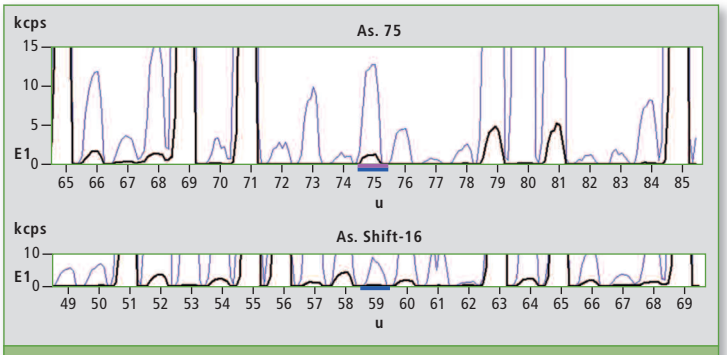

Figure 2: Development Assistant window in LabSolutions ICP-MS software for ^{75}As in beer sample. Dark curve corresponds to DBG mode and blue to DBN measurement mode.

ing production, beer processing, conservation and bottling. This influence is greater than expected because during the beer-making process both raw and processed products are often in long contact with materials such as stainless steel, copper, glass and other equipment.

The determination of copper is important because high concentrations are disadvantageous to the colloidal stability and taste of the beer. The same goes for zinc, which is an essential trace element for yeast that influences metabolic processes such as protein synthesis and nucleic acid metabolism. Typical concentration levels of copper and zinc in beer are 0.2 mg/L [2].

Furthermore, the determination of arsenic, antimony, cadmium and lead is important because these elements are toxic when present in beer or the brewing water.

The source of these elements in beer and other alcoholic beverages could be the contamination of raw material or technological processes.

Arsenic released by Kieselguhr filtering material

Arsenic is released into beer from a filtering material called Kieselguhr, or diatomaceous earth, which is used to remove yeast, hops and other particles and give the beer a crystal clear appearance. Diatomaceous earth consists of fossilized remains of diatoms, a type of hard-shelled algae that lived millions of years ago.

Diatomaceous earth finds wide use in filtering of beer and wine, and is an ingredient in other products as discussed by Professor Mehmet Coelhan from the Research Center Weihenstephan for Brewing and Food Quality [3].

For simultaneous quantitative determination of the inorganic elements in beer, ICP-MS is the most preferable tool for quality control because of its high sensitivity (trace detection), wide dynamic range and high sample throughput. The Shimadzu ICPMS-2030 is an easy to operate and fast system meeting these requirements.

Furthermore due to the unique Eco-Mode associated with Minitorch, ICPMS-2030 can drastically reduce running costs by as much as half.

The octopole collision cell assures high accuracy for all measurements of elements. Using helium gas and Kinetic Energy Discrimination principle (KED), this cell suppresses most of the spectroscopic interferences (polyatomic interferences).

The efficiency of suppression of interferences and enhancement of sensitivity is improved by a cooled cyclonic chamber and well controlled torch positioning.

Parameter	Setting
RF generater power	1.2 kW
Plasma gas	8 L/min
Auxilliary gas	1.1 L/min
Carrier gas	0.7 L/min
Nebulizer type	MicroMist
Sampling depth	5 mm
Spray chamber temperature	5 °C
Coll. cell gas flow (He) DBG mode only	6 mL/min
Quantified isotopes	^{75}As, ^{111}Cd, ^{65}Cu, ^{202}Hg, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{66}Zn
International standards (ISTD)	^{69}Ga, ^{71}Ga, ^{115}In, ^{205}Tl

Table 1: ICPMS-2030 measurement parameters

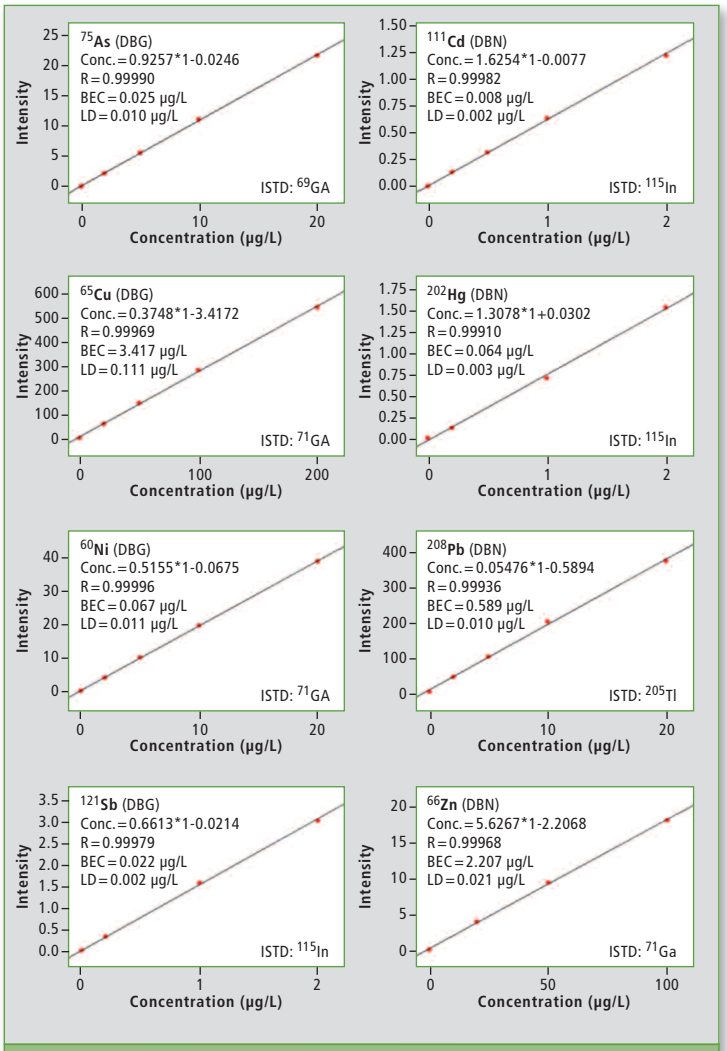

Figure 3: Calibration curves obtained using 1 % HNO_3 and 5 % EtOH. DBN analysis are made without gas in collision cell. DBG analysis are purged with He gas in collision cell (KED).

Element	Beer 1	Beer 2	Beer 3	Beer 4	Beer 5
^{75}As	2.05	3.49	2.39	1.46	0.39
^{111}Cd	0.07	0.05	0.07	0.08	0.15
^{65}Cu	29.10	28.70	40.50	38.20	22.40
^{60}Ni	2.25	5.62	1.53	2.58	4.47
^{208}Pb	—	—	> LQ	—	—
^{121}Sb	0.39	0.19	2.15	0.45	0.55
^{66}Zn	5.28	23.90	5.04	2.83	29.20

Table 2: ICPMS-2030 results for each beer sample [µg/L]

Moreover, ICPMS-2030 is able to save all mass issued from sample measurement. The development assistant of LabSolutions ICP-MS software can propose the optimum parameters for each element in the sample. Method development has never been easier and faster.

Experimental setup on ICPMS-2030

In the experimental work, five commercially available beers were evaluated: St. Bernardus Abt 12 from Belgium, and Becks Gold, König Pilsener, Erdinger and Bitburger Pils, all originating from Germany.

Thanks to the ICPMS-2030 system, analysis of beer could be performed without any sample preparation. All analyzed samples were degassed using only ultrasound. After this treatment, they were aspirated directly to the ICPMS-2030.

Eight different elements were quantified simultaneously: As, Cd, Cu, Hg, Ni, Pb, Sb and Zn. Analytical measurements conditions are summarized in table 1 (page 23).

For each element studied, calibration curves include five points in the concentration range from 0.1 to 200 µg/L in a matrix-matched solution using 1 % nitric acid and 5 % ethanol.

Beer samples were measured in triplicate, and three of them were measured as quality control samples (Becks, König and St. Bernardus), spiked with 0.5 ppb, 5 ppb or 50 ppb resp., depending on the element concentration.

An internal standard solution in 1 % nitric acid (^{69}Ga, ^{71}Ga, ^{115}In, ^{205}Tl) was mixed online with sample, before being aspirated in the nebulizer.

As shown in figure 3 (page 23), all correlation coefficients r achieve a 0.999 level. Moreover, low values of detection limits (LD), calculated automatically by LabSolution ICP-MS software with 3σ method, indicate the high suitability and ability of ICPMS-2030 for trace contaminant analysis. For each beer, results are summarized in table 2.

The quantitation results in table 2 demonstrate that ICPMS-2030 is able to simultaneously quantify the various elements present in beer samples.

In order to determine the method accuracy, three of five beer samples were spiked with each element (0.5 ppb, 5 ppb or 50 ppb). Results are shown in table 3 and calculated according to:

$$\text{Recovery (\%)} = \frac{\text{Value after spike} - \text{Initial value}}{\text{Initial value}} \times 100$$

Conclusion

Beer is one of the favorite alcoholic beverages in European countries with a statistical per capita consumption of around 68 L.

Quality is therefore expected to be high and continuous quality control is essential. However, beer may contain a variety of heavy metals such as arsenic, lead and cadmium at low levels.

High-sensitivity analytical tools such as the ICP-MS are best suited to detect these low level contaminants to permanently ensure the highest quality of beer.

Sample	Recovery rate (%)		
	Beer 1	Beer 2	Beer 5
^{75}As	100[1]	97[1]	109[1]
^{111}Cd	113[2]	101[2]	92[2]
^{65}Cu	99[3]	82[3]	92[3]
^{60}Ni	84[1]	95[1]	85[1]
^{208}Pb	95[1]	92[1]	99[1]
^{121}Sb	84[2]	87[2]	94[2]
^{66}Zn	92[3]	98[3]	97[3]

Table 3: Spike-Recovery rates in beer: 1 spike of 5 ppb. 2 spike of 0.5 ppb. 3 spike of 50 ppb.

Literature

[1] Pfenninger, H.: Brautechnische Analysenmethoden (1996)

[2] J.S. Hough et al., Malting and Brewing Science (Springer US, 1982).

[3] M. Coelhan et al., Am. Chem. Soc. "Widely Used Filtering Material Adds Arsenic to Beers" (2013), https://www.acs.org/content/acs/en/pressroom/newsreleases/2013/april/widely-used-filtering-material-adds-arsenic-to-beers.html

Safety of people in modern transport

One metal shaving, and five minutes are enough

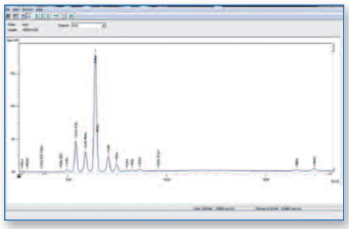

Figure 3: EDX spectrum of GH2036 shaving

Figure 1: EDX-7000P/8000P

Timely diagnosis of engine wear is key to safety of people using aircraft, automobiles or railway trains. Analysis of engine oils is one of the main types of such applications.

Engine oils contain fine wear products as well as particles of metals and alloys in the form of shavings. Elemental analysis of such pieces permits determination of the engine part wearing out, and measurement of concentrations of main alloy/steel components in oil helps to estimate the degree of wear of that part.

Testing laboratories of many major airlines use X-ray fluorescence spectrometers for fast analysis of small metal shavings. Energy dispersive X-ray fluorescence spectrometers such as Shimadzu's EDX-7000P/8000P (figure 1) are suitable tools for such analysis.

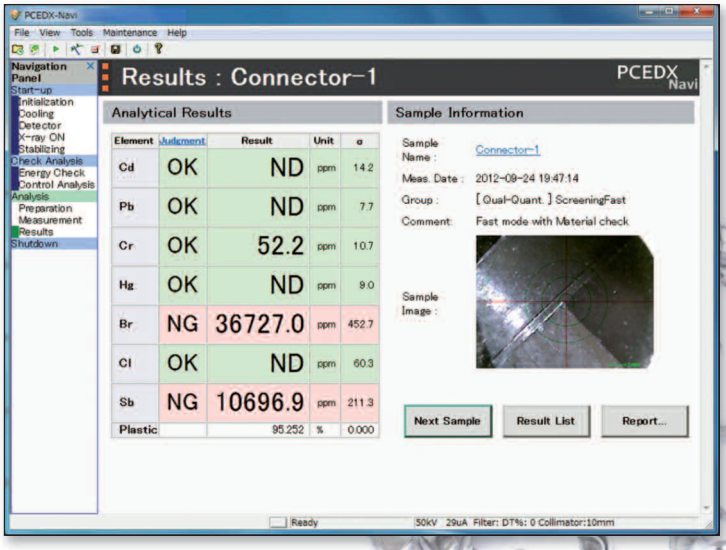

Figure 2: Sample display screen in PCEDX Navi

The EDX-7000P and EDX-8000P instruments are BfS (safety standards of the German Federal Institute for Safety) type approval certified.

Both spectrometers are equipped with an automatic collimator switching system and a sample observation camera for local analysis and small sample measurements. Advanced PCEDX Navi software is specially designed for less experienced users.

Standardless quantitative fast analysis of small metal particles

Can the EDX-7000P/8000P spectrometers be used successfully for standardless quantitative fast analysis of small metal particles? In an experiment, measurement of one stainless steel shaving by EDX-8000P was performed to estimate the capabilities of EDX spectrometers for standardless quantitative elemental analysis of metal microparticles by Fundamental Parameters (FP) method. Stainless steel is used in the production of valves for aircraft, automobile and tractor diesel engines and fastenings for engines.

One shaving of stainless steel GH2036 (China) in the native form was placed in the center of the sample compartment (figure 2). A collimator of 1 mm diameter was selected for the analysis. A routine measurement procedure of unknown sample by FP method was used, as included in the standard spectrometer software. The spectrum of the sample is shown in figure 3.

Total analysis time including placement of the sample in the cell was less than five minutes.

Element	Concentration, wt %	
	Quantitation value	Certified value
Cr	12.84	12.87
Mn	8.156	8.23
Ni	7.65	7.85
V	1.369	1.39
Nb	0.49	0.49
Mo	1.097	1.14

Table 1: Quantitative Value of GH2036 sample by FP Method

Conclusion

Results of the analysis are shown in table 1. The results show an excellent match of quantitation and certified values.

The analysis results show that the EDX-7000P/8000P can be used successfully for standardless quantitative fast analysis of small metal particles without any sample preparation.

On the safe side with MCERTS accreditation

Online TOC-4200 reveals its strengths during field tests

TOC-4200

Shimadzu's online TOC-4200 analyzer has been granted MCERTS accreditation based on the performance standards and test procedures set for continuous water monitoring equipment.

MCERTS is the certification system of the Environmental Agency of England and Wales (UK) for measurement equipment. It provides the framework conditions and quality objectives for companies to meet in order to comply with the authority requirements for environmental monitoring.

MCERTS is quickly becoming a required performance and reliability standard by organizations around the world. With accredited equipment, companies and authorities ensure that they are doing everything possible to protect their environment. Requirements for obtaining this certification include laboratory testing and a 3-month field test under real conditions.

TOC-4200

The TOC-4200 is a powerful analyzer that is operated under catalytic combustion at 680 °C. The analyzer removes the inorganic carbon content automatically from the sample and subsequently injects an aliquot onto a 680 °C hot platinum catalyst where all organic compounds are oxidized to carbon dioxide.

The resulting CO_2 is transferred by a carrier gas stream to a highly sensitive and CO_2-selective NDIR detector where it is measured. The TOC concentration is calculated using an external calibration. The integrated dilution function allows TOC analyses up to 20,000 mg/L. In addition, it allows automated dilution of the sample when the measurement range is exceeded.

The automated dilution as well as the self-calibration functions and

Test point	1	2	3	4	5
Ref. value (ppm)	5	25	50	75	100
Measurement 1	4.89	24.33	49.65	75.77	101
Measurement 2	5.01	24.71	50.15	75.19	99.57
Measurement 3	4.9	24.75	49.57	75.34	100.7
Measurement 4	4.95	24.69	49.57	74.86	101.3
Measurement 5	4.94	24.35	50.03	76.1	99.24
Measurement 6	4.95	24.25	49.16	74.13	101.5
Mean value	4.94	24.51	49.69	75.23	100.55

Table 1: Results for the measurement range 0 - 100 mg/L

the optimized sampling allow a virtually independent operation of the measurement system.

Numerous alarm and status signals simplify the detection of exceeded limit values or the need for maintenance. In addition to the conventional options, Modbus communication is also available. An optional web browser enables a "view" of the instrument from any networked computer.

Laboratory tests

The TOC-4200 performance data, such as the mean measurement error, linearity and reproducibility were determined in laboratory tests. For this purpose, the TOC-4200 was installed in the laboratory and calibrated as a function of the measurement ranges. Subsequently, five measurement points were measured six times each: 10, 25, 50, 75 and 100 % of the respective measurement range.

Mean deviation

For the determination of the mean measurement deviation, the mean deviation from the reference value was calculated for each measurement point. The highest value is listed in the certification report. To pass the test, this value must be less than 10 %.

The mean deviation for the measurement range 0 - 100 mg/L is 1.99 %. The test for this range was therefore passed. For the linearity determination, a linear plot was determined from the mean values of the measurement points. The deviation of the measured data from the straight line was subsequently calculated in %. The maximum value may not exceed 5 %.

Linearity

For the measurement range 0 - 100 mg/L, the linearity is -2.23 %, which meets the test requirements for this range. For the reproducibility, the standard deviation and the relative standard deviation were calculated from the measured data of each measurement point. Again, the highest value may not exceed 5 %.

Reproducibility

The reproducibility for the 0 - 100 mg/L measurement range is 0.93 %. The test for this range was therefore passed. Measurements were also carried out for the measurement ranges 0 - 500 mg/L, 0 - 1.000 mg/L and 0 - 10,000 mg/L. All values obtained were below the specified limits. In addition, data were obtained to determine drift, matrix influence and response time.

Field test

For the field test, data collected over three months from a customer installation in a wastewater application (measurement range 0 to 100 mg/L) was evaluated. Particular attention was paid to operating time and downtime. Downtime includes time for calibration, maintenance, service and troubleshooting. The resulting availability should be higher than 95 %. The TOC-4200 reached 100 %.

Conclusion – unique TOC on the market

The TOC-4200 achieved a 100 % availability in the field test, highlighting its robustness and reliability. It is the only online TOC analyzer utilizing catalytic combustion oxidation available on the market with MCERTS accreditation. This technology offers a clear advantage for anyone involved in the analysis of water and wastewater with a high salt content, solids or suspended matter as well as complex organic compounds.

The certificate (MC160311/00) was issued for the TOC measurement ranges 0 - 100, 0 - 500, 0 - 1.000 and 0 - 10,000 mg/L.

Test point	1	2	3	4	5
Ref. value (ppm)	5	25	50	75	100
Run 1	-2.25	-2.75	-0.70	1.02	0.99
Run 2	0.20	-1.17	0.30	0.25	-0.43
Run 3	-2.04	-1.01	-0.87	0.45	0.70
Run 4	-1.01	-1.26	-0.87	-0.19	1.28
Run 5	-1.21	-2.67	0.06	1.45	-0.77
Run 6	-1.01	-3.09	-1.71	-1.17	1.48
Mean Error (%)	**-1.22**	**-1.99**	**-0.63**	**0.30**	**0.54**

Table 2: Mean error in %

Test point	1	2	3	4	5
Ref. value (ppm)	5	25	50	75	100
Mean value	4.94	24.51	49.69	75.23	100.55
Value of the linear regression line	5.012	25.06	50.12	75.18	100.24
Deviation	-0.07	-0.55	-0.43	0.05	0.31
Deviation in %	**-1.46**	**-2.23**	**-0.87**	**0.07**	**0.31**

Table 3: Linearity

Reproducibility					
Test Point	1	2	3	4	5
Standard deviation	0.043	0.226	0.357	0.694	0.935
Relative STD	**0.87**	**0.92**	**0.72**	**0.92**	**0.93**

Table 4: Reproducibility

Further information on this article:

- Product Conformity Certificate: MC160311/00

Literature

www.csagroupuk.org/wp-content/uploads/2017/02/MCERTSCertifiedProductsCWMSPart2.pdf

New solutions for tomorrow

Launch of Shimadzu European Innovation Center

Figure 1: Dr. Teruhisa Ueda (r./CEO Shimadzu Corporation) and Dr. Hiroki Nakajima (Chief of European Innovation Center) are painting the traditional „Daruma."

In early March, Shimadzu opened its European Innovation Center. In presence of Dr. Teruhisa Ueda, President and CEO of Shimadzu Corporation, Duisburg's Mayor Sören Link, Yasunori Yamamoto, CEO Shimadzu Europa, Japanese Consul Ryuta Mizuuchi, and Shuzo Maruyama, General Manager Analytical & Measuring Instruments Division, Shimadzu Corp., cut the tape.

In addition, a Daruma mask was painted in a Japanese ceremony to bring happiness and success. Numerous opinion leaders, thought leaders and experts from markets and science were invited as guests.

Shimadzu's European Innovation Center innovations-oriented is a Think Tank combining scientific and technological know-how in order to use Shimadzu's expertise to provide even more customer-focused service. It applies a decentralized structure to be in close local proximity to scientists and related markets. This provides direct access to the users as well as to projects and samples.

Clinical applications, imaging technology, food, and composites

With their leading-edge research expertise, highly-reputed scientists from well-known European universities cover the academic part of the Shimadzu European Innovation Center. For years, they have cooperated with Shimadzu in various projects. Their scientific focus areas include clinical applications, imaging technology, food, and composites, with an emphasis on new methods, tools, techniques, diagnostics, and solutions. Their work will, for example, further facilitate will help to increase analytical and medical-diagnostic research with focus on patients' health as well as consumer and environmental protection.

Innovations-oriented exploration of four perspectives

With regard to clinical, imaging, food, and composites, the Shimadzu European Innovation Center explores four focus areas:

- Trends & Demands: based on European needs and demands
- Adaptation & Development, i.e. special accessories and jigs, adaptations, special software, new and special methods
- Compliance to European regulations, such as official regulations and standards, and local rules for limits of hazardous substances
- Strong cooperation: between Shimadzu's Innovation Centers and Shimadzu's R&D team in Japan, developing global solutions based on global needs.

Analyzers involved in the European scientists' research projects in particular include chromatography, mass spectrometry, and material testing.

So far, other Shimadzu Innovation Centers are located in Maryland, USA, Singapore and Beijing, China where they serve as drivers of joint research and new product developments.

Shimadzu live

EBC European Brewery Convention	Euromedlab	CSI Conference
Ljubjana, Slovenia Mai 10 - 18, 2017 www.ebc2017.com	Athens, Greece June 11 - 15, 2017 www.athens2017.org	Pisa, Italy June 11 - 16, 2017 www.csi-conference.org
GAS Analysis	**HPLC**	**Automotive testing expo**
Rotterdam, Netherlands June 13 - 15, 2017 www.gasanalysisevent.com	Prague, Czech Republic June 18 - 22, 2017 www.hplc2017-prague.org	Stuttgart, Germany June 20 - 22, 2017 www.testing-expo.com/europe

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