

**PAHs: simple analysis with
high detection limits**

Determination of PAHs or mineral
oils in water using fluorescence
spectroscopy

**Higher safety for avionics and
automotive**

Very high cycle fatigue assessment
of laser additive manufactured parts

»This car really smells new«

Emissions testing of motor vehicle
interiors



APPLICATION

Higher safety for avionics and automotive – Very high cycle fatigue assessment of laser additive manufactured parts 4

»This car really smells new« – Emissions testing of motor vehicle interiors 6

Drug residues in surface waters – New fast LC-MS/MS method using the LCMS-8060 8

PAHs: simple analysis with high detection limits – Determination of PAHs or mineral oils in water using fluorescence spectroscopy according to ASTM D 5412 12

Paper clip fashion show – Color control in the production of coated metal paper clips 16

Tracing contaminants in polymeric kitchen utensils – Evidence of WEEE relevant substances in polymeric food-contact articles 18

How healthy is beer? The German Beer Purity Law of 1516 22

Extra virgin olive oil: genuine or fake? – Reveal adulteration through FTIR spectroscopy 24

LATEST NEWS

How clean is clean? Cleaning validation in the food industry 2

25 years Technical Offices in Jena and Berlin, Germany 11

58 real life applications on food quality and food safety 14

Materials testing goes extreme – New HPV-X2 ultra-high-speed camera 21

Small explorers in the laboratory – Elementary school students playfully explore the world of analysis 27

How clean is clean?

Cleaning validation in the food industry



For decades, cleaning validation has been an established method in the pharmaceutical industry. It refers to the effective cleaning of pharmaceutical production equipment such as reactors or fermenters. Cleaning validation is also applied increasingly in production and processing in the food industry.

Drugs are often manufactured in discontinuous production processes. As soon as a batch of the active ingredient is sent to processing, the production equipment used is already being cleaned so that the next batch can be produced. The actual cleaning process is very strictly specified and is subsequently validated analytical-

ly, whereby a sample from the production equipment is analyzed for specific parameters. As long as a specific limit value is not exceeded, the production equipment is considered to be clean and can be used again. This process is called cleaning validation.

There is also great interest in cleaning validation of equipment used in the production or processing of foods in the food industry. The IFS Food (International Featured Standards for the assessment of food quality and safety), for instance, requires validation of the effectiveness of cleaning measures according to a specified sampling scheme using suitable methods [1].



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But what are these suitable methods?

Single-substance analysis is widely practiced in the pharmaceutical industry. For instance, it is possible to analyze a particular active substance in rinsing water. However, various sum parameters, such as electrical conductivity or TOC, are established as well.

The TOC (Total Organic Carbon) can detect all the carbon present in organic compounds in one single analysis and is, therefore, particularly suitable for the determination of contamination by organic compounds.

Different methods are used for TOC analysis. In most widely used methods, the sample is first treated with acid in order to eliminate inorganic compounds such as carbonates and hydrogen carbonates. These are converted to CO₂ and are then purged using a sparging gas. Subsequently, an aliquot of the sample is injected onto a hot platinum catalyst. The organic substances are oxidized into CO₂ and transferred via a carrier gas to an NDIR detector where they are detected.

Single-substance analysis versus TOC

Compared to the more complex single-substance analysis, TOC determination for cleaning validation has several advantages. TOC determination is quick and simple; it takes just a few minutes. In addition, no lengthy sample preparation is required. All that is needed is a TOC analyzer and only small amounts of a 1-molar hydrochloric acid solution.

Furthermore, TOC analysis not only detects an individual compound but a multitude of compounds and is, therefore, product-independent and highly flexible. When different products are being manufactured by one company or in one production system, TOC determination can be carried out for all products as long as they contain organic compounds. Foods are generally not considered as pure substances but to contain different organic compounds such as carbohydrates,

fats or proteins. TOC analysis also detects surfactants that are used for cleaning, next to the actual product.

Proven methods for production equipment validation

Two sampling methods for production equipment validation have become established:

- direct sampling and
- indirect sampling.

Direct sampling is carried out using the swab test. This involves careful wiping of a defined, accu-

ical areas. Due to the generally small extraction volume, lower detection limits can be achieved, compared to the final-rinse method with which a considerably larger area of the production equipment can be evaluated. TOC determination via the swab method is more time-consuming and is only used for smaller parts of the entire production system.

In the indirect sampling method, a final rinse with water is carried out after cleaning. This final rinse water is subsequently analyzed. The advantage of the final-rinse

Two methods, one analyzer

Rinsing water and swab extracts can be examined using a TOC analyzer. Modern analyzers such as Shimadzu's TOC-L series automatically take over sample preparation (acidification and sparging). For high sample throughputs, sample preparation can already be carried out in the autosampler, saving much time. The systems are equipped with a highly effective platinum catalyst operating at a combustion temperature of 680 °C. A special syringe unit enables automated dilution of the samples when the calibration range is exceeded. Standards are also diluted automatically to create calibration curves in equidistant concentration intervals.

However, cleaning validation via TOC determination also has limitations. It is only useful if the organic compounds are water-soluble. The use of organic solvents, for instance to dissolve lipophilic compounds (such as fats) is excluded by definition. Here, a diluted sodium hydroxide solution is used in a limited number of cases.

In addition to the food industry, cleaning validation is also important in other industries such as in the production of cosmetics or cleaning agents. Especially in contract manufacturing, such as in the production of private brands or for contract manufacturing in the field of crop protection products, cleaning validation can be an invaluable tool for quality control.

Read for you

'Nachrichten aus der Chemie' 9/2015

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TOC-L

rately measured surface of the production equipment using a swab. The swab is subsequently extracted in a vial containing ultrapure water. The extract is analyzed for its TOC content. In swab analysis, the results are usually expressed in mg/cm².

The advantage of the swab method is the very accurate examination of small and particularly crit-

ical areas. Due to the generally small extraction volume, lower detection limits can be achieved, compared to the final-rinse method with which a considerably larger area of the production equipment can be evaluated. TOC determination via the swab method is more time-consuming and is only used for smaller parts of the entire production system.

In practice, a combination of the swab method and the final-rinse method is mostly used in cleaning validation. In this way, the entire production system as well as specific critical areas can be analyzed with the highest possible sensitivity.

Higher safety for avionics and automotive

Very high cycle fatigue (VHCF) assessment of laser additive manufactured (LAM) parts



Figure 1: Overview of the Shimadzu ultrasonic fatigue testing system USF-2000

Selective laser melting (SLM) is a laser additive manufacturing process where parts are additively manufactured using powder material with the aid of laser energy. A three-dimensional CAD model is provided as an input to the SLM machine which scans the geometry after slicing it into 2D layers. The laser energy selectively melts the powder particles at the desired location of the component to be manufactured.

The unique manufacturing capability of SLM process makes it suitable for aerospace, automotive and biomedical applications. Several alloys like aluminum, titanium, steel and nickel-based alloys have been processed by SLM technique [1,2]. Although the fatigue strength diminishes for SLM processed materials in the “as-built” condition due to the process-inherent surface roughness, fatigue performance after post-pro-

cessing is suitable for many applications in the aviation and medical industry [1].

Contrary to the previous assumption that the materials do not fail under fatigue if the applied stress is below the so-called fatigue li-

mit; with the availability of the novel very high cycle fatigue (VHCF) testing techniques, it has been found that materials do fail under fatigue loading even when the stresses are below the conventional fatigue limit, suggesting the non-existence of such a limit

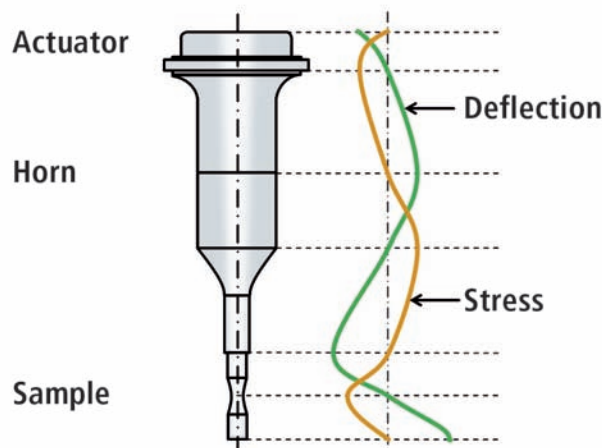


Figure 2: Functional principle of specimen loading at ultrasonic fatigue testing system USF-2000

[3, 4]. Some alloys of both lattice types, bcc (body-centered cubic) and fcc (face-centered cubic), show a change in crack initiation site from surface to subsurface in a region from HCF (high cycle fatigue) to VHCF [5].

Experimental methodology

The test samples of AlSi12 alloy were manufactured using a commercially available SLM system in an inert environment using argon gas. Details of the processing set-up and parameters can be viewed in [1].

Quasi-static tensile tests were carried out according to ISO 6892-1:2009. Continuous load increase tests were executed starting at low stress amplitude of 30 MPa. Stress amplitude was increased slowly at a rate of 10 MPa / 10^4 cycles. Load increase tests and constant amplitude tests were carried out at a frequency of 20 Hz. The results of process optimization, quasi-static properties, high cycle fatigue properties and the measurement methodology for characterization of process-induced defects are published in [2, 6].

Two types of configurations are investigated in this study. For batch I, no pre-heating of the base plate was applied; whereas samples of batch II were manufactured with base plate heating (BPH) at 200 °C.

Very high cycle fatigue (VHCF) tests were carried out on an ultrasonic fatigue testing system at a frequency of 20 kHz. Figure 1 shows an overview of Shimadzu's USF-2000 testing system while figure 2 explains the detailed principle of the test setup. A Piezo-electric crystal is used in the actu-

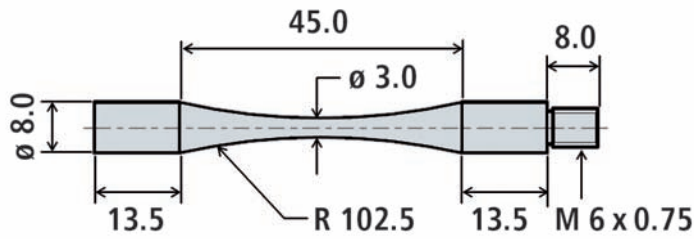


Figure 3: Specimen geometry for ultrasonic fatigue tests

ator which resonates at a fixed frequency of 20 kHz. In the ultrasonic fatigue testing system, vibrations are designed so that the longitudinal waves, transmitted through the solid body, resonate.

The specimen with geometry shown in figure 3 is clamped only at one threaded end on USF and is free at the bottom end. The specimen is designed so that maximum stress is experienced at its middle and the maximum displacement occurs at its free end. To eliminate the temperature effect due to high test frequency, the specimens were cooled with compressed air during tests, and the tests were performed at a pulse-pause ratio of 50:50, i.e. the system was set to resonate for 200 ms and then stopped for the next 200 ms to cool down.

Experiments for determination of the fatigue strength at 10^9 cycles were performed according to staircase method. If a specimen at ultrasonic frequency failed at less than 10^9 cycles, the stress amplitude is decreased by 5 MPa for the next experiment. If the specimen did not fail at 10^9 cycles, the stress amplitude is increased by 5 MPa in the subsequent test. Failure of the specimen is based on the change in resonance frequency. When the micro-crack leads to final fracture, the natural frequency of the system reduces the operating frequency of the system and the test is terminated.

Results

Figure 4 shows exemplary surface micrographs for the two batches investigated. The remnant porosity is viewed only as the gas porosity. A difference in the pore fraction of the samples without and with base plate heating is observed. In the samples with base plate heating, large size gas pores are absent which are very critical

in fatigue performance. The reduction of large pores is attributed to the de-gassing in the manufacturing chamber due to pre-heating.

Figure 5 represents S-N curves for batches I and II in the region from high cycle fatigue to very high cycle fatigue. Experiments showed that fatigue fracture occurs beyond high cycle fatigue region in

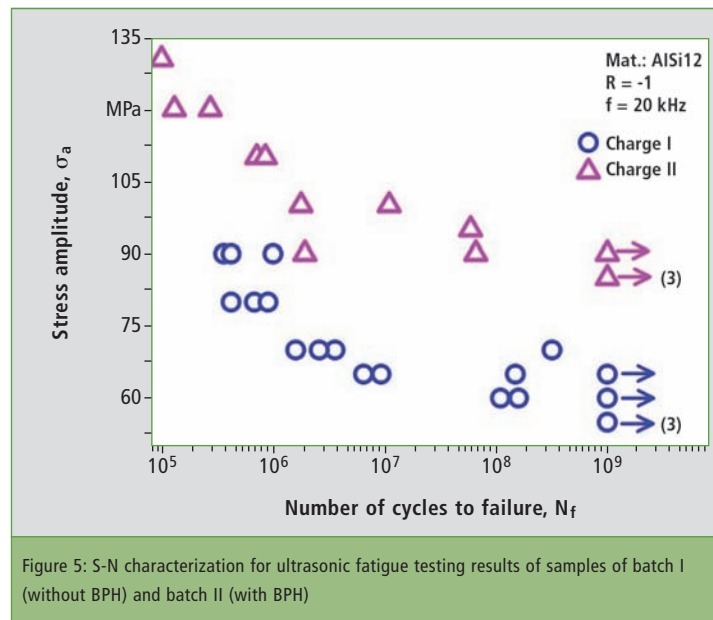


Figure 5: S-N characterization for ultrasonic fatigue testing results of samples of batch I (without BPH) and batch II (with BPH)

both the batches. The results of the experiments indicate that fatigue strength in very high cycle regime of samples manufactured with base plate heating is about 45 % higher than fatigue strength of sample without base plate heating. Fatigue strength at one giga cycle for batches I and II is 60.5 ± 4.7 MPa and 88.7 ± 3.3 MPa respectively. This increase in strength is attributed to elimination of the micro pores.

Outlook

New developments in testing machines enable going beyond previously known limits of knowledge. This opens the door to more in-

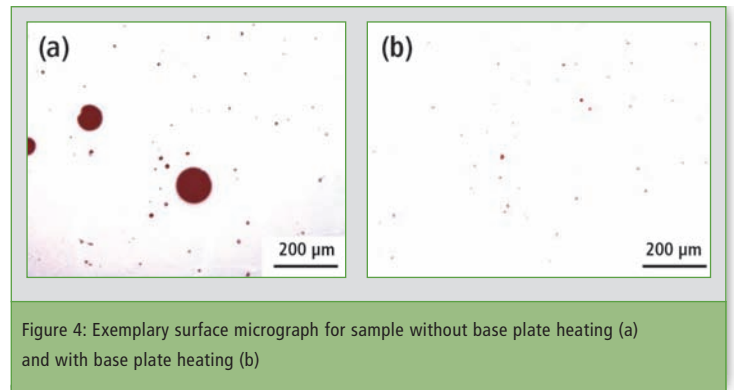


Figure 4: Exemplary surface micrograph for sample without base plate heating (a) and with base plate heating (b)

tensive testing in most realistic conditions. The new capabilities in testing machines provide researchers with powerful tools to further investigate the effect of processing parameters on resulting functional performances in a wide range.

processed by selective laser melting.

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»This car really smells new«

Emissions testing of motor vehicle interiors in accordance with VDA-278

Indoor air quality in new vehicles is an important topic for the automotive industry. More and more people spend increasing amounts of time in their cars. Others have been saving for a long time to make their dream of a new car come true. They can hardly wait to take their first ride in their dream car with that 'new

ted not only from the product surface into the air, but they can be resupplied slowly to the surface from the interior of the product via migration processes.

Due to the chemical diversity of VOCs, there is a wide range of harmful effects on human health. Some emissions may be carcino-

genic or cause nerve damage in high concentrations. Other emissions may 'just' be an odor nuisance. Adverse health effects that may occur include nose and throat irritations, coughing, headache – or more generally: flu-related and allergy-related reactions as well as skin irritations.

Quality assurance in accordance with VDA (German Association of the Automotive Industry)

Various analytical methods are available for investigating the

emission behavior of materials and components in car interiors. Although there is no uniform regulation, responsible governmental departments, automotive manufacturers and the large group of suppliers are interested in a worldwide harmonization of testing methods, also from financial aspects.

In Germany, car manufacturers place the highest demands on the materials used in their vehicles and they are increasingly demanding 'low emission synthetic materials' with low VOC and FOG values (the term FOG refers to less volatile compounds that have, for instance, precipitated in the form of a film onto the interior windscreen). To determine these values, the VDA-recommended VDA 278 standard (or GMW 15634) is the generally accepted reference method. Moreover, nearly every car manufacturer has its own additional, often stricter requirements for quality assurance at the highest level.

The VDA 278 standard includes the determination of volatile (VOC) and semi-volatile (FOG/SVOC) compounds in non-metallic materials that are used in molded components in motor vehicle interiors, such as textiles, floor carpeting, adhesives, sealing com-

pounds, foams, leather, plastic parts, films, lacquers or combinations of different materials, using coupled thermal desorption GC-MS analysis.

Thermal desorption GC-MS analysis

This technique features the determination of the sum parameters of VOC values (boiling range up to C25) and FOG values (boiling range from C14 to C32), as well as individual components and their concentrations, in a single method. During thermal desorption, a representative aliquot (usually 10–50 mg) of a sample is placed in a desorption tube and then heated. A helium stream is used to transfer the resulting gases into a cryo trap, where they are condensed and enriched. The condensed substances are rinsed from the cryo trap by a helium gas flow in opposite direction into the GCMS system where they are detected both qualitatively and quantitatively following gas chromatographic separation.

In the present application example, upper layer of fairing parts were analyzed for volatile compounds in accordance with VDA 278 (October 2011). The effects of storage of the components on their VOC and FOG content were also investigated.

Sample preparation and analytical conditions

The VDA 278 standard specifies a strict workflow, starting with testing instrument performance using a control standard solution consisting of 18 components (see figure 1). In the next step, two calibration standards are measured. Toluene is used to determine the response factor for the VOC calibration and hexadecane respectively for determination of the response factor for the FOG calibration. Desorption tubes filled with Tenax (an absorber material)

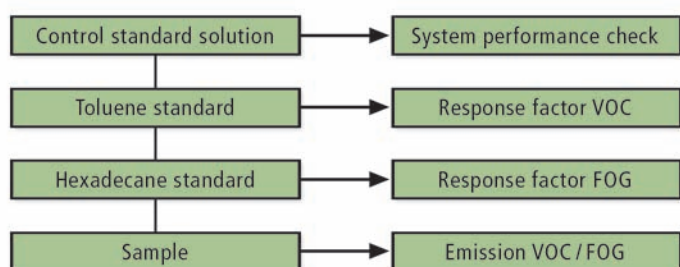


Figure 1: Workflow according to VDA 278

car smell.' However, these 'pleasant' odors are emissions from non-metallic automotive components. These emissions are, at least potentially, hazardous to human health.

Studies have shown that the content of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) in new vehicles is often considerably higher than recommended for, e.g., offices, schools or homes [1]. Even when, over time, the 'new car smell' disappears and the indoor air concentration of these chemicals decreases, their concentrations can quickly increase again to hazardous levels in a closed car when temperatures rise during summer.

VOCs with harmful effects on human health

The VOC chemical cocktail is composed of various volatile organic compounds, such as solvent residues, small synthetic components as well as additives (for instance plasticizers, solubilizing agents, anti-oxidants, stabilizers, flame retardants) and cleaning product residues. VOCs are emit-

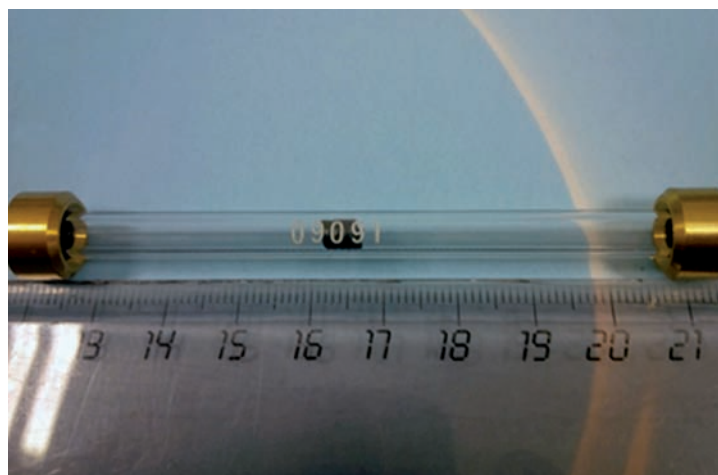


Figure 2: Correct placement of the sample in the desorption tube

were used for the preparation of the calibration samples. After injection of the standard solution, the solvent is evaporated for five minutes under a continuous flow of nitrogen (100 mL/min).

The sample to be investigated (upper layer of fairing parts) is removed from its packaging immediately prior to analysis and cut into small pieces (approx. 10 mg) which are then placed in the middle of a carefully cleaned desorption tube (see figure 2). Each sample is measured twice – first to determine its VOC value (desorption at 90 °C) and subsequently also to determine its FOG value (desorption at 120 °C).

Implementation

Sample measurement was carried out using a Shimadzu TD-20 thermodesorber, coupled to the GCMS-QP2010 SE quadrupole mass spectrometer. In accordance with VDA 278, the samples were desorbed for 30 minutes at the appropriate temperature. Due to the high concentration of the toluene and hexadecane calibration standards, the applied sample amount was reduced by a factor of four. Nevertheless, the measurements had to be carried out at a high split ratio (100:1) in order to prevent saturation of the detector. Data acquisition was carried out in scan mode over a mass range of 29 - 450 u. The chromatogram of the control standard solution is shown in figure 3.

As required by the VDA 278 standard, both o-xylene and n-nonane components are baseline separated. Although undecane and 2,5-dimethylphenol are not chromatographically separated, it is not a problem to identify both peaks unequivocally by means of their characteristic mass spectra (see detail in figure 3).

As required, the recovery rates of the various substances are be -

tween 60 and 140 %. For toluene, the recovery rate is 98 %. Based on the calibration standards, response factors calculated for VOC and FOG were 0.08 and 0.06 respectively. For the determination of the sum parameters (VOC and FOG value), the areas of all the substance peaks originating from the sample lying above the baseline were determined. Figure 4 shows an example of chromatograms for the measurement of VOC and FOG.

To investigate the effect of storage on the sample, the same measurements were repeated after seven days. Table 1 shows a comparison of the measurements. As expected, storage plays an important role, which can be seen clearly in the drastic reduction of the VOC value. In comparison, the content of less volatile substances (FOG value) does not decline as much.

This example very clearly illustrates the effect of storage and time of sampling on the emission values, as well as on their reproducibility and reliability. In this context sample preparation should also not be neglected, which should be carried out as quickly as possible at not too elevated temperatures.

Conclusions

Because of its simple and user-friendly sample preparation, Shimadzu's thermal desorption system consisting of the TD-20 thermodesorber and the GCMS-QP2010 SE is optimally suited for the determination of emission values of motor vehicle components in accordance with the VDA 278 standard. All sample tubings are inert thanks to a Silco-steel coating. This ensures particularly good recovery rates and minimal sample carry-over, also for high-boiling point substances. Moreover, the system provides Peltier cooling which does not require additional cooling agents

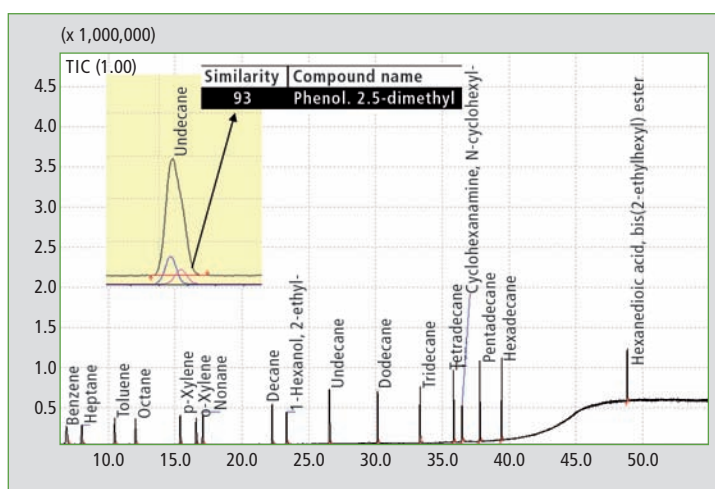


Figure 3: Chromatogram of the control standard

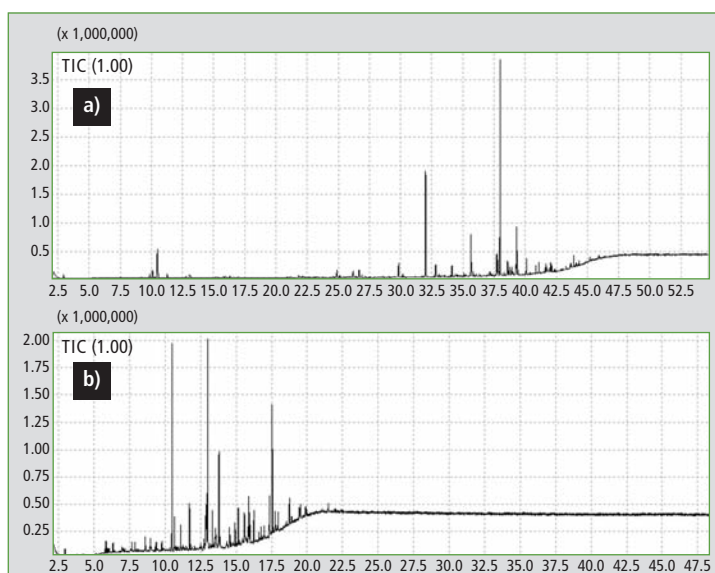


Figure 4: Chromatogram of the upper layer material of fairing parts measured under VOC (a) and SVOCs/FOG (b) conditions.

(for instance liquid nitrogen), as well as a direct transfer line and a separate carrier gas control (AFC). In this way, the emission values of materials used in new vehicles can be monitored reliably and a consistently high quality can be ensured.

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Further information on this article

• Application Note:
Analysis of VOC and FOG emissions from moulded components for automobiles according to VDA 278(SCA_280_081)



Without storage		7 Days storage without packaging	
Emission VOC 1:	299 µg/g	Emission VOC 1:	160 µg/g
Emission VOC 2:	290 µg/g	Emission VOC 2:	156 µg/g
Emission FOG:	234 µg/g	Emission FOG:	164 µg/g

Table 1: Emission values (VOC und FOG) from the upper layer material of fairing parts without storage and after seven days of storage without packaging



Drug residues in surface waters

New fast LC-MS/MS method using the LCMS-8060

According to 2013 OECD statistics, the use of pharmaceuticals in OECD countries has increased tremendously within a decade. While new therapeutic options and a comprehensive health care system are invaluable, there is also a downside: once drug residues have been released into the environment, they can be found in surface waters and

in groundwater. Thanks to modern instrument technologies, it is now possible to detect traces of drug residues, even in drinking water.

How do pharmaceuticals end up in surface waters?

Chemically speaking, most medicines are intended to be very sta-

ble because in the body sufficient intact active ingredient molecules should arrive at the disease site. As a consequence, however, much of the ingested drug substances remain unchanged or are excreted in the form of metabolites. Sewage systems convey these substances to wastewater treatment plants where their stability turns out to be a problem. Biological decom-

position becomes increasingly difficult and binding to particles hardly takes place, so that the first treatment stage is not very effective. While some of the active substances are degraded during conventional sewage clarification processes, many residues remain unaltered and end up in surface waters and, in part, also in our drinking water.

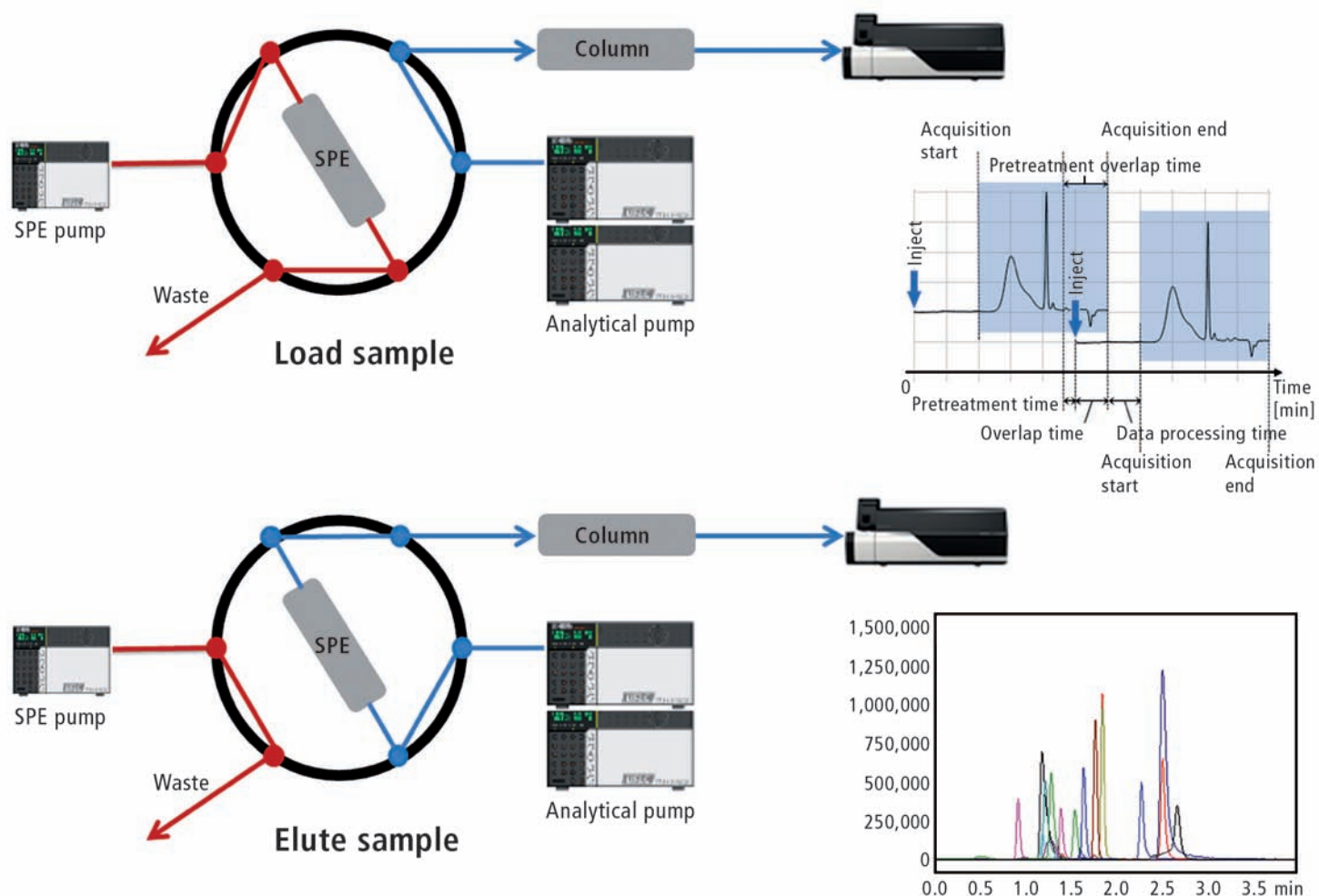


Figure 1: Design and functionality of the analytical online SPE system

Households are the main source of water pollution. This is hard to avoid. A higher, avoidable proportion of the pollution can be attributed to improper disposal of old or unused medicines. They are often flushed down the toilet or sink instead of being disposed of as household refuse. Large quantities of pharmaceuticals are also being used in intensive livestock farming, and may be mixed with

animal feed. Via dung and liquid manure, these drugs end up in the soil where they leach into the groundwater and ultimately arrive in our rivers and lakes.

Possible consequences of drugs in surface waters

While drug concentrations measured in surface waters are many orders of magnitude below the

effective concentration for humans and, therefore, do not pose any risk to human health, harmful effects on other organisms in the environment have been well documented.

A variety of antibiotics are particularly problematic. While penicillins are very easily biodegradable, sulfonamides, for instance, belong to the active substances that may render microorganisms in biological wastewater treatment plants inactive. On the other hand, the abundance of antibiotics may promote the development of resistant bacteria. Multi-resistant microorganisms have already been detected repeatedly in watercourses downstream of sewage treatment plants.

In addition to the widely discussed antibiotics, the current focus is on substances with endocrine (hormonal) effects. Very low concentrations (ng/L) will already

have a lasting effect on the reproduction of fish and frogs.

Another example is the widely used analgesic diclofenac, which can lead to liver and kidney damage in fish. Certain species of vulture in India and Pakistan are particularly sensitive to this substance – three vulture species are meanwhile almost completely extinct because they feed on dead cattle that were treated with diclofenac [2].

Drug residues are now found almost everywhere and all year round in a wide variety of water samples. Concentrations of the residues detected are low and usually in the nanogram per liter range. Due to optimized measurement methods, however, it is now possible to detect previously unknown residues in real samples. ♦

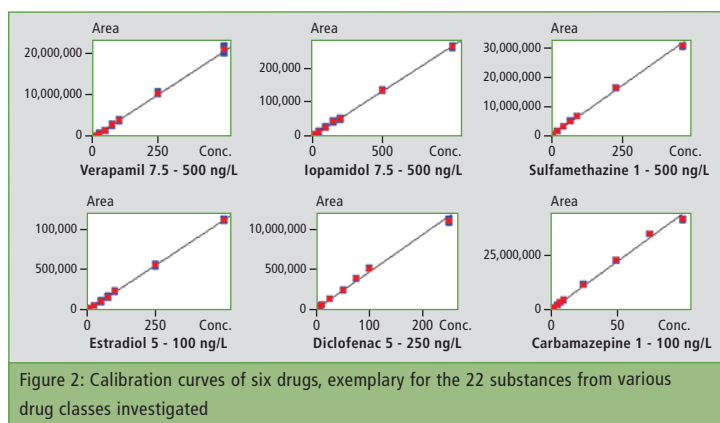


Figure 2: Calibration curves of six drugs, exemplary for the 22 substances from various drug classes investigated

Control standard QC 75 ng/L (n = 6)					
	Accuracy [%]	% RSD		Accuracy [%]	% RSD
Erythromycin	98.7	2.7	Progesterone	107.9	2.7
Atorvastatin	98.5	6.6	Sulfamethazine	108.1	2.1
Caffeine	110.2	3.1	Sulfamethoxazol	107.2	3.0
Carbamazepine	104.4	1.4	Verapamil	97.4	4.2
Diclofenac	103.9	3.2	Estradiol	101.3	4.5
Atenolol	108.7	3.6	Chloramphenicol	105.4	3.3
Lidocaine	103.4	1.2	Diphenylhydantoine	104.6	4.1
Lovastatine	105.9	4.1	Ibuprofen	101.3	2.4
Bezafibrat	106.8	1.7	Indomethazine	109.7	4.8
Paracetamol	107.5	1.9	Iopromide	106.0	7.4
Paraxanthine	106.4	3.6	Iopamidol	96.7	8.7

Table 1: Statistical evaluation of the quality control at a concentration of 75 ng/L

The ultrafast LC-MS method presented here is suitable for trace analysis of drug residues of different drug classes in water such as antibiotics, sulfonamides, anti-inflammatory medicines, analgesics, psychiatric medicines and X-ray contrast agents.

Material and methods

The water samples were analyzed using a Shimadzu Nexera X2 UHPLC system including an online SPE precolumn, coupled to a triple quadrupole LCMS-8060 mass spectrometer. In this combination, automated sample pretreatment using an online solid-phase extraction column is particularly timesaving and user-friendly. In the first step, the water samples are pretreated on a Strata-X online SPE column (2.0 mm x 20 mm, 25 µm) and the eluate is subsequently transferred onto an analytical column (Raptor Biphenyl, 2.1 mm x 100 mm, 2.7 µm) for further separation using a binary gradient (figure 1).

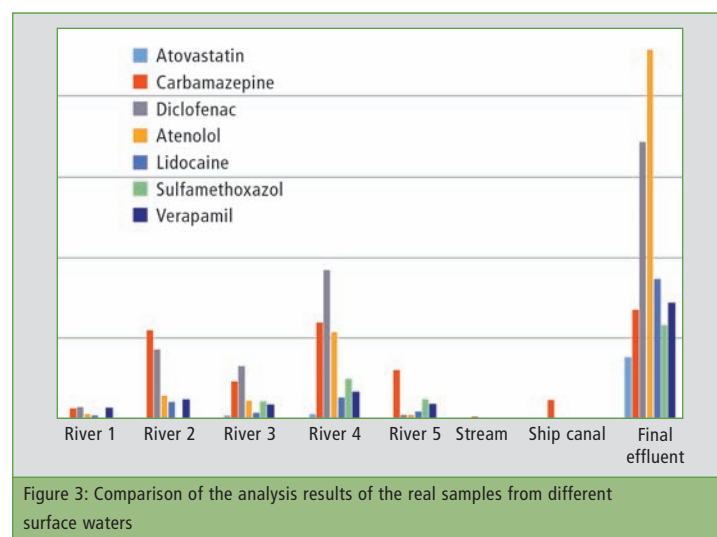
For optimal utilization of the system, the LabSolution software offers an elegant overlapping sample injection program. With this software function, it is possible to inject a second sample onto the SPE column while the first sample is still eluting from the analytical column. Rinsing of the SPE column can take place in parallel to equilibration of the analytical column, thereby saving time.

Thanks to the superior scan speed of the LCMS-8060 and the ultrafast polarity switching time, chemically very different compounds of different polarities can be detected.

Even when some substance peaks overlap, unequivocal peak assignment is possible. The combination of outstanding instrument technology and elegant software functions enables highly sensitive measurements in just five

minutes, including sample preparation.

Real samples from five smaller rivers, one stream and a ship canal were investigated for their pollution through drug residues.



minutes, including sample preparation.

Figure 2 shows an example of the calibration curves within a range of 1 - 500 ng/L for diclofenac, sulfamethazine, carbamazepine, estradiol, verapamil and iopamidol, representing the 22 drugs investigated from different drug classes. For the calibration curves, duplicate determinations of individual concentration levels were carried out subsequent to previous online SPE sample preparation. The correlation coefficient (r) was greater than 0.99 for each of the 22 substances. In addition, the precision and the percentage standard deviation at a mean concentration of 75 ng/L (six repetitions) were determined as an indicator of the reliability of the method (see table 1).

Low concentrations of some substances could be detected. Figure 3 shows the detected substances and the different pollution levels of various water bodies.

Large bodies of water such as rivers and ship canals that do not have any further tributaries are contaminated only slightly. Smaller rivers with their tributaries already exhibit increased drug residue concentrations. As expected, the pollution level of the final effluent of a wastewater treatment plant is the highest, because the investigated substances could not be filtered out or degraded during the water treatment processes presently applied.

Analysis results in just five minutes

In recent years, the effects of drug residues on flora and fauna are being systematically investigated. Questions on the ecological effects are becoming more and more urgent due to population growth and increasing use of medicines. The present application describes a reliable method for qualitative and quantitative determination of 22 medicines in surface waters at the required sensitivity. Using a combination of Shimadzu's HPLC Nexera X2 with the ultrafast LCMS-8060 which is optimally suited for high sample-throughput, the entire analysis can be completed in just five minutes – including the user-friendly online SPE sample preparation step and column equilibration. This immense saving in time is due to the optional overlapping sample introduction function, the highest possible MRM data acquisition rate and a polarity switching time of only five ms.

Literature

- [1] Homepage of the German Federal Environmental Agency
- [2] Hannelore Gießen, Pharmazeutische Zeitung 04/2011

25 years Technical Offices in Jena and Berlin, Germany

Specialized expertise meets individual support on-site

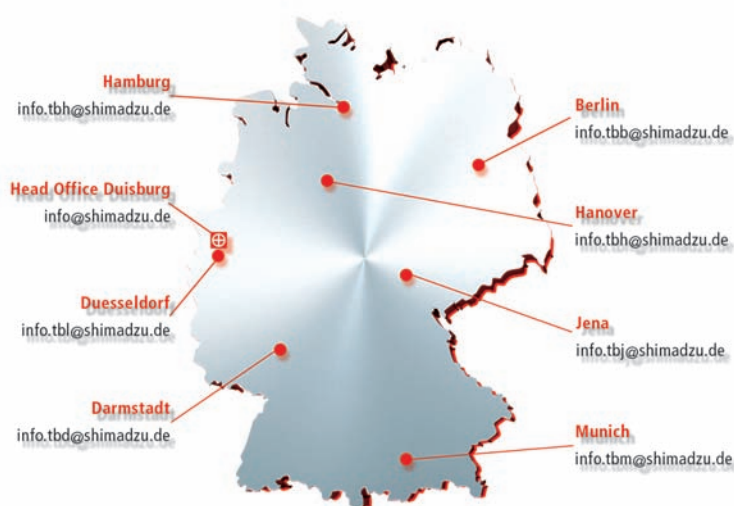


Figure 1: The nationwide service network guarantees close proximity to customers

With six Technical Offices all across Germany, Shimadzu offers a comprehensive sales and service network in regional catchment areas. In two cities, Berlin and Jena, the Shimadzu offices celebrate their 25th anniversary this year. Both of them have grown steadily and have long-lasting customer relationships. Each office started out initially with three employees, and since then, staff numbers have quadrupled. This growth also reflects the increased order volume.

Technical Office Jena: ambitiously meeting challenges

After the Berlin Wall went down, Shimadzu made fast inroads into the pharmaceutical industry in the greater Jena area. This key industry has always had a great demand for analytical systems. Through its local presence, Shimadzu could establish long-lasting partnership with its customers. Today, the Technical Office serves all relevant pharmaceutical companies located in the region.

Shimadzu's solutions are also demanded in the chemical industry, governmental and private laboratories focusing on clinical and environmental issues, or at universities, colleges and public institutions. Dr. Volkmar Schulz, head of the Technical Office Jena, knows why: "Thanks to the excellent teamwork across all our business areas, such as sales, applications and services, we can offer our customers optimal tailor-made solutions. The individual support plays a decisive role."

Technical Office Berlin: product innovations based on close cooperation

The office's earliest customer relationships even date back to before the fall of the Berlin Wall. One close relationship in particular led to an innovative product that is known internationally today: TOX.IS, the HPLC system for the determination of poisons and drugs in urine. In the 1990s, a Berlin hospital laboratory needed an automated instrument which could identify toxic compounds in human urine within a short

amount of time. In close cooperation with the customer and a research group at Berlin's Humboldt University, the Shimadzu team developed a prototype that met these demands.

Of course, commercial products cannot result from every single cooperation with clients, but the quality of these relations is exemplary for many of our long-standing customer relationships, ex-

plains Dr. Michael Schulze, Head of the Berlin Technical Office. "Customers from the pharmaceutical and chemical industry, academic research, institutes and biotechnology have known and valued our staff for many years – and conversely, our staff knows the circumstances in these companies and institutes. In this way, we can quickly adjust to the current needs of our customers."



Figure 2a



Figure 2b: 140 years meet 25 years: The teams of the Berlin (figure 2a) and Jena Technical Offices together with a puppet representing company founder Genzo Shimadzu. It will travel around the world in 2015 for a snapshot with Shimadzu's employees, documenting the company's 140-year anniversary.

PAHs: simple analysis with high detection limits

Determination of PAHs or mineral oils in water using fluorescence spectroscopy according to ASTM D 5412

Fluorescence spectroscopy:
little sample preparation, fast results

An alternative analytical technique leading to fast results with little sample preparation is fluorescence spectroscopy. Because of its sensitive measurement principle, detection limits for contaminations in the lower ppb range are easily achieved. The regulation or the standard for this analysis has been established by the American Society for Testing and Materials (ASTM). The D 5412 standard testing method includes determination of complex polycyclic aromatic hydrocarbons (PAHs) or mineral oils in water [1].

The PAHs or mineral oils are quantified in aqueous samples using fluorescence spectroscopy. Appropriate calibration standards exhibiting similar emission and synchronous fluorescence spectra are used for calibration. According to the ASTM, this test method is suitable for contaminations from mineral oils, fuel oils and

What do drinking water and wastewater have in common? Contamination. With wastewater, it's likely to think about the total sum of contamination, whereas with drinking water more detailed information on contaminations at trace level may be obtained. Contaminations in drinking water are considered to occur in the ppm concentration range or lower.

Various analytical techniques are available to address a wide range of analytical problems:

- Hydrocarbons (C5 – C44, and up to a chain length of C60) are chromatographically separated and determined quantitatively using GC analysis in accordance with DIN DEV 38409-H53 and ISO 9377-2.

- FTIR spectroscopy is still used, in part, to determine hydrocarbon mineral oils and aromatic hydrocarbons in drinking water in the ppm down to the ppb range (DIN 38409-H18, although this standard expires due to a ban on the solvents used)
- The total organic carbon content in drinking water and wastewater is determined using TOC analysis. The relevant TOC standard is EN 1484 'Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). This standard applies to a measurement range of 0.3 - 1,000 mg/L.

The techniques mentioned above are ideally suited for detection of impurities or contaminations in

the lower ppb range. These techniques are subject to corresponding national and EU regulations.

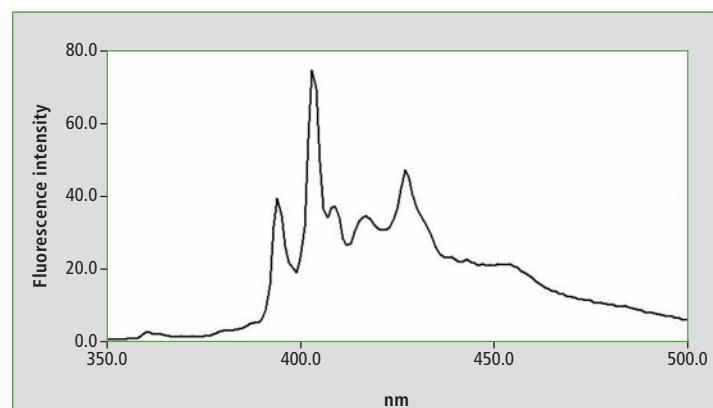


Figure 1: Fluorescence spectrum of a mixture consisting of five polycyclic aromatic hydrocarbons (PAHs) in a measuring range of 350 - 500 nm using an excitation wavelength of 300 nm

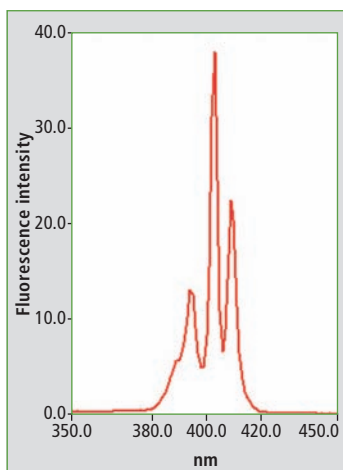


Figure 2: Synchronous scanning fluorescence spectrum of benzo[a]pyrene in a measuring range of 350 to 450 nm with an offset of 6 nm between excitation and emission wavelengths.

tar oils. Industrial organic contaminants cannot be excluded.

In accordance with the ASTM standard method, the PAHs or mineral oils are dissolved in cyclohexane. The initial concentration of an unknown sample should be approximately 100 µg/L for a fluorescence measurement. It may be necessary to dilute this solution in order to bring the fluorescence signal into the linear range and to suppress self-absorption effects of the matrix. Cyclohexane has been recommended as a suitable solvent for this analytical method. Alternative solvents can be substituted but they should comply with the ASTM requirements. The 10 mm layer thickness cuvette must be made of non-fluorescent quartz.

Representation of selective fluorescence-active organic compounds

Fluorescence spectroscopy enables representation and quantification of selective fluorescence-active organic compounds in mixtures. Fluorescence spectrometers allow measurement of excitation and emission spectra, which can be used for substance identification. When a mixture contains several fluorescence-active compounds, excitation of one compound can trigger excitation of a second compound resulting in decreased fluorescence for that compound. Synchronous scanning is used to

minimize these overlapping effects.

In synchronous scanning, the two monochromators in Shimadzu's RF-6000 spectrofluorophotometer are scanned simultaneously. To obtain a standard fluorescence spectrum, the excitation wavelength is set to the desired analytical wavelength and the emission is measured over the UV-VIS measuring range. Under synchronous scanning conditions, the monochromators are scanned synchronously at a fixed wavelength interval offset. For example, an excitation wavelength of 220 nm is selected and the resulting fluorescence is measured from a wavelength of 230 nm. Synchronous scanning is thus carried out at an offset of 10 nm. The desired effect is that the measurement acts as a background correction of the fluorescence arising from 'neighboring' compounds. It is known that fluorescence always occurs with a slight time delay with respect to excitation to higher wavelengths as a stray light phenomenon.

chemical ring systems respond to the UV light by emitting fluorescence. The 300 nm excitation wavelength is not selective for this compound mixture.

Some of the PAHs emit fluorescence following excitation of 300 nm. When the measurement is repeated using synchronous scanning, one signal group is isolated. Upon comparison of this result with a synchronous scan of benzo[a]pyrene, this PAH could be identified. Due to the distinct isolation of this PAH, it is also possible to quantify this substance.

Several examples of measurement of various mineral oils are described in the ASTM standard method. Figure 1 shows the fluorescence spectrum of the PAH mixture using a fixed excitation wavelength. Figure 2 shows the synchronous scan spectrum of benzo[a]pyrene at an offset of 6 nm. The isolation of benzo[a]pyrene from the mixture is shown

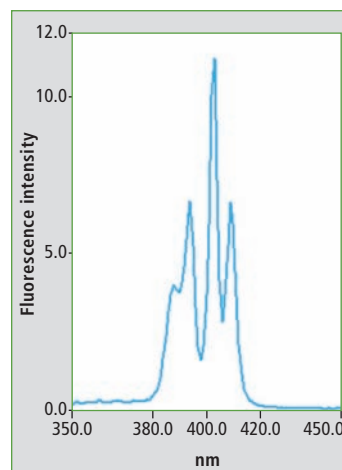


Figure 3: Synchronous scanning fluorescence spectrum of the mixture (fig. 1) in a measuring range of 350 to 450 nm with an offset of 6 nm between excitation and emission wavelengths

In accordance with the ASTM standard, this method can detect concentrations of 0.5 ppm of oils in water. Detection limits are dependent on the individual fluorescence activities of the PAHs and the mineral oils.

Literature

- [1] ASTM D 5412 – 93 (Reapproved 2000), Standard Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water



RF-6000

In the example shown here, a mixture of five different PAHs was prepared. The goal is to show that the synchronous scan can represent one of the substances.

Response of the organic compounds to UV light

Figure 1 shows the fluorescence spectrum of a mixture of five compounds. An analytical wavelength of 300 nm was used for excitation of the solution. Most of the organic compounds containing

in figure 3. This spectrum was also measured with an offset of 6 nm for comparison.

Conclusion

Fluorescence spectroscopy is highly suitable for the analysis of PAHs or mineral oils in aqueous samples. In the above-mentioned case, the benzo[a]pyrene spectrum could be obtained using synchronous scanning. Due to its high quantum yield, benzo[a]pyrene is detectable in low concentrations.



58 real life applications on food quality and food safety

Application Handbook: Food, Beverages, Agriculture

Over 200 pages, the new Application Handbook “Food, Beverages, Agriculture” covers 58 real life applications related to hot subjects such as food scandals which recently have alarmed consumers all around the world. The edition contains most advanced technolo-

gies and solutions such as chromatography, mass spectrometry, spectroscopy, life science, sum parameter (TOC/TN) and materials testing and inspection.

The book is free of charge and can be downloaded at: <http://bit.ly/FoodBeveragesAgriculture>

Regarding food, water, beverages and agricultural cropland, the increasing world population is one of the biggest challenges of mankind.

How can access be provided to sufficient and safe food as well as clean water? How can crop failure

be prevented? Can new food sources be explored?

Analytical tools for food and beverages industries

Determination of pesticides in vegetables, identification of horse meat in lasagne and quantification of heavy metals in drinking water: in food and beverages industries, analytical instrumentation methods are essential to ensure high product quality during many steps in the production process such as quality control of raw materials (e.g. natural products) and their treatment during and after production. The food and beverages spectrum is so widespread that dedicated analytical technologies must be applied to meet the challenges regarding consumer and product safety.

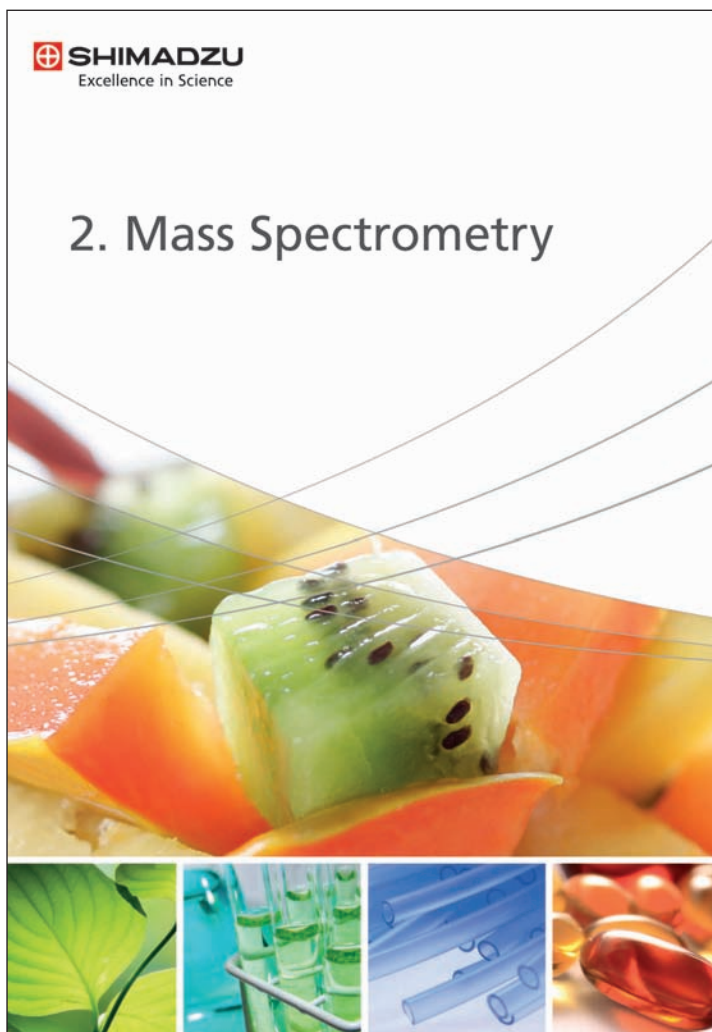
This is a quick overview of the technologies and their use:

Chromatography

- Chromatographic separation and analysis of volatile and semi-volatile components in food, beverages, liquors and packaging materials are widely used in food quality control. GC is a key technique in qualitative and/or quantitative analysis of food composition, natural products, food additives, flavor and aroma compounds and contaminants such as pesticides and environmental pollutants.
- HPLC and UHPLC systems are able to quantitatively analyze substances in mixtures containing multiple ingredients by separating and detecting target substances. They are also used to purify specific substances once they are separated.
- GC-MS is a hyphenated technique combining the separating power of gas chromatography (GC) with the detection power of mass spectrometry to identify different substances within a sample, for example the fast screening of residual pesticides in food using fast GC-MS/MS.
- LC-MS is a powerful technique that brings together very high sensitivity and high selectivity.

Its application is oriented towards the separation, general detection and potential identification of chemicals of particular masses in the presence of other chemicals (e.g. complex mixtures). It is widespread in food

- Energy dispersive fluorescence spectrometry allows the quantitative analysis of element distribution in food samples. This technique provides non-destructive and fast measurements of liquids and solids and is best



safety applications such as Multi-residue analysis of pesticides in food samples by Triple Quadrupole UHPLC-MS/MS.

Spectroscopy

- Atomic absorption spectroscopy (AAS) or inductively coupled plasma optical emission spectroscopy (ICP-OES) is the method for quantitative analysis of element concentrations in food samples and beverages. AAS allows the sequential analysis of elements, and ICP-OES is used for the simultaneous analysis of major, minor and trace elements in drinking water, mineral water, wine and other beverages.

suited for analysis of the elemental range from sodium/carbon to uranium, covering the majority of the metallic elements.

- Molecular spectroscopy is used for analysis of metals, ions, colors and molecules in the ultraviolet and visible range of the light spectrum. Determination of wine color and quality control of the wine bottles are typical applications in food and food packaging industries using UV-VIS-NIR spectrophotometers.
- Fourier transform infrared (FTIR) spectroscopy is used for quantification and identification of substances from the near to

the far infrared range. Tea bags made of PET are identified using single reflection ATR in combination with infrared spectrometry.

Sum parameter

- The TOC sum parameter determines organic compounds in different matrices, especially in all kinds of water. In the food and beverage industry, water is used as solvent, product or rinsing solution.

Material testing and inspection

- Besides food flavor, texture such as crispiness, glutinousness, feel on tooth and tongue influence the perception of food.

Shimadzu provides complete solutions including soft- and hardware to evaluate physical properties of food.

Further information on this article

- About the Application Handbook and download link: <http://bit.ly/FoodBeveragesAgriculture>



Paper clip fashion show

Color control in the production of coated metal paper clips

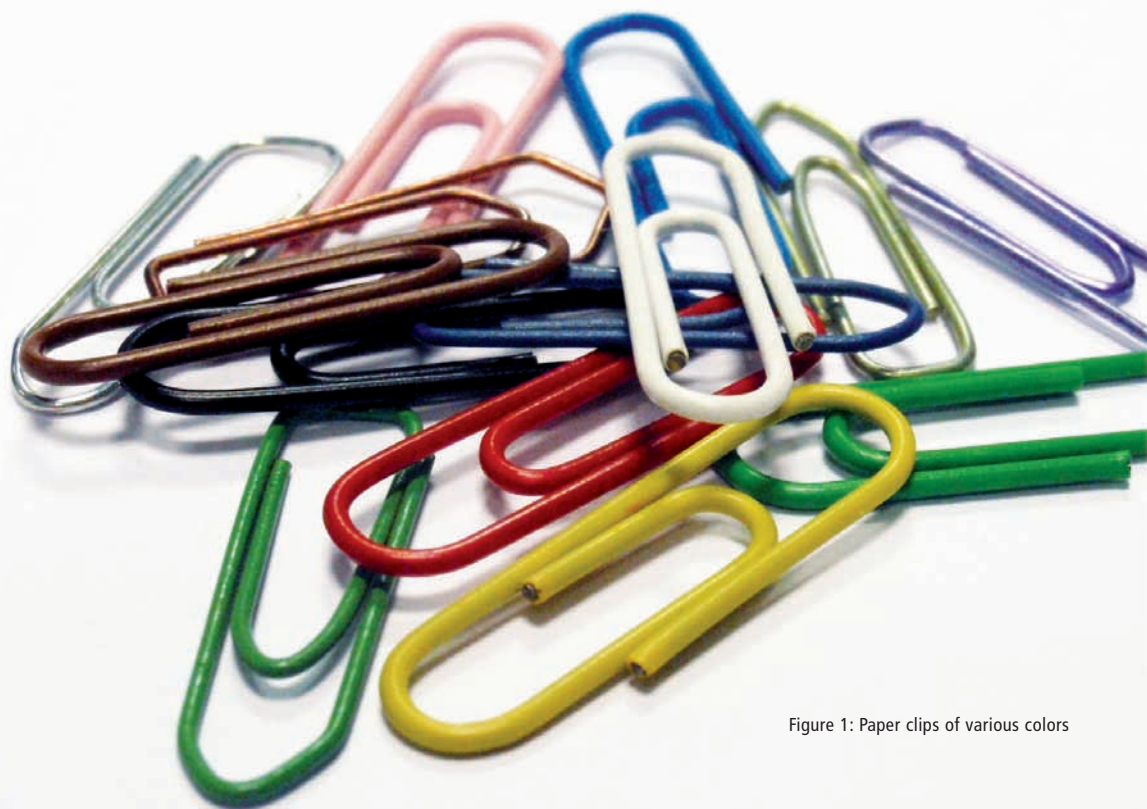


Figure 1: Paper clips of various colors

Commodities and natural foods have one thing in common: their visual appearance and their reproducibility, which are key for sales. This is equally true, for example, for apples and pears and their packaging as well as for colors of beverages or clothing. Consumers are conditioned to perceive something

being wrong in case of deviating colors. This is why many everyday products are subject to color inspection.

It is well known that people perceive and describe a specific color in different tones, e.g. of red or blue. In order to automate color management in the production

process, measuring instruments and physical properties tables are available that define the colors.

Color determination is standardized through fixed table values. Color is classified in three primary colors known as RGB colors that reflect the proportion of red, green and blue in a color blend. Tristimulus values (XYZ) according to the CIE standard take human color perception into account in the evaluation of spectral characteristics of color [1]. Color perception also depends on the illumination source and the viewing angle. Depending on the source of light, brightness, yellowness and other color characteristics can be determined.

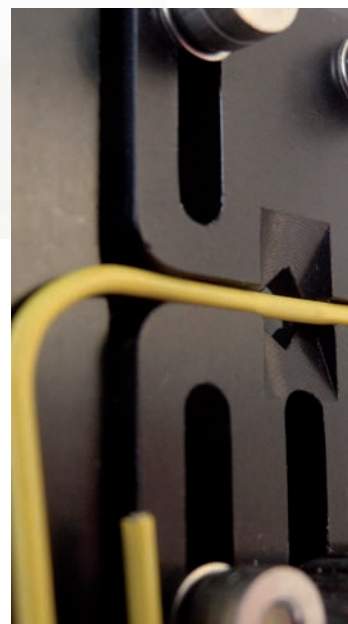


Figure 2: Detail of a clamped yellow paper clip with the 3 x 3 mm measuring window in view

Spectroscopy and paper clips

Color is a domain of UV-VIS spectroscopy. This technology can be used to simulate the visible range in which humans perceive color, to measure materials and to analyze and categorize the spectra obtained. UV-VIS analysis is well

Paperclip color	Line color of the UV-VIS spectrum
Neutral (bare wire, 1 mm ø)	Dark grey
White (no color absorption)	Dark violet
Black (complete color absorption)	Black
Brown	Brown
Green	Green
Yellow	Yellow
Red	Red
Blue	Blue
Pink	Pink

Table 1: Paper clips with a diameter of 1.25 mm and their colors, as well as the classification of the line colors as shown in Figure 4

known in the investigation of liquids, glasses and films. Standard liquid cuvettes can handle sample sizes with an area of, for instance, 1 x 4.5 cm up to areas of several centimeters. The application discussed here focuses on small solid sample sizes. Of interest is the color of a coated wire with a diameter of approximately one millimeter.

Colorful paper clips have been selected here as a simple example for this type of material. The wires coated with a colored polymer have a diameter of approximately 1.25 mm. Figure 1 shows the paper clips.

Sample preparation

A micro sample holder was used for the measurements. This holder has a measuring window of 3 x 3 mm. The sample is fixed between two plates in the holder. Figure 2 shows a yellow wire clamped in a micro sample holder and figure 3 shows a paper clip. This holder is attached to an integrating sphere (Ulbricht sphere) and is irradiated directly with UV-VIS light. Nine different sam-

Illumination: C Standard daylight		Observer: 10 degrees						
Color scales		Tristimulus values			Chromaticity coordinates		Dominant wavelength [nm]	
Visual color	Sample	X	Y	Z	X	Y	dWL	File Name
Blue	1	2.88	3.21	5.98	0.2388	0.2661	475.1	CLIP_Blue
Brown	2	2.57	2.53	2.42	0.3412	0.3369	581.2	CLIP_Brown
Green	3	2.85	3.58	3.02	0.3018	0.3787	536.0	CLIP_Green
Pink	4	6.49	6.10	6.78	0.3349	0.3151	*486.6	CLIP_Pink
Yellow	5	4.99	5.19	2.52	0.3930	0.4083	571.5	CLIP_Yellow
Red	6	2.42	2.36	2.61	0.3281	0.3192	617.8	CLIP_Red

Table 2: Color analysis of the paper clip spectra using the color tables in accordance with CIE [1]

ple colors (table 1) were selected, including black, white and non-coated (bare).

Figure 4 shows the UV-VIS spectra of the measured paper clip colors. The colored lines of the spectra represent the colors of the paper clips. The colors are listed in table 1.

For determination of the tristimulus value, the non-coated, black and white paper clips were excluded from the color value calculation because, according to physics and the spectral result, they do not show any color absorption.

The other paper clip colors can be determined and are listed in table 2.

The dominant wavelength represents the visual colors. The green wire absorbs radiation at 536 nm, which corresponds to the color green. The pink paper clip is marked with an asterisk. The color absorption of this color is in the extreme violet and red spectral range, also called the 'purple boundary' or 'line of purples'. Since the horseshoe-shaped chromaticity diagram cannot assign any analytical

thing involved in product manufacturing, from the colored raw material to the finished product and to adjust the production parameters.

Literature

- [1] Colorimetry – Part 1: CIE standard colorimetric observers (ISO 11664-1:2007); German version EN ISO 11664-1:2011

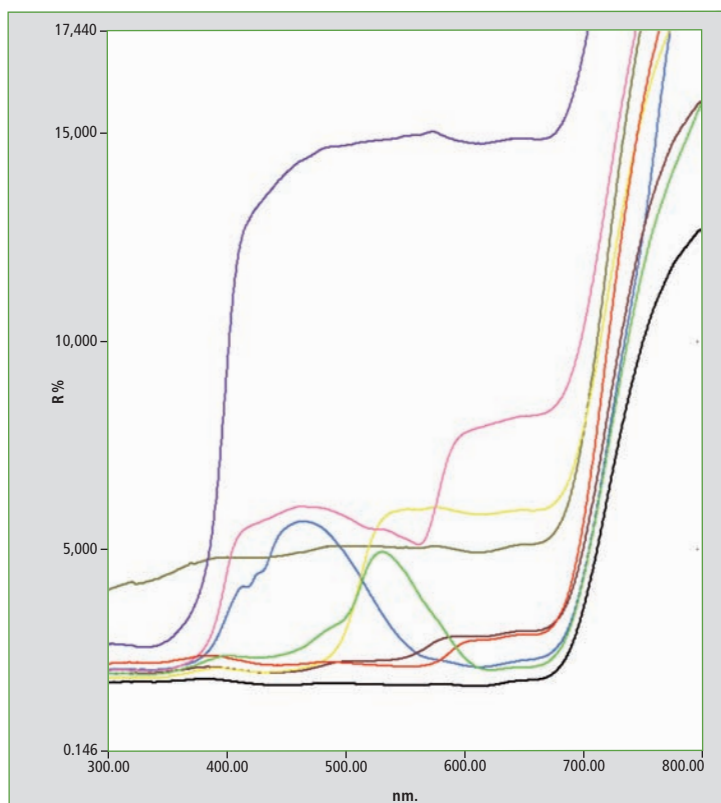


Figure 4: UV-VIS reflectance spectrum of unicolor paper clips for which the line color of the spectrum was classified in table 1



Figure 3: Micro sample holder with a clamped white paper clip

wavelengths in this range, the color lying opposite (complementary) in the diagram is assigned. In this example, it is the wavelength at 486.6 nm, which corresponds to a bluish-green color.

Result

The performance capability of UV-VIS spectroscopy is not limited to liquids. Solid samples with a diameter of three millimeters can be analyzed easily and quickly without sample destruction.

The colors of the materials used can be determined correctly for quality control. With this knowledge, it is easy to check every-

Tracing contaminants in polymeric kitchen utensils

Evidence of WEEE relevant substances in polymeric food-contact articles (FCAs)

The amount of polymeric waste is increasing steadily, due for example to shorter life cycles of many technical con-

ing substances, oligomers, colorants, additives or surface additives that are basic constituents of the polymeric FCA. If they mi-

grate into food, they cause an unacceptable change. The regulation also covers the so-called 'positive list' of authorized monomers,



Figure 1: Combined analytical techniques for analysis of different kinds of contaminants in plastics: XRF, ICP-OES, FT-IR, GC-MS

sumer products. This is why recycling of polymeric/plastic waste becomes more and more important. This process has to be carried out in a secure way, otherwise hazardous substances or materials can harm the environment or humans. This is why recycling of polymeric substances has been regulated, mostly depending on the subsequent use. Accordingly, Food Contact Articles (FCAs) are treated in a special way.

Polymeric FCAs are regulated within the European Union by the European Commission Regulation 10/2011 [1]. It describes an overall migration test using defined food simulants measuring the amount of non-volatile substances released from a material or FCA. Using olive oil, an overall migration test evaluates the inertness of the FCAs releasing not more than 10 mg of constituents per 1 dm² as the maximum permitted limit.

These migrating non-volatile substances may be monomers, start-

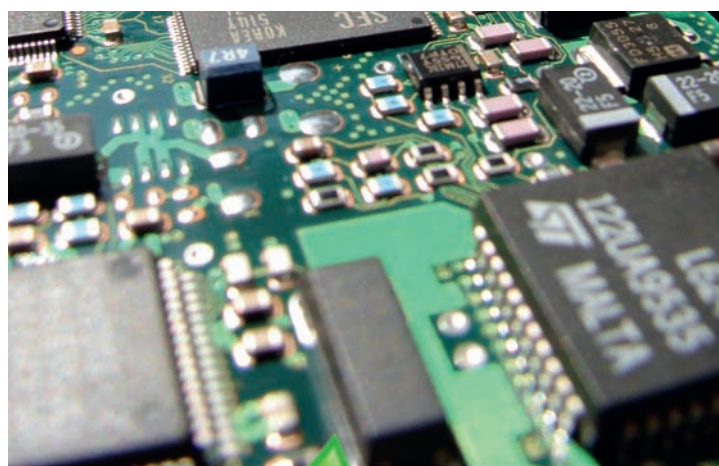


Figure 2: Electronic Waste in Food Contact Articles such as thermocups?

Sample	Sample	Colour	Main polymer ^a	Detected monomers (Pyrolysis GC-MS)	Macromolecular contamination ^a	Br content ^b (mg kg ⁻¹)	Detected BFRs ^c
1	Egg cutter	Black	PP/PE	4-ethenyl-cyclohexene; styrene; α -methylstyrene; Benzoic acid	HIPS/PBT or PET	57	TBBPA, decaBDE
2	Electric frying pan	Black	PBT	1,4-butadiene; 4-ethenyl-cyclohexene; styrene; α -methylstyrene	HIPS or ABS or SAN	5975	TBBPA, DBDPE
5	Movable lid (thermocup cover)	Black	ABS	Methylmethacrylate; Benzoic acid	PMMA/PBT or PET	504	TBBPA, decaBDE
10	Screwable closure (thermocup cover)	Black	PP/PE	Methylmethacrylate; styrene; α -methylstyrene	PMMA/ PS or PBT or PET	n.d.	n.d.

Table 1: Sample list (excerpt) with sample description and results showing macromolecular contaminants, Br content and BFR identification

Notes: ^a The main polymer and possible polymeric contaminants were interpreted from FTIR spectra combined with pyrolysis GC-MS data · ^b Measured by XRF; n.d. means not detected and implements a limit of detection of 40 mg kg⁻¹ · ^c Measured by thermal desorption GC-MS

other starting substances, macromolecules, additives and polymer aids [2, 3].

All chemicals listed were evaluated individually for their toxicity and migration behavior by EFSA (European Food Safety Authority) which defined a specific migration limit for controlled migration and evaluation of the FCA. The positive list is still expanding as new toxicological data on substances is obtained [2, 3].

Investigated samples

In total, ten polymeric FCAs were analyzed. Only black-colored items were selected as it is suggested that black polymeric items are more likely to be contaminated by recycled polymers. Technically speaking, a melt of recycled polymeric material with virgin material does not look attractive; however, after color unification with black pigments it is again visual appealing.

All ten black polymeric FCAs were purchased randomly from different distributors within Europe between 2012 and 2013. From this rather small group of samples, three samples were typical kitchen utensils, while seven samples were used as lid closures of thermo-cups for hot drinks (figure 2). They were chosen for two reasons:

- they come into direct contact with the mouth
- their usage for hot drinks anticipates a higher rate of migration of contaminants into the food/drink.

Brominated flame retardants in FCAs?

So far, brominated flame retardants (BFRs) are not included in the positive list and, as a consequence, are not allowed to be used as initial substances for the manufacture of FCAs sold on the European market. But BFRs are often present in technical products in order to decrease flammability.

To explore whether waste from electrical and electronic equipment (WEEE) is used as raw material in the manufacture of polymeric Food Contact Articles, the presence of BFRs in final products is a first indicator.

X-ray fluorescence spectroscopy (with EDX-7000) has been used to check polymer samples for Bromine (Br). This spectral method is very effective and can quickly screen many test points on one sample non-destructively without time-consuming sample treatment. Samples with a total elemental Br concentration of higher than 40 mg/kg were considered as Br-positive and may therefore contain BFRs.

Complementary to XRF analysis, BFRs were identified by thermal desorption GC-MS (PY-2020iD, Frontier Laboratories, coupled to Shimadzu's GCMS-QP2010 series) to learn more about the specific kind of BFR and to finally assure that the Br identified by XRF is related to BFRs.

Thermal desorption is a sample introduction method using heat to extract/vaporize additives from a polymer matrix or a sample ex-

tract. In this case, sample extracts were prepared from selected polymer samples (24-h static migration in toluene). Toluene as an extraction/dilution solvent is favored since most of the commercially available BFRs are easily soluble in this solvent.

The results of Br analysis are summarized in table 1 (excerpt). From the ten samples selected, seven samples contained BFRs.

The highest Br level was found in a PBT (polybutylene terephthalate) sample with 5,975 mg/kg Br from TBBPA (tetrabromobisphenol A) and DBDPE (decabromodiphenylethane), while the lowest detectable Br level was found in a PP/PE (polypropylene/polyethylene) sample containing 57 mg/kg Br from TBBPA and decaBDE (decabromodiphenylether). For all Br-positive samples with a Br level higher than 40 mg/kg, TBBPA was detected in all seven samples as the most abundant BFR. Interesting was the fact that no RoHS-regulated BFRs [4] were detected. The BFRs in this case were definitely just contamination. The level required to achieve flame retardancy starts at around 0.8 weight % and ranges up to approx. 8 weight %. So this level of Br is quite surprising, since all are too low to achieve sufficient flame retardancy (< 0.6 weight %).

What kind of polymers are in use?

For identification of the polymer matrix, ATR-FTIR analysis was performed with the IRTracer-100. The instrument is equipped with a single reflectance diamond

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ATR crystal. All spectra were compared with standard spectra from databases that are commercially available, e.g. RoHS, ATR-Polymer2, IRs Polymer2 and T-Polymer2, all running on LabSolutions IR software combined with in-house libraries. For the identification of the main polymers, the match with the libraries was 90 % or higher.

Similar to XRF analysis, the ATR-FTIR technique is non-destructive and samples can be stored afterwards or used for further analysis. In addition to confirming FTIR results concerning main polymers, the pyrolysis technique can give an insight into macromolecular contaminants as an additional hint for pureness or impureness of the materials the polymeric FCAs are made of. ATR-FTIR in combination with pyrolysis GC-MS is a powerful tool to obtain the full compositional overview of polymer matrix.

The use of recycled polymers was reconfirmed, as macromolecular contamination was present in all samples, indicating that none of them were pure material (table 2, excerpt). This is why further analysis techniques were applied to find further proof as to whether waste from electrical and electronic equipment (WEEE) was used during recycling, besides the fact that BFRs were present.

Elemental Contamination

Sb is definitely a key element in electronic applications, generally added to polymers as Sb_2O_3 involving a highly efficient FR (flame retardance) system in combination with halogen-containing FRs. In addition, non-rare earth elements (non-REEs) of interest were selected: As, Be, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb and Zn.

All these elements are used in electric and electronic equipment.

Measurements of selected rare earth elements (REEs) such as Ce, Dy, Er, La, Nd, Pr, and Y were also performed. The criteria in choosing these REEs came from their abundance in WEEE based on the available literature and the demand from industry.

Element	Sample 1	Sample 2	Sample 5	Sample 10
As	4.0	7.2	4.0	–
Cd	2.0	– a	5.5	–
Ce	8.9	7.3	–	–
Cr	19	2.4	6.5	–
Cu	37	–	20	–
Dy	0.42	–	–	–
Fe	1,200	59	75	4.8
Hg	0.14	0.019	0.81	–
La	2.4	–	–	–
Nd	2.5	–	–	–
Ni	3.0	1.9	2.4	0.54
Pb	99	–	26	–
Pr	4.5	–	–	–
Sb	–	500	110	–
Y	2.0	–	–	–
Zn	100	30	38	25

Table 2: Elemental composition of the samples (excerpt). All data in mg/kg.

Note: a "–" means not detected with a value below the LOD for the selected element

All measurements were performed by simultaneous ICP-OES (ICPE-9820), after all samples were microwave digested. There are two advantages when using simultaneous ICP-OES:

- the analytical plasma can be observed axially and radially
- all elements are measured at the same time.

Both plasma observations can be combined in a single method, meaning that traces can be measured using a real axial view and major elements for the same sample by using a real radial view, thereby enlarging the dynamic range. To increase sensitivity especially for the toxic elements Hg and As, the hydride vapour technique was also applied.

Results

In four of the seven cases, concentration of Sb was higher in FCAs containing BFRs, corresponding to the use of Sb_2O_3 as a synergist FR with halogenated FRs. In all cases of Br detection at elevated concentrations (> 200 mg/kg of Br), Sb was also detected (table 2). For example sample 2, a PBT sample, contained Br at a level of 5,975 mg/kg combined with a concentration of 504 mg/kg of Sb. The presence of Sb in PBT or PET can be justified as Sb_2O_3 is commonly used as a catalyst in such matrices, however, the presence of Sb and Br together is not common

in PBT or PET applications unless applied to give flame retardancy.

In most of the BFR-positive samples, typical elements used in electronic equipment like ferrous elements and the selected heavy elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb and Zn) were present either at trace level or at elevated concentrations. The presence of these elements was expected as they appear in many applications within electrical and electronic equipment.

Typical REEs (Ce, Dy, La, Nd, Pr and Y) found in many electronic and electric applications nowadays were present in four of the seven Br-positive samples, while in Br-negative samples no traces of REEs were detected.

Conclusion

To conclude, it can be stated that BFRs were present in polymeric FCAs and these FCAs contained in addition different macromolecular contaminants, indicating the use of recycled material with WEEE as one source for raw material being assumed. Results of elemental analysis confirmed this assumption.

Even expensive elements like REEs which have no functional use in polymers applied in, e.g. upper parts from thermo-cups (lid closures) were present in the samples.

Combining the GCMS-QP2010 series, IRTTracer-100, EDX-7000 and ICPE-9800 series analytical instruments, much information can be obtained from just one sample. It implies that materials need to be regulated more strictly in order to avoid hazardous substances that can harm the environment or humans.

Authors

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Read for you in

Franky Puype, Jiri Samsonok, Jan Knoop, Marion Egelkraut-Holtus & Markus Ortlieb (2015) "Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold in the European market", Food Additives & Contaminants: Part A, 32:3, 410 - 426

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- [3] Regulation (EC) No. 202/2014 of 3 March 2014 amending European Commission Regulation (EU) No. 10/2011
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Materials testing goes extreme

2015 Summer School expert meeting – New HPV-X2 ultra-high-speed camera



Figure 1: Lecture event



Figure 2: HPV-X2

» Be a millionaire – Materials testing goes extreme« was the working title of the HPV Summer School 2015 at the beginning of July in the historical city of Potsdam, Germany. 15 experts in ultra-high-speed materials testing, materials research as well as micro and nanofluid systems used this occasion for in-depth exchange of experiences.

Some of the topics leading to particularly lively discussions were

on research of novel composite materials like CFRP (carbon fiber reinforced plastics) at the German University of Dortmund, HDPE (high-density polyethylene) at the Federal Institute for Materials Research in Berlin, as well as 'drop-lets and microbubbles' research at the Technical University of Twente in the Netherlands. These technical presentations provided an up-to-date overview on ultra-high-speed investigations at several research institutes.

An additional highlight of the first day was the experimental part in the afternoon where Nobuyuki Tokuoka, an R&D engineer of Shimadzu's technical department for ultra-high-speed cameras introduced the new HPV-X2 ultra-high-speed camera. The HPV-X2 not only continues the tradition of its previous versions but also outperforms them in crucial technical data. In this way, the HPV-X2 can record up to 10 million frames per second and features extremely high sensitivity with a newly developed FTCMOS2 sensor. Particularly under poor lighting conditions, this sensor achieves a significantly improved recording quality compared to all other cameras in this performance class, of course without 'blooming' effects. Furthermore, it is possible to synchronize two cameras allowing high-speed recording from two observation directions.

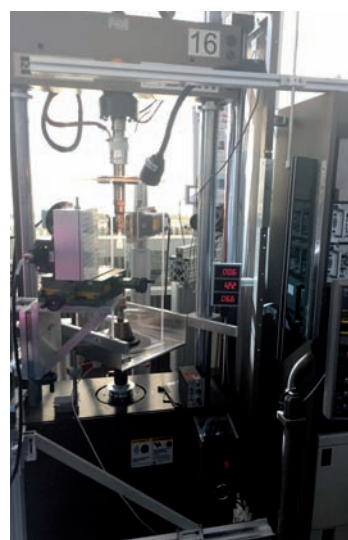


Figure 4: High-speed experiment at the Federal Institute for Materials Research and Testing

behavior under high-speed conditions were carried out using a Shimadzu HPV series ultra-high-speed camera.

On the second day, the group visited the Federal Institute for Materials Research and Testing (BAM, Bundesanstalt für Materialforschung und -prüfung) in Berlin-Steglitz.

At the Institute's Division 5.2, real-life experiments on material



Figure 3: Bus tour 'Alter Fritz.' The first day's program was concluded with a tour of the Prussian King 'Alter Fritz' castle in a historical bus, looking at Potsdam and its famous castles and parks from a different perspective with charming and humorous anecdotes and stories.

How healthy is beer?

The German Beer Purity Law of 1516

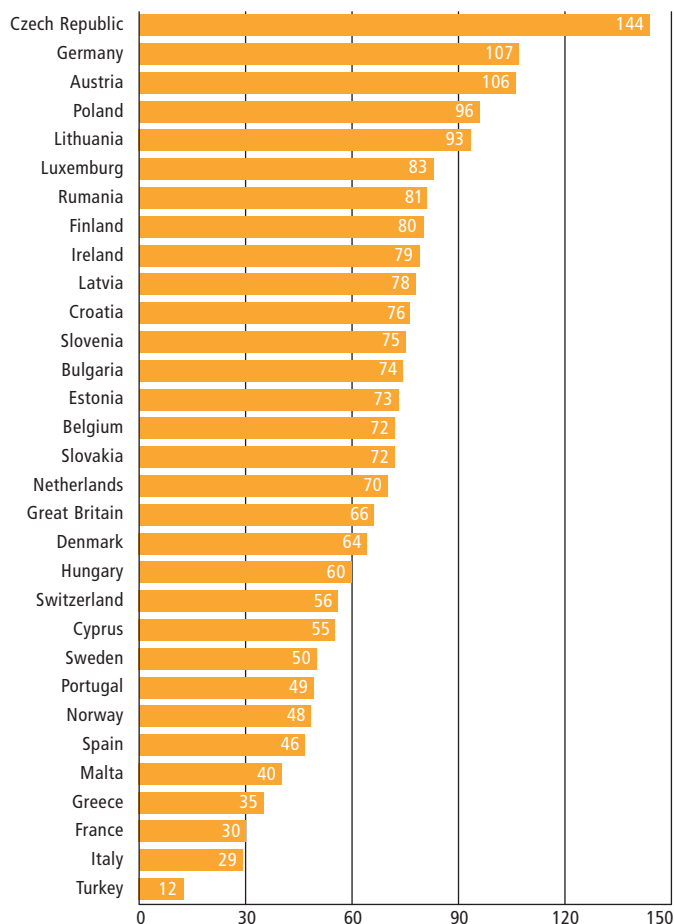


Figure 1: Beer consumption in Europe

Beer is the most popular alcoholic beverage in Europe.

In Germany, beer enjoys a particularly high status due to the German Beer Purity Law of 1516 (the “Reinheitsgebot”), which uniquely defines the ingredients of beer to be hop, malt, yeast and water. This makes the German Beer Purity Law the oldest food law in the world which is still valid today and makes beer, in addition to drinking water, one of the most researched food products with the highest standards regarding quality, freshness, appearance and flavor.

In 2014, the German brewing industry has further extended its leading position as Europe’s largest beer producer. According to the latest Barth Report on Hops

[1], German brewers with a beer output of 95.6 million hectoliters ranked first in Europe ahead of Russia (81.6), Great Britain (41.2), Poland (39.8) and Spain (33.5). With more than 1,300 breweries, Germany clearly states its core competency in the European beer sector.

China is production world champion; the Czech Republic is the thirstiest country

While beer sales in 2014 have increased slightly in Germany in comparison to the previous year, world beer production fell by 11.8 million hectoliters (–0.6 %) to a total of 1.96 billion hectoliters. In a worldwide comparison, Germany came in fourth. With an estimated yearly production of

492.1 million hectoliters, China remains the world’s largest beer producer, followed by the United States with a 225.9 million hectoliter output and Brazil (140.4 million).

Statistically, per capita beer consumption in European countries was 68 liters in 2013. The highest per capita beer consumption was determined for the Czech Republic (144 L), followed by Germany (107 L) and Austria (106 L) [2]. For these levels of consumption, the question arises: just how healthy is beer?

The dose makes the poison

Experts agree that, on the one hand, excessive consumption is unhealthy because too much alcohol impairs brain and liver cells, causes addiction and can promote the development of cancer. On the other hand, it is clear that beer consumption in small amounts is rarely harmful, but can even be conducive to good health. Consumed in moderation, beer is said to protect against heart attacks and stroke, diabetes and kidney stones and to prevent dementia.

However, what is considered to be ‘small amounts’ varies from country to country. According to the German newspaper ‘Die Welt’, men in Portugal are recommended to consume no more than 40 grams of alcohol per day, which corresponds to approximately one liter of beer. In Germany, on the other hand, the German Federal Center for Health Education (BZgA) recommends no more than 20 grams per day, i.e. half a liter. For women, one quarter of a liter per day, i.e. approximately twelve grams, should already suffice [3].

What does beer contain?

In accordance with the German Beer Purity Law of 1516, German beer contains the ingredients hops, malt, yeast and water, as well as all major B vitamins. Vitamin B2 and B6, which are important for metabolism, are particularly abundant in beer. In addition, bitter substances and essential oils are indisputably effective against loss of appetite, gastric disorders and states of anxiety.

Japanese scientists have found active ingredients in 24 types of



Figure 2: Nexera XR UHPLC with RF-20Ax fluorescence detector

beer that inhibit so-called heterocyclic amines and thus the onset of cancer. This has been confirmed by German scientists, who see the same tumor-preventing effects of the polyphenolic flavonoids as are claimed for red wine.

Last but not least, beer is diuretic, and its phenolic ingredients support the cardiovascular system. In addition, beer contains minerals and trace elements (e.g. Ca, Na, Mg and Zn) that are important for human nutrition. However, undesirable substances such as heavy metals (for instance Cd, Pb, Hg and As) are also found.

The heavy metal arsenic can be released into beer during the filtering process and, in specific cases, may reach concentrations of up to 24 micrograms per liter. This is significantly higher than the WHO guideline for drinking water of ten microgram, considered to be the limit in Germany. Arsenic may be released from the diatomaceous earth filter used for filtration. Diatomaceous earth is made up of the skeletons of fossil diatoms.

In unfiltered beer such as wheat beers, arsenic concentration is lower. Arsenic can, however, also end up in beer by way of natural processes via water. This is why water used specifically for the brewing process is often purified or sourced from brewery-owned wells. However, by selection of suitable filter materials and constant monitoring, arsenic contamination has declined over the past three years. [4]

In addition to these inorganic contaminations, undesirable substances of organic origin, the so-called mycotoxins such as ochratoxin A (OTA) can also be formed on grains/brewers barley by fungi of the *Aspergillus* and *Penicillium* genera and thus represent a potential contamination risk for the popular beer.

Analysis

For the determination of ochratoxin A, high-performance liquid chromatography (HPLC) in combination with a fluorescence detector (FLD) is a frequently used



Figure 3: ICPE-9820 simultaneous ICP-OES spectrometer with 'dual view'

method that is also described in the European standard EN 14133 (2009). Although raw materials must be analyzed for their mycotoxin content, several studies independently report on the OTA contamination of beers. Because of the average per capita consumption of over 100 liters per year in some European countries, regular residue analysis is advisable, even if discussions on the maximum OTA content at EU level are still ongoing.

Sample analysis was carried out using a Shimadzu Nexera XR UHPLC system equipped with an RF-20Axs fluorescence detector. Excitation wavelength was 335 nm and emission wavelength was 465 nm; detector response was set to 1.5 s and sensitivity was set to 'high.' A 100 x 3 mm, 1.8 µm Nucleodur phenyl-hexyl separation column (Macherey Nagel, Düren, Germany) was used. Injection volume for all measurements was 10 µL. The mobile phase flow rate (isocratic 50/50 (v/v) deionized water + 0.1 % formic acid/acetonitrile [Sigma, Altenkirchen, Germany]) was adjusted to 0.6 mL/min. The limit of detection (LOD) was < 0.1 ng/mL and the limit of quantification (LOQ) was 0.3 ng/mL with respect to the measurement solution [5].

Sequential determination of the element concentrations was carried out using an atomic absorption spectrometer, like Shimadzu's AA-7000 in combination with a GFA-7000 graphite furnace for electrothermal atomization, and

also an HVG-1 hydride vapor generator for the determination of hydride-forming elements.

For simultaneous multi-element analysis, an atomic emission spectrometer with an inductively-coupled plasma like the ICPE-9820 (figure 1) with vertical minitorch position and 'dual view' (axial and radial) plasma observation is suitable.

This method enables the analysis of samples with low concentrations of just a few µg/L (axial) such as Pb, Cd, Mn, Hg, As and Sb and high concentrations of

standard solutions. Figure 4 shows the calibration curves for 24 elements.

Conclusion

Beer has been brewed in Germany for many years according to the German Beer Purity Law. Still, beer may contain heavy metals such as arsenic and additional undesirable substances such as mycotoxins. Using sensitive analytical systems such as the Nexera XR UHPLC with the RF-20Axs fluorescence detector and simultaneous ICP-OES ICPE-9820 spectrometer, the quality of beer is permanently ensured. Beer drinkers do not need to worry, neither now nor in the future ...

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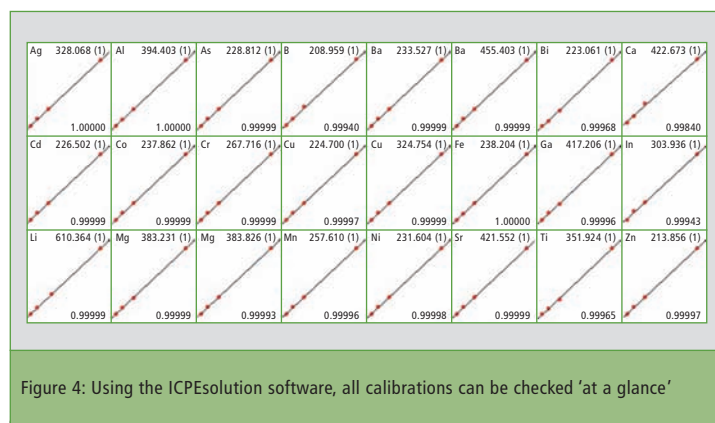


Figure 4: Using the ICPEsolution software, all calibrations can be checked 'at a glance'

approximately 0.5 mg/L up to 150 mg/L (radial) such as Na, K, Ca and Mg within a single analysis sequence. Implementation of this method is carried out in accordance with DIN EN ISO 11885 (2009). The beer samples were degassed for 5 minutes in an ultrasonic water bath and subsequently diluted with water to 1:1 and 1:5 respectively. Calibration was performed against aqueous



Extra virgin olive oil: genuine or fake?

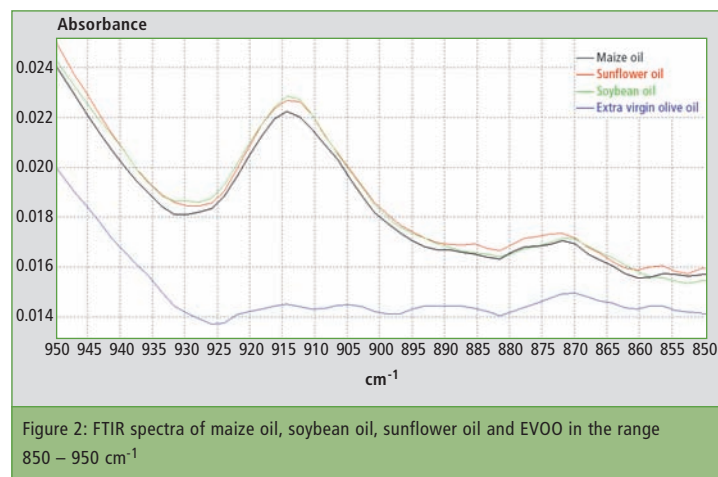
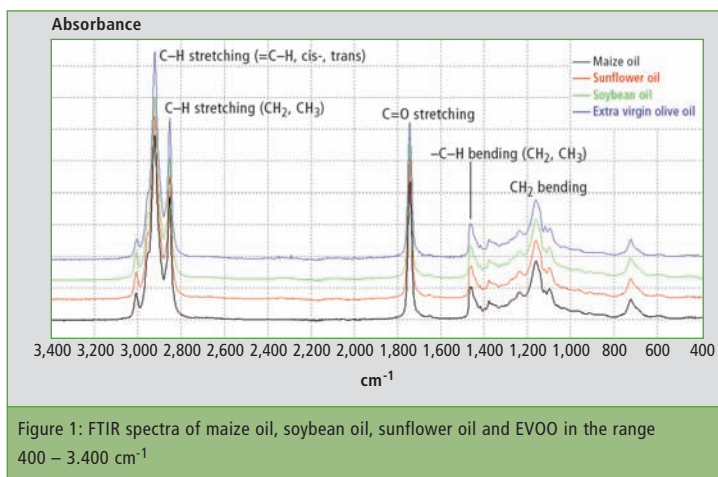
Reveal adulteration through FTIR spectroscopy

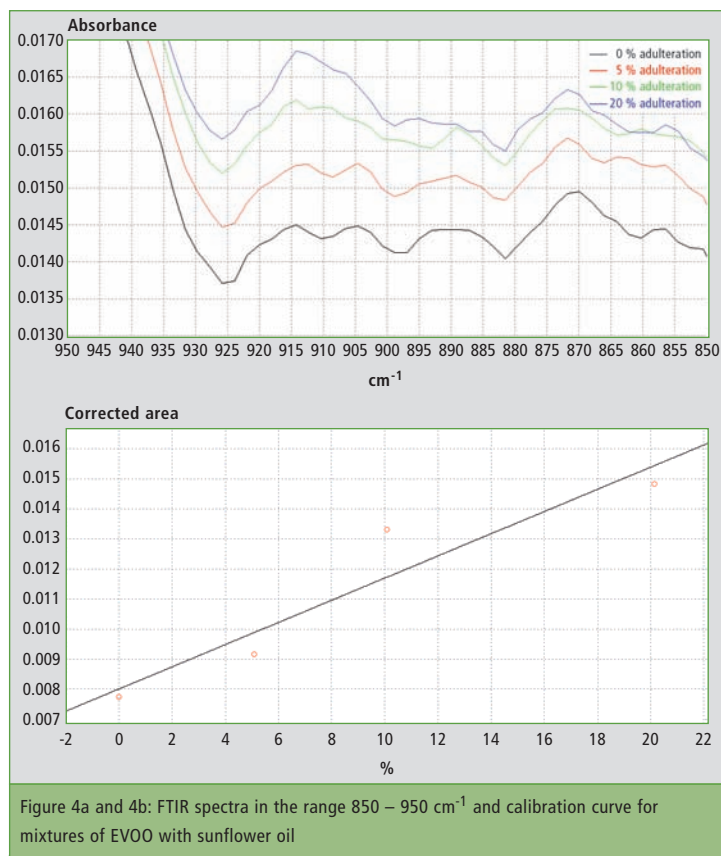
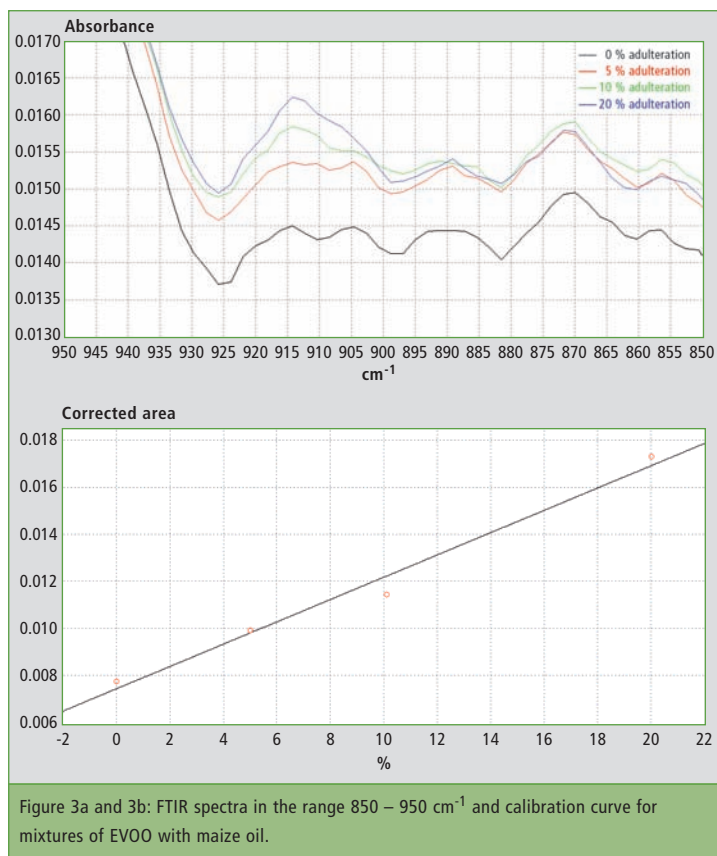
Consumer demands and their preoccupation with a rational and healthy diet require

a high consumption of vegetable oils rich in unsaturated fatty acids. In Central and North European

countries, this has led to increased imports of expensive oils. Extra virgin olive oil (EVOO) is one of

the favorite products of European consumers. High prices of EVOO cause some producers and traders





to focus on their partial or total substitution through cheaper oils (sunflower oil, soybean oil).

Establishing the authenticity of EVOO continues to be of great interest to scientists and consumers, and detecting adulteration of EVOO for economic gain is an ongoing concern for regulatory agencies. Many of the official methods used to detect adulteration of EVOO are labor intensive, time consuming and generally require more than one method. This study proposes a FTIR method without the need of sample preparation, to establish rapidly the authenticity of EVOO product.

Methods and materials

Mixtures of EVOO with maize oil, soybean oil and sunflower oil at various ratios (w/w) were measured using a Shimadzu IRAffinity-1S FTIR spectrometer and a single reflection diamond ATR attachment. The data collected were processed after performing ATR correction using 1,000 cm⁻¹ as a reference wavenumber. The origin of oil samples was well

known and the authenticity was checked with appropriate chromatographic methods.

Results and discussion

The FTIR spectra of EVOO, maize oil, sunflower oil and soybean oil are shown in figure 1.

Adulterant	Equation	r ²
Maize oil	Corrected Area = $4.741 \times 10^{-4} \cdot (\% \text{ Adulterant [w/w]}) + 7.435 \times 10^{-3}$	0.98
Sunflower oil	Corrected Area = $4.576 \times 10^{-4} \cdot (\% \text{ Adulterant [w/w]}) + 7.857 \times 10^{-3}$	0.97
Soybean oil	Corrected Area = $3.694 \times 10^{-4} \cdot (\% \text{ Adulterant [w/w]}) + 8.002 \times 10^{-3}$	0.90

Table 1: Results of linear regression for mixtures of EVOO with maize oil, sunflower and soybean oil

All of them are characterized by the same well evident peaks at 900 – 1,400 cm⁻¹, 1,700 – 1,800 cm⁻¹ and 2,800 – 3,100 cm⁻¹. The spectral structure of edible oils is mainly due to lipid molecules containing fatty acids. The similarity of the spectra reflects the similarity in the chemical composition of these oils. Nevertheless, minor differences appear in a more detailed analysis in terms of small band shifts and of small differences in relative intensity.

With closer inspection of the FTIR spectra of these oils, some differences located at around

900 cm⁻¹ are evident in figure 2. From the literature, it can be evinced that the band at ca. 914 cm⁻¹ is related to the out-of-plane bending vibration of the =C–H group. This vibration is present due to trans-fatty acids, which are totally absent in EVOO but are present in all refined oils.

Thus adulteration of EVOO with any of these seed oils can be determined by measuring the absorbance at ca. 914 cm⁻¹.

In the FTIR spectra of EVOO, this band is best defined in the range from ca. 895 to 925 cm⁻¹. By using the corrected area between 895 and 925 cm⁻¹ for the determination (i.e. by setting the spectral points at 895 and 925 cm⁻¹ as baseline points), the effects of the horizontal shifting of the band and of the vertical shifting of the baseline for different ratios of EVOO and adulterant are canceled.

Table 1 shows the results obtained using different mixtures (w/w) of EVOO with maize oil, sunflower oil and soybean oil. The relevant spectra and calibration curves for maize oil, sunflower oil and soybean oil are shown in figure 3, figure 4 and figure 5 respectively. ♦

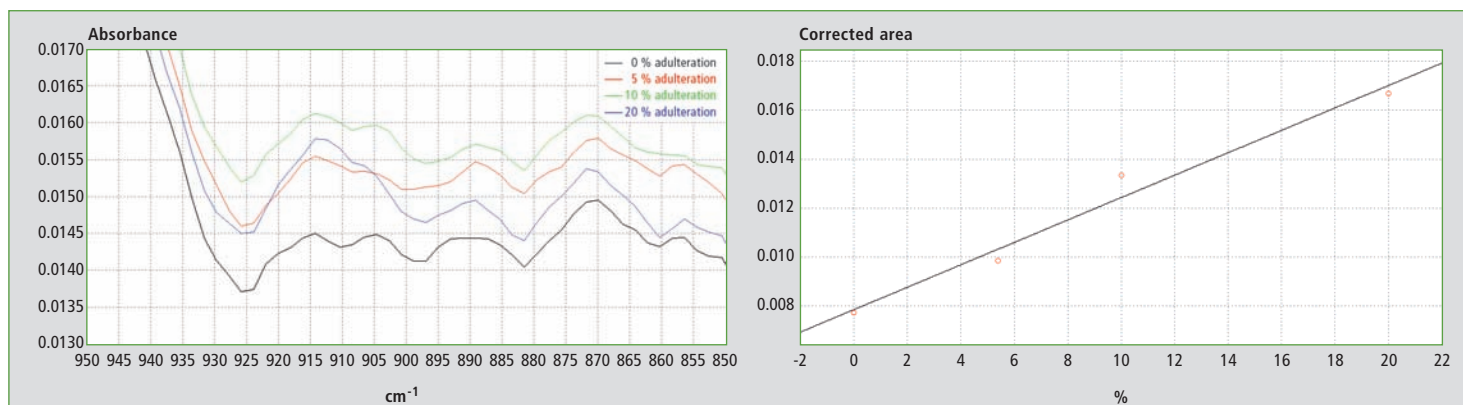


Figure 5a and 5b: FTIR spectra in the range 850 – 950 cm⁻¹ and calibration curve for mixtures of EVOO with soybean oil

It is noteworthy, not only that the results are linear, but also that a single calibration curve can be constructed for all of these adulterants (figure 6). The results are

This method is suitable for detecting adulteration of EVOO down to 3 %. For lower detection limits, horizontal attenuated total reflection HATR or the classical



shown in table 2. The LOD and LOQ values determined based on the residual standard deviations of the overall regression line were 3 % and 9 % (w/w) respectively.

Conclusions

FTIR spectroscopy provides a good means for the fast determination of adulteration of EVOO with maize oil, soybean oil and sunflower oil. The proposed method does not require sample preparation and eliminates the need for using organic solvents. The band at ca. 914 cm⁻¹ is an excellent target for this determination since its data are linear and produce similar results for the adulteration of EVOO irrespective of the adulterant being used (maize oil, soybean oil or sunflower oil).

transmission mode techniques may be used. Both need more sample preparation and solvents.

For sophisticated adulteration, official chromatographic methods or in-house developed methods from expert contract laboratories are more appropriate.

Authors

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Equation	r ²
Corrected Area = $4.326 \times 10^{-4} \cdot (\% \text{ Adulterant [w/w]}) + 7.780 \times 10^{-3}$	0.92

Table 2: Results of linear regression for mixtures of EVOO with maize oil, sunflower oil and soybean oil

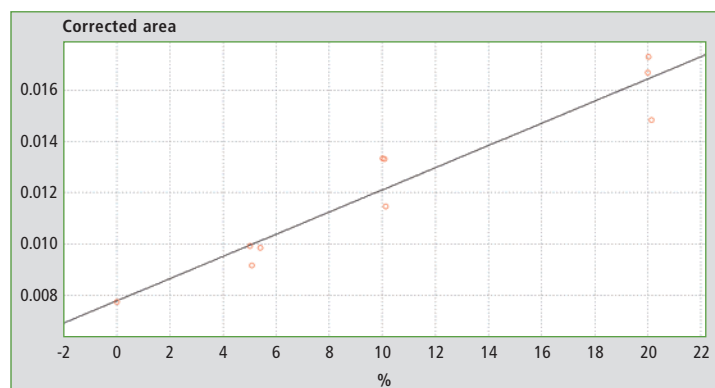


Figure 6: Calibration curve for mixtures of EVOO with maize oil, sunflower oil and soybean oil

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Application note:
SCA_110_017 Iodine
number determination
using FTIR-ATR-Spec-
troscopy



Small explorers in the laboratory

Elementary school students playfully explore the world of analysis

It is as quiet as a mouse in Shimadzu's materials testing laboratory where 26 elementary school students of the Albert Schweitzer elementary school are eagerly holding their breath. Finally a faint click occurs, then a deep breath and surprised faces. This is what it sounds like when the testing machine breaks through a chocolate bar. The experiment is part of Shimadzu's Summer School to which the company has, for the first time, invited 4th grade students of an elementary school in Duisburg. Here, the children can playfully learn how analytics and related technologies play a role in daily life – without anyone being aware.

As an example, the chocolate bar product specialist Mirnes Hasan-basovic demonstrates in a test how much force teeth and jaws must exert to bite through a bar of chocolate. And the difference between milk chocolate and dark chocolate plays a role; the darker the chocolate, the harder the choc-



olate bar. This is how product manufacturers ensure that biting into your favorite chocolate bar or into an ice cream bar always imparts the same feel – and sound. Even uniform popping sounds are important. The boys were interested not only in food testing but especially in the harder materials: “What kind of objects or materials can Shimadzu's instruments destroy? Also trucks, airplanes or

even titanium?” These are also possible, but of course everything must first be disassembled into testable individual parts. Hearing this, their eyes light up.

Chromatography to trace down felt-tip pen and perfume

From the testing laboratory, the young students now move on to the conference room. There they

sit down at their tables like ‘grown-ups’ and can finally do some testing themselves. Product specialist Dr. Ute Potyka presents a ‘child-friendly’ introduction to chromatography. Equipped with test tubes, felt-tip pens, paper strips and wooden sticks, it is now time to experiment. They observe how two narrow bands of ink slowly spread out over the entire piece of paper. This exciting spectacle is triggered as soon as the paper comes into contact with the water in the test tube. The fascination is great and the neighbor's test tube is also eyed curiously – since depending on the color, the bands migrate up the paper at different speeds. On a flip chart Dr. Ute Potyka explains to the children in a few words how their experiment relates to instrumental chromatography. Although the term ‘chromatography’ may still appear to be somewhat awkward, the children could relate to the principle.

In the adjacent laboratory the students discover another aspect of chromatography: the perfume test. What perfumers had mixed together with loving attention to detail into a fragrance is now decomposed by Shimadzu's GCMS-QP2010 into its individual scents. Is it possible to recognize these scents in the smell test? While the GCMS instrument is adjusting automatically to the correct temperature, the children curiously marvel at the giant instruments in the laboratory.

Dr. Hendrik Schulte explains how the autosampler works and demonstrates the closing force of the small door behind which the sample is analyzed. No jerking and tugging can open this door. “Not even ten elephants?” asks an interested student. “That would need to be tested,” ponders Schulte. ♦



However, the children quickly arrive at the conclusion that the elephants would not all fit in the laboratory at the same time. The proof of that experiment will have to wait ...

The perfume is now prepared and ready for the smell test. Standing on a small stool, the children apply their noses to the 'sniffer' to smell the scents. English terms? No problem! The students have been learning English since the 1st grade. It is, however, more difficult to smell the individual scents: caramel, chamomile or perhaps something completely different? The solution is surprising and the children want to try again right away to find out if they can better recognize the scent with this new knowledge.

Spectroscopy – plunging into the colorful world of light

But it is also possible to analyze product components using Shimadzu's instruments without first disassembling them. Product specialist Jan Knoop demonstrates this with a yellow toy car. While the students look at the peaks on the monitor with great interest, Knoop explains what they mean: "This old toy car still contains cadmium. In your toys, this is clearly no longer the case – much too unhealthy." Even when cadmium is an unfamiliar term to the children, they do understand that the instrument helps to make their toys safer.

Concentrating hard, they build their next testing object: a spec-

troscopy box. Product specialist Marion Egelkraut-Holtus explains how a spectroscopy grating disperses the light. Once assembled, one looks through a pinhole to see the color composition of the light, which falls through a slit onto the opposite end of the box. "A rainbow, way cool!" cries out a girl excitedly. Depending on the light source, the children see colorful bands of different thickness in the box. While some children do not want to put the box aside, others already answer the questions eagerly in the final small quiz. A quick glance at the neighboring table confirms: the box is checked correctly.



From young explorer to young scientist

When you learn so much, you get hungry. At the end of the day, giant pizzas already await the children in Shimadzu's cafeteria. While the young explorers satisfy their appetite, Uta Steeger, coordinator of the Summer School



comes to a positive conclusion: "I am very happy that the children had so much fun. This encourages us as a company, to be able to offer students practical insights into the sciences and to awaken enthusiasm for these subjects." This seems to have worked – before the young scientists are getting ready to go home, an urgent question: "How old do you have to be to become a trainee at Shimadzu?" Clearly, there is no shortage of future young talents at Shimadzu's Duisburg location. And the class teacher is also convinced that the children have picked up many new experiences: "Even if they may not have understood the principles of all the experiments, there will be a moment later during physics lessons, when they 'get it' – practical knowledge has a long-term effect."



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