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# NEWS 01 2018

50th ANNIVERSARY Shimadzu Europa

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50th anniversary of Shimadzu in Europe

# How X-ray fluorescence can support consumer prices stability

## Aluminum fluoride all-in-one analysis with EDX-8000P

Figure 1: Aluminum cookware: the easiest way to cook and transport various food dishes

Nowadays, aluminum as a chemical element plays an important role in everyday life. Due to its low weight and good thermal conduction, aluminum and its alloys are the basis for modern aviation industry, aerospace engineering, production of automobiles, rolling stock for high speed trains, sea and river vessels...

Moreover, this element is extremely popular in the production of cookware or foils used for packaging in the food industry.

Aluminum is produced by electrolysis of alumina dissolved in a molten cryolite bath. The process of electrolysis requires a huge amount of electricity. Some industrial processes using aluminum fluoride $AlF_3$ (approximately 5 - 15 %) and other additives have been developed to decrease the melting point to 930 - 950 °C and to increase conductivity of the electrolyte solution. This reduces energy consumption and greatly decreases the cost of the aluminum.

Before being used as an additive, aluminum fluoride has to be analyzed in order to check the content of the main component. At the same time, the main impurity (aluminum oxide) as well as harmful elements such as silicon, phosphorus and iron are examined in order to prevent main product contamination (metallic aluminum).

### $AlF_3$ quality analysis: a constant challenge for laboratories

According to the Russian GOST regulation (national standard of the Russian Federation and CIS countries), standard chemical analysis of aluminum fluoride includes many time-consuming sample preparation steps including fusion and dissolution. In addition, different analysis methods are used for each compound: titration for quantitative analysis of $AlF_3$, free aluminum oxide ($Al_2O_3$) determination by trilo-

nometric measurement of aluminum, and photometric analysis of silicon, phosphorus and iron oxides ($SiO_2$, $Fe_2O_3$ and $P_2O_5$). So, complete analysis of one sample (including sample preparation) takes more than twelve hours and requires many chemical reagents and devices.

Use of the EDX-8000P Energy Dispersive X-ray fluorescence spectrometer appears to offer a valuable alternative way to simplify and dramatically decrease analysis time. This spectrometer is in fact able to analyze all elements from carbon up to uranium in a simultaneous measurement. Moreover, target concentration ranges are compatible with the EDX spectrometer sensitivity. The EDX-8000P is BfS (safety standards of the German Federal Institute for Radiation Safety) type approval certified.

## New fast and easy X-ray fluorescence method for $AlF_3$ analysis

Samples of $AlF_3$ were prepared for analysis by grinding in the mixer mill and pressing in the pellet press. The same sample preparation is used for single $AlF_3$ standard sample with a known content of the main component and $Al_2O_3$. Calibration samples for analysis of $SiO_2$, $P_2O_5$ and $Fe_2O_3$ were prepared by adding known amounts of element oxides to $AlF_3$ standard sample and subsequent mixing, grinding and pressing.

A routine measurement procedure of unknown sample by Fundamental Parameters (FP) method is included in the standard spectrometer software (PCEDX). Nevertheless, a single standard sample was used to perform methods calibration in order to improve accuracy of results. Aluminum fluoride content was calculated on the basis of fluorine element concentration. Aluminum oxide $Al_2O_3$ concentration was then evaluated by the aluminum peak after aluminum fluoride subtraction. Results of X-ray and chemical (titration and photometry) analysis obtained for fluorine and aluminum are given in table 1.

| | Concentration, wt. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Russian Standard GOST 19181-78 | Sample 1 | | Sample 2 | | Sample 3 | | Sample 4 | |
| | | Chem. | EDX | Chem. | EDX | Chem. | EDX | Chem. | EDX |
| $AlF_3$ | > 93 | 94.5 | 94.9 | 95.8 | 95.2 | 96.1 | 96.0 | 96.0 | 95.9 |
| $Al_2O_3$ | > 4 | 2.7 | 2.6 | 2.5 | 2.3 | 1.9 | 2.1 | 2.1 | 2.2 |

Table 1: Comparison of results of main component and $Al_2O_3$ in $AlF_3$ analysis by chemical methods (Chem.) and EDX-8000P

| | Concentration, wt. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Russian Standard GOST 19181-78 | Sample 1 | | Sample 2 | | Sample 3 | | Sample 4 | |
| | | Chem. | EDX | Chem. | EDX | Chem. | EDX | Chem. | EDX |
| $SiO_2$ | > 0.25 | 0.15 | 0.18 | 0.16 | 0.16 | 0.11 | 0.14 | 0.09 | 0.12 |
| $P_2O_5$ | > 0.05 | 0.026 | 0.025 | 0.026 | 0.024 | 0.03 | 0.027 | 0.018 | 0.021 |
| $Fe_2O_5$ | > 0.08 | < 0.02 | 0.015 | < 0.02 | 0.015 | < 0.02 | 0.01 | 0.030 | 0.027 |

Table 2: Comparison of results for $SiO_2$, $P_2O_5$ and $Fe_2O_3$ analysis by chemical methods (Chem.) and EDX-8000P

The other contaminants (silicon, phosphorus and iron oxides) were analyzed using calibration curve method with corresponding element specific Kα lines. Calibration curves for each oxide are shown in figure 3. The results of X-ray and chemical analyses are given in table 2.


Figure 2: Energy dispersive X-ray fluorescence spectrometer EDX-8000P

Total analysis time of all elements including sample preparation was only approximately thirty minutes.

## Conclusion

All EDX results shown in tables 1 and 2 showed excellent correlation with official regulation analysis methods results. This demonstrates that the EDX-8000P analysis procedure is a valuable alternative to traditional time-consuming methods. By decreasing analysis time and chemical product consumption, this new strategy can contribute to reduced aluminum material prices and in the end to price stability of consumer prices for food packaging, convenience foods and freshly prepared meals on wheels.

## Acknowledgements

We gratefully acknowledge the valuable advice and assistance in EDX analysis of our colleagues from the accredited Analit Company (St. Petersburg, Russia) laboratory.

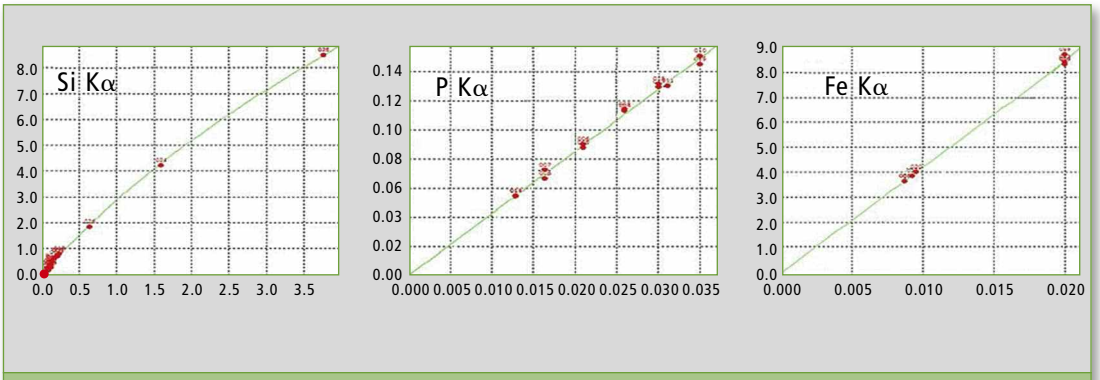


Figure 3: Calibration curves obtained for each targeted contaminant

# Into the microwave!

## Analysis of fatty acids in foods


The EU regulation on the provision of food information to consumers (No. 1169/2011) [1] requires all food manufacturers to label their products with information on the content of saturated and unsaturated fatty acids. The new regulation aims to provide more transparency to consumers so that they have a sound basis for making a decision on whether or not to buy a product.

Analysis of fatty acids is based on determination of the total fat content using the Weibull-Stoldt method (ISO 8262-1 [2]), followed by derivatization of the fatty acids to volatile fatty acid methyl esters (FAMEs) according to ISO 12966-2:2011, and their GC analysis according to ISO 12966-4:2015 [3]. The ISO standards form the basis of a new method recently developed at the University of Applied Sciences in Krefeld, Germany that uses microwave-assisted extraction and analysis of saturated and unsaturated fatty acids. This method has already been presented in the journal Chromatography Today 5-6/16.

Whereas the ISO method determines total fat by means of digestion in hydrochloric acid followed by Soxhlet extraction, the microwave method involves simultaneous digestion and extraction of the lipids. The microwave used for this was a Discover SP-D® instrument manufactured by the German-based CEM company.

| Injector | SPL (Split) |
|---|---|
| Injection volume | 1 µL |
| Injector temperature | 250 °C |
| Split ratio | 1:100 |
| Column type | FAME WAX |
| Column length | 30 m |
| Inner diameter | 0.25 mm |
| Film thickness | 0.25 µm |
| Detector | FID |
| Detector temperature | 250 °C |
| Mobile phase | Helium |
| Carrier gas flow | 35 cm/s |

Table 1: Parameters for GC analysis of the FAMEs using a GC-2010 Plus instrument

Total fat contents of the reference materials investigated – milk powder and chocolate – were recovered completely. All non-certified samples also gave very good recovery rates of > 90 wt.-% total fat with standard deviations between 0.6 and 3.7 wt.-%. This clearly demonstrates that successful determination of the total fat in real samples using the microwave method is matrix-dependent.

In particular, the homogeneity of the sample influences the completeness of the extraction. This especially affects foods such as potato chips and infant formula powder due to their inhomogeneity or to the complexity of their composition. The recovery rate of these samples can be increased by approx. 15 % by means of repeated extraction (cold). These steps are carried out with fresh solvent after digestion. As a compromise between complete recovery and required analysis time and consumption of chemicals, three extraction steps were carried out for each analysis.

### ISO vs. microwave

In the long term, the microwave method of determining total fat presents an attractive alternative because it offers considerable savings in resources. Experiments showed that a single determination of total fat using the microwave method takes 1.5 h, whereas the ISO method takes up to 9.5 h. The microwave method thus offers a time saving of 8 h while also requiring less instrumentation. Furthermore, it requires much smaller quantities of chemicals, particularly organic solvents (figure 3).

The actual analysis of fatty acids is carried out using gas chroma-

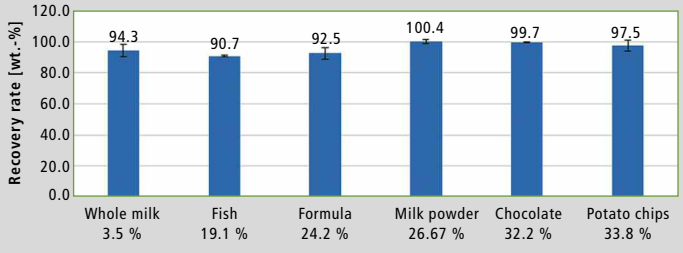


Figure 1: Recovery rates of the total fat contents of all food samples investigated; the milk powder and chocolate are certified reference materials. For the other samples, a reference value was determined with the ISO method.

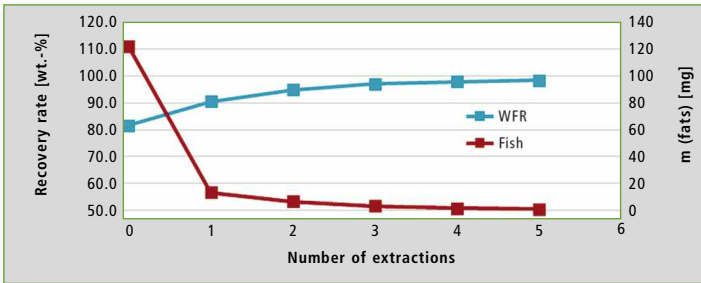


Figure 2: Plot of the fat extracted per extraction and increasing recovery rates (RR) for the extraction of a salmon sample using the microwave method

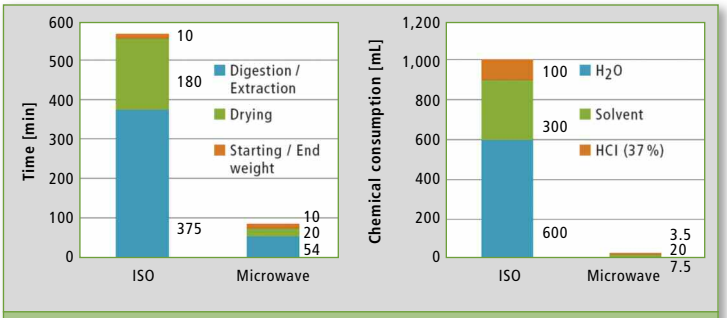


Figure 3: Required time and consumption of chemicals for a single total fat determination using the microwave and ISO methods

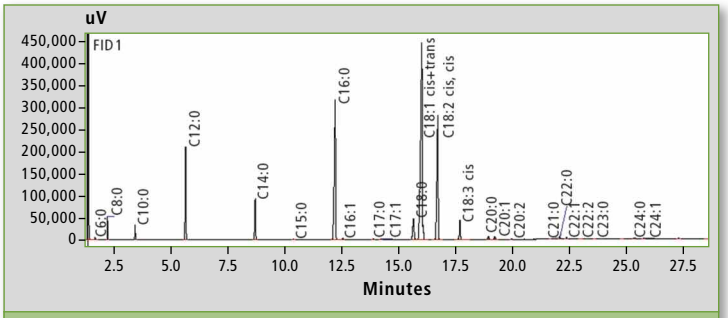


Figure 4: Chromatogram of the FAMEs from infant formula powder using the microwave method

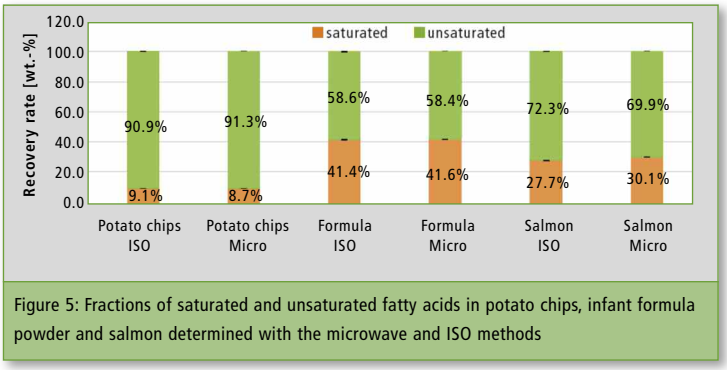


Figure 5: Fractions of saturated and unsaturated fatty acids in potato chips, infant formula powder and salmon determined with the microwave and ISO methods

tography. With respect to required time and consumption of chemicals, the new microwave derivatization is very similar to the general methods described in ISO 12966-4. An alkali- and an acid-catalyzed derivatization step are each carried out to convert both bound and free fatty acids to FAMEs. Parameters used for GC analysis of the FAMEs with a GC-2010 Plus from Shimadzu are summarised in table 1.

The 37-component FAME mix from Supelco company was used for identification. The GC method applied was able to separate all FAMEs present, except for the cis/trans isomers of oleic acid (C18:1). Figure 4 shows the chromatogram of the FAMEs present in a sample of infant formula powder.

The peak areas have a linear relationship with the mass fractions so that summation over the peak areas enables determination of the percentage fractions of the saturated and unsaturated fatty acids. The microwave method for the infant formula powder (chromatogram) gives a fraction of 41.6 ± 0.12 wt.-% for saturated fatty acids and 58.4 ± 0.12 wt.-% for unsaturated. Figure 5 compares the percentage mass fractions of three samples obtained using the ISO and the microwave methods.

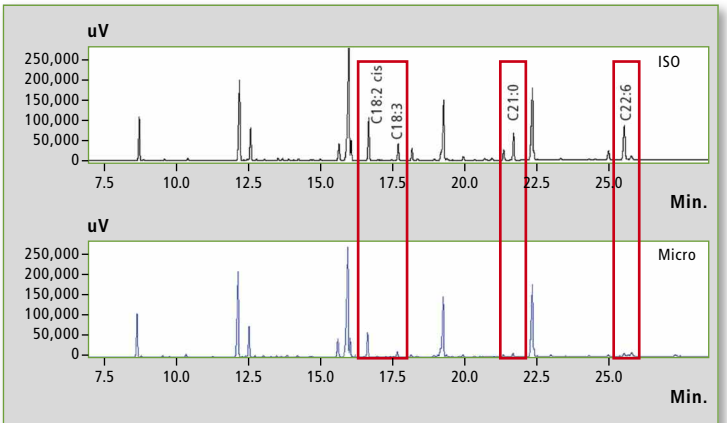


Figure 6: Top chromatogram: Analysis of salmon using the ISO method. Bottom chromatogram: Analysis of salmon using the microwave method.

This shows that the mass fractions of saturated and unsaturated fatty acids obtained with the two methods are in agreement, and the microwave method is thus qualitatively equivalent to the ISO method. This also applies to the sample of potato chips, which contained an enormously high fraction of unsaturated fatty acids.

Some samples, e.g. salmon, gave slight deviations in the ratio of saturated to unsaturated fatty acids. A closer look at the chromatograms of the salmon sample reveals slight differences for both methods. For example, fatty acids C21:0 and C22:6 were not found using the microwave method, in contrast to the ISO method. Further investigations are necessary in this context.

## Conclusion

GC-FID is a simple way of determining saturated and unsaturated fatty acids in foods. For sample preparation, the microwave method of extracting fatty acids in foods can be used as the basis for analyzing a wide range of food samples. Compared to conventional ISO methods, it saves resources with respect to both chemicals and time and also gives comparable results.

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## Literature

[1] The European Parliament and Council of the European Union, "Regulation No. 1169/2011 of the European Parliament and of the Council," No. 1169. pp. 18-63, 2011.
[2] Deutsches Institut für Normung e.V., "Bestimmung des Gesamtfettgehalts in Fleisch und Fleischerzeugnissen- Gravimetrisches Verfahren nach Weibull-Stoldt" (Determination of the total fat content in meat and meat products – Gravimetric determination using the Weibull-Stoldt method). Beuth Verlag Berlin, 2014.
[3] Deutsches Institut für Normung e.V., "Animal and vegetable fats and oils – Gas chromatography of fatty acid methyl esters – Part 4: Determination by capillary gas chromatography (ISO 12966-4:2015)". Beuth Verlag Berlin, 2015.

# New solutions for treating plastic waste

## FTIR analysis of biodegradable polymers from everyday life

Every year, an estimated 140 million tonnes of plastic are produced from fossil fuels [1]. Much of this is intended for the production of consumer goods such as food packaging or disposable tableware. But what happens to plastic after it has been disposed of?

Recycling large proportions of the plastic requires much effort. After a few cycles, however, it becomes plastic waste and ends up in landfills. From there, it makes its way into the environment as microplastic [2]. The microplastic then becomes part of the food chain, and returns sooner or later to the consumer.

In 2014 on the Dutch island of Texel, the stomach contents of fulmars were tested for polymers, a scientific project driven by Dr. J. A. van Franeker, Wageningen University & Research. On average, about 0.3 g of plastic per bird (700 g) stomach was found; compared to a human with 70 kg, this is equivalent of the capacity of a lunch box filled with plastic [3]. This illustrates the problem of microplastics in the environment. For many years, research has addressed the situation. The solution to the problem is called biodegradable plastics.

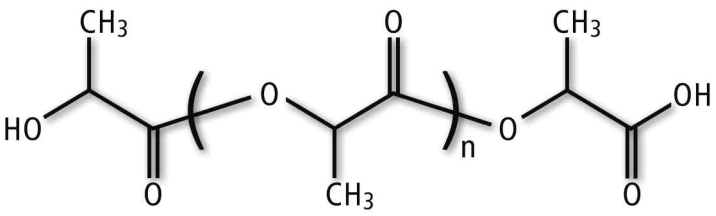



Figure 1: Chemical Structure of Polylactic Acid (PLA)

## Biodegradable plastics in food packaging

Analysis of food packaging reveals traces of biodegradable plastics. So far, about 200 plastic packaging of foodstuffs have been analyzed for their main components using infrared spectroscopy (FTIR). This was done with the IR-Tracer100 FTIR spectrophotometer in combination with an ATR (attenuated total reflection) diamond reflection unit. Five of the samples tested are labelled as "biodegradable", more specifically: two teabags, one garbage bag, disposable cutlery and the lid of a disposable coffee cup (figure 2). The samples were from England, Germany and the Netherlands.

Figure 3 shows that the ATR spectrum of the disposable spoon has similarities to the spectrum of modified polylactic acid (PLA). The additional peaks at 1,010 $cm^{-1}$ and 667 $cm^{-1}$ are due to the stretching and deformation vibrations of the Si-O bond, suggesting the presence of talc as a filler [4].

## Which polymers are in disposable dishes?

PLA is a polymer consisting of lactic acid monomers that can be produced by lactic acid bacteria. Biodegradation is carried out by microorganisms, or rather through their excreted enzymes (esterases, proteases, lipases). In the simulated composting of a PLA bottle, it was found that it took about six weeks until over 80 % of the bottle was broken down into $CO_2$ and water [1]. PLA is therefore a desirable alternative to plastics such as PP, PE or PS.

A big disadvantage of PLA, however, is its high brittleness. The disposable spoon, for example, is very rigid and breaks easily, strongly limiting applications of the biological plastic as a packaging material. To circumvent this difficulty, attempts have been made to add low-molecular plasticizers to PLA [1]. Other disadvantages are the low heat resistance and higher production costs.

In addition to packaging materials, 3D printing and medical technology are other possible fields of application for PLA. Medical technology benefits above all from the degradation properties of PLA. Implants made of PLA (e.g. screws) can be designed so that they are absorbed by the body over a defined period of time. Other applications in the medical field include sutures and microspheres for the release of active ingredients [5].


Figure 2: Analyzed samples consisting of biodegradable polymers (declaration on the products)

## Biodegradable polymers in a tea bag

Analysis of the biodegradable tea bags showed that both are also made of PLA. This polymer replaces the commonly used PET (polyethylene terephthalate). Earlier research has shown that PET teabags contain about 200 ppm of antimony, leading to significant contamination of the tea during the brewing process [6]. Due to the harmful properties of

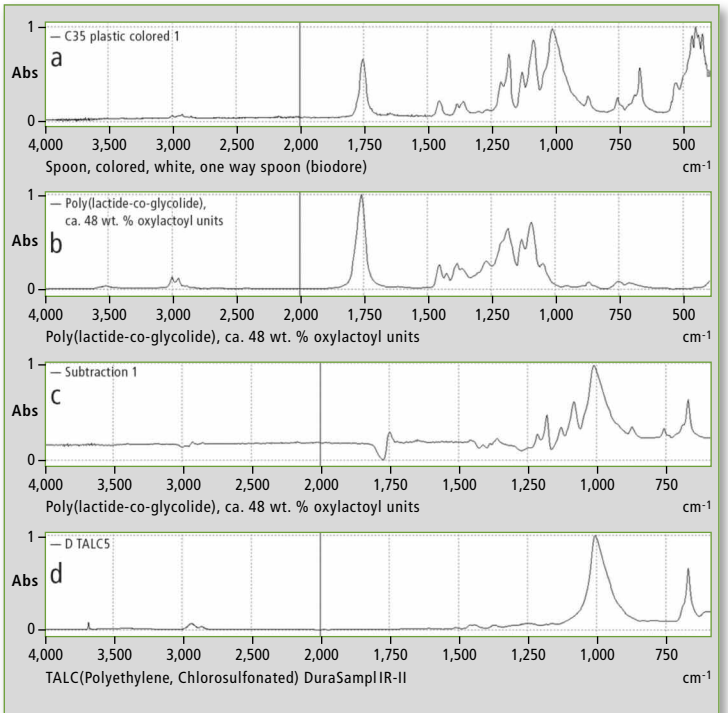



Figure 3: IR spectrum of plastic spoon (a), IR database spectrum of modified PLA (b), differential spectrum of a and b (c), IR database spectrum of talc (d)

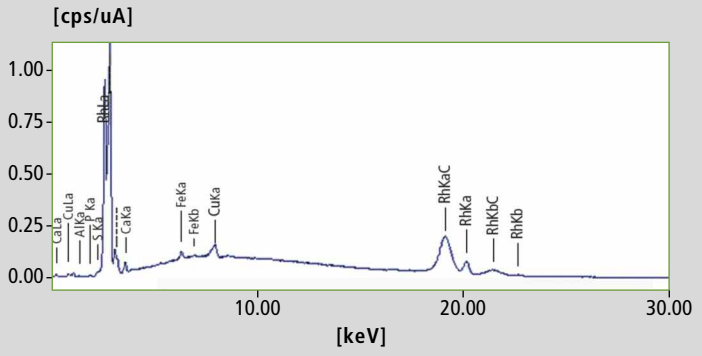



Figure 4: EDX spectrum of a PLA teabag (excitation energy 50 kV). Neither antimony nor other harmful heavy metals have been detected.

antimony, the use of PET in teabags may present a health risk. EDX (energy-dispersive X-ray fluorescence) analysis of the PLA tea bags shows that neither antimony nor other harmful heavy metals are detectable here. This makes PLA more environmentally friendly, and also safer as a material for tea bags.

### PBT in garbage bags

Finally, the "biodegradable" garbage bag should be mentioned. FTIR analysis confirms that this is not PLA but polybutylene terephthalate (PBT). There is also evidence of glycogen in the IR spectrum, a widely branched polysaccharide that acts as a storage medium in the human body. It is made up of numerous glucose units and, in the case of the garbage bag, connects the PBT chains [7]. At the same time, it offers a point of attack for breaking down of the chains by chemical or biological hydrolysis. Unlike PLA which can be broken down microbially to water and $CO_2$, the decomposition here is really a reduction of chain length.

### Summary

PLA bioplastic is a popular alternative to fossil-based polymers. It is already being used in a wide variety of applications but has not yet prevailed over conventional plastics in the food packaging sector. In addition to cost reasons, this is mainly due to inadequate material properties. ATR analysis of the samples presented shows that FTIR spectroscopy is a suitable method to identify biodegradable polymers and their additives non-destructively in a minimal amount of time. Additionally, with the EDX technique, it is possible to easily determine the elemental composition of the polymer and to assess the safety of the product.

### Literature

[1] Madhavan Nampoothiri K., Rajendran Nair N., Pappy John R., An overview of the recent developments in polylactide (PLA) research, NIIST, India, 2010.

[2] Amass W., Amass A., Tighe B., A Review of Biodegradable Polymers: Uses, Current Developments in the Synthesis and Characterization of Biodegradable Polyesters, Blends of Biodegradable Polymers and Recent Advances in Biodegradation Studies, POLYMER INTERNATIONAL, 1998, VOL. 47, NO. 2.

[3] Van Franeker, J. A., Fulmar Litter EcoQO monitoring in the Netherlands – Update 2014. IMARES Report C123/15. IMARES, Texel. 55 pp., 2015.

[4] Farmer V. C., The infrared spectra of talc, saponite and hectorite, The Macaulay Institute for Soil Research, Aberdeen, Scotland, 1958.

[5] Ruffieux K., Wintermantel E., Resorbierbare Implantate. In: Medizintechnik Life Science Engineering, Springer, Berlin, Heidelberg, 2008.

[6] Egelkraut-Holtus M., Knoop J., Ortlieb M., Antimony in Breakfast Tea? Consequences Going Hand in Hand with Today's Materials, G.I.T. Laboratory Journal 1-2/2015, 26-27.

[7] www.chemie.de/lexikon/Glykogen.html

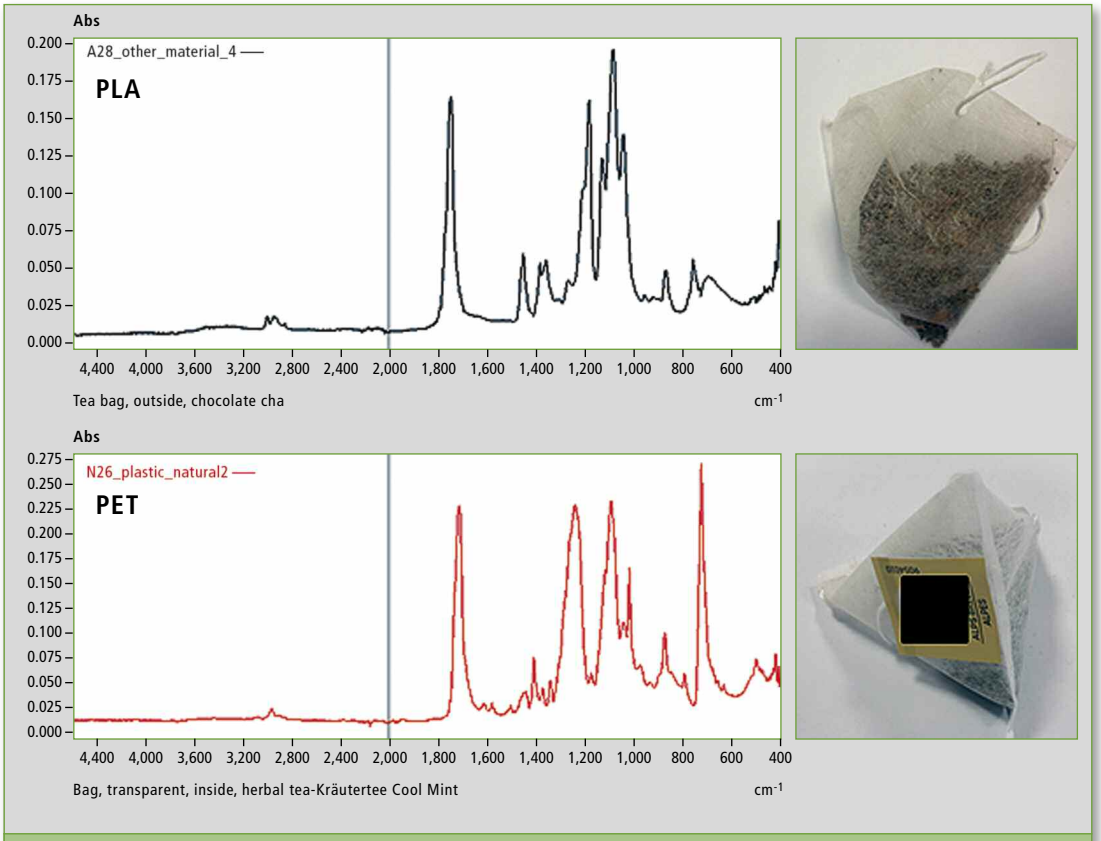



Figure 5: Comparison of spectra of PLA teabag with a conventional PET teabag

# New micro-flow LC-MS solution

## Nexera Mikros provides high sensitivity, durability and ease-of-use

The Nexera Mikros is a brand-new LC-MS accommodating a wide range of flowrates, from semi-micro flowrates (100 to 500 µL/min) which are often used for analysis in existing systems, to micro flowrates (1 to 10 µL/min). This system achieves both durability and operability while enabling analysis with a significant increase in sensitivity.

Nexera Mikros complements the Nexera series, featuring Nexera X2, XR, MP, Nexera-i and Nexera UC systems to maximize analytical productivity. The Nexera series is a unique approach to delivering high-quality, high-speed LC-MS analysis combining the Nexera UHPLC and any Shimadzu single or triple quadrupole UFMS solution as a seamlessly integrated system.

With Nexera Mikros, Shimadzu contributes to improving productivity at pharmaceutical companies and clinical contract research organizations. The new LC-MS sets a new standard in instrument operability, processing speed and ease-of-use as well as sample throughput.

Nexera Mikros

### Ten times more sensitivity

Compared to existing LC-MS systems, Nexera Mikros provides at least ten times more sensitivity. This is achieved by the LC-Mikros, a solvent delivery pump with a new control system, reducing pulsation while delivering a stable solvent flow even at low micro flowrates. In addition, positioning of the ionization interface has been optimized for more efficient sample introduction into the mass spectrometer.

### UF-Link achieves both high-sensitivity analysis and improved operability

Microscopic gaps (dead volume) in the piping connectors lead to a decrease in sensitivity by causing peak dispersion. UF-Link, a connection mechanism between Shimadzu's newly developed analytical column and the mass spectrometer, ensures high sensitivity and, at the same time, enables one-touch connection between the analytical column and the ionization interface for the mass spectrometer. In addition, UF-Link is compatible with connections between commonly used analytical columns and the ionization interface, so column selection is flexible to suit the target sample.

### Higher efficiency of investments in R&D

The LC-Mikros solvent pump delivers a wide flowrate range, from micro flowrates of 1 µL/min to semi-micro flowrates of 500 µL/min. By enabling analysis comparable to existing LC-MS systems, and high-sensitivity analysis at micro flowrates, this single unit improves the operational efficiency of the LC-MS system and shortens research and development times.

# Hot, Hotter, Bombfire

## Pungency of Currywurst

Every culture has its own famous fast food dish or street food, to use a current buzzword. The UK is famous for its fish and chips, Denmark for its hot dogs, The Netherlands for Frikandel, and Germany for its fried pork sausage with curry sauce, the so-called Currywurst. Although Berlin claims to have invented this dish, the Ruhr area with 5 million people in the west of the country has the highest density of fast food restaurants offering Currywurst seasoned with curry ketchup, a sauce based on spiced ketchup or tomato paste. The dish often comes with French fries.

Over 800 million curry sausages are consumed annually in Germany [1], some with hot or very hot sauces added. According to owners of "Die Currywurst", their Ruhr area-based snack bar provides the world's hottest Currywurst. Shimadzu has received some samples for analysis, including the hottest sauce. Guests eat them at their own risk, and they are served with the warning: "may threaten health".

The pungency (hotness) of a product is measured in Scoville Heat Units (SHU). Tabasco has a pungency of 2,500 to 5,000 Scoville, while the "Bombfire" sauce, own creation of the "Die Currywurst" snack bar, has up to 666,000 Scoville.

### Pungency level determination with HPLC

Pungency of the various sauces depends on the amount of capsaicinoids which are naturally present in bell peppers or chili peppers. The two main components, capsaicin (69 %) and dihydrocapsaicin (22 %), are almost twice as strong as the capsaicinoids nordihydrocapsaicin (7 %), homodihydrocapsaicin (1 %) and homocapsaicin (1 %), which are smaller in comparison. Therefore, only capsaicin and dihydrocapsaicin are studied to determine capsaicin levels in the various sauces and pure chili peppers [2].

To measure the exact content, the i-Series LC-2040C 3D compact HPLC system was used for high-speed analysis. Equipped with a photodiode array (PDA) and fluorescence detector, standards of the two main components were analyzed first. The method parameters applied are based on an existing Shimadzu application (No. L335) and are listed in table 1.

First, capsaicin and dihdrocapsaicin standards are tested in different concentrations (5, 10, 25, 50, 75 and 100 µg/mL) to create a calibration curve. Fluorescence detection exhibits approximately 16-fold higher sensitivity than detection with the PDA, as shown in figure 1.

Focus will therefore only be on the fluorescence detector analyses. The assignment of the two peaks is shown in figure 2, where the

| Column | Shim-Pack GIST C18 (2.1 x 100 mm i.D., 2 µm) |
|---|---|
| Mobile phase A | 1.0 % aqueous solutions of acetic acid |
| Mobile phase B | Acetonitrile |
| Flow rate | 0.9 mL/min (40 Vol.-% B) |
| Column oven temperature | 50 °C |
| Detection | PDA 280 nm, RF-20Axs Ex 280 nm, Em 325 nm |
| Injection volume | 1 µL |

Table 1: Method parameters for analysis of capsaicin and dihydrocapsaicin

| Sample | Capsaicin | Dihydrocapsaicin | Scoville |
|---|---|---|---|
| | µg/g (sample) | µg/g (sample) | |
| Home Grown | 1,501.4 | 388.5 | 30,427 |
| Habanero | 1,693.4 | 782.2 | 39,857 |
| Piri Piri | 4,877.7 | 2,273.0 | 115,125 |
| Bhut Jolokia | 24,356.1 | 8,818.6 | 534,113 |

Table 2: Results of measurements of chili peppers

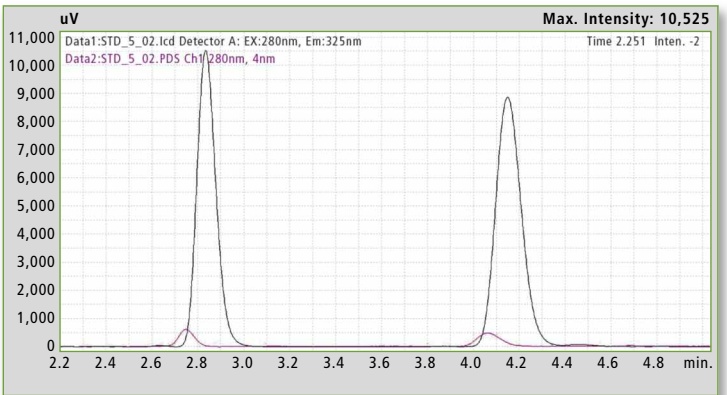



Figure 1: Comparison of RF (black) with PDA detection (violet)

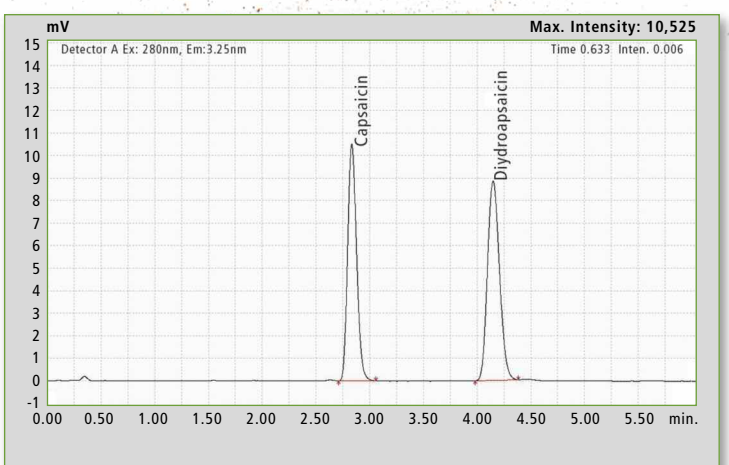



Figure 2: RF chromatogram of the standard 5 µg/mL

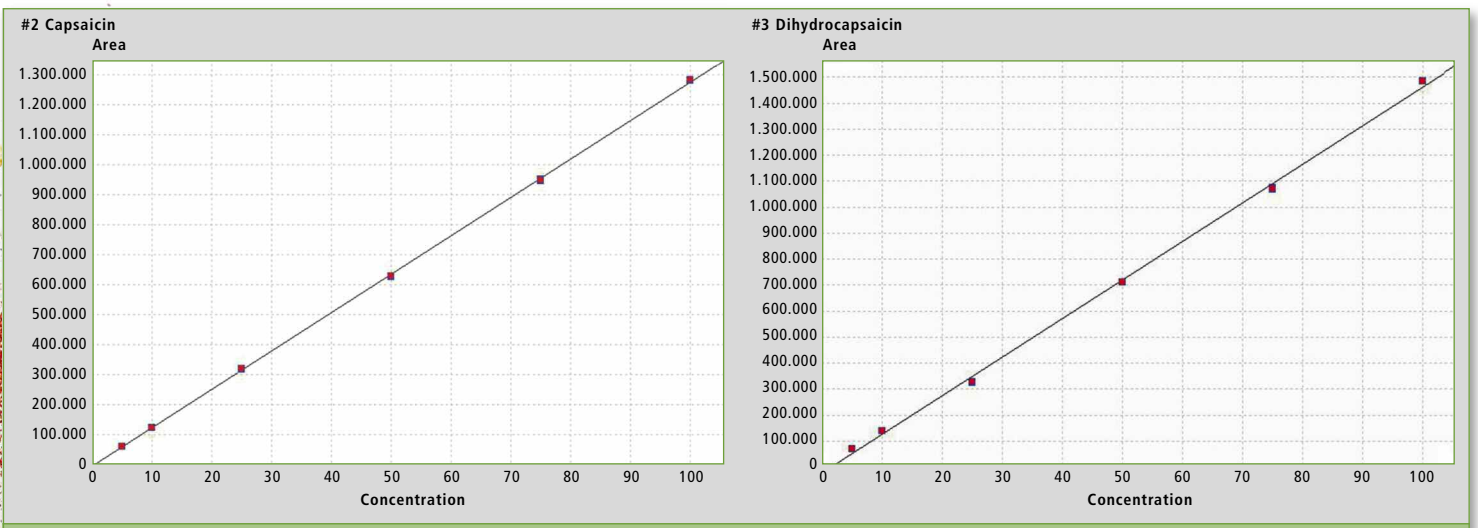



Figure 3: Calibration curves of capsaicin and dihydrocapsaicin

capsaicin is the peak eluting at 2.84 min and the dihydrocapsaicin is the peak later eluting at 4.16 min.

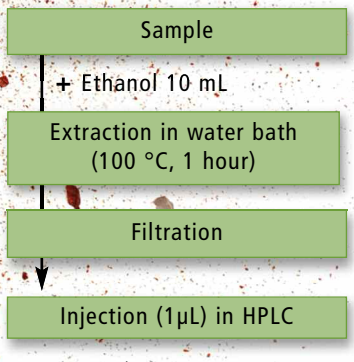



Figure 4: Sample preparation

## Comparison of chili peppers and chili sauces

The two calibration curves of capsaicin (figure 3 left) and dihydrocapsaicin (figure 3 right) serve as a basis for later determination of the capsaicin content in the extracted chili peppers and the chili sauces.

For sample preparation of the dried chilies and sauces, a defined amount of sample is first weighed (1 g chili pepper, 2 g sauce) and dissolved in 10 mL ethanol. After one hour of extraction in a water bath (100 °C) and filtration of the solution, 1 µL is injected (figure 4).

In total, four chili peppers and five sauces with distinct degrees of pungency were examined. Figure 5 shows the chromatogram of a sauce with a pungency of level seven, i.e. medium to high, in which capsaicin, dihydrocapsaicin and also nordihydrocapsaicin can be identified.

## Formula for the degree of pungency

The calibration curves of capsaicin and dihydrocapsaicin are used for quantification. To determine the degree of pungency, the concentrations are ascertained according to the peak areas and converted to the initial weight. The result can then be converted to the Scoville scale using the formula below (without nordihydrocapsaicin) to determine the degree of pungency of chili peppers and sauces.

$$SHV = C + D + N$$

C = (µg capsaicin per gram) × 16,1
D = (µg dihydrocapsaicin per gram) × 16,1
N = (µg nordihydrocapsaicin per gram) × 9,3

The results are shown in tables 2 and 3.

## Summary

The method depicted shows an easy sample preparation and fast analysis of chili products. The results obtained enable an approximate estimation of the expected level of pungency, but due to the non-inclusion of the nordihydrocapsaicin and a possibly incomplete extraction, Scoville results are considered to be too low.

As expected, the results reveal a significantly higher degree of pungency of pure chili peppers than for Currywurst sauces. This difference is a result of the same sample processing for both types of samples and the diluting effect of the sauce, which contains components of pure chili peppers. However, the goal was to make the expected trend of pungency visible analytically for sauces with different degrees of pungency, and this has been achieved. This is clearly shown for the examples in table 3.

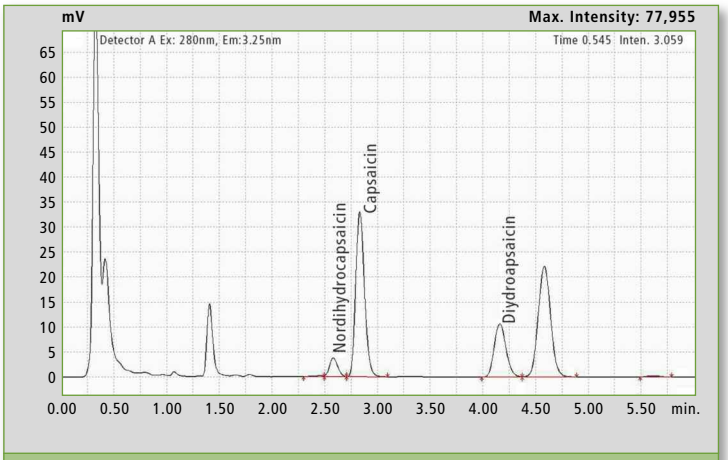



Figure 5: Chromatogram of the sauce with pungency level 7

| Sample | Capsaicin | Dihydrocapsaicin | Scoville |
|---|---|---|---|
| | µg/g (sample) | µg/g (sample) | |
| Sauce 3 | 5.9 | 12.0 | 289 |
| Sauce 5 | 6.8 | 11.6 | 296 |
| Sauce 7 | 405.6 | 120.9 | 8,478 |
| Sauce 10 | 1,103.2 | 442.3 | 24,882 |
| Sauce 10+ | 4,867.0 | 3,182.4 | 129,594 |

Table 3: Results of trial measurements of chili peppers and hot sauces

## Literature

[1] wikipedia.org/wiki/Currywurst
[2] wikipedia.org/wiki/Capsaicin

**Further information on this article:**
- Application note: Shimadzu Application News No. L335

# Olive oil is top source of vitamin E

## A quantitative fluorescence analysis of tocopherols

Tocopherols are methyl-substituted chromanols with a side chain consisting of three isoprenes. The four α-, β-, γ- and δ-tocopherols differ in the number and position of the methyl groups in the phenolic part of the chroman ring. The α homologue contains three methyl groups, while the β- and the γ-homologues are dimethylated positional isomers. The δ homologue is mono methylated. These substances all exhibit vitamin E activity, but the biological potential of R,R,R-α-tocopherol clearly surpasses the other homologues with 1.49 IU/mg [1].

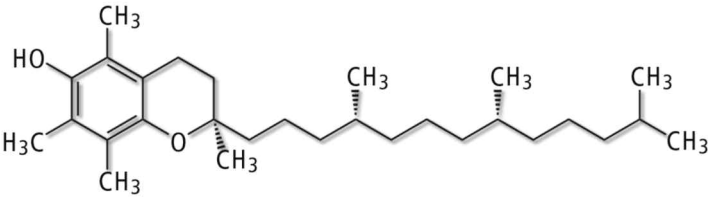



Figure 1: Chemical structure of α-tocopherol

Tocopherols are used, for example, in the food industry, because they effectively inhibit fat oxidation in food [2]. This effect is also evident in other biological systems such as the human body.

### 20 % of vitamin E requirements are contributed by fats and oils

The largest sources of vitamin E are vegetable oils. Based on data from the National Health and Nutrition Survey (NHAVES II), it is evident that fats and oils contribute more than 20 % to vitamin E requirements [1]. The daily dose required increases when the diet contains a large proportion of unsaturated fatty acids. For example, the necessary α-tocopherol consumption is 0.09 mg/g for monounsaturated fatty acids and 0.4 - 0.6 mg/g for diunsaturated fatty acids [3]. According to the National Research Council (1989), a 10 mg daily intake of vitamin E for men and 8 mg for women is recommended.

According to nutritional beliefs, extra virgin olive oil, despite its high content of monounsaturated fatty acids, is suitable for supplementing the daily vitamin E intake and for protection from vitamin E deficiency [4, 5]. Today, it is recognized worldwide as a health promoting oil, which is why extra virgin olive oil is becoming increasingly important in many countries. As a result, large volumes of oil are exported from Italy, Spain and Greece to the United States, Australia and Japan [6, 7].

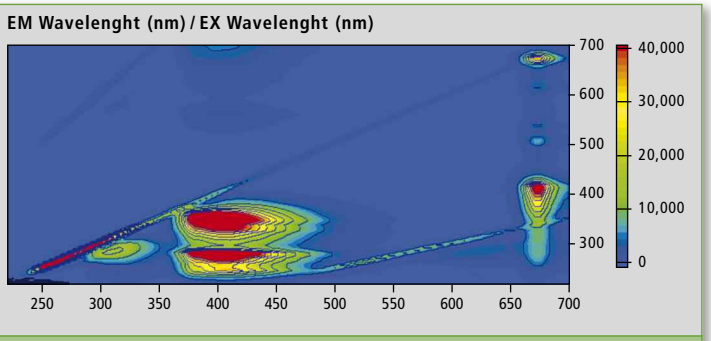



Figure 2: 3D scan of hexane diluted olive oil (1 vol.-%)

### High sensitivity of fluorescence spectroscopy

Fluorescence spectroscopy is very suitable for component analysis of olive oils. The method has a higher sensitivity than, for example, UV/Vis spectroscopy, since the signal-to-noise ratio is significantly higher. Also, fluorescence spectroscopy can be applied in three dimensions, which is an advantage for particularly complex compositions of samples.

In 3D fluorescence spectroscopy, the associated emission spectra are applied for a range of excitation wavelengths. Figure 2 shows a 3D spectrum of commercial olive oil. In addition to the excitation wavelength, fluorescence activities in the range of 290 - 340 nm, 350 - 450 nm and 660 - 680 nm are present. The emission at around 670 nm (Ex: 400 nm) is typical for chlorophyll, while the broad band between 350 nm and 450 nm is caused by polyunsaturated fatty acids and their oxidation products. The last remaining emission peak at about 320 nm is attributable to vitamin E [8].

The concentration of fluorescence-active chromophores in pure olive oil is very high. In order to reduce the intensity of the fluorescence, it is possible to rotate the sample 30° or 60° to the excitation beam. In this way, the volume traversed by the excitation beam is reduced.

However, this does not affect quenching effects within the sample. In order to reduce this, olive oil is diluted with n-hexane (1 vol.-% olive oil) for measurement. This also impacts on quantification of vitamin E in olive oil, since significantly fewer matrix effects occur [4]. Figure 3 shows a comparison of the measurement of a dilute hexane solution (1 vol.-%) with a higher concentration (30 vol.-%). The spectrum of the higher concentrated oil-hexane solution (black) clearly shows the matrix, in addition to the tocopherol peak at about 320 nm, which makes it difficult to evaluate the peak area amongst others.

### Quantitative assessment of vitamin E content

To quantify the vitamin E content in olive oil, an external calibration is performed. To test the dynamic

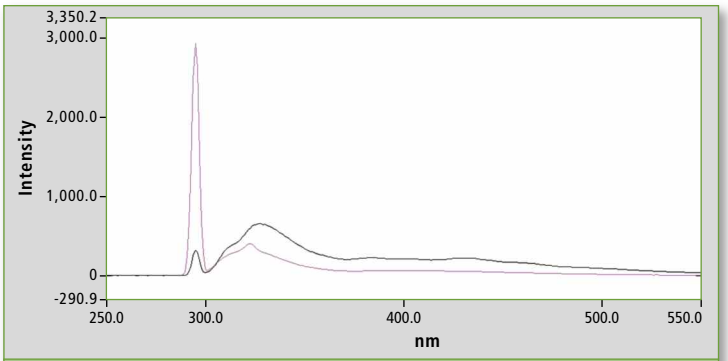



Figure 3: Range of diluted olive oil 1 % v/v, in n-hexane (purple), spectrum of diluted olive oil 30 % v/v, in n-hexane (black)

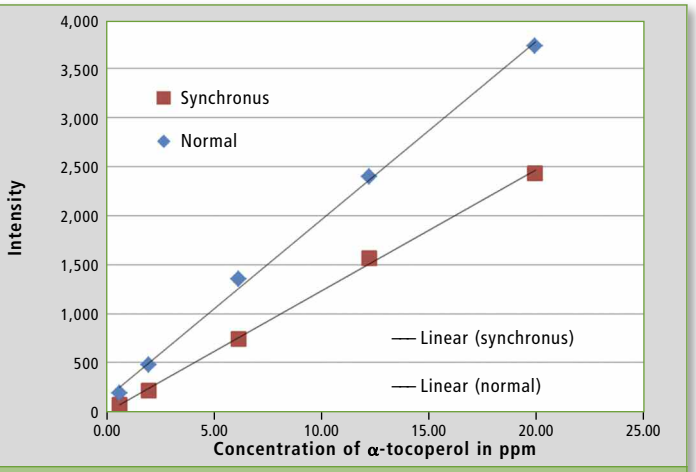



Figure 4: Calibration of α-tocopherol in hexane normal and with the synchronous technique and respective calibration lines

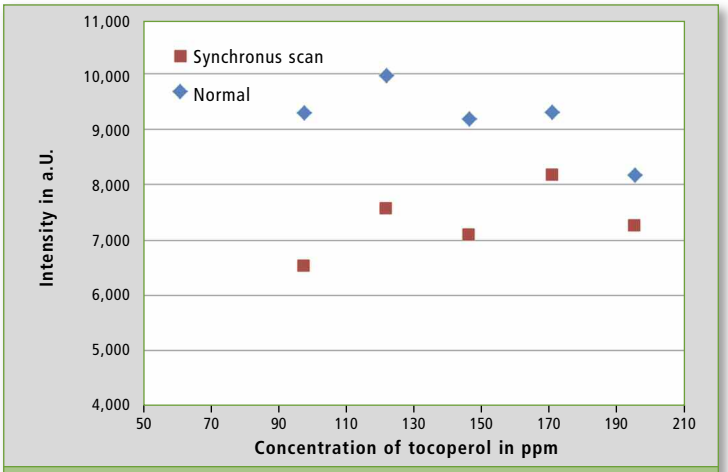



Figure 6: Calibration of an α-tocopherol-hexane solution in the range of 80 - 200 ppm (Ex: 290 nm)

range, calibration solutions with 0.6 - 75 ppm α-tocopherol prepared in hexane are used and measured at an excitation wavelength of 290 nm. It is noticeable that the sensitivity to the higher α-tocopherol concentrations decreases, so a calibration in the range of 1 - 20 ppm is therefore the most suitable.

All measurements were also done with the synchronous technique. Excitation and emission wavelengths were scanned, with both wavelengths at a constant distance from each other. Excitation peak in the spectrum was significantly attenuated, as well as second order light and matrix effects of the sample. This resulted in much narrower peaks. These are usually easier to evaluate, but have a lower intensity [9].

## Normal and synchronous measurement

For testing, an olive oil-hexane solution (1 vol.-%) was measured normally and synchronously. The α-tocopherol peak is very small, so that the sample can be arranged at the lower end of the calibration line. Oil-hexane solution thus contains approximately 1 - 2 ppm α-tocopherol, while a slightly higher value is deduced using calibration with synchronous technology. For a reliable calibration, it is recommended to increase the proportion of olive oil in the hexane solution by a few percent. A compromise between good quantifiability and as few matrix effects as possible for the olive oil concentration has to be found.

Additionally, fluorescence spectra of hexane solutions with higher α-tocopherol concentrations have been measured in order to see how the fluorescence reacts at higher concentrations. The resulting plot of intensities versus concentration (figure 6) shows that above a concentration of 100 ppm, quenching effects occur within the sample and a linear correlation between intensity and concentration is no longer present. Therefore, it makes no sense to measure undiluted olive oil.

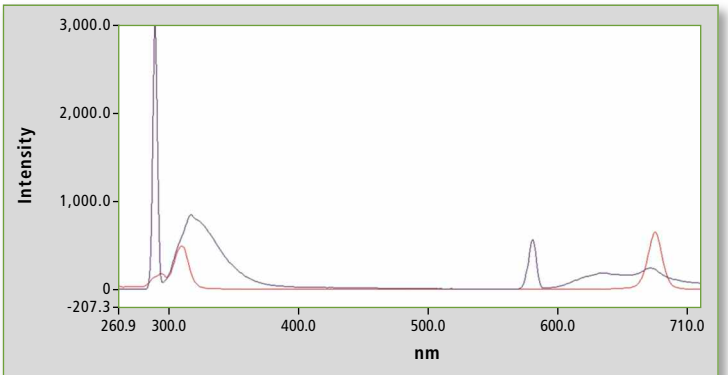



Figure 5: Fluorescence spectrum of an olive oil sample (black); Synchronous scan of an olive oil sample (red)

## Summary

Vitamin E is a quality feature of olive oil, but quantification by fluorescence spectroscopy is challenging. In general, sufficient dilution of the olive oil with hexane to minimize quenching within the sample and to ensure system calibratability is necessary. However, the sample should only be diluted to the extent that the α-tocopherol concentration is still approximately 10 - 15 ppm. For samples with a high amount of matrix, it may be useful to measure the fluorescence in synchronous mode, as it minimizes interfering effects.


## Authors

Aurelia Bertini, Hochschule Niederrhein
Manos Barbounis, Asteriadis S.A.
Vassilis N. Kamvissis, Sevitel


## Literature


[1] Eitenmiller, R. R.; Landen, WO, Jr. Vitamin E. Tocopherols and tocotrienols. In Vitamin Analysis for the Health and Food Sciences; CRC Press: Boca Raton, FL, 1999; p 109.

[2] Kamal-Eldin, A; Andersson, R. A multivariate study of the correlation between tocopherol content and fatty acid composition in vegetable oils. J. Am. Oil Chem. Soc. 1997, 74, pp. 375-380.

[3] Belitz, HD; Grosch, W. Food Chemistry, 2nd Ed.; Spinger publishing house: Berlin, Germany, 1999.

[4] Kafatos, A; Comas, G. Biological effects of olive oil on human health. In Olive Oil; Kiritsakis, AK, Ed.; American Oil Chemists' Society: Champaign, Il, 1990; Chapter 17, pp. 157-181.

[5] Lenart, EB; Willet, WC; Kiritsakis, AK. Nutritional and Health aspects of olive oil. In Olive Oil Kiritsakis AK Ed: Food and Nutrition Press: Trumbull CT, 1998; Chapter 16, pp. 299-322.

[6] Petrakis, C. Good Manufacturing Practice (GMP) guidelines for virgin olive oil production. Grasas Aceities 1994, 45, pp. 53-54.

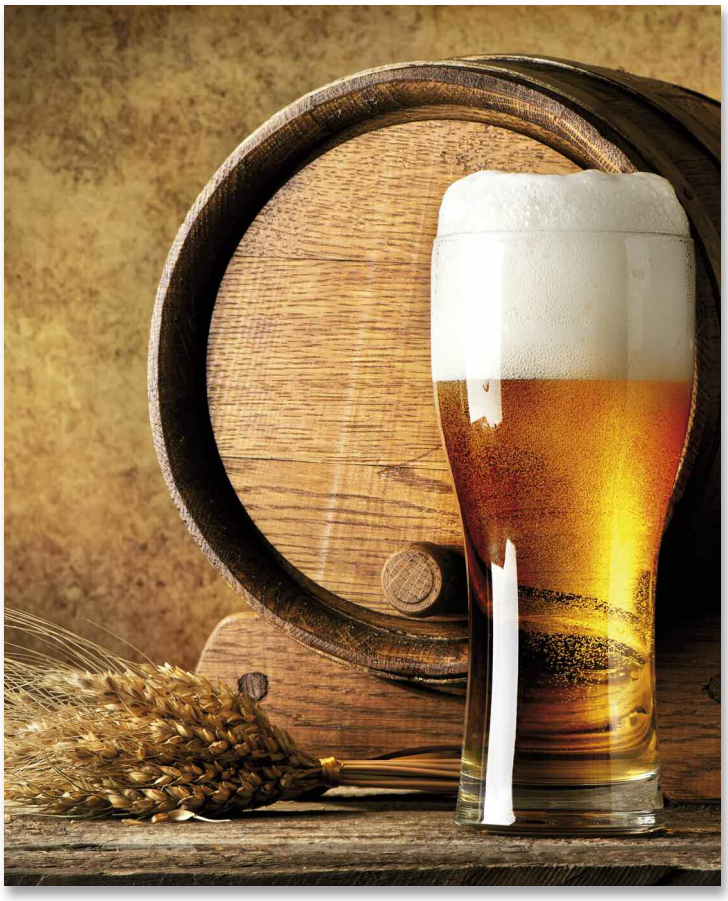
[7] Eleni Psomiadou, Maria Tsimidou, Dimitrios Boskou, a-tocopherol Content of Greek Virgin Olive oils, J. Agric. Food Chem., 2000, 48 (5), pp. 1770-1775.

[8] Kyriakidis & Skarkalis: Journal of AOAC Internattional Vol. 83, No. 6, 2000.

[9] Sikorska E., Khmelinskii I., Sikorski M., Analysis of Olive Oils by Fluorescence Spectroscopy: Methods and Applications, InTech (2012).

# Flavors in beer determined by Headspace-GC

## GC-2010 Plus in the Quality Control procedure of a large Greek brewery



Beer flavor is formed by a complex mixture of many components giving each brew its own distinctive personality. This mixture mostly includes alcohols, esters, acids, sulphur compounds and vicinal diketones.

Esters represent one of the most important flavor groups and play a considerable role in the organoleptic characteristics of the beer. Production of esters is influenced mainly by wort composition and fermentation parameters during the brewing process. Additionally, esters are often the target-compounds in authentication and quality control methods.

Furthermore, monitoring for vicinal diketones (VDKs) including 2,3-butanedione (diacetyl) and 2,3-pentanedione, is also a critical step in determination of flavor in beer. VDKs are considered to be extremely important since they are known to affect the taste of the beer. These components are responsible for the sweet butter flavor and are considered as non-beneficial at high levels.

Another important task (in the brewing process) is monitoring of acetaldehyde. As known, acetaldehyde is reduced to ethanol by yeast during secondary fermentation, but this process may be reversed due to extensive oxidation, converting ethanol back to acetaldehyde. Acetaldehyde can also be a product of bacterial spoilage caused by Zymomonas or Acetobacter.

Dimethyl sulphide (DMS) is a sulfur compound with the taste and aroma of sweet corn. This derives either from the malt (as a result of fermentation process) or bacterial infection. Sulfur components could be considered acceptable at low concentrations, but in higher levels, they give off an unpleasant taste and smell.

This shows that rapid and reliable methods are highly desirable for determination of aroma profile of the beer due to its importance.

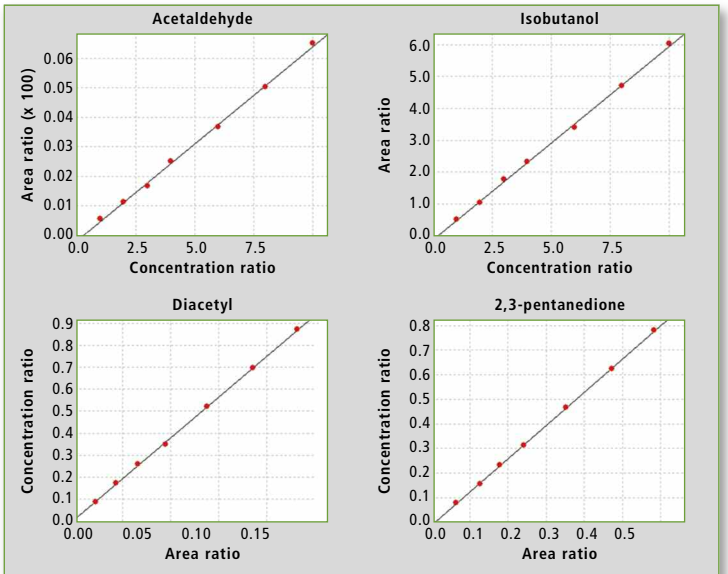



Figure 1: Typical calibration curves

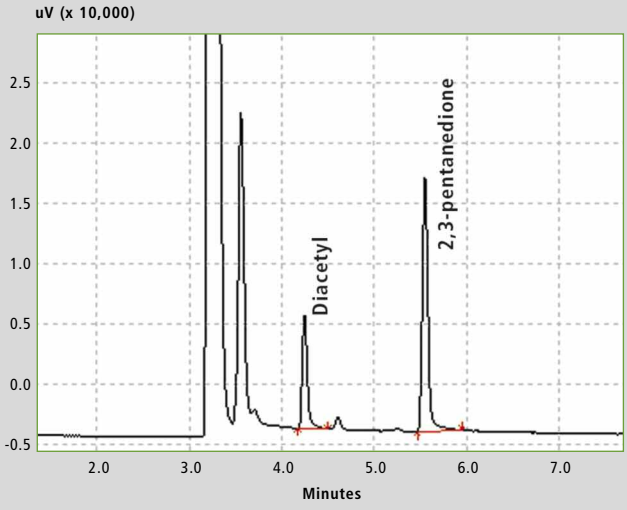



Figure 2: Analysis of VDKs in a standard

## Worldwide established: Headspace-GC

Headspace sampling coupled with gas chromatography (HS-GC) is a widely used technique for the analysis of beer throughout the world. It is also considered important in quality control (QC) in order to identify problems or changes occurring in brewing or fermentation processes that could affect the quality of the final product, i.e.:

- significant increases of ethyl formate, acetone and/or methanol in cases of contamination caused by inadequately disinfected tanks or leaks in cooling systems
- an abnormal increase in ethyl capronate related to yeast and fermentation problems.

The aim of this current work was the successful development of the HS-GC technique to successfully implement it in the Quality Control of a large brewery in Greece.

## Sample preparation

Beer samples require degassing prior to headspace analysis for two reasons. Firstly, it is critical to prevent dissolved carbon dioxide ($CO_2$) from influencing vial pressure during the headspace heating process, and secondly, $CO_2$ eluting during chromatography disturbs the GC baseline.

Samples were prepared by transferring the beer to a wide mouth beaker and sonicating them briefly. After degassing, 2.5 mL of beer sample was placed into a 20 mL headspace vial, the internal standard was added with a gas tight syringe, and the vial was sealed with a rubber septa. It was then placed in the rack of the headspace autosampler for incubation and injection.

## Instrumentation

**Gas chromatograph**
Shimadzu GC-2010 Plus, two Split/Splitless injectors, two lines, one with an ECD detector (analysis of VDKs) and the second with a FID detector (analysis of esters, DMS, acetaldehyde).

**Headspace autosampler**
Shimadzu AOC-5000 with a 2.5 mL headspace syringe.

**Capillary columns**
- Line 1 (VDKs): Varian CP SIL 8 CB column (50 m, 0.53 mm ID and 1 µm film thickness)
- Line 2 (esters): Varian CP Wax 52 CB column (60 m, 0.32 mm and 1.20 µm film thickness)

## Results and discussion

Following the identification of the compounds, calibration was carried out using an aquatic solution of 5 % in ethanol. The substances used for each analysis were as follows:

- VDKs: diacetyl and 2,3 pentanedione and 1,2-dichloropropane as internal standard.
- Esters etc: acetaldehyde, DMS, acetone, ethyl formate, ethyl acetate, methanol, ethyl propionate, propanol, isobutanol, isoamyl acetate, amyl alcohols and ethyl capronate and n-butanol as internal standard.

The calibration curve used for each substance consisted of seven points, and the correlation coefficients ($r^2$) are listed in table 2, varying from 0.9965 to 0.9999. Some typical calibration curves are also shown in figure 1.

## Experimental data

Nine repetitions of the highest concentration VDKs standard were performed, and the relative RSDs are shown in table 3. Repeatability was very good and in all cases RSD was less than 3 % (see also table 3).

## Conclusion

The headspace-GC technique is a fast and reliable method for routine analysis of odor compounds in beer. Due to minimum sample pretreatment, high sensitivity and excellent repeatability of the Shimadzu GC-2010 Plus gas chromatograph and Shimadzu

| Line 1 (VDKs) | Line 2 (Esters) |
|---|---|
| Injector temperature: 135 °C | Injector temperature: 135 °C |
| Split ratio: 3 | Split ratio: 3 |
| Column oven: 75 °C for 12 min | Column oven: 35 °C (25 min), 10 °C/min to 150 and hold 10 min |
| FID temperature: 150 °C | FID temperature: 150 °C |
| Pressure: 35 KPa | Pressure: 73 KPa |
| Carrier gas: Helium | Carrier gas: Helium |

Table 1: Method parameters

| Compound | Correlation Coefficient | RSD (%) |
|---|---|---|
| Diacetyl | 0.9995 | 1.04 |
| 2,3-pentanedione | 0.9999 | 1.08 |
| Acetaldehyde | 0.9984 | 2.51 |
| Dms | 0.9989 | 2.20 |
| Acetone | 0.9989 | 1.3 |
| Ethyl formate | 0.9976 | 2.25 |
| Ethyl acetate | 0.9987 | 1.30 |
| Methanol | 0.9965 | 2.43 |
| Ethyl propionate | 0.9984 | 1.75 |
| Propanol | 0.9991 | 2.89 |
| Isobutanol | 0.9989 | 2.50 |
| Isoamyl acetate | 0.9965 | 1.35 |
| Amyl alcohols | 0.9986 | 2.85 |
| Ethyl capronate | 0.9973 | 2.93 |

Table 2: Correlation coefficients of the related substances

| ID#1 Compound name: Diacetyl | | |
|---|---|---|
| Titel | Ret. time | Area |
| mixture&ISTD9.gcd | 4.249 | 36,193 |
| mixture&ISTD8.gcd | 4.249 | 36,457 |
| mixture&ISTD7.gcd | 4.248 | 36,336 |
| mixture&ISTD6.gcd | 4.248 | 36,657 |
| mixture&ISTD5.gcd | 4.247 | 36,830 |
| mixture&ISTD4.gcd | 4.247 | 36,652 |
| mixture&ISTD3.gcd | 4.246 | 36,530 |
| mixture&ISTD2.gcd | 4.245 | 36,923 |
| mixture&ISTD1.gcd | 4.243 | 35,667 |
| Average | 4.247 | 36,472 |
| %RSD | 0.049 | 1.038 |
| Maximum | 4.249 | 36,923 |
| Minimum | 4.243 | 35,667 |
| Standard deviation | 0.002 | 379 |
| **ID#2 Compound name: 2,3-pentanedione** | | |
| Titel | Ret. time | Area |
| mixture&ISTD9.gcd | 5.552 | 89,233 |
| mixture&ISTD8.gcd | 5.551 | 89,539 |
| mixture&ISTD7.gcd | 5.551 | 89,407 |
| mixture&ISTD6.gcd | 5.550 | 91,125 |
| mixture&ISTD5.gcd | 5.549 | 91,484 |
| mixture&ISTD4.gcd | 5.548 | 90,068 |
| mixture&ISTD3.gcd | 5.547 | 89,663 |
| mixture&ISTD2.gcd | 5.546 | 90,701 |
| mixture&ISTD1.gcd | 5.543 | 88,497 |
| Average | 5.548 | 89,971 |
| %RSD | 0.052 | 1.075 |
| Maximum | 5.552 | 91,484 |
| Minimum | 5.543 | 89,497 |
| Standard deviation | 0.003 | 967 |

Table 3: Repeatability data of VDKs (screenshot from GC Solution software)

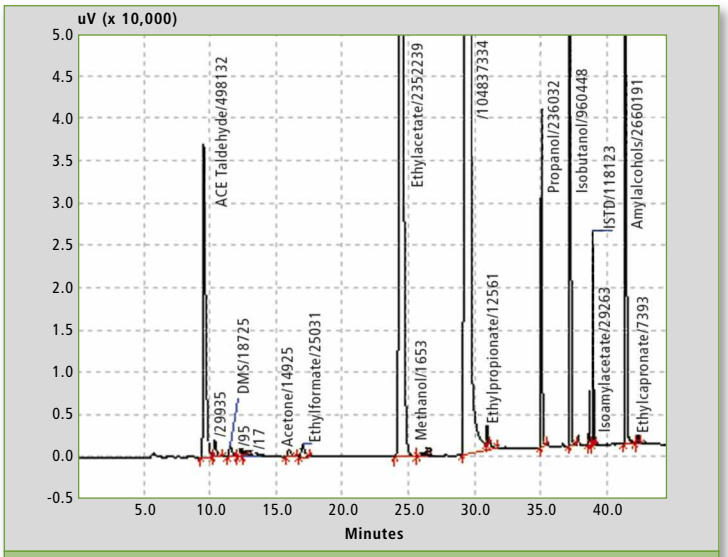



Figure 3: Analysis of esters etc. in a standard

AOC-5000 autosampler, it was quite easy to implement it in the Quality Control procedure of a large brewery plant in Greece.

**This application can be done in the same way using the new Nexis GC-2030.**


### Authors

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### Literature


[1] Tomáš Horák, Jirí Culík, Vladimír Kellner, Marie Jurková, Pavel Cejka, Danuša Hašková and Josef Dvorák, J. Inst. Brew. 116(1), Analysis of Selected Esters in Beer: Comparison of Solid-Phase Microextraction and Stir Bar Sorptive Extraction, pp. 81-85, 2010.

[2] Li Huimin, Li Hongjun, Liu Xiuhua, Chen Bing
Int J Agric & Biol Eng, 21 (Vol. 5), Analysis of volatile flavor compounds in top fermented wheat beer by headspace sampling-gas chromatography, 2012.




# Guardian in the chemical park

## TOC process measurement at Leuna Chemical Park, Germany

As a method of analysis that has been established for decades, the sum parameter TOC (Total Organic Carbon) measures the total contamination of organic components in a matrix in a single analytical run – whether in a laboratory environment or online during an industrial process. This makes the TOC a versatile and universal parameter, as demonstrated by InfraLeuna Chemical Park in Leuna, Germany.

The Leuna Chemical Park, located in the heart of central Germany, stands for dynamism, innovation and maximum efficiency. As an independent operator of the entire infrastructure, InfraLeuna ensures the synergy of the Leuna chemical site and provides the framework for local companies for a cost-effective and efficient production.

The comprehensive offer of InfraLeuna consists of the redundant provision of steam, electricity, fresh water and drinking water as well as sanitation and other services. This also includes complex logistics services. The focus is on the business success for the customers and the further development of the chemical site as a whole.

Analytical monitoring of water quality is an integral part of these services. It is an important tool for safe running of all processes, and protection of equipment and the environment. It is carried out at various points where different water qualities occur, such as waste water, ultrapure water or water vapor.

### The TOC

To quickly measure the level of organic component contamination in water, the TOC value is determined. This can be done offline in the lab as well as online during the process. Shimadzu's TOC-4200 is an example of a TOC process for online monitoring.

An automatic sampling station withdraws process water steadily and feeds it to the analyzer. It is important to adjust the extraction to the respective water quality: If it contains particles, it has to be treated differently than saline particle-free water. Shimadzu offers various sampling modules for this purpose. Up to six different sample streams can be connected to one station and can be measured by a single analyzer.

Important for the determination of the TOC is the differentiation between organic and inorganic carbon. After all, carbonates and bicarbonates can be found in every natural water. The most commonly used method for TOC determination is therefore the so-called NPOC (Non Purgeable Organic Carbon) method. The sample is acidified in order to convert the carbonates and bicarbonates contained to $CO_2$. Subsequently, the resulting carbon dioxide is expelled by a gas stream which is passed through the sample.

This sample preparation is done automatically by the TOC-4200. Once the inorganic carbon is removed, an aliquot is injected automatically onto a 680 °C platinum catalyst where all existing organic compounds are oxidized to carbon dioxide. The resulting $CO_2$ is conducted by a carrier gas flow to a highly sensitive $CO_2$-selective NDIR detector and subsequently measured. Based on an external calibration, the TOC concentration is then calculated.

### Wastewater treatment

At the chemical site of Leuna, about 300 $m^3$ per hour of wastewater is produced that needs to be cleaned. For this purpose, the site operates its own multi-stage wastewater treatment plant. In order to protect the biological treatment stage of the sewage treatment plant, the entrance of

the biological treatment stage is meticulously controlled. An online TOC system closely monitors the inflow, as excessive amounts of organic load can severely disrupt or even kill the plant's sensitive biology. In order to detect potential incoming volatile solvent loads, NPOC and also POC (purgeable organic carbons) as option are measured in the feed.

To control the efficiency of the wastewater treatment plant and the clarification process, output of the wastewater treatment plant is also monitored. For this, two streams are analyzed:

- waters from the various purification stages of the sewage treatment plant
- surface waters resulting from precipitation events.

Analytical monitoring of water quality by TOC measurement is essential for efficient processes in the Leuna Chemical

If the appropriate limits are not exceeded, the water may be discharged to the river. To avoid environmental damage, the TOC-4200 systems used for this purpose are connected to a mechanical gate valve system. If the limit value is exceeded, the valve is closed automatically and the water is sent to a containment tank and then returned to wastewater treatment.

## Ultrapure water

In many areas of the chemical park, ultrapure water is used, either for chemical processes or for thermal processes in waste heat or boiler plants. InfraLeuna produces about 350 $m^3$ ultrapure water per hour. In this manufacturing process, different techniques are combined. The raw water is first decarbonated, filtered through a gravel filter and a candle filter, then purified by reverse osmosis and desalted by ion exchange.

TOC impurities in ultrapure water can have a negative impact on chemical processes. Especially in the production and processing of high purity chemicals, contamination can have a negative influence on the quality of the product. An important specification of ultrapure water is thereby described by the TOC: it must not contain more than 0.2 mg/L of organic carbon. The ultrapure water is therefore examined continuously before feeding into the supply lines. To perform such sensitive measurements, a special high-sensitivity catalyst is used. The platinum-plated quartz wool of the catalyst enables injection of higher volumes. Detection limits below 50 µg/L TOC are achieved in this combination.

## Steam / condensate

One of the most important sources of energy in the Leuna Chemical Park is steam. It is used to heat reactors and is sometimes even part of the manufacturing process. InfraLeuna supplies their customers and their own plants with steam at different pressure levels. The steam is generated with high efficiency, using cogeneration system in a combined cycle power plant.

Contaminants in the water used for steam production can have negative effects on the plant. In addition to inorganic substances such as salts or $CO_2$, organic contaminants can also cause damage. In steam generation, some organic substances are decomposed. Decomposition products, e.g. organic acids, lead to increased corrosion of system components such as heat exchangers or the blades of steam turbines.

In the return condensate, organic substances can accumulate. The condensate is therefore also monitored and only reused if a maximum limit of 0.8 mg/L TOC is met. If the measured TOC concentration is higher, the condensate is treated by suitable procedures before reuse. To protect the system components in the steam-condensate circuit, TOC is carefully monitored.

## Recooling Water

For condensation in the water-steam circuit, additional cooling circuits are needed. The cooling towers used for this purpose with their large amounts of water are an open system, in contrast to the closed water-steam circuits. From the outside, various environmental influences affect the water quality of the so-called recooling water. In addition, with temperatures between 20 °C and 40 °C, it presents an ideal breeding ground for microorganisms of all kinds. To reduce microbial contamination, chemicals are added to the recooling water. This water is also monitored continuously for its organic impurity level.

## Sampling

At the Leuna chemical site, process TOC devices are used in many places to monitor the water. Sampling, on the other hand, is carried out in all used systems by means of counter flow-extraction. The sampling system consists of a curved overflow pipe into which a sampling capillary is inserted.

The sampling point is located directly behind the pipe bend, so that a turbulent flow of the sample homogenizes a multiphase mixture which may be present. The TOC-4200 draws the flowing sample out of this capillary against its direction of flow, and then washes it back with rinse water. The sampling device thus contains no moving parts or filters and is effectively maintenance free. The flowing medium flushes particles or deposits away from the capillary, so that no blockages can occur.

## Conclusion

Many varied fields of application with TOC analysis are in operation in a chemical park such as in Leuna. Whether sewage, rainwater, condensate, ultrapure water or recooling water, whether with or without salts and particles – all waters have their own requirements for analysis, which can be met by appropriate options.

**Read for you** in Laborpraxis December 2017

**Further information on this article:**

- www.laborpraxis.vogel.de/per-toc-messung-im-prozess-die-wasserqualitaet-im-chemiepark-ueberwachen-a-669678/


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# Troubleshooting via YouTube

## Video tutorials using the new GC generation Nexis GC-2030 as an example

Figure 1: YouTube: Touchscreen display & LabSolutions Direct

Figure 2: YouTube: Septum and Liner

Regular analysis of customer requests from around the world revealed that users would like easier access to GC analysis and simplification of daily maintenance tasks, such as changing the column.

With its new troubleshooting channel on YouTube, Shimadzu takes a new approach using video and voice to give practical tips & tricks relating to chromatography. The Nexis GC-2030 as part of the new GC generation is used as an example to show how this high-precision technology can be conveniently maintained and just how easy daily work with the Nexis GC-2030 really is.

### Consistent user guidance

Self-explanatory icons on the GC-2030 color touchscreens guide users intuitively through the procedure for setting up all required method parameters. The same icons and structure of the typical GC modules are also used in the LabSolutions software. The "LabSolutions Direct" interface can be used to see the status of a running GC analysis as well as remotely restarting sample measurements using a tablet PC or smartphone, provided the GC-2030 has network access (figure 1).

Figure 3: YouTube: ClickTek and oven lamp

### Simple maintenance

Another video shows just how easy it is to change the septum and liner as part of routine maintenance work on the GC injector (figure 2). After the work is complete, the simple diagnostic function of the GC-2030 provides clear information on whether the injector is again gas-tight and ready for use.

Changing the column is a standard procedure if the GC is used for different types of applications (figure 3). The unique Click-Tek technology reduces this procedure to a few well-defined steps. A simple snap hook mechanism is sufficient to verify whether the column has been installed correctly as there are only two possible positions: "open" and "shut". Furthermore, an optional LED oven lamp gives a clear view inside the GC-2030 oven.

Replacing the gas filter in the line of the split gas outlet is carried out less frequently, but can also be done quickly without a tool (figure 4). The filter prevents contamination of the electronic unit controlling the carrier gas. An indicator in the filter changes color when replacement is necessary.

These videos can be watched simply by clicking on the links in the Shimadzu News App. Alternatively, "GC-2030" can be entered in the search mask of YouTube.com.

An additional video tutorial details changing of the desolvation line on the LCMS-8060 triple-quad mass spectrometer. More videos will be added soon.

**Further information on this article:**

- bit.ly/Troubleshooting_ShimadzuEurope

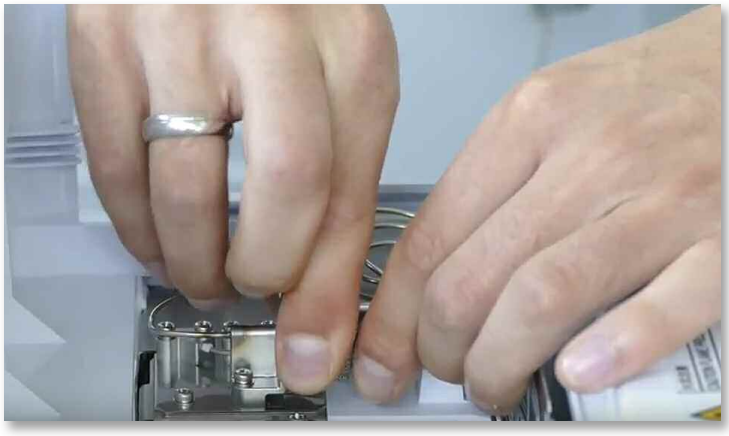


Figure 4: YouTube: Filter Nexis GC-2030

# Less than a teaspoon of blood can predict Alzheimer's disease risk

An international collaborative research team led by the Japanese National Center for Geriatrics and Gerontology (NCGG), Koichi Tanaka Mass Spectrometry Research Laboratory at Shimadzu Corporation, and the Australian Imaging, Biomarker and Lifestyle Study of Aging (AIBL) groups has established a highly sensitive blood test able to identify individuals at risk of developing Alzheimer's disease. (The research also involved collaborators at The University of Tokyo, Kyoto University, Kindai University, and Tokyo Metropolitan Institute of Gerontology.) The results have been published online, on 31 January 2018, in Nature, one of the world's leading scientific journals.

One of the essential pathological signatures of Alzheimer's disease is deposition in the brain of an abnormal protein, called Aβ-amyloid (Aβ). About three decades before the onset of dementia symptoms, the deposition starts silently, without any sign of cognitive abnormalities. It is estimated that about 20 - 40 % of the general elderly population have a significant Aβ burden in their brain. While the Aβ deposition does not necessarily mean a fast progression to Alzheimer's dementia, these individuals are considered to be "at risk" of developing Alzheimer's disease at some future point. The new blood test can identify individuals with abnormal Aβ deposition in the brain,with about 90 % accuracy.

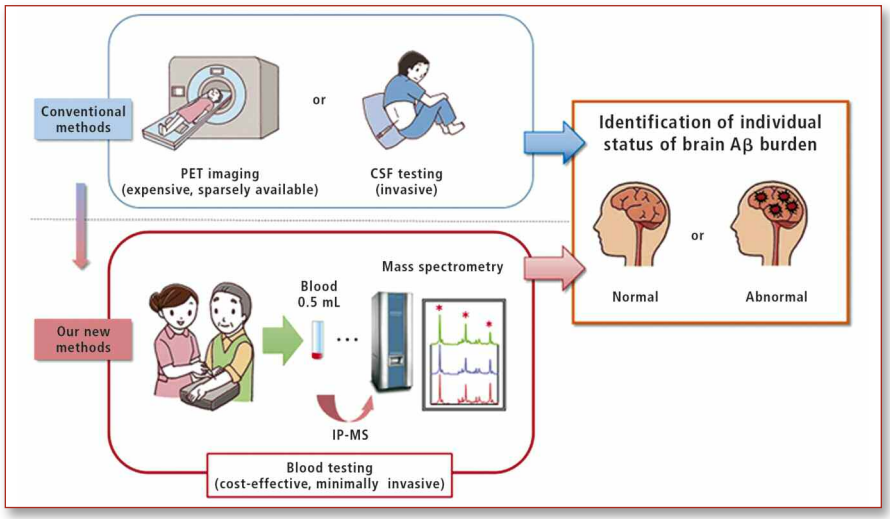
"Currently, only positron emission tomography (PET) imaging or cerebrospinal fluid testing are available to ascertain brain Aβ burden, however, these tests are expensive and/or invasive" says Akinori Nakamura, Laboratory Chief at NCGG. "Therefore, a minimally invasive and cost-effective blood test is strongly desired; however, it has proven to be very difficult to develop despite much research effort. Our study is important because it not only demonstrates the high performance of this blood test, but also its reliability and reproducibility as it was successfully validated in two independent large datasets from different countries, Japan (121 samples) and Australia (252 samples)."

Koichi Tanaka at Shimadzu Corporation, who achieved the Nobel Prize in Chemistry in 2002 for developing a method for mass spectrometric analyses

One key point for their success is that the test employed a new method called immunoprecipitation and mass spectrometry (IP-MS). "From only 0.5 mL of a blood sample, the IP-MS method can quantitatively measure several Aβ-related peptides, such as Aβ1-42, Aβ1-40, and APP669-711, in plasma, even though their concentration in plasma is extremely low. We found that the ratio of these peptides, APP669-711/Aβ1-42, Aβ1-40/Aβ1-42, were an accurate surrogate for the brain Aβ burden. This technique was established by our colleague Naoki Kaneko, who also first found APP669-711 in plasma," says Koichi Tanaka at Shimadzu Corporation, who achieved the Nobel Prize in Chemistry in 2002 for developing a method for mass spectrometric analyses.

"Scientists at Shimadzu Corporation will need to scale up the test so that it can be widely used, but once this issue is resolved, this new test has the potential to eventually disrupt the current PET/CSF technologies. In the first instance, however, it is likely to be used for screening," says Colin L. Masters, Professor at the Florey Institute, The University of Melbourne, who led the AIBL project.

"Our blood test may also have a transformative potential to facilitate the development of effective drugs for Alzheimer's disease," says Katsuhiko Yanagisawa, Director-general of Research Institute at NCGG. He continues, "Although drugs for Alzheimer's disease are still under development, the best chance for the efficacious interventions are considered to be before the onset of the dementia symptoms. Our blood test is expected to enable population-based screening to identify "at risk" individuals to be recruited in preclinical and prodromal prevention trials with reasonable cost-benefit and scalability."




**Authors of the article, published in Nature:**

Akinori Nakamura, Naoki Kaneko, Victor L. Villemagne, Takashi Kato, James Doecke, Vincent Doré, Chris Fowler, Qiao-Xin Li, Ralph Martins, Christopher Rowe, Taisuke Tomita, Katsumi Matsuzaki, Kenji Ishii, Kazunari Ishii, Yutaka Arahata, Shinichi Iwamoto, Kengo Ito, Koichi Tanaka, Colin L. Masters & Katsuhiko Yanagisawa

**Further information on this article:**

- www.nature.com/articles/nature25456

# Pop the corks: 50th anniversary of Shimadzu in Europe

## Time to celebrate

This year, Shimadzu celebrates the 50th anniversary of its presence in Europe. This is an exciting year with lots of innovations to be expected, and it is also a time to celebrate with the clients, employees and the business communities of analytical instrumentation and medical technology.

It started in 1968 with five employees: Shimadzu Europa commenced operations in Düsseldorf, the capital of Germany's most populous federal state. In 1987, after 20 years of growth, Shimadzu relocated a few miles further to Duisburg, a city with the largest inland port in Europe, which since then hosts Shimadzu's European Headquarters for the Shimadzu Corporation (Kyoto, Japan). Today, Shimadzu employs almost 700 people in Europe and has developed into a large European network with offices and trade partners in 81 cities from 48 countries.

**"Excellence in Science"**

The headquarter in Duisburg provides the technological and application-oriented knowhow. Through trainings and seminars in the over 1,500 sqm Laboratory World, it is regularly shared with the sales and service forces who transfer it into the markets. They are one of the world's largest providers of analytical instrumentation and X-ray diagnostic imaging solutions. Whereas medical technology covers Angiography, Fluoroscopy and Radiography as well as Mobile X-ray Systems, the analytical instrumentation focuses on advanced solutions in Chromatography, Mass Spectrometry, Spectroscopy, Total Organic Carbon analysis, Imaging, Life Sciences, Material Testing and Measuring Technology.

"Excellence in Science" stands for Shimadzu's core value proposition representing the company's scientific and technological approach to always providing business, medical and research solutions with advanced analytical and diagnostic imaging systems, ensuring better consumer, patient and environment protection as well as product safety. Numerous world firsts which have meanwhile become industrial and clinical standards today substantiate this tag line.

**Paradigm shifts in business**

Developing, running and growing a company for 50 years (and on a global scale it is more than 140 years) is not just a question of offering the right products and services, it is also a matter of adapting successfully to societal, political, economic and technological changes as well as aligning to clients' expansion plans, needs and structures to fully support their competitiveness. These all influence the ways of doing business, cooperating with clients and driving a company.

Just to mention a few: the digital revolution, i.e. the transition from the industrial era to the information age, caused a technological paradigm shift regarding new applications, precision and conducting systems. A similar impact in a political context was the raise of the Iron Curtain which gave access to new markets and target groups, and also led to a new political and market order all over Europe.

**Quiz 'n' Win**

Throughout the year, Shimadzu takes the opportunity to celebrate with its clients and the business communities. In the coming months, exciting competitions will be run with lots of attractive prizes to win. Just visit the **www.shimadzu.eu/50th-anniversary** website and apply to take part in the quiz with questions around Shimadzu's history, portfolio and milestones. Don't worry, you don't have to be an expert! **Good luck!**

## Shimadzu live

**analytica**
Munich, Germany
April 10 - 13, 2018
www.analytica.de

**Wire**
Düsseldorf, Germany
April 16 - 20, 2018
www.wire.de

**ISCC**
Riva del Garda, Italy
May 13 - 18, 2018
www.iscc42.chromaleont.it

**IFAT**
Munich, Germany
May 14 - 18, 2018
www.ifat.de

**EPRW**
Munich, Germany
May 22 - 25, 2018
www.eprw2018.com

**Automotive Testing Expo**
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June 05. - 07, 2018
www.testing-expo.com

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