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New milestone

The new Nexis GC-2030

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Nexera UC/s – Analysis and evaluation of chiral drugs

A century of experience

Shimadzu celebrates 100 years of testing machines

The Next Industry Standard

Nexis GC-2030 – a new milestone in precision and sensitivity

Figure 1: Milestones in GC development – Nexis GC-2030

It has been 60 years since Shimadzu initiated the development of GC systems with the introduction of its GC-1A. Since then, numerous innovations have made gas chromatography one of the most important analytical techniques. Based on longstanding experience in the development of GC systems as well as continuous exchange of ideas with users, Shimadzu has set a new milestone in precision and sensitivity with its Nexis GC-2030.

The Nexis GC-2030 stands for 'Next Industry Standard.' Meeting this demand requires a clear view of present day GC requirements. Gas chromatography is used in all areas of research and development that ultimately enrich but also influence our daily life through foods, consumer goods, electronics, health and environment. Growing concern over the extent to which technological advances negatively influence people and the environment has led to an increased demand to learn more about the complex composition of products as well as their emission into the environment and their resulting interactions.

To meet these demands, an analysis system must fulfil many requirements:

- chromatographic solutions for separation of complex samples
- high detection sensitivity for the smallest traces of toxic impurities

- highest precision for reliable results
- simple instrument control and operation, also for novice GC users
- high reliability supported by automated diagnostic routines
- safety when handling hydrogen carrier gas.

Simple operation via self-explanatory user interface

The new color touchscreen display offers fast and intuitive access to the Nexis GC-2030. Self-explanatory icons guide users through the entire system operation (figure 2). The same icons are found in the new LabSolutions software, which offers optional conventional or graphically controlled operation of the GC. Network-operated control also offers all advantages of the World Wide Web. Direct access via iPhone or iPad to the status of an ongoing analysis as well as launching of new measurement sequences is possible at any time and any place.

Maintenance without tools

Regular maintenance tasks on the Nexis GC-2030 such as septum, liner and column replacement no longer require any tools and can be performed quickly and efficiently (figure 3a). The new Click Tek connector technology also

Figure 2: Color display with the Nexis GC-2030 touchscreen

enables simple column installation by hand without the use of any tools. An optional oven lamp is available for illumination and offers an excellent view inside the oven (figure 3b).

Flexible choice of carrier gas control with highest precision

Intelligent and ultrafast carrier gas control (AFC – Advanced Flow Control) enables superior reproducibility of the Nexis GC-2030 through high-precision gas flow rate control. Carrier gas flow can be adjusted and controlled based on constant linear velocity, volume flow or pressure.

Highest sensitivity worldwide

Redesigned detectors such as the flame ionization detector (FID), electron capture detector (ECD) and flame photometer (FPD) open up new dimensions in trace analysis. The unique barrier ionization discharge (BID) detector allows simultaneous detection of inorganic and organic components in the low-ppb range.

Efficiency for fast results and high sample throughput

Special techniques such as backflushing, detector splitting and heartcutting are supported by the GC system and can be integrated into the chromatographic configuration as simple modules. In this way, the graphical support allows easy access to advanced chromatographic techniques.

Fast GC is the technique of choice for obtaining fast results or high sample throughput. High-resolution capillary columns allow separation of complex samples in the shortest amount of time by using high carrier gas flow velocities and high heating rates of the GC oven.

This, however, requires an ultrafast responding detector system in order to capture sharp signals at full height and symmetry. Each detector of the Nexis GC-2030 system can be adjusted optimally to any chromatographic technique by setting the data acquisition rate (up to 500 Hz) and the filter time constant (2 - 2,000 ms).

Safety with hydrogen as carrier gas

For most GC applications and particularly for fast ones, hydrogen is the ideal carrier gas. However, its use presents risks in the event of leakages.

The Nexis GC-2030's automatic gas leak check assures adequate safety.

A residual risk remains at higher gas flows in low pressure ranges. Here, the optional hydrogen sensor offers additional safety. The GC-2030 oven is monitored continuously and the GC system is shut down before an explosive hydrogen concentration can form.

Summary

Over the past decades, gas chromatography has developed into a comprehensive technique. With the Nexis GC-2030, Shimadzu makes this available to every user. Simple self-explanatory operation facilitates access for 'GC novices' intending to use GC analytical technologies in their fields of expertise. Sensitive detectors also measure in the ultra-trace range with highest precision. Sophisticated diagnostic techniques provide information on the system's operational capability at any time. Daily tasks are carried out with just a few steps. Safety for economical operation using hydrogen as carrier gas is assured via optional sensors. As the new standard, the Nexis GC-2030 combines high performance with simple operating conditions and reliable long-term operation.

Figure 3a and 3b: Maintenance without tools: liner replacement of the split injector (SPL) or column installation in the GC oven. The optional oven light facilitates these steps by providing good illumination of the column connections.

Further information on this article:
- www.shimadzu.eu/gc-2030

Harmful substances in textiles

Detection of harmful substances in textiles using LC-MS/MS

There is hardly anything that we allow as close to our body as our clothing. It protects us against cold, moisture or the sun. We choose our clothing carefully and wear it next to our skin, and children often like to put pieces of clothing into their mouths.

Many different chemicals are used in textiles and clothing production. These chemicals have specific properties such as vivid colors, wind and moisture impermeability, antibacterial effects, crease resistance and much more.

In the manufacture of clothing, the number of additives and finishing agents is vast. Nearly 6,000 preparations are available, e.g. refinement agents for fibers and yarns such as bleaching or hydrophilic agents for pretreatment, additives for dyeing and printing, as well as dispersing agents, protective colloids, dye accelerators, oxidation, mordant or resist agents. The list appears to be endless.

Additive chemicals are used as optical brighteners (optical white) or to reduce creasing and shrinking. They are used as stiffening agents, anti-electrostatics, water and oil repellents, protection against pests, flame retardants and antimicrobial agents. In total, these preparations include about 600 different chemical compounds, whereby dyes are not yet taken into account.

Not all of these substances are environmentally safe. Some are suspected of causing allergies. Others do not degrade in the environment and accumulate in fatty tissues or are suspected of being carcinogens.

Children are considered to be particularly at risk in their mental development. A multitude of compounds can potentially harm the brain, but they are neither regulated nor tested for harmful effects on fetuses and children. Experts are calling for better protection of children from the effects of toxic chemicals, the so-called 'silent epidemic' [1].

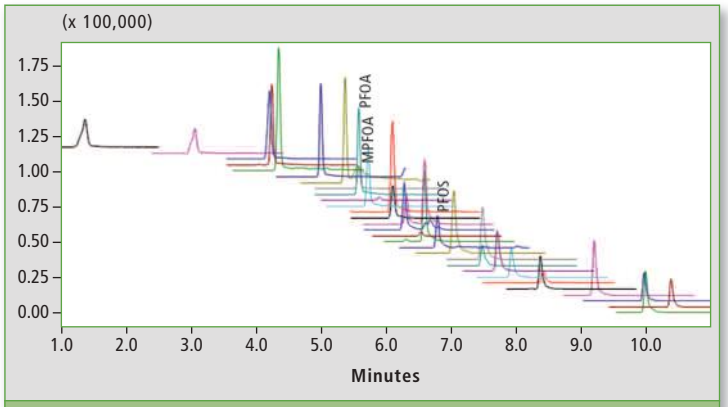

Figure 1: MRM Chromatogram of a PFC standard with 26 PFCs in a textile matrix (concentration: 1,000 pg/mL, internal standard ^{13}C-PFOA = M-PFOA concentration: 500 pg/mL)

Legal foundations

The European Textile Labelling Regulation merely requires that information is provided on the textile fibers used. Labelling of the additives used is, however, not yet required. Textiles are considered to be commodities, and in this case the general prohibition applies that the manufacture and treatment of commodities must not be harmful to human health. Compliance with the legal provisions is primarily the responsibility of the manufacturer. Monitoring of compliance with the legal provisions is the responsibility of the federal states. Since there is no mandatory authorization or reporting requirement for textiles – only information on the fibers used is required – there is no comprehensive knowledge of potential risks [2].

Experts and consumer organizations have long been demanding a precise declaration of 'ingredients.' However, some harmful substances are already prohibited in clothing, such as carcinogenic azo dyes or certain flame retardants. A labelling requirement applies to formaldehyde and a maximum concentration of 5 mg/kg textile applies to pentachlorophenol in accordance with the German Chemicals Prohibition Ordinance. However, these are only

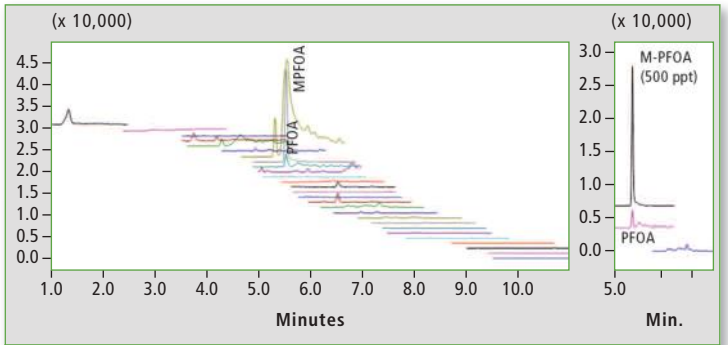

Figure 2: MRM Chromatogram of a methanol extract of the textile GS with internal standard (M-PFOA, 500 pg/mL). Traces of PFOA could only be detected in this sample.

specific legal provisions. Unlike, for example, cosmetic products, there is no standardized, comprehensive regulation for textiles or leather.

Over 90 million tons of textile fibers were produced in 2015, a large proportion of which in countries that do not adequately regulate the use of harmful substances. This is a huge problem. The textiles produced are contaminated with harmful substances, and the release of these harmful substances into the environment is immense. The majority of the chemicals used for finishing are transferred untreated into rivers, and sooner or later will enter the drinking water and food chains.

PFCs also get into foods

Just how far-reaching the input of chemicals into the environment can be, is shown by example of the so-called PFCs (perfluorinated and polyfluorinated chemicals). This substance group includes more than 800 compounds which do not occur naturally. Due to their outstanding water, oil and dirt repellant properties, PFCs are often used in the production of home textiles such as carpets, curtains, table cloths and pillow cases as well as upholstered furniture. PFCs are found in virtually all rainproof, breathable outdoor textiles, they are used as anti-grease ingredient in coated paper such as paper cups or pizza boxes, or as non-stick coating in Teflon pans.

The problem is: PFCs are extremely stable. They do not degrade in the environment but are only distributed. In 2015, a Greenpeace expedition found PFCs in all snow and water samples collected from seemingly untouched and remote locations around the world (among others, in China at an altitude of 5,000 meters and in a Chilean national park).

Persistent harmful substances are distributed via the air and flowing waters throughout the world and finally also reach our food. They accumulate in the body, bind to proteins in blood, liver and kidneys and can be passed on to the fetus or the baby during pregnancy.

No.	Name	RT (min)	Range (pg/mL)	R^2	LOD (pg/mL)	LOQ (pg/mL)	RSD (%), n = 6 (50 pg/mL)	RSD (%), n = 6 (1,000 pg/mL)
1	PFBA	1.379	50~5,000	1.000	15.6	47.3	3.5	3.7
2	PFPA	3.063	50~5,000	0.9993	11.5	34.8	6.9	1.0
3	PFBS	4.211	20~5,000	0.9991	6.1	18.5	3.5	3.4
4	PFHxA	4.245	50~5,000	0.9995	16.6	50.2	5.7	3.6
5	HPFHpA	4.353	20~5,000	0.9993	2.8	8.5	4.5	2.2
6	PFHpA	5.004	50~5,000	0.9992	13.8	41.8	9.1	3.9
7	1H,1H,2H,2H-PFOS	5.373	50~5,000	0.9992	14.9	45.3	9.3	5.7
8	PFOA	5.594	20~5,000	0.9996	5.8	17.7	5.9	1.3
9	PFHxS	5.733	50~5,000	0.9992	11.8	35.6	10.7	2.1
10	FOEA	5.896	1,000~5,000	0.9988	246.3	746.3	N.A.	12.6
11	PFNA	6.112	50~5,000	0.9996	13.3	40.2	6.3	6.7
12	PFHpS	6.285	50~5,000	0.9991	8.7	26.3	9.6	3.5
13	PF-3,7-DMOA	6.308	50~5,000	0.9996	15.3	46.5	14.4	4.1
14	PFDA	6.592	50~5,000	0.9998	9.6	29.0	7.8	7.2
15	PFOS	6.793	20~5,000	0.9990	5.3	16.1	12.8	6.1
16	H4PFUnA	6.541	500~5,000	0.9973	82.3	249.3	N.A.	12.4
17	PFUdA	7.045	20~5,000	0.9995	5.3	16.0	11.1	4.8
18	PFDoA	7.484	50~5,000	0.9990	11.5	35.0	10.4	3.4
19	PFDS	7.721	50~5,000	0.9991	15.3	46.2	8.0	3.6
20	PFTrDA	7.928	50~5,000	0.9991	15.2	46.0	13.5	8.3
21	PFTeDA	8.372	50~5,000	0.9991	13.4	40.6	7.6	8.8
22	FOSA	8.420	50~5,000	0.9995	11.6	35.0	14.0	8.2
23	PFDHxA	9.198	20~5,000	0.9985	1.4	4.1	14.7	2.5
24	N-MeFOSA	9.955	200~5,000	0.9986	60.8	184.1	N.A.	6.2
25	PFODA	9.980	20~5,000	0.9982	5.0	15.1	11.0	1.7
26	N-EtFOSA	10.369	100~5,000	0.9984	32.1	97.2	N.A.	6.0
IS	M-PFOA	5.556	500	Not available				

Table 1: Limits of detection and quantification for 26 PFCs, including PFOS, PFOA, as well as reproducibility data (n = 6) for the concentration levels 50 pg/mL and 1,000 pg/mL

Sensitive detection of PFCs in textiles using LCMS

Because of these alarming properties, consumer protection and environmental organizations are focusing on PFCs. The most prominent representatives are the perfluorooctane sulfonic acid (PFOS) and the perfluorooctanoic acid (PFOA), both of which are likely to be carcinogenic.

While the use of PFOS and its components is already prohibited as a substance in goods in the EU REACH Chemicals Regulation, PFOA is still on the list of candidates. Unintentional trace impurities are exempted and for textiles there is a threshold of 1 µg/m² of the coated material. A fast and sensitive method for testing textile samples is presented below.

Figure 1 shows the MRM chromatogram of a PFC standard in a textile matrix with 26 components, including ^{13}C-PFOA (= M-PFOA) as internal standard. The measurements were performed using the LCMS-8050 triple quadrupole mass spectrometer coupled to a Nexera UHPLC. Separation of the compounds was achieved in less than twelve minutes with an excellent limit of detection for PFOS (LOD = 5.3 pg/mL) and PFOA (LOD = 5.8 pg/mL). Further important statistic features of the method are listed in table 1. (Detailed information on the methods can be downloaded via the QR code at the end of the article.)

Analysis of real samples

PFC concentrations in five different articles of clothing (designated as BS, GS, YS, WS and BR) from local stores were determined using the method described. As shown in figure 2, traces of PFOA (650 pg/g = 0.65 ppb) were only found in sample GS. None of the 26 PFC compounds could be detected in the other four samples.

Dyes

Dyes not only represent the largest group, they are also the most important group of substances used in textile manufacturing with regard to health risks. For the assessment of health aspects, a classification based on the dyeing process is helpful. Water soluble direct dyes are incorporated in the hollow spaces (cavities) of the fibers. Water soluble reactive dyes, in contrast, are firmly bound to the fiber by means of a covalent bond. These dyes are usually harmless because they are poorly absorbed by the skin.

Disperse dyes are lipophilic substances that are directly dissolved in the chemical fiber. For technical reasons, only small molecules with the addition of organic solvents (dye accelerators, carriers) are considered suitable as disperse dyes. In case of incorrect treatment like over-dyeing or incomplete removal of the carrier, health risks due to these lipophilic substances, some of which are readily absorbed via the skin, cannot be ruled out.

No.	Compound	RT (min)	Range (ppb)	Linearity	LOQ	LOD	RSD (%), n = 6	
							10 ppb	50 ppb
1	2,4-toluenediamine	1.148	1 - 1,000	0.9992	0.68	0.22	1.92	3.73
2	Benzidine	1.506	1 - 1,000	0.9960	0.52	0.17	4.89	3.88
3	4,4′-oxydianiline	1.268	0.5 - 200	0.9944	0.26	0.09	4.47	4.12
4	4,4′-diaminodiphenylmethane	1.583	0.5 - 1,000	0.9992	0.35	0.12	1.28	2.31
5	o-anisidine	1.733	0.2 - 200	0.9993	0.15	0.05	4.90	2.81
6	o-toluidine	2.049	0.2 - 200	0.9998	0.16	0.05	2.67	1.58
7	p-cresidine	3.975	0.1 - 200	0.9992	0.06	0.02	3.08	1.36
8	2,4′-diaminoanisole	3.975	1 - 200	0.9995	0.58	0.19	6.72	2.61
9	2,4′-xylidine	3.933	1 - 200	0.9994	0.73	0.24	1.65	2.33
10	3,3′-dimethoxybenzidine	4.514	0.2 - 200	0.9951	0.20	0.06	2.01	1.12
11	4-chloroaniline	4.094	1 - 200	0.9997	0.78	0.26	3.75	1.93
12	o-tolidine	4.395	0.5 - 200	0.9992	0.28	0.10	3.64	1.83
13	4,4′-methylene-bis(2-methylaniline)	4.484	0.5 - 200	0.9993	0.21	0.07	2.62	2.77
14	2,6-xylidine	4.991	1 - 200	0.9995	0.85	0.28	3.21	3.23
15	2,4,5-trimethylaniline	5.001	0.5 - 200	0.9995	0.29	0.10	3.22	1.30
16	2-naphthylamine	5.472	0.2 - 200	0.9994	0.10	0.03	3.54	1.72
17	4,4′-thiodianiline	5.457	0.5 - 1,000	0.9993	0.19	0.06	2.91	2.00
18	4-chloro-o-toluidine	6.282	0.2 - 500	0.9997	0.15	0.05	1.99	2.08
19	Basic Red 9	6.139	0.05 - 100	0.9931	0.02	0.01	1.22	1.93
20	4-aminobiphenyl	6.612	0.5 - 1,000	0.9996	0.45	0.15	1.81	2.45
21	Basic Violet 14	6.479	0.05 - 100	0.9977	0.02	0.01	2.78	1.42
22	5-nitro-o-toluidine	6.888	5 - 1,000	0.9994	1.98	0.65	10.86	8.18
23	Disperse Blue 7	7.459	1 - 200	0.9991	0.71	0.24	3.10	1.33
24	Disperse Yellow 9	7.805	5 - 1,000	0.9997	5.00	1.50	15.16	4.16
25	Disperse Blue 3	7.921	0.5 - 200	0.9994	0.28	0.09	5.14	1.91
26	Disperse Red 11	7.936	0.5 - 100	0.9967	0.20	0.06	3.04	2.32
27	Disperse Blue 102	8.294	2 - 200	0.9991	0.97	0.32	16.32	7.61
28	Disperse Red 17	8.489	0.5 - 200	0.9992	0.50	0.15	6.16	3.78
29	4-aminoazobenzene	8.815	2 - 200	0.9995	1.23	0.41	10.43	3.95
30	3,3′-dichlorobenzidine	8.789	2 - 200	0.9994	1.47	0.48	11.04	6.06
31	4,4′-methylene-bis-2-chloroaniline	8.978	2 - 200	0.9993	2.00	0.60	4.77	4.59
32	Disperse Blue 106	8.938	0.1 - 200	0.9994	0.04	0.01	10.34	3.56
33	Disperse Orange 3	9.128	0.1 - 200	0.9994	0.08	0.03	5.81	2.01
34	Basic Violet 3	9.2	0.05 - 200	0.9990	0.02	0.01	4.42	2.45
35	Disperse Yellow 3	9.203	0.5 - 200	0.9991	0.21	0.07	3.97	2.74
36	Disperse Orange 11	9.273	0.5 - 200	0.9992	0.34	0.11	11.59	4.69
37	Disperse Brown 1	9.289	1 - 200	0.9993	1.00	0.33	6.24	8.33
38	Disperse Red 1	9.571	0.2 - 100	0.9942	0.20	0.07	3.16	5.54
39	Disperse Blue 35	9.875	5 - 1,000	0.9980	1.98	0.65	10.54	5.99
40	Disperse Yellow 1	8.438	2 - 200	0.9960	2.00	0.63	10.43	8.29
41	Disperse Yellow 49 (Leather)	10.099	0.5 - 200	0.9996	0.26	0.09	3.63	2.40
42	Disperse Blue 124	10.163	1 - 500	0.9981	0.78	0.26	4.70	4.74
43	Disperse Blue 26	10.779	5 - 200	0.9986	4.09	1.35	7.08	12.85
44	Disperse Orange 37	10.864	5 - 200	0.9970	4.05	1.34	4.31	3.35
45	Disperse Yellow 23	11.049	0.2 - 200	0.9969	0.17	0.06	5.19	1.75
46	Disperse Orange 1	11.195	0.2 - 200	0.9979	0.12	0.03	2.57	1.23
47	Disperse Orange 149	12.069	1 - 200	0.9975	0.73	0.24	4.80	7.42

Table 2: Limits of detection and quantification for 47 dyes, as well as reproducibility data (n = 6) for the concentration levels 10 ppb and 50 ppb

Carcinogenic amines in azo dyes

By far, the most important group of dyes are the azo dyes, about 500 of them are synthesized on the basis of carcinogenic amines. Even today, 150 of these compounds are still commercially available. Following absorption by the body, azo dyes can be cleaved enzymatically (for instance by intestinal bacteria, certain liver enzymes or skin bacteria) back into the original potentially carcinogenic amines.

The German industry already has given up the use of azo dyes for a long time which can cleave into carcinogenic aromatic amines. Imported textiles, however, may well contain such harmful dyes even though, as stated in the REACH regulation, no textiles treated with such dyes may be brought on the market if limit values of 30 mg/kg are exceeded.

In the literature, a total of 49 dyes are described as contact allergens in the context of textile-related contact allergies. About two-thirds of them are disperse dyes. In addition, the BfR (Federal Institute for Risk Assessment, Germany) specified eight disperse dyes several years ago, that should no longer be used in clothing textiles.

Screening and quantitative determination of 47 azo dyes

The following application example describes a method for quick and reliable detection of 47 dyes from different dye groups, 23 azo dyes, 21 disperse dyes and three triphenylmethane. These also include seven of the eight disperse dyes specified by the BfR (disperse blue 35, 106 and 124, disperse yellow 3, disperse orange 3 and 37/76; disperse red 1).

Separation of the 47 components is achieved within twelve minutes, as shown by the MRM chromatogram in figure 3. To develop the analytical method, a dye-free textile sample was spiked with the corresponding standard dyes and the instrument parameters were optimized. The measurements were performed using Shimadzu's LCMS-8040 triple quadrupole mass spectrometer coupled to Shimadzu's Nexera UHPLC. (A detailed description of the method can be downloaded via the QR code at the end of the article).

Table 2 lists the limits of detection and limits of determination as well as calibration linearity data and reproducibility measurements.

Analysis of random samples from clothing stores

A total of three light-colored articles of clothing, designated as 0B, 0G and 0Y, were purchased in local textile stores and analyzed using the method presented. One of the 47 dyes could be identified unequivocally in one of the three random samples: disperse red, which is regarded as a contact allergen belonging to the eight BfR banned dyes (figure 4).

Conclusion

Fast and sensitive detection methods for harmful chemicals in textiles are necessary to enable random monitoring of, for instance, clothing. The introduction and monitoring of limit values not only serves to protect persons

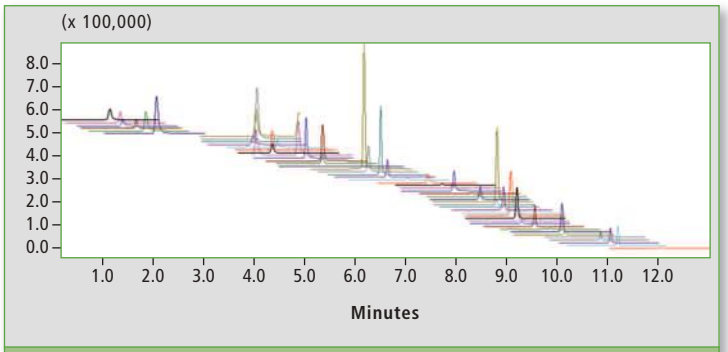

Figure 3: Chromatogram of MRM-traces of 47 dyes of different dye groups in one run (concentration 20 ng/mL (20 ppb) each; injection volume: 5 µL)

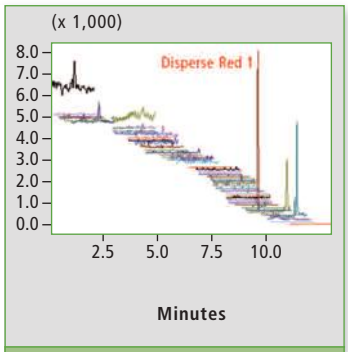

Figure 4: MRM Chromatogram of the real sample 0G with detection of the disperse dye 'Disperse Red 1'

wearing the piece of clothing but also to support sustained protection of the environment. Even when some manufacturers are committed to stop the use of known harmful substances in clothing, contaminated clothes are still found in random samples collected by environmental and consumer organizations [3]. Using LC-MS/MS, even small traces of harmful substances can be determined accurately and quantitatively.

Literature

[1] Focus online 06.03.2014: In Billigländern produziert – Krebs- und Allergiegefahr: So giftig ist unsere Kleidung.
[2] BfR, Bundesinstitut für Risikobewertung; Einführung in die Problematik der Bekleidungstextilien. Aktualisierte Stellungnahme Nr. 041/2012 vom 06. Juli 2012
[3] Greenpeace Homepage, Report: Chemie in unberührter Natur und Gefährliche Chemikalien in Outdoor Ausrüstung (Greenpeace Produkttest 2016)
[4] UBA, Umweltbundesamt, Homepage Themenseite PFC

Further information on this article:

- Poster: SAP-ADSC ASMS 2016 poster LCMS-8050 for 26PFC in textile
- Poster: SAP-ADSC – ASMS 2016 poster LCMS-8040 for 47 dyes in textiles

One-stop solutions for clinical market applications

Shimadzu has acquired AlsaChim, a specialist for high-quality analytical isotope labeled standards

ALSACHIM
a Shimadzu Group Company

Shimadzu has joined forces with the France-based AlsaChim company specializing in stable isotope-labelled compounds, metabolites and pharmaceutical related substances. AlsaChim is now by 100 % part of the Shimadzu family. The brand name will be kept for the future complemented by the subtitle "a Shimadzu Group Company." Through this acquisition, Shimadzu will further develop and extend its activities in the clinical market which is one of the focus areas for the European Innovation Center (EUIC). AlsaChim technology complements Shimadzu's product and solution portfolio in the clinical market. Now, Shimadzu is able to enter the market with complete solutions consisting of hardware and software as well as application kits. Clients now benefit from one-stop solutions of complex analytical systems.

European Headquarters in Duisburg, Germany

Analysis and evaluation of chiral drugs in biological samples

Nexera UC-MS/MS for highly sensitive SFC analysis

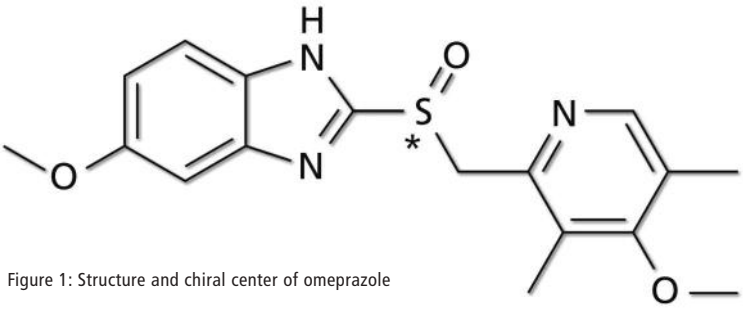

Figure 1: Structure and chiral center of omeprazole

Projects in drug discovery and safety are constantly aiming at the development of novel and safer drugs, therapeutics and diagnostics. During API (active pharmaceutical ingredient) development, drug stereoisomerism is recognized as an issue having clinical and regulatory implications.

Enantiomers have essentially identical physical and chemical properties, while potentially showing large differences in toxicity.

Stereoisomeric composition of a drug with a chiral center should therefore be well documented. To evaluate the pharmacokinetics of a single enantiomer or any mixture of enantiomers, manufacturers must develop quantitative assays for individual enantiomers early in the drug development stage.

One of the challenges of chiral separations is the fact that enantiomers exhibit the same physical and chemical properties, so they can only be separated in a chiral environment.

For chromatographic separations chiral stationary phases are available that enable the separation of stereoisomers. In order to determine the stationary phase that offers optimum selectivity for the chiral separation problem at hand, screening runs are usually performed, testing several chiral columns at a time. Normal phase HPLC is often the method of choice, however, SFC has frequently been proven to be the superior method for the separation of chiral compounds.

Figure 2: Nexera UC SFC-MS system

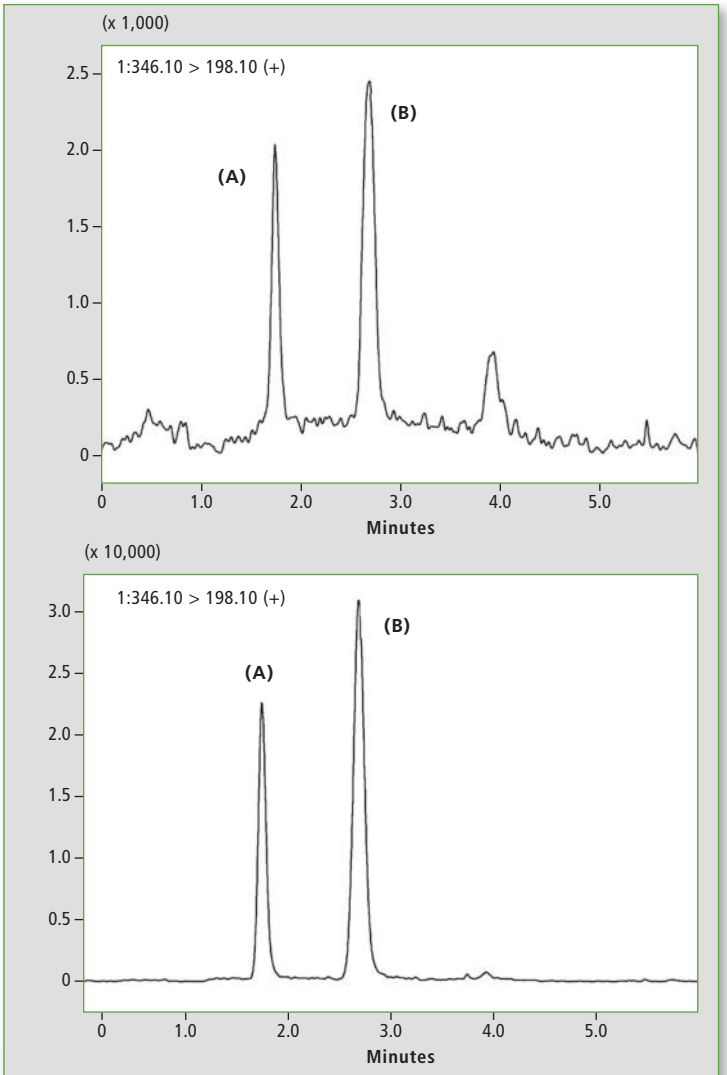

Figure 3: Chromatogram of a plasma sample spiked with a) 2 µg/L and b) 20 µg/L omeprazole, analysed with the Nexera UC LC/SFC switching system

This article presents an example of the selectivity and sensitivity of drug level monitoring in a biological sample and the evaluation results of the analytical method as an application to pharmacokinetics research of chiral drugs using SFC-MS/MS, after having selected an appropriate column.

Analysis of omeprazole in a plasma sample

The applicability of human plasma matrix to SFC was evaluated using the enantiomeric drug omeprazole, a well-known proton pump inhibitor, as an example. Figure 1 shows the chemical structure of

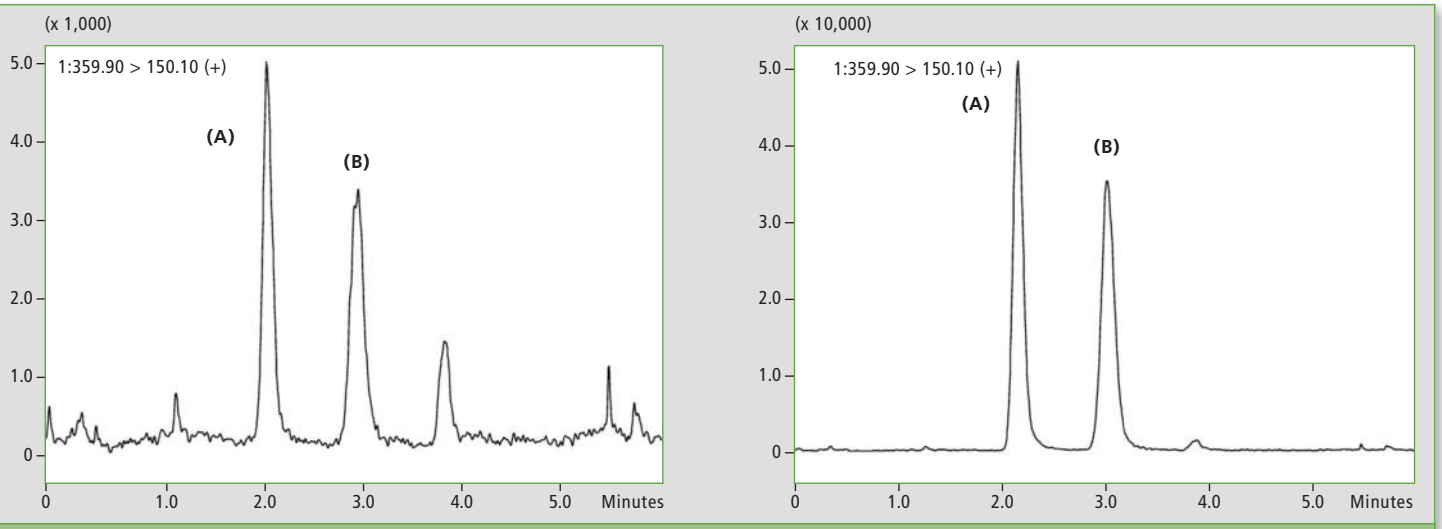

Figure 4: Chromatogram of a plasma sample spiked with a) 3 µg/L and b) 30 µg/L rabeprazole, analysed with the Nexera UC LC/SFC switching system

omeprazole. For the preparation of a blood plasma sample, 20 µl of plasma were mixed with 250 µl of acetonitrile for protein precipitation. The supernatant was mixed with acetonitrile and alkalized with 28 % aqueous ammonia. Three µl of the resulting sample solution were injected for analysis. The analytical conditions for SFC-MS/MS analysis are displayed in table 1.

Daicel's CHIRALPAK® IC-3 analytical column was identified as the most appropriate separation column in an initial column screening. Detection was performed using the Shimadzu LCMS-8050 triple quadrupole mass spectrometer.

A calibration curve was created using human plasma samples containing 1, 2, 10, 20 and 100 µg/L of omeprazole standard. Figure 3 shows the MRM chromatograms of the samples spiked with 2 µg/L and 20 µg/L respectively, and the two omeprazole enantiomers (A) and (B) are well separated. Linearity of the calibration was $R^2 > 0.99$ for both isomers.

The method produced good repeatability tested by five injections of the 2 µg/L sample with RSD values of peak area of 4.4 % for both omeprazole (A) and (B). Recovery was determined from a 10 µg/L sample compared to analysis of stock solution. Recovery rates of 101.1 % and 100.5 % respectively were obtained.

Analysis of rabeprazole in a plasma sample

Rabeprazole, known as a gastric acid secretion inhibitor, has a similar chemical structure to omeprazole, suggesting the possibility of successful chiral separation under similar analytical conditions. Rabeprazole was therefore analyzed in a plasma sample using the same analytical conditions as described for omeprazole in the previous section. The chemical structure of rabeprazole is shown in figure 4, where the structural similarity to omeprazole can easily be recognized.

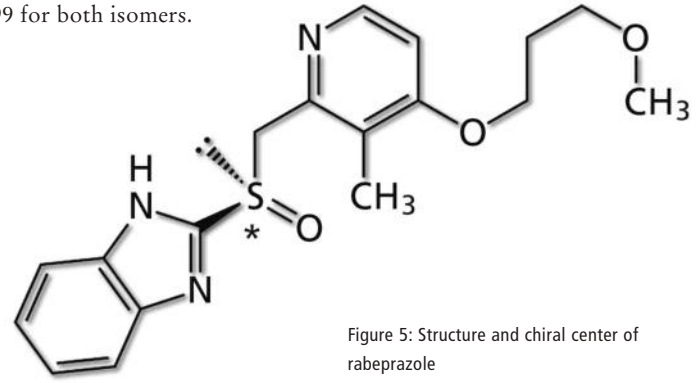

Figure 5: Structure and chiral center of rabeprazole

Column	CHIRALPAK®, IC-3 (100 × 3.0 mm, 3 µm)
Mobile phase	CO_2 / Methanol (80 : 20 v/v)
Flow rate	3 mL/min
Column temperature	40 °C
Injection volume	3 µL
BPR pressure	10 MPa
BPR temperature	50 °C
Detector	LCMS-8050 (ESI, MRM mode)
Make-up solvent	Methanol
Make-up flow rate	0.1 mL/min

Table 1: Analytical conditions

	Linearity (R^2)	Repeatability (% RSD peak area)	% Recovery (4)
Omeprazole (A)	0.99996 (1)	4.4 (3)	101.1
Omeprazole (B)	0.99998 (1)	4.4 (3)	100.5
Rabeprazole (A)	0.99996 (2)	1.8 (4)	102.5
Rabeprazole (B)	0.99999 (2)	2.4 (4)	100.1

Table 2: Results for linearity, repeatability and recovery rate for the determination of omeprazole and rabeprazole in plasma samples

A calibration curve was generated using human plasma samples containing 0.3, 1, 3, 10 and 30 µg/L of rabeprazole standard. Figure 5 shows MRM chromatograms of the samples spiked with 3 µg/L and 30 µg/L respectively. The two rabeprazole enantiomers (A) and (B) are well separated. Linearity of the calibration was $R^2 > 0.99$ for both isomers.

The method achieved good repeatability tested by five injections of the 10 µg/L sample with RSD values of peak area of 1.8 % and 2.4 for rabeprazole (A) and (B) respectively. Recovery was compared to analysis of stock solution as 102.5 % and 100.1 %. Table 2 summarizes the linearity, peak area repeatability and recovery rate for each compound. These results verify the applicability of this method to the practical analysis of plasma samples.

Simple and fast characterization tool for biosensor development

UV-spectroscopy with Thermal Melt Analysis System – microvolumes in spectral focus

One of the key aspects in the development of DNA-based biosensors relies on understanding the molecular binding event to be detected. DNA is a polymer comprised of nucleotides forming four bases (adenine, thymine, guanine and cytosine). These nucleotides are bonded together via phosphodiester bonds. In a double helix, two strands of DNA are held together via hydrogen bonding between adenine and thymine with two bonds and guanine and cytosine with triple bonds respectively. The study of DNA is central to the understanding of many biological processes that have been identified in many human diseases.

At the University of Bath, the Biosensor Research Laboratory has been pioneering the development of DNA-based electrochemical sensors for the detection of a wide range of biomarkers ranging from DNA, microRNAs, proteins and cells. The addition of the UV-Vis spectrophotometer together with Thermal Melt Analysis System has been a very useful tool to understand the biosensor development approach.

Biosensor, signal and target DNA

A biosensor is an analytical device that can be used for detection of an analyte (pollutant, viral DNA, antigen or protein) by combining a biological component (enzyme, DNA, antibody or aptamer respectively) that acts like a probe and binds to the target. Such a binding event gives rise to a signal which is detected by a transducer (mass sensitive, optical or electrochemical) [1].

In order to get a signal, it is important that the specific molecular event occurs, which in the case of a DNA biosensor means the capture of the target DNA. Therefore, it becomes inevitable to have the right probe that binds specifically to the target. A controlled fabrication strategy is to monitor each step of the development of the biosensor. Hence, it is important to know if the probe which in this case is a single-stranded DNA and the target sequence are binding. Shimadzu UV-1800 with Thermal Melt Analysis System finds its place in such a development phase of the biosensor (figure 1).

Figure 1: Shimadzu UV-1800 with Thermal Melt Analysis System (TMSPC-8) consisting of eight series micro multi-cell cuvette

Nucleic acids, as single or double strands of DNA and RNA, absorb ultraviolet (UV) light due to the heterocyclic rings of the nucleotides. The absorption properties are normally used for quantification, since all absorb around 260 nm.

Furthermore, the absorption can be used to detect sample hybridization in solution as a function of temperature, for example. In ssDNA, the bases stack on top of each other, but this conformation is maximized in dsDNA. The hybridization stabilizes the helical structure of DNA and also RNA. Such a feature has been proven to be useful in understanding of the base-pairing of double-stranded DNA [2]. Such a property was used to understand the melting curve of the sequences of DNA-based biosensor development. Figure 2 demonstrates a schematic of a gold electrode surface after the modification with thiolated single-stranded DNA probe with a spacer molecule (6-mercapto-1-hexanol) to control the probe surface density.

Methods

For characterization of the nature of hybridization of the probe DNA and target DNA, an 8-series micro cell was used with silicone plugs, which fits inside the TMSPC-8 temperature controlled accessory. A Shimadzu UV-1800 spectrophotometer equipped with the TMSPC-8 was applied for the thermal melt experiment.

1 µM concentration of probe DNA (5'- SH(CH6) -TTTT-TATTGTGACAGACCATTGC-TACA-3'), target DNA (5'-TGTAGCAATGGTCTGTCA-CAAT-3') and the mixture of probe and target DNA was prepared separately in 10 mM phos-

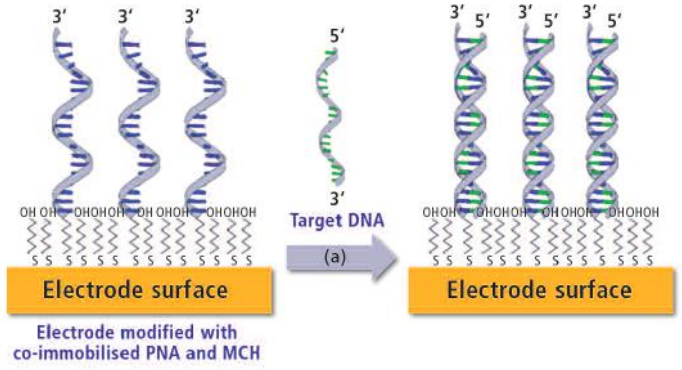

Figure 2: Schematic of a DNA biosensor. Left shows the co-immobilization of thiolated DNA probe with a spacer molecule (6-mercapto-1-hexanol). Right represents post capture of target DNA resulting in the formation of a duplex strand.

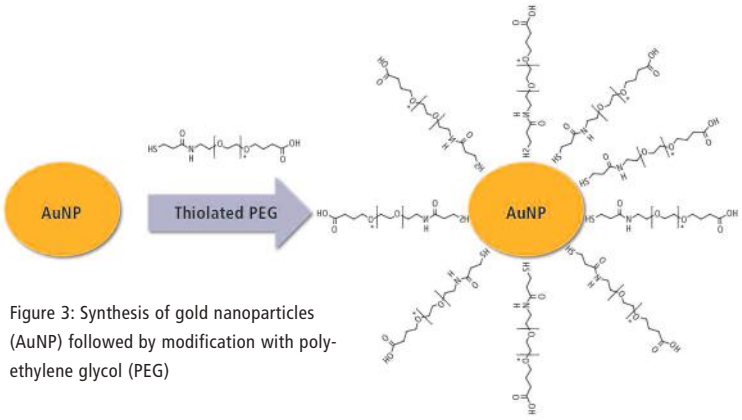

Figure 3: Synthesis of gold nanoparticles (AuNP) followed by modification with polyethylene glycol (PEG)

phate buffer saline (PBS, pH 7.4). The first cell was just used to measure the blank with PBS buffer, followed by the use of two cells each for probe DNA, target DNA and mixture (probe + target) respectively. The program was set with a complete cycle where the temperature was raised from 19 °C to 90 °C and back. Using a ramp rate of 0.5 °C/min, the absorbance was recorded at a wavelength of 260 nm.

Figure 3 shows the schematic of gold nanoparticle (AuNP) before and after modification with polyethylene glycol (PEG). Synthesis of 17 nm AuNP was adopted by the protocol reported by Gao, Jie, et al [3]. Briefly, 5 mL HAuCl4 gold (III) chloride hydrate (0.2 % w/w) from Sigma-Aldrich was added to 90 mL water and was heated to 80 °C with constant stirring. Later, 5 ml of trisodium citrate dihydrate solution (1 % w/w) from Sigma-Aldrich in water was added quickly leading to changing of the color to deep red.

Thereafter, the synthesized AuNP was modified by polyethylene glycol (PEG). 1 mL of AuNP was incubated with 100 uL of 0.5 mM (O-(3-Carboxypropyl)-O'-[2-(3mercaptopropionylamino) ethyl] -polyethylene glycol (PEG) from Sigma-Aldrich [MW 3000 Da]) for 16 hours at 4 °C with constant stirring. The modification of AuNP before and after the modification was monitored using Shimadzu's UV-1800, looking at the absorbance spectrum in the wavelength from 400 to 800 nm.

Results and Discussion

Figure 4 shows the real-time melting curve obtained for the DNA probe and target DNA from 19 °C to 90 °C and back. Two DNA strands hybridize at room temperature and with the increase of temperature, the conformation changes until 60 °C. Up to this value, the double helix denatures, increasing the absorbance. When the temperature decreases, the single strands hybridize again and the absorbance reduces. The temperature at which half of DNA strands are in the single-stranded (ssDNA) state is termed as melting temperature (Tm). From the software analysis, the Tm in 10 mM PBS (pH 7.4) was found to be 66 °C.

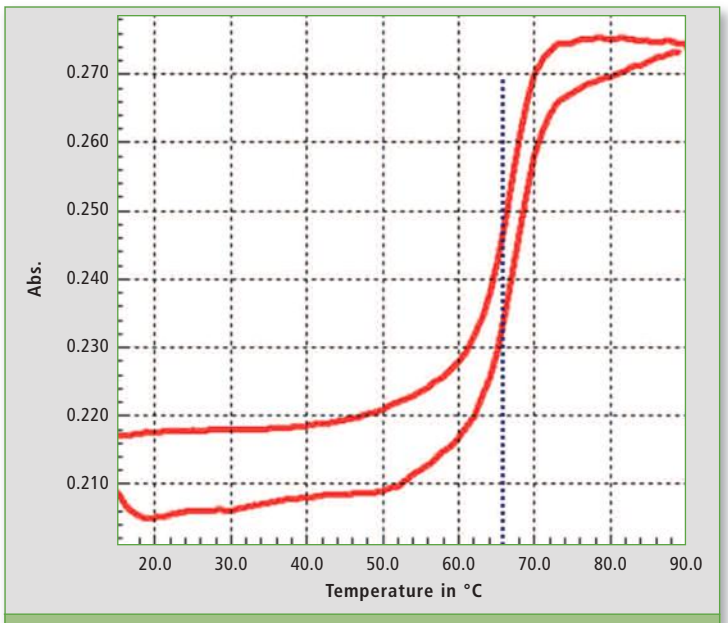

Figure 4: Melting curve of DNA probe and target DNA in 10 mM PBS buffer, pH 7.4

The analysis confirmed that the two strands obtained hybridized well due to their complementary properties. Different nucleotide sequences lead to different denaturation temperatures which can be analysed with UV light. Similarly, hybridization events can be confirmed using this technique.

Figure 5 shows the absorbance curve obtained for the synthesised AuNP. The graph shows characteristic peaks of 20 nm AuNPs at 520 nm. After the modification of AuNP with PEG molecules, the characteristic peak shows a 3 nm displacement which is well in accordance with the reported literature [3].

Conclusion

In conclusion, the impetus of this application news was to demonstrate how the Shimadzu UV-1800 together with Thermal Melt Analysis (TMSPC-8) system can be utilized as a characterizing tool to develop a biosensor. The UV-1800, when incorporated with the TMSPC-8 System is capable of monitoring the changes in absorbance of the dsDNA melting as a function of temperature and determining Tm values for the dsDNA in the buffer applied. It was also used to understand the nature of hybridization and to confirm the use of right sequences for the development of DNA-based sensor. UV-1800 was also applied to monitor the changes in absorbance on the modification of gold nanoparticles with PEG. With the 8-channel micro cell, multiple curves can be captured simultaneously for the analysis of repetitive sample. Another advantage of using such a cell is the need of low sample volume (100 µL) enabling analysis of samples in a most efficient way by reducing necessary resources and cost.

Instrumentation

Shimadzu UV-1800 including computer control software UVProbe, high precision cell holder: The TM analysis system (TMSPC-8) is an accessory for UV-Vis, comprising of a thermo-electrically temperature controlled micro multi-cell holder employing a Peltier element and PC software specially designed for the purpose.

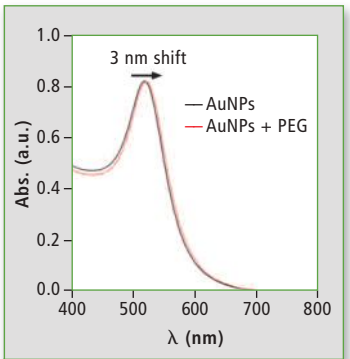

Figure 5: Absorbance curve of gold nanoparticle (AuNP) before and after modification with polyethylene glycol (PEG)

Authors

Pawan Jolly [1], Marina Batistuti [2], Pavel Zhurauski [1], Pedro Estrela [1]

[1] University of Bath, UK; [2] University of São Paulo, Brazil

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Lighting up

Determination of quantum efficiency of fluorescence standards with high quality

One of our first experiences with materials lighting up at night is definitely the glowing dial of a wristwatch. A wide variety of materials exhibit this property in which energy supplied from an external source leads to the emission of light (fluorescence or phosphorescence). This physical principle of fluorescence is used in the development and quality control of lighting systems, displays or monitors, as well as in biotechnology and medicine. For these applications, modern instrumental analysis makes use of reliable and precise measurement technologies to characterize this fluorescence.

In fluorescence spectroscopy, there is an interdependence between instrument technology and the wavelength of the light. Modern instruments can perform computational spectra correction in order to reliably compare different instruments. Such a correction takes into account the characteristics of the emission optics as well as the excitation optics. The spectra corrected for these characteristics are subsequently used to determine the so-called quantum yield of the fluorescing materials (fluorophores). The quantum yield describes the probability of how effectively a material can convert the irradiated energy by the excitation light into the emitted fluorescent light.

Quantum yield: relative and absolute method

In the past, this determination was carried out using a relative method, in which a known reference standard was measured and its fluorescence intensity was then compared to that of a sample. For unknown compounds, however, these quantum yields must be determined in a different way via an absolute method – known as 'quantum efficiency' (QE).

In this case, the quantum yield is calculated directly from a spectrum measured from the fluorescent substance using an integrating sphere, which effectively collects all fluorescence quanta and passes these to the emission detector. Figure 1 illustrates the approach and mathematics for the determination of the quantum efficiency.

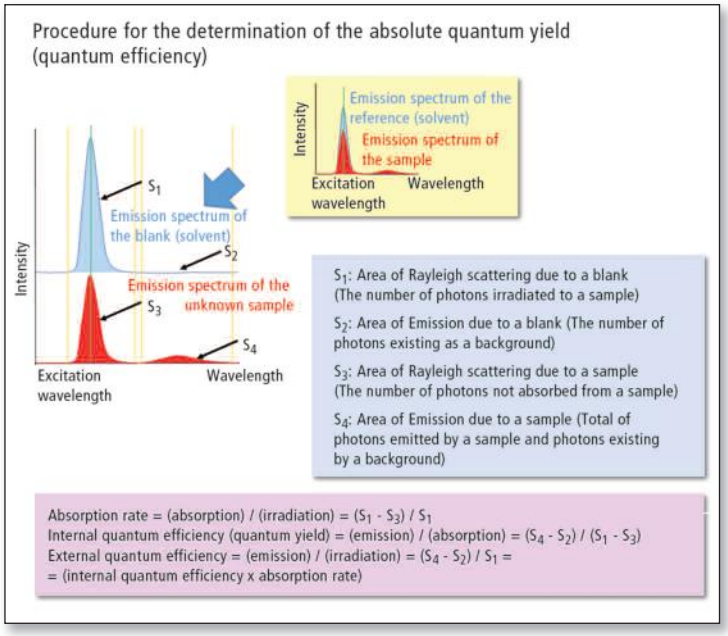


Figure 1: Determination of the absolute quantum yield

In 2011, IUPAC published a technical report [1] in which the quantum yields of various fluorescence standards were compared based on the existing literature. As a small set of well-established standards, quinine sulfate, fluorescein and rhodamine 6G are listed. In addition, the review also includes 9,10-diphenyl anthracene, beta-carboline, (norharmane), harmaline, rhodamine 101 and cresyl violet as well as 28 other frequently used substances [1].

	Concentration	Solvent	Excitation at	Area range evaluation Excitation	Area range evaluation Emission
Quinine sulfate	5 x 10^{-5} M	0.05 M H_2SO_4	350 nm	330 - 365 nm	370 - 635 nm
Fluoresceine	10^{-7} M	0.1 M NaOH	488 nm	470 - 500 nm	500 - 700 nm
Tryptophan	10^{-5} M	Destilled water	270 nm	250 - 290 nm	300 - 480 nm

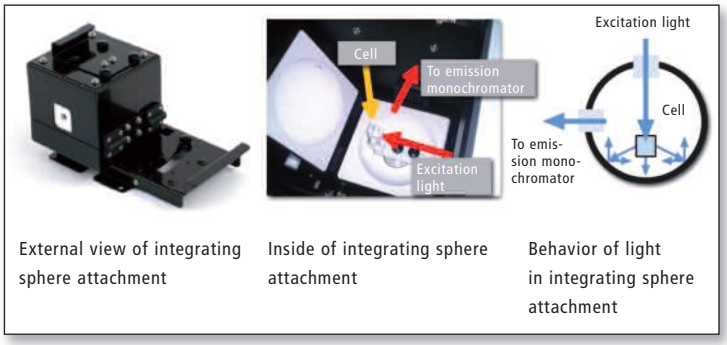
Table 1: Conditions for evaluation of the measured spectra for quantum efficiency determination

Fluorescence standards dependent on solution conditions

When considering the selection of the standard, the conditions of the solution in which the standards are prepared are important. Solvent concentration, pH value in aqueous solution and also temperature must be taken into account. Different solvents used to prepare the fluorescent standards lead to different quantum yields.

In addition to these aspects, the IUPAC report also discusses the measurement technology applied. Two variations are the rule:

- relative measurement of quantum yield using a cuvette in a standard sample holder of a fluorescence spectrometer.
- absolute measurement of quantum efficiency using an integrating sphere.



External view of integrating sphere attachment | Inside of integrating sphere attachment | Behavior of light in integrating sphere attachment

Figure 2: Integrating sphere for the RF-6000; left: integrating sphere; middle: cuvette in the opened sphere; right: graphical representation of the light path of excitation and emission within the sphere.

Source of the QE values	QE value Fluoresceine	QE value Quinine sulfate	QE value Tryptophan
IUPAC [1]	0.91 ± 0.05	0.60 ± 0.02	0.15 ± 0.01
Reevaluation [2]	0.88 ± 0.03	0.60 ± 0.02	0.15 ± 0.01
LabSolutions RF	0.9045	0.5898	0.152

Table 2: Comparison of absolute quantum yields (QE, quantum efficiency) for fluorescein, quinine sulfate and tryptophan measured with an integrating sphere (data obtained from the literature) with quantum yields obtained using the RF-6000 with integrating sphere

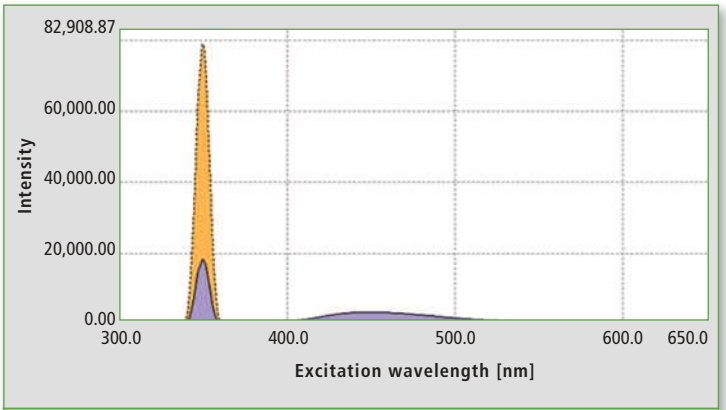


Figure 3: Determination of the quantum efficiency of a quinine solution at a concentration of 5 x 10^{-5} M; QE was calculated as 0.5898

The present application not only demonstrates the absolute determination of the quantum efficiency of three fluorophores using Shimadzu's RF-6000 with integrating sphere (figure 2) but also the good correlation of these results with corresponding literature values. In this application, the quantum efficiencies of fluorescein, quinine sulfate and tryptophan were determined as examples.

Carrying out the measurement

Prior to measurement, the appropriate concentration of the solution is adjusted and the diluted fluorophore is transferred to a cuvette with four polished sides. This cuvette is placed into the integrating sphere of the RF-6000 and measurement is subsequently started.

The measurement parameters selected in the LabSolutions RF software are listed in table 1. A measurement was carried out with an average speed of 600 nm/min. The instrument was set to a slit width of 5 nm for excitation as well as for emission. Detector sensitivity was set to low.

The 'Quantum Efficiency' function of the LabSolutions RF software was used to evaluate quantum efficiency. The areas used for signal integration are listed in table 1. As an example, the quantum efficiency measurement of quinine sulfate is shown in figure 3. Table 2 compares the measured absolute quantum efficiency with the data obtained from the literature.

All three QE values of the fluorescence standard examined lie exactly within the range of the described target value.

Conclusion

The RF-6000 is excellently suited to quantum yield measurements. With its high signal-to-noise ratio in combination with its high speed and quantum yield/efficiency software, absolute quantum yields can be determined quickly and accurately.

Literature

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[2] Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector Kengo Suzuki, Atsushi Kobayashi, Shigeo Kaneko, Kazuyuki Takehira, Toshitada Yo-shihara, Hitoshi Ishida, Yoshimi Shiina, Shigero Oishic and Seiji Tobita; Phys. Chem. Chem. Phys., 2009, 11, 9850-9860; DOI: 10.1039/b912178a

How spectrometers take care of human health

Inclusions in packagings analyzed with EDX-7000P/8000P

In the last issue of Shimadzu News, the first part of this EDX article series focused on safety application in aircraft, automobiles and railway locomotives, in particular the analysis of engine oils containing fine wear products as well as particles of metals and alloys in the form of shavings. Testing laboratories of many major airlines use X-ray fluorescence spectrometers for fast analysis of small metal shavings. This second part of the EDX article series covers food packagings.

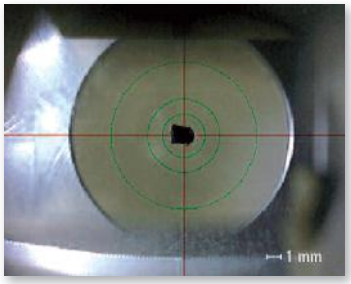


Figure 1: Photo of the inclusion at PC screen

Contaminants in packaging materials

Human health can be influenced by the choice of food – in a positive as well as in a negative way. Despite their apparent quality and healthiness, food products still have to be analyzed for the presence of harmful and dangerous contaminants. Such impurities or residues can get into the products from packaging materials – for example, bags cans, jars, and bottles. Although glass packaging materials seem to be the safest, they can also contain contaminants that have entered the glass during the manufacturing process from furnace, piping or melting forms.

These inclusions can be hazardous to human health. In addition, they can influence the durability of the packaging. For a typical measurement, the analyst breaks the sample and dissolves part of it with inclusion in the appropriate reagent. Such sample preparation is time-consuming and dissolution is usually associated with the use of hydrofluoric acid, requiring special utensils and a separate work area.

All this can be avoided by using the energy dispersive X-ray fluorescence spectrometer EDX-7000P or EDX-8000P for the analysis. These are used for non-destructive elemental analysis of solid, powder and liquid samples while offering excellent maintenance performance. Both instruments are BfS (safety standards of the German Federal Institute for Radiation Safety) type approval certified. The sample observation camera and automatic collimator switching system allow local analysis of different parts of the sample.

Standardless quantitative fast analysis of single extraneous inclusion in glass jar

In an experiment, single extraneous inclusion on the outer surface of glass jars was measured using EDX-8000P. A glass jar was placed in the sample compartment so that the inclusion was in the center of the area to be analyzed. A collimator of 1 mm diameter was selected for the analysis (figure 1). A routine measurement procedure of unknown sample by Fundamental Parameters (FP) method was used, as included in the standard spectrometer software. The spectrum of the sample is shown in figure 2.

Conclusion

The results of the sample analysed are listed in table 1. They show that the analysis of extraneous inclusions by EDX-7000P/8000P can be done successfully without their separation from glass, which eliminates time-consuming sample preparation and use of chemical reagents.

Element	Concentration wt %
SiO_2	68.624
Al_2O_3	12.534
SO_3	8.048
CaO	3.570
K_2O	2.987
Fe_2O_3	2.766
TiO_2	0.999
ZrO_2	0.129
SrO	0.123
MnO	0.089
CuO	0.067
Rb_2O	0.064

Table 1: Results of analysed example

Moreover, it greatly reduces time of analysis. Data acquired helps to determine the possible source of contamination (cast iron melting form, furnace lining or other).

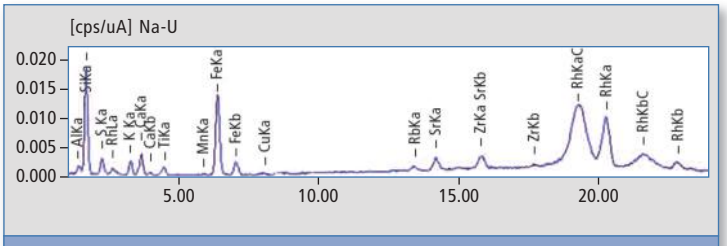
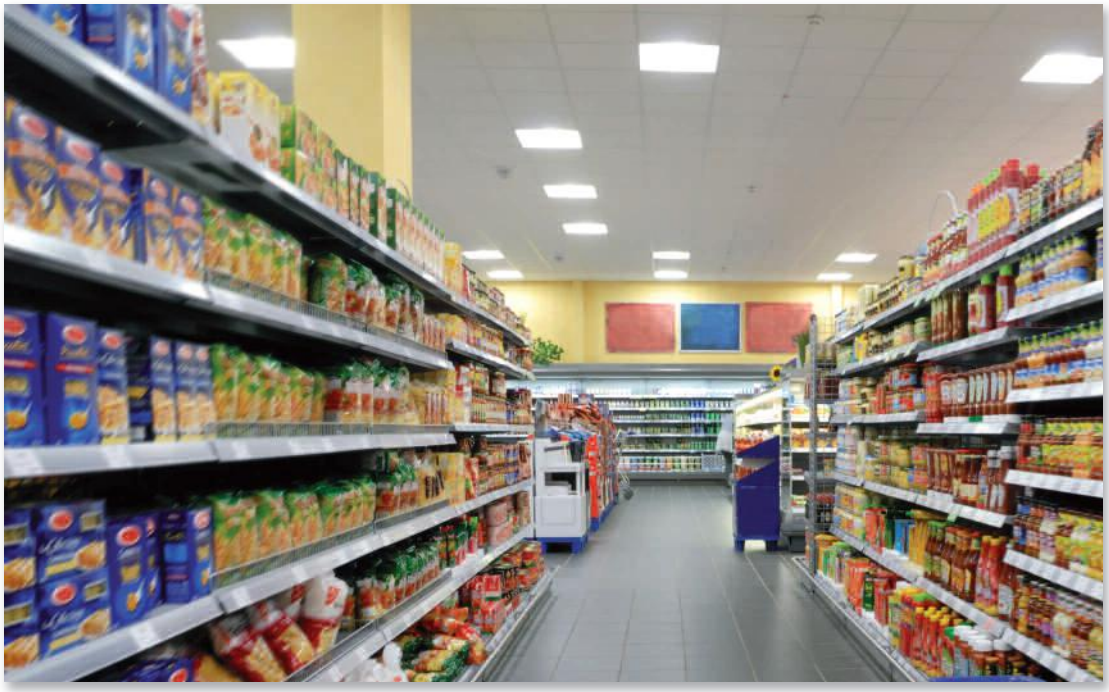


Figure 2: EDX spectrum of inclusion on outer surface of glass jar. Total analysis time including placement of the sample in the cell was approximately three minutes.

Food and food packaging: non-intentionally added substances

FTIR, EDX and LC-GC-online Technique for colored, non-transparent plastic packaging



Food can be contaminated not only through direct contact with its packaging, but also along the entire production and commercial chain. So far, legislation on the migration of substances from plastic packaging into food in particular has covered the starting materials used in the plastics manufacturing. Regarding health risks related to the transfer of substances, the so-called NIAS (non-intentionally added substances) should be focused on more strongly; these substances are added non-intentionally during manufacturing of plastic packaging materials. These can include impurities originating from raw materials, reaction and degradation products in manufacturing as well as impurities arising from transport and production [1].

Contamination during the production process

Possible sources for impurities can be found in the production process, including preservation and bottling, in which metals can migrate into food and beverages. Often, raw as well as processed products are in prolonged contact with materials such as stainless steel, copper, glass and other equipment.

Figure 1: Occurrence of various plastics among the 43 samples investigated

Impurities in the packaging material

Another source is the packaging material. It is in close contact with the food – during the entire transport, storage in retail as well as in the consumer's home.

Currently, there is much discussion on food packaging with saturated and aromatic mineral oil hydrocarbons (MOSH – mineral oil saturated hydrocarbons and MOAH – mineral oil aromatic hydrocarbons).

The MOSH fraction consists of linear and branched alkanes as well as alkyl substituted cycloalkanes, whereas the MOAH fraction consists of alkylated polyaromatic hydrocarbons with up to four aromatic rings. The main focus is on the aromatic fraction, which is suspected of being potentially carcinogenic and mutagenic [2]. The proportion of the aromatic fraction is approximately 15 - 30 % of the total mineral oil fraction.

In addition to the mineral oil fractions MOSH and MOAH, the so-called POSH (polyolefinic oligomeric saturated hydrocarbons) are focused, i.e. oligomers that can migrate from plastic packaging (PE, PP).

Scope of the new plastics regulation

In principle, the Commission Regulation (EU) No. 10/2011 on plastic materials and articles that come into contact with food stipulates that impurities as well

Figure 2: PET tray for tomatoes; Sample 08

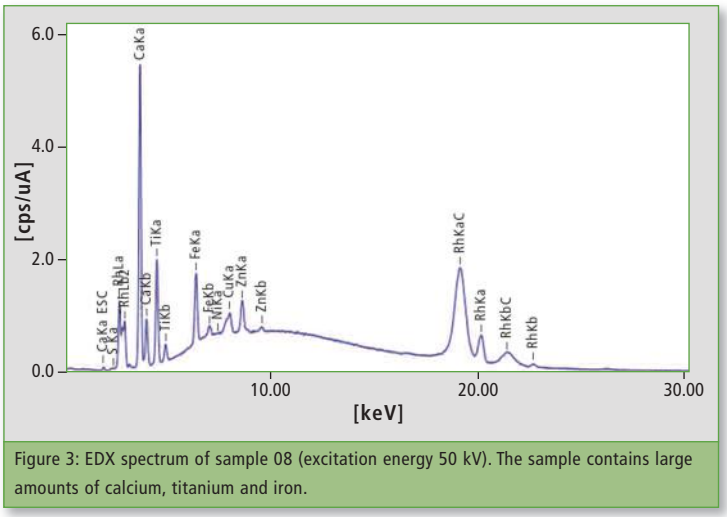


Figure 3: EDX spectrum of sample 08 (excitation energy 50 kV). The sample contains large amounts of calcium, titanium and iron.

as reaction and degradation products must be assessed by the manufacturer in accordance with internationally accepted scientific principles of risk management.

As of 1 January 2016, the amended test conditions described therein fully apply. In addition to overall migration (migration limit: 60 mg/kg food), there are many other specific migration limit values that must be adhered to.

'Multi-material multi-layer materials' are also included in the new plastics regulation as well as materials or objects consisting of two or more layers of different materials of which at least one consists of plastic [3]. As reported in the Shimadzu News 1/2017, a total of 32 transparent, colorless and 50 imprinted food packagings were investigated. This article now focuses on colored non-transparent plastic packagings. The plastics were analyzed using FTIR and EDX spectroscopy as well as an LC-GC online system. Spectroscopic methods offer the advantage of non-destructive sample analysis with little time expenditure. The chromatographic method can be fully automated.

Within the scope of the investigation, 43 samples of different origin were analyzed. This included, for instance, caps or closures of bottles and cups, vegetable nets and trays. First, the samples were identified using FTIR spectroscopy and later analyzed for non-intentionally added substances such as heavy metals and mineral oil hydrocarbons.

Identification of plastics using FTIR spectroscopy

All samples were analyzed in the first step using FTIR spectroscopy. This enabled a non-destructive investigation of surfaces in which the main components of the outer and inner surfaces of the plastic packagings could be identified. The absorption was measured using Shimadzu's IR Tracer-100 equipped with a diamond ATR. In this method, the IR beam penetrates the sample to a depth of about 2 µm, whereby the intensity of the reflected light is attenuated with respect to the irradiated light.

Figure 4: MOSH/MOAH application system

In a second complementary step, an EDX analysis was executed using Shimadzu's EDX-8000P. Upon suitable excitation, each element emits characteristic X-rays allowing the element's identification. Using energy dispersive X-ray fluorescence analysis, elements from carbon up to uranium can easily be detected in the lower ppm range.

To analyze the samples, a total of 48 IR and 40 EDX spectra were recorded. Table 1 lists samples that include packagings consisting of one or two main polymers. Most of them were black or white, while otherswere blue, yellow, orange, green or gold.

The most frequently used polymers are polypropylene (PP), polyethylene (PE) and polystyrene (PS). Due to its high heat resistance, PP is used for packaging hot-filled or sterilized products while PS is used mainly in disposable items due to its high susceptibility to breakage [4].

Figure 1 shows polymer composition of the investigated samples which shows great similarity to the composition of maritime microplastics occurring on a remote Maldive island, as investigated in a study by the Germany-based Bayreuth University. The microplastics particles found consisted mainly of PE, PP and PS [5].

Quantitative analysis of heavy metals using EDX spectroscopy

EDX spectroscopy allows the identification of fillers and ROHS elements that may be present in the sample. Most samples contain larger amounts of the elements silicon, calcium, titanium and aluminum. This confirms the presence of fillers such as kaolinite (SiO_2/Al_2O_3) and calcite ($CaCO_3$). The titanium is present as titanium oxide and serves not only as a white pigment but also as a stabilizer. By absorbing UV irradiation, it protects against photo-oxidation of the polymer [6].

PET is produced using an antimony trioxide catalyst [7]. For this reason, PET-containing samples were screened for antimony residues using a fast screening method specifically optimized for ROHS elements as well as for antimony and chloride. Table 2 shows the analysis results for sample 08. It contains 311.3 ppm antimony. In other PET-containing samples, antimony concentrations of several hundred ppm were found.

Sample 08 from table 1 still contains antimony residues. Many of the food packagings investigated consist of an outer PET layer and an inner PE layer. In this way, the food contained is not in direct contact with the antimony-contaminated PET layer. The examples show that a combination of

FTIR and EDX spectroscopy offers access to a multitude of information on plastics and their contents. Both methods are completely non-destructive and require minimum time.

MOSH/MOAH analysis using online LC-GC technology

Undesirable mineral oil residues often enter products through the use of mineral oil based printing inks which can be found in food and food packagings. This effect has been increasingly detected not only in recycled materials but also in packagings consisting of fresh raw materials. In many products, the concentration of saturated (MOSH) and aromatic (MOAH) hydrocarbons is particularly high.

For this analysis, a MOSH/MOAH application system is now available based on LC-GC coupling and was developed in accordance with EN 16995:2016 'Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with online HPLC-GC-FID analysis; German and English version FprEN 16995:2016.'

No.	Sample	Color	Polymer (inner surface)	Polymer (outer surface)	Recycling symbol	Additive
01	Fast Food	white	PS	PS	06 PS	Si, Al
02	Cutlery	gold		PP	—	Si, Al, Cu, Ti, Zn, K
03	Soft Drink	silver		PE	—	Ca, Ti, Al, Si, K
04	Coffee	black	PE	PET	—	Al, Si, S, Fe, K, Ba
05	Milk	blue		PE	—	Ti, Al, Si, S, Ca
06	Sweets	black		PP	01 PET	Ca
07	Potatoes	yellow		PE	—	Ti, Al, Ca, Si
08	Tomatoes	black	PET	PET	01 PET	Ca, Ti, Si
09	Pears	black	PS	PS	06 PS	Si, Al, Ca, S, Ti
10	Sausages	black	PE	PA (Nylon6)	—	Si

Table 1: Organic and inorganic main components of ten selected food packagings

Element	Result	3-sigma [ppm]
Cd	ND	[18.0]
Pb	ND	[10.8]
Cr	3.9 ppm	[4.4]
Hg	ND	[2.0]
Br	ND	[2.1]
Cl	53.5 ppm	[59.5]
Sb	311.3 ppm	[62.0]

Table 2: Results of EDX screenings for ROHS elements, antimony and chlorine of sample 08. ND = not detected; 3-sigma = triple standard deviation.

The system consists of the following components:

- Shimadzu's LC-20ADXRpump unit with UV detector and degasser
- Shimadzu's GC-2010 Plus with two FIDs
- CTC autosampler
- Semrau CHRONECT® LC-GC (figure 4).

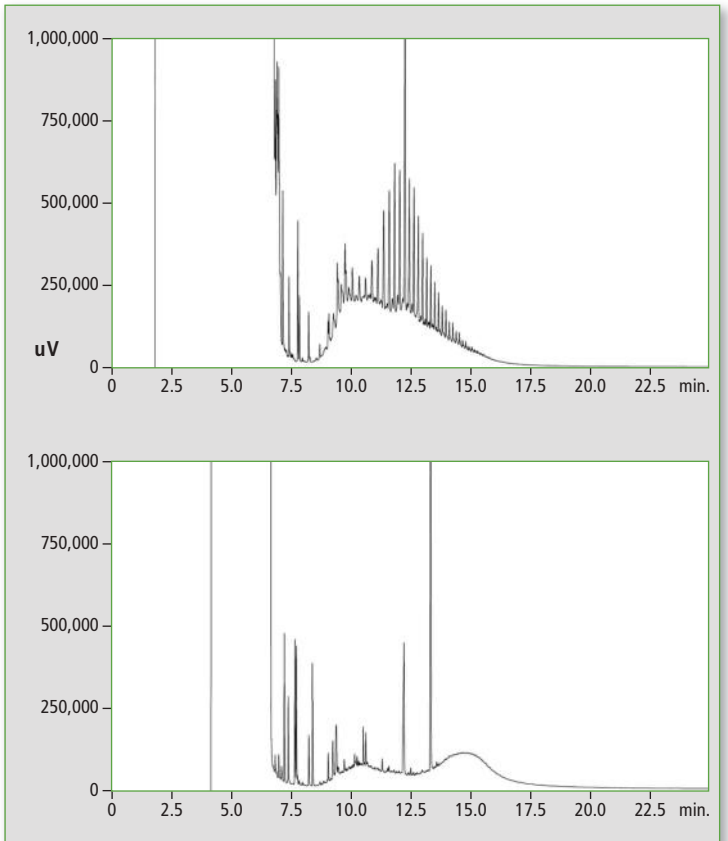


Figure 5: Chromatogram of the MOSH and MOAH fractions

The method offers high sample throughput, reproducible results and good sensitivity. The system enables LC-GC measurements with a reproducibility comparable with conventional split/splitless injection in a gas chromatograph. Direct coupling reduces the risk of contamination in manual methods. The advantage of the system is the configuration of two FID detectors, allowing parallel determination of MOSH and MOAH within a single run and leading to characteristic chromatograms as shown in figure 5.

Conclusion

The Commission Regulation (EU) No. 10/2011 on plastic materials and articles that come into contact with food (also referred to as 'Plastics Implementation Measure', PIM) has been in force since 4 February 2011. As of 1 January 2016, the test conditions prescribed therein apply fully. In addition to overall migration (migration limit 60 mg/kg food), many other specific migration limits must be adhered to.

Shimadzu offers a comprehensive solution for the analysis of non-intentionally added substances (NIAS) including heavy metals (antimony trioxide) and mineral oil fractions (MOSH/MOAH).

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Further information on this article:

- Flyer MOSH/MOAH Analyzer

Life can be hard

Contamination of bread - Particle analysis with FTIR-ATR single reflection ATR technique and EDX for inorganic analysis

With a bright smile, the author has bought healthy full grain bread, persuaded to do something good for the body. Being hungry, he ate the bread straight away and may-be a little too fast. Suddenly – a cracking sound, he has bitten on something incredibly hard. Oh no, the teeth! Is one broken? Repair is so expensive, it would be a disaster. Quickly checked, everything okay. But a hard particle needs investigating...

Once isolated, the particle looked like a rice corn which had dried to be hard as a stone.

Let's name this particle (figure 1). It has a size of 3 to 5 mm and a shape like a rice corn. Under the stereo microscope, it showed an orange color. Under normal day light, it appeared white. Having

Figure 1: The contaminant in wholegrain bread has a size of 2 x 5 mm; this photo was obtained with a camera integrated in a stereo microscope

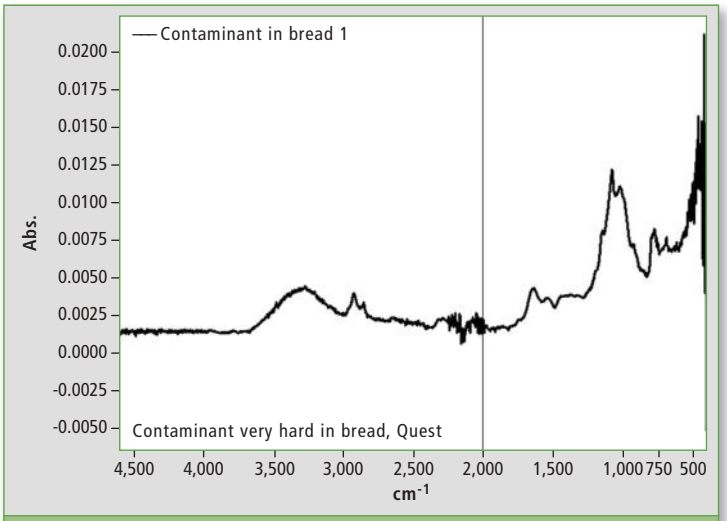

Figure 2: Low-pressure: infrared spectrum from the surface of the particle, which is dominated by cellulose

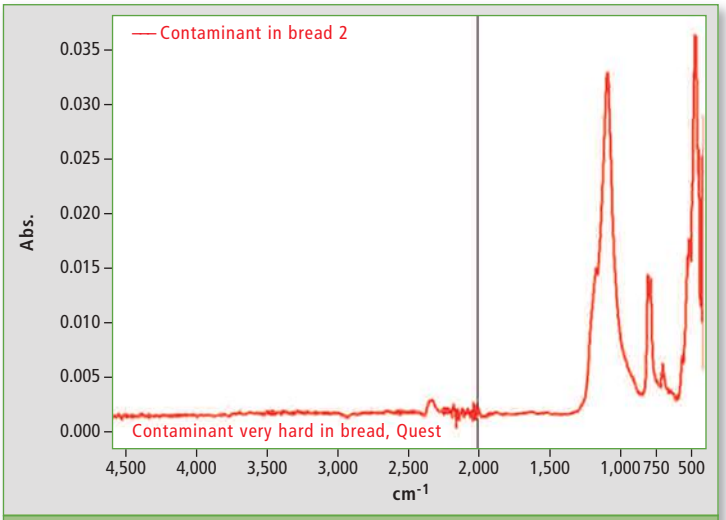

Figure 3: Middle- pressure: infrared spectrum from a collection of particles from the corn, mostly identified as SiO_2

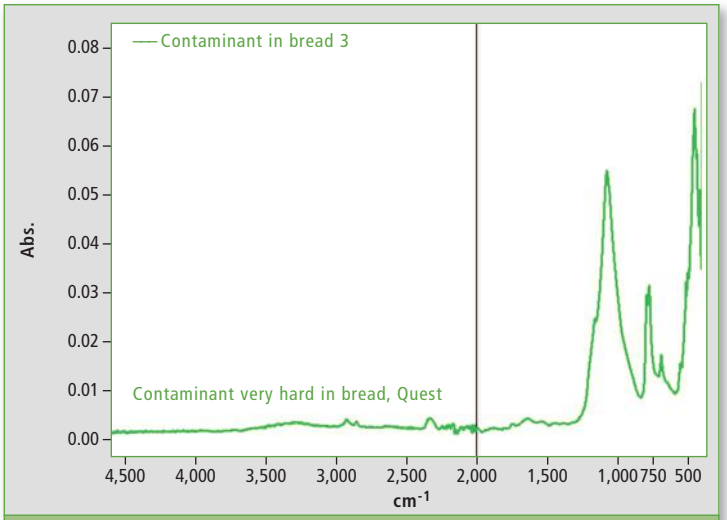

Figure 4: high-pressure: reconfirming the result from 2, a collection of fine crystals from the particle separated powder

being hurt by this particle, it was of interest to analyze the real chemical consistence.

Particle measurement techniques

For a rough screening and identification of materials, two non-destructive analysis techniques are available: EDX and FTIR. Non-destructive means that the sample keeps its form and that a chemical treatment is not needed.

EDX (energy dispersive X-Ray fluorescence spectrometer) makes the analysis easy due to the "place and measure" nature of its application. Infrared spectroscopy (FTIR Fourier Transform Infrared Spectroscopy) is a measurement technique which helps to identify very hard material using the single reflection ATR (Attenuated Total Reflection) tool without any other physical treatment. This is possible because the ATR unit Specac Quest™ has an integrated diamond window which makes it possible to analyze very hard solid materials at their surfaces (penetration depth of the infrared beam of ~2 µm). The hardness of the diamond will help to do so.

Sample preparation and spectral analysis using FTIR

No special sample pretreatment was used. The particle had a rice-corn shape of 3 by 5 mm. It was simply placed on the diamond window of approx. 2 mm size and the anvil (accessory) was screwed down to press the corn onto the diamond window, breaking it into smaller, still very hard pieces. At this moment, it became obvious that an inorganic material was present. FTIR measurement was done in a range of 400 to 4,600 cm^{-1}. Infrared reflection spectra are presented in figures 2 to 4.

Anvil pressure was set in three levels. With low pressure a cellulose spectrum was measured at the effective top surface. This is acceptable because the environment of this specific corn was previously bread. Traces of cellulose remained on the surface of the particle.

Figures 3 and 4 show measurements of fragments from the corn and of the crystal dust. The dust appeared after the particle cracked and was collected from the measurement crystal. Both measurements with different pressure – middle (fragment) and high pressure (particle dust) resulted in an inorganic spectrum. The spectrum is most probably the SiO_2 spectrum. A library search resulted in a good match dedicated to diatomaceous earth.

Sample preparation and X-ray analysis with EDX-8000

In addition to FTIR-ATR measurements, EDX technique was applied to obtain elemental composition of the sample in the ppm to percentage level without the need of sample preparation. Standards for calibrating the instrument are useful to increase accuracy of measurement results, but are not mandatory. The analysis is non-destructive, making the technique very useful for screening of unknown samples.

For this measurement, the particle was transferred to a special plastic cup. With a collimator (standard accessory) the measurement range was narrowed down to 1 mm. Using a camera (standard accessory), the exact position of the sample within the sample chamber was confirmed.

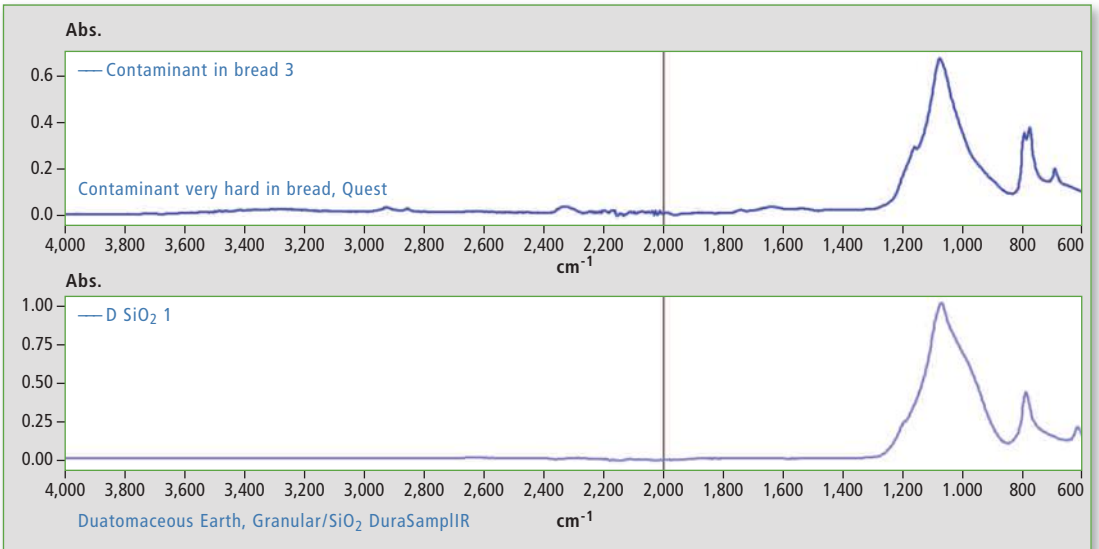

Figure 5: Library search and hit with diatomaceous earth, granular/SiO_2 DuraSamplIR

Analyte	Result [%]	[3-sigma]	Proc.-Calc.	Line	Int. (cps/uA)
SiO_2	91.851	[1.891]	Quan-FP	SiKa	3.0173
K_2O	6.601	[0.246]	Quan-FP	K Ka	0.7465
Fe_2O_3	0.949	[0.016]	Quan-FP	FeKa	3.7834
CaO	0.371	[0.018]	Quan-FP	CaKa	0.3355
SO_3	0.213	[0.029]	Quan-FP	S Ka	0.1533
CuO	0.016	[0.002]	Quan-FP	CuKa	0.3445

Table 1: EDX results using Fundamental Parameter (FP method)

For the measurement, a simple standardless FP (fundamental parameter) method was used. Calibration of the instrument was not needed. No filters (standard accessory) or vacuum condition (optional accessory for measurement of light elements) were used.

Results

It was clear that the main compound of the sample was SiO_2, i.e. a stone. Other elements present such as Fe are typical elements occurring in stones and minerals.

Instrumentation

- IRTracer-100 with LabSolutions IR software
- Single reflection unit – Specac Quest™
- Shimadzu Libraries
- EDX-8000
- EDXIR Contaminant Library

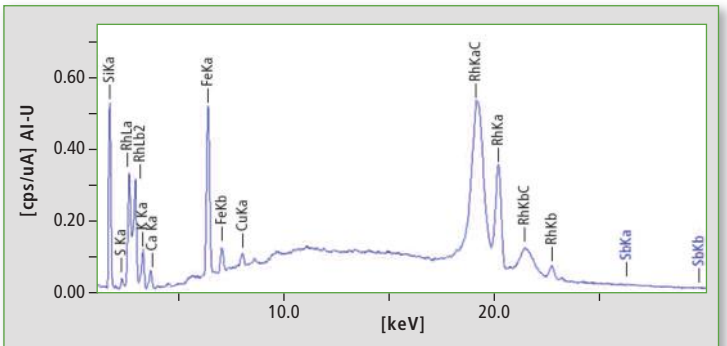

Figure 6: EDX spectrum of the particle

Conclusion

Infrared spectroscopy can identify the major components in natural and complex sample material. The domain of infrared is the identification of substances from organic or inorganic characteristics. As inorganics have more unspecific signal groups, EDX is a good complementary analysis for the elemental distribution in a small particle such as the corn in this case.

Feed to Food

Strategies for measurement of pesticides in water and foods

Water is not only the basis for all life, but it is also an important resource for many types of production processes, particularly in agriculture. Fresh water sources especially in surface and ground water are of vital importance to humans, but they occur in low amounts only. Water plays a role in various applications, for instance as a foodstuff in the form of drinking water or as a basis for food and beverage preparation. Water is also important in the production or supply of raw materials in industry and agriculture [1, 2].

This is why water plays a central role in the food chain and why contaminations have a direct effect on human health. Plant protection products (PPPs) are used extensively and comprehensively in agriculture to increase production. As a result, PPP residues can persist on foods and feedstuff or leach into surface and ground water via various routes. In addition, PPPs are prone to conversion and degradation processes which may lead to the formation of many different metabolites over time. In monitoring programs these metabolites, with their often widely varying physicochemical properties, must also be taken into account, resulting in highly complex requirements on analysis strategies.

Method: Analysis of plant protection products

In food analysis, the QuEChERS (quick, easy, cheap, rugged and

safe) method as described by Anastassiades et al. has become increasingly popular in recent years [3]. In this method, the sample is extracted with acetonitrile, the extract is subsequently mixed with buffer salts and purified by the addition of suitable additives (PSA, C18, GCB). The extract can then be measured directly using GC-MS or LC-MS.

In recent years, much work has been carried out to validate this method for many different food matrices [4 - 11]. The development of multi-analyte methods in the fields of GC-MS and LC-MS technology has advanced considerably whereby it is now possible to simultaneously determine more than 100 analytes within a single analytical run. If a limit of determination of 10 µg/kg has to be achieved, a system determination limit of 10 µg/L is usually sufficient for these methods and is, in general, easily achievable using state-of-the-art instrumentation.

The situation is different in residue analysis of water intended for human consumption in accordance with EU Council Directive 98/83/EC [12], where a single substance must be quantified with a limit of determination of 0.1 µg/L. For pesticides in particular, which must be determined using LC-MS in the ESI (electrospray ionization) negative mode, this limit of determination often cannot be achieved without additional sample preparation, such as an enrichment step.

It is also known that the ESI ionization source is highly sensitive to matrix effects [13]. Especially, fluctuating salt concentrations and organic compounds such as humic substances very often lead to ionization suppression but also to ionization amplification [14]. This can subsequently lead to false-low or false-high measurement results in pesticide analysis. The required sample enrichment step and, in particular, the removal of undesirable matrix components, often necessitates unavoidable sample preparation methods such as solid-phase extraction (SPE) in water analysis. Such steps usually require expenditures in time, personnel and resources.

Online-SPE-HPLC-ESI-MS/MS

One possibility to achieve complete automation with minimal sample and solvent amounts is the use of online SPE-LC/MS systems. Water samples of just a few milliliters can be simultaneously enriched, purified and measured using multi-analyte methods. HPLC buffers are simultaneously used for sample extraction as well as for analysis. The total analysis times for sample preparation and measurement can thus be reduced to just a few minutes, as demonstrated by ESW Consulting Wruss, a company in the field of environmental analytics, using Shimadzu's LCMS-8040 [15].

Conclusion: Automated online analysis of water samples

Particularly in view of the large number of PPPs (> 1,000) used worldwide, analytical systems must be very flexible and easily applicable with regard to the substances to be analyzed. Sample throughput and analysis time play an essential role in routine laboratories. Economical use of materials and solvents and the required sample amounts are of great importance in the context of extensive monitoring programs.

By using such automated online systems, errors in the sample preparation process can be reduced to a minimum and analysis becomes more robust with respect to a wide range of matrices in the extraction of water samples of different origins.

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Brave helper in allergen management

Cleaning validation in specialty foods production

While the TOC serves as a universal parameter for the analysis of the level of cleanliness in a food production plant, the TN_b is a more selective assessment parameter with regard to contamination by proteins. Together, they serve as a measure of food safety, and thus aid consumer protection, which is particularly important to food allergy sufferers.

The German Allergy and Asthma Association (DAAB) estimates the number of food allergy sufferers needing treatment to be around six million. While in children and infants, cow milk, soy, wheat, peanuts and hazelnuts are the main trigger, adolescents and adults generally react more strongly to raw vegetables and fruits, nuts, fish, shellfish and mollusks. Allergic reactions often occur on the skin and mucous membranes, in the neck and around the nose, in the bronchi or in the gastrointestinal tract. The most severe and life-threatening allergic reaction is the so-called anaphylactic shock, which can lead to circulatory collapse and even death.

Persons with food allergies are sensitive to certain food ingredients, so-called allergens. To provide information on the consumption of allergen-containing foods to those persons affected, the 14 most frequent food allergy triggers (for example mustard, eggs, celery, peanuts etc.) are subject to appropriate package labelling. If a food contains one of these ingredients, this must be clearly indicated on the packaging.

During food production or processing, traces of allergens can inadvertently get into foods via preliminary or intermediate products, without being labeled on the packaging as an ingredient. To avoid such cross-contamination, many food manufacturers rely on cleaning validation.

Cleaning validation

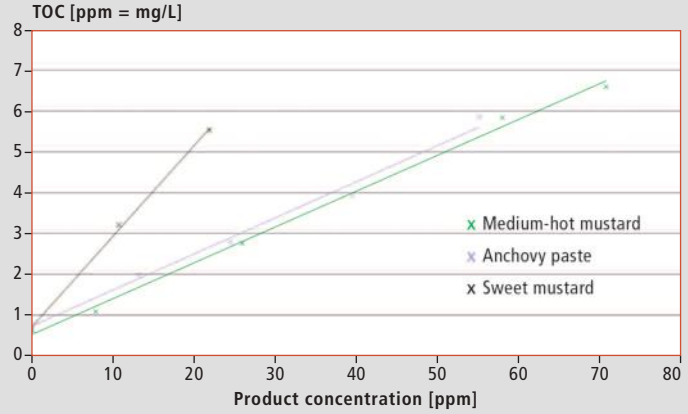
Many foods are produced discontinuously in multi-purpose production plants. Following production and packaging, foods are ready to enter the market and the food production plant is subsequently cleaned in order to produce new batches of the food or other foods of different formulations. In addition to optical inspection and microbiological swabs and to confirm the effectiveness of this cleaning process, the final rinse water is examined for possible residues and ingredients. For this purpose, a widely-used parameter is the TOC (total organic carbon). It detects the total amount of carbon originating from organic compounds.

TOC as universal parameter

For TOC determination, a mineral acid is first added to the rinsing water, converting the carbonates and hydrogen carbonates in the water to CO_2. A rinsing gas removes the carbon dioxide from the sample. Subsequently, an aliquot of the prepared sample is injected onto the hot catalyst where the organic substances are converted to CO_2. A carrier gas transfers the CO_2 to an NDIR detector and the amount of carbon dioxide is measured.

Modern analyzers such as the Shimadzu TOC-L series carry out automated sample preparation (acidification and degassing). The systems use a highly effective platinum catalyst and operate at a combustion temperature of 680 °C. A special injection unit enables automated dilution of the sample upon exceeding the calibration range of the samples. This is also the case for the preparation of standards to create calibration curves in equidistant concentration steps.

As nearly all foods consist of organic matter, the TOC is a universal parameter in cleaning validation and is suitable for a variety of products. In addition, TOC determination also detects cleaning agent residues. An additional advantage of TOC determination is its simplicity and speed. A triple TOC determination of final rinse water generally takes less than 15 minutes. If a corresponding limit



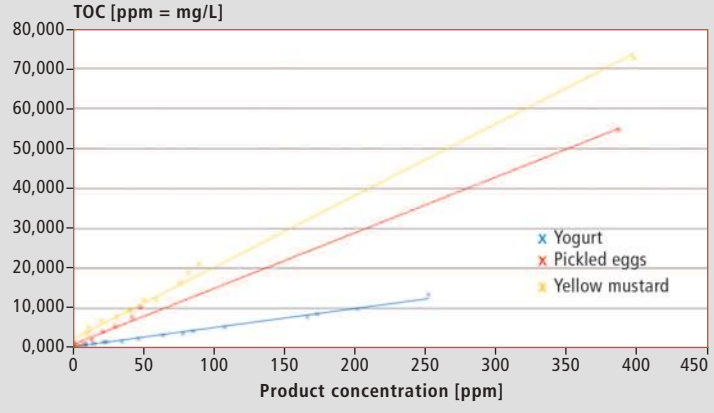


Figure 1a and 1b: TOC results of various allergen-containing foods in different concentrations

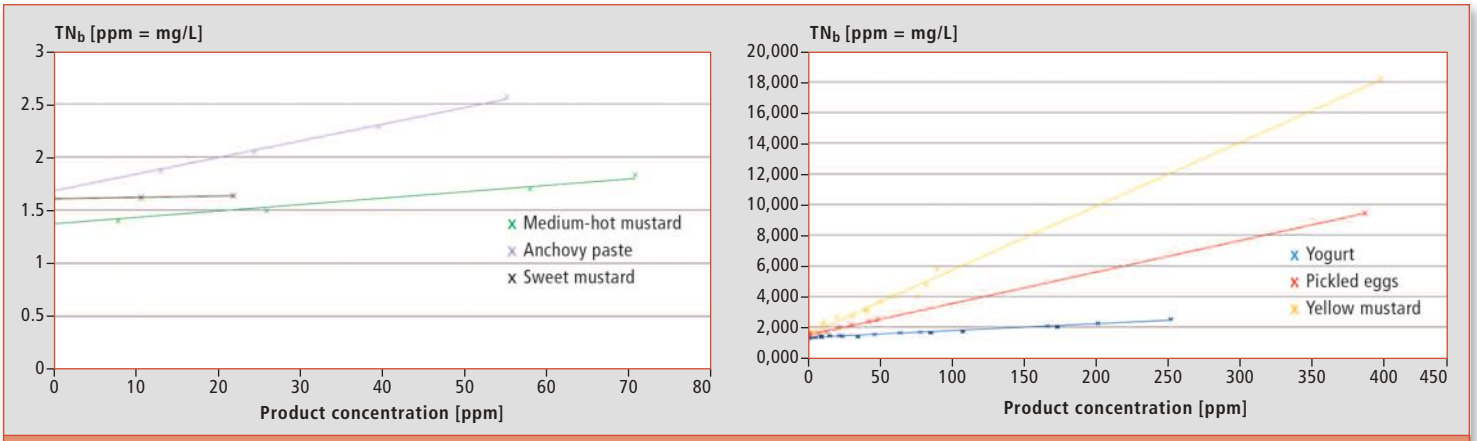


Figure 2a and 2b: TN_b results of various allergen-containing foods in different concentrations.

value is not exceeded in the final rinse water, the cleaning of the food production plant has been validated analytically.

The TN_b

In a TOC analysis of the final rinse water, combustion does not only produce carbon dioxide from organic substances. At temperatures above 700 °C, nitrogen-containing compounds are converted to nitrogen monoxide. A carrier gas transports the NO produced to a chemiluminescence detector where the measuring gas is brought into contact with ozone.

Ozone is a strong oxidizing agent, which oxidizes NO to nitrogen dioxide. In this reaction, light quanta (photons) are emitted (chemiluminescence) and are detected. The TN_b sum parameter (total bound nitrogen) is a measure of the organic and inorganic nitrogen compounds present in a sample. TOC and TN_b determination can be performed simultaneously using Shimadzu's TOC-L systems – one injection yields two measurement results. The combustion temperature is set to 720 °C and both detectors are connected in series.

Cleaning validation results can also be used to estimate a possible allergen contamination. This is performed via a 'worst case' scenario that assumes that all organic substances are allergens.

As allergens present in foods are almost exclusively proteins containing nitrogen atoms, the TN_b parameter provides considerably more information for the assessment of allergen carryover in a worst-case scenario than the TOC parameter.

Figure 3: TOC-L with autosampler for TOC and TN_b determination

Specialty foods manufacturer tests TN_b parameter for allergen carryover determination

Employees of the Germany-based Develey Mustard & Specialty Foods company have carried out extensive studies with different allergen-containing foods and determined that the TN_b sum parameter is suitable for the assessment of allergen carryover in the production of foods.

For these tests, contaminated rinse water samples were prepared, i.e. defined concentrations of an allergen-containing raw material or a product were prepared in tap water. Subsequently, the samples were analyzed for their TOC and TN_b content. As expected, it was concluded that both the TOC and the TN_b concentrations increase linearly with increasing product concentration.

While a TOC value from an unknown rinse sample could originate from innumerable compounds such as carbohydrates, fats, surfactants etc., the TN_b parameter provides significantly more selective information on the presence of proteins. This allows for a worst-case scenario assessment with respect to allergens contained in the final rinse with respect to medical reference dosages. This calculation ensures that no relevant amounts of allergens can be carried over to subsequent production. The assessment obtained here is intended to exclude allergen carryover within a food production plant and to confirm cleaning validation. In addition, the method cuts costs because complex allergen testing is avoided.

Conclusion

Cleaning validation is a useful tool to verify the effectiveness of a cleaning procedure in food production. The TOC serves as a universal parameter for the analysis of the level of cleanliness of a food production plant.

In addition, the TN_b parameter enables a more selective assessment regarding contaminations by proteins. A worst-case scenario is useful in assessing possible contamination by allergens, helping to ensure food safety and, consequently, protection of affected consumers. Moreover, this type of measurement provides an objective, analytically valid measurement result, which is suitable as a basis for the assessment of consumer risks in order to ensure that the cleaning process safeguards consumer protection. Thus, if a product label contains the following information: 'May contain traces of allergen XY', this constitutes a quantified assessment of the allergy risk and does not merely provide precautionary information for reasons of liability.

Read for you in Laborpraxis 12/16

Current state of process analysis technology

2nd TOC Process Analysis day in Duisburg features lectures and discussions between experts

Figure 1: Lively discussions and interesting lectures at the second TOC Process Analysis day in Duisburg, Germany

In mid-March 2017, Shimadzu hosted the TOC Process Analysis day for the second time. Users, planners and engineers from industry and academia met to discuss the current state of process analysis technology.

TOC (Total Organic Carbon) determination is of great importance in many industries. The TOC sum parameter specifies the total content of organic carbon in a single analytical measurement value. TOC determination can be carried out safely and simply in the laboratory as well as during online process analysis. With its TOC-4200 series, Shimadzu currently offers online TOC systems for continuous process analysis.

Two years ago, Shimadzu organized the TOC Process Analysis day for the first time as a platform for sharing experiences and networking for users of process analysis technologies. It now takes place in alternate years with the TOC User Meeting that has meanwhile existed for 15 years. Just like the first TOC Process Analysis day in 2015, speakers from industry and academia presented application-related lectures and shared their experiences with participants.

Monitoring purified water

In many applications, the TOC parameter is a measure of undesirable contaminations. Monitoring of water quality is especially important when using purified water. Dr. Raoul Schröder (Bürkert Werke, Germany) showed that the use of peripheral equipment also influences water quality.

Bürkert, manufacturer of valves and valve technologies, investigates the influence on water pollution caused by components of fluid plants. When flowing through a fluid plant water comes into contact with various types of equipment such as pumps, pipes or valves. This can lead to mobilization of different compounds from these components, which contaminate the water. The magnitude of these contaminations may only be in the lower ppm range but these contaminations become important when using ultrapure water and most certainly in regard

Figure 2: Seminar speakers (from left to right): Dr. Raoul Schröder (Bürkert Werke GmbH & Co. KG), Bettina Gierszewski (Shimadzu Europa GmbH), Mischa Dings (Shimadzu Deutschland GmbH), Ralf Kienle (Clariant Plastics & Coatings Deutschland GmbH), Dr. Tomas Sauter (Covestro Deutschland AG), Andreas Gräfe (Lanxess Deutschland GmbH) and Sascha Hupach (Shimadzu Deutschland GmbH).

to quality assurance for manufacturers of water-bearing components.

Higher quality requires higher data density

Demands on modern production processes are steadily increasing. Not only is there a growing demand to cut costs as well as to save energy and raw materials, but production capacity, efficiency and flexibility should also be increased. And all this with ever higher quality requirements. "In order to meet these demands, it is necessary to generate higher data density for automated process control", says Andreas Gräfe of Lanxess Germany, when discussing the general benefits of process analysis technology (PAT).

The use of laboratory analysis is more and more taking a backseat. Nowadays, hardly any large-scale plant is started up without having to supply corresponding process analysis data for process control. The demands placed on the systems used are based primarily on achieving the highest possible availability as well as on increasing data density. In this way, PAT is of benefit to plant and process safety and also to employee and environmental protection.

TOC data density allows for more precise process control

Modern online measuring systems technology features availability of 99 % or higher and thus offers the required reliability for automated process control. Andreas Gräfe illustrated this with a practical example: Prior to the use of process technology, wastewater monitoring had been carried out by appropriate laboratory analyses. A TOC analysis took approximately 40 minutes including sampling and sample transfer to the laboratory. By using Online-TOC, analysis results are delivered automatically in ten minute intervals. Because of the increased amount of data, the wastewater is more closely monitored. The company thus obtains more information on its wastewater and can control its production process more precisely. Cleaning costs incurred in the wastewater treatment plant can now be more efficiently allocated (in accordance with the 'polluter pays principle'). Based on the higher data density, reporting to the authorities is also more precise.

MCERTS certified performance and reliability standard

In order to verify the high availability of process analyzers, the Environmental Agency of England and Wales (UK) has developed a certification system for measurement equipment – the MCERTS accreditation. It provides the framework conditions and quality objectives for companies to meet in order to comply with authority requirements for environmental monitoring. MCERTS is quickly becoming a required performance and reliability standard by organizations around the world. With accredited equipment, companies and authorities ensure that they are doing everything possible to protect their environment.

Requirements for obtaining MCERTS certification include various laboratory tests and a 3-month field test under real conditions. Measurements are performed by an independent testing facility according to predefined testing methods. MCERTS accreditation has been issued to measurement systems in Shimadzu's TOC-4200 series. TOC product manager Bettina Gierszewski at Shimadzu, in her presentation on MCERTS, discussed the test measurements performed as well as the results of the TOC-4200 field test.

TOC content of wastewater a decisive criterion for disposal

Ralf Kienle, Clariant Plastics & Coatings Germany, reported on the use of laboratory and online measurements for monitoring of industrial wastewater effluents. The pigment production process generates wastewater during various purification stages, which is discharged at regular intervals into the wastewater treatment plant of the Hoechst Chemical Park, Germany.

Figure 3: Shimadzu TOC-4200 with MCERTS accreditation

TOC content of the wastewater is considered as a decisive criterion for disposal. Until recently TOC analysis was performed reliably using a laboratory system. The use of an online measuring system now saves time. In addition, by connecting the analyzer to the process control system, untimely discharge of wastewater due to human error can be prevented. During the analysis, the process control system automatically locks all pumps.

Planning stages and project management for process analysis

The final speaker on the 2nd TOC Process Analysis day was Dr. Thomas Sauter of Covestro Germany. He presented an interesting insight into the various planning stages and project management for process analysis in investment projects. He showed the tried and tested project phases for the construction of 'plug and play' analysis containers. These were designed, built and transported to their places of destination, for example a chemical factory in China, by Covestro PAT specialists. Thomas Sauter pointed out what needs to be taken into consideration and how many different contacts are involved as well as specialist departments that need to be included.

Read for you in LABO Mai 2017

A century of experience

Shimadzu celebrates 100th anniversary of testing machines

100 years testing machines

After 100 years of experience and continuous development in materials testing technology, Shimadzu's product range today includes static and dynamic universal testing machines, hardness testing instruments and capillary rheometers as well as the HPV-X high-speed camera, the most powerful in its class – with 10 million frames per second. Shimadzu's testing machines are at the cutting edge of technology regarding control systems, sensor technology and information processing, to reliably support developers and users.

What started in 1917 with fiber and cement testing machines, continued in the following decades with hydraulic, dynamic and fully automated testing instruments including an ultrasound fatigue testing system as well as a particle size analyzer.

Testing innovative and increasingly high-performance materials

Material characteristics vary widely and behave differently depending on ambient conditions and forces exerted. Research and development departments need highly precise and reliable data for production and quality control of innovative and increasingly high-performance materials, for instance composite or jointing materials.

Precision universal testing machine for research and development

Just one representative example of the versatility and performance of Shimadzu's materials testing systems:

Shimadzu's AG-Xplus series includes especially powerful and versatile electromechanical testing machines. With their rigid frames and precise load cells, they are optimally equipped for all requirements, in particular for research and development.

For customer-specific requirements, numerous solutions are available, for instance a dual space testing system, without the need to switch testing accessories for compression and tensile testing.

With its user-friendly Trapezium X software, all settings required can be applied in the shortest possible time.

Further information on Shimadzu's testing machine expertise is available on page 28.

Wine tasting and wine testing

Secrets of wine analysis: from sniffing and tasting to measuring

Which substances in red wine promote health and prolong life? Which aromas are responsible for the wine's varietal character? Which aroma concentration range can the human nose detect? How can illegal aromatization be identified? Do histamines play a role in wine intolerance?

In wine, there seems to be more than just one truth. Sometimes, there is also true criminal intent: counterfeit foods, such as labelling fraud, product counterfeiting or falsified content generate fat profits for the fraudsters and cause considerable financial harm to the original manufacturers. In addition, there are economic and often consumer health damages.

Professor Erich Leitner of the Graz University of Technology, Austria, Head of the Institute of Analytical Chemistry and Food Chemistry, has been focussing for years on food quality from a scientific perspective. He has led Shimadzu's exclusive two-day seminar 'the Secrets of Wine Analysis and Wine Tasting.'

In addition to the determination of species-relevant flavouring substances via GC analysis, theoretical and practical aspects were discussed on other methods to characterize wine and its ingredients (metals, polyphenols, dyes as well as residues). In a wine tasting tutorial of the wines analyzed, the participants were able to establish a direct link between sensory quality and analytics.

Furthermore, they compared the performance of the human nose with the instrument's sensitivity.

This seminar series will be continued, again by personal invitation, in order to give all participants sufficient time to be introduced onsite to the various analytical techniques using real samples.

New – Materials Testing Application Handbook

100th anniversary of materials testing equipment

Shimadzu's Materials Testing Application Handbook is now available and can be downloaded via www.shimadzu.eu. It covers 112 applications in eight industries such as automotive, aerospace, biomaterials and medical, composites, food, metal, railroad, rubber and plastics industries to support consumer and environmental protection as well as product reliability.

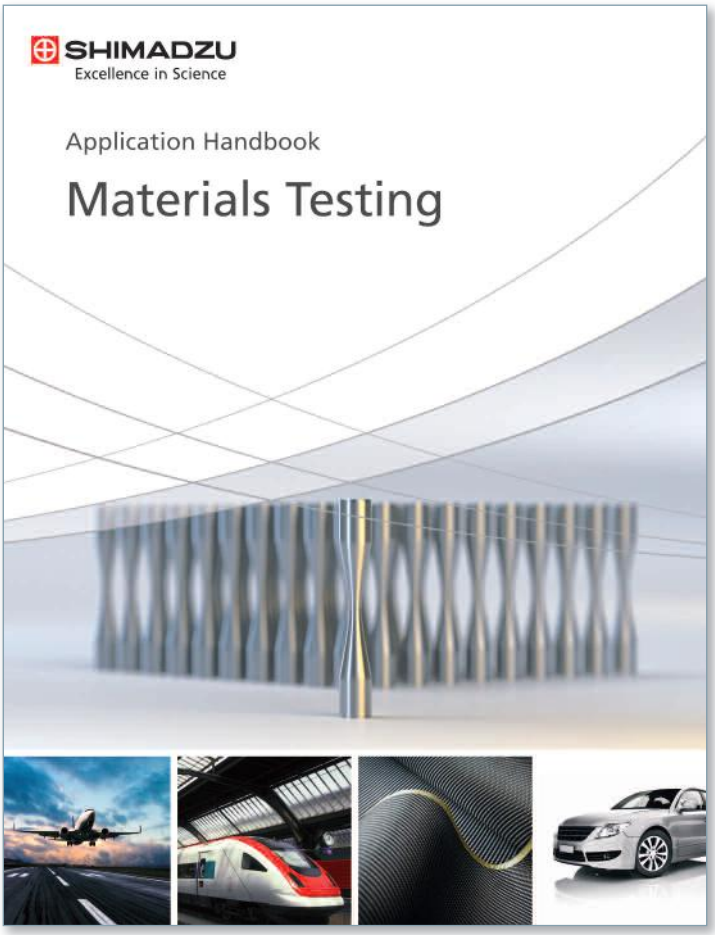
The Materials Testing Application Handbook is hands-on and solution-oriented. The applications described cover most-modern technologies, e.g. universal, fatigue and hardness testing and also high-speed video camera application.

Since 1917, Shimadzu has a proven track record in manufacturing testing machines designed to meet the diverse needs of customers worldwide.

To date, the company has sold tens of thousands of testing machines. In addition, Shimadzu has marketed thousands of application-specific systems tailored to the unique needs of clients, and remains committed to providing customers with this same level of service in the future.

Please see also other Application Handbooks on
- Liquid Chromatography
- Food & Beverages
- TOC
- Clinical
- GC/GC-MS.

Further information on this article:
- Application Handbook Materials Testing



Shimadzu live

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