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Biogenic Fuels and Renewable Energies – A Challenge for Elemental Analysis?

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Renewable raw materials are becoming increasingly important. This is not only because of the knowledge that natural resources such as crude oil, natural gas and coal will become more scarce over the next few decades, but also as a result of environmental protection (CO_2 emission).

With the use of biogenic materials for the production of fuels and combustibles, their content of harmful substances is particularly important. The most important of these substances are nitrogen, sulfur and chlorine-containing hydrocarbon compounds. They not only have a negative effect on the further processing procedure, for example, through the formation of undesired by-products or the contamination of catalysts, they also have a subsequent detrimental effect on the performance characteristics and applications of the finished products. Because of this, a precise inspection of the used raw materials, intermediate stages, and end products is required.

Special tasks require special systems

The requirements for analysis technology are just as diverse as the measuring tasks for the production of biogenic energy sources. While the elements C/N/S/Cl are of note for all materials, the features of the sample matrices to be examined and the contents to be determined vary greatly.

The raw materials are primarily inhomogeneous solids that can be contaminated with various other components. The elements to be analyzed appear at the macro level. Therefore, an ideal analysis system must be robust and low-maintenance. It should permit quantitative digestion without the use of a catalyst, and dosing of representatively large sample volumes to avoid time-consuming sample preparation and costs.

The end products, on the other hand, are primarily highly volatile flammable liquids. The elements sulfur, nitrogen and chlorine only appear as undesirable contamination at the trace level. Therefore, the analysis technique used must allow extremely sensitive detection. It should enable an automatically optimized, safe, and thereby complete combustion, as implemented with flame sensor technology.

multi EA® series systems offer both. They are optimally matched to the special features of the particular measuring task.

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Instrumentation

Analysis technique

All measurements with elemental analyzers of the multi EA$^®$ series (see Figure 1) were conducted with the following configuration:

Figure 1:
a) The elemental analysis systems of the multi EA$^®$ series, b) Solid autosampler FPG 48

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multi EA® 5000 – for determinations at macro and trace level:

- Base device with double furnace and high-performance gas box
- Automatic Boat Drive – sample feed with flame sensor technology
- UV fluorescence detector – for the determination of sulfur content
- Chemiluminescence detector – for the determination of nitrogen content
- Microcoulometric chlorine module – for the determination of chlorine content
- NDIR detector – for the determination of carbon content
- MMS 5000 – multi matrix sampler for the automatic sampling of solids and liquids

multi EA® 4000 – for determinations at macro level:

- Base device with high-temperature furnace
- FPG 48 – sampler for the automatic sampling of solids
- NDIR detector – for the determination of sulfur content
- NDIR detector – for the determination of carbon content
- Microcoulometric chlorine module – for the determination of chlorine content

Sample measurement

The samples were directly analyzed without pretreatment with the multi EA® 5000 or the multi EA® 4000. The introduction and conveyance of the samples occurred automatically.

The determination of the sulfur, carbon and chlorine content was completed with the multi EA® 4000 in a single-phase process at 1450°C (C/S) or at 1000°C (Cl) in an oxygen stream, without the use of a catalyst.

The determination of sulfur, nitrogen, carbon and chlorine content with the multi EA® 5000 took place in a two-phase process at 1050°C, also without the use of a catalyst. In the first process phase, the safe evaporation and pyrolysis of the samples took place in the inert gas flow; in the second phase, the complete combustion of the formed pyrolysis products took place in pure oxygen. The intelligent flame sensor technology optimizes the combustion process, thereby enabling a fast, safe and complete reaction, even with difficult sample matrices.

The measurements of the gaseous reaction products (CO_2, SO_2, NO_x and HX) formed during combustion were recorded after the test gas drying using the detection principles listed in Table 1. Because of the matrix-optimized combustion processes, a threefold determination is normally sufficient.

Calibration

For the determination of sulfur and carbon content at macro level, the elemental analyzer multi EA® 4000 was calibrated with a certified carbon standard. The chlorine determination at macro level requires no calibration. Only a system check with a 0.01 M HCl standard solution was carried out (* see Table 1).

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The elemental analyzer multi EA$^®$ 5000, which was calibrated with liquid standard kits, was used for the determination of sulfur, nitrogen and chlorine contents at trace level. The solvent isooctane was used as a matrix for the sulfur, nitrogen and chlorine standards or as standard substance for the carbon calibration.

Element	System	Detection	Calibration substance	Range
Sulfur	multi EA$^®$ 5000	UVFD	Dibenzothiophene	0.01 – 10,000 ppm
Nitrogen	multi EA$^®$ 5000	CLD	Pyridine	0.03 – 10,000 ppm
Chlorine	multi EA$^®$ 5000	Coulometric	2,4,6-Trichlorophenol	0.1 – 10,000 ppm
Carbon	multi EA$^®$ 5000	NDIR	Isooctane	0.1 ppm – 100%
Sulfur	multi EA$^®$ 4000	NDIR	Carbon 0.65% S	15 µg – 8 mg S abs.
Carbon	multi EA$^®$ 4000	NDIR	Carbon 78.8% C	10 µg – 500 mg C abs.
Chlorine	multi EA$^®$ 4000	Coulometric	--- *	1 µg – 20 mg Cl abs.

Table 1: Used detection systems and calibration substances

Results and discussion

The analyzed samples are real samples. The multi EA$^®$ 4000, a robust high-temperature combustion system, was used for the analysis of samples 1–5. This instrument was specially developed for the determination of high element contents, primarily in solid sample matrices. Its notably large sample capacity of up to 3 g allows the dosing of a representative amount, even for inhomogeneous materials. Materials such as shredded plant remains can also be measured without difficulty and with good reproducibility. The results of the multi-element analysis of these samples are summarized in Table 2.

No.	Sample	TC ± RSD [%]	TS ± RSD [%]	TCl ± RSD [%]
1	Wood	53.8 ± 0.8	**	0.14 ± 10.3
2	Biomass (straw)	46.1 ± 0.5	**	0.25 ± < 0.01
3	Biomass (wood)	50.8 ± 0.3	**	0.1 ± < 0.01
4	Derived fuel	48.5 ± 0.4	0.31 ± 0.01	0.41 ± 0.04
5	Heating oil	88.3 ± 0.1	0.89 ± 0.07	0.57 ± 0.05

Table 2: Multi-element analysis of various solid biomass samples and their secondary products
** Below the detection limit of 15 µg S absolute.

The TC, TS and TCl content of the tested biogenic raw materials or waste products are high, as expected, and reach into the upper mass percent range. Figure 2 is representative of the measurement curves of the analysis of a derived fuel.

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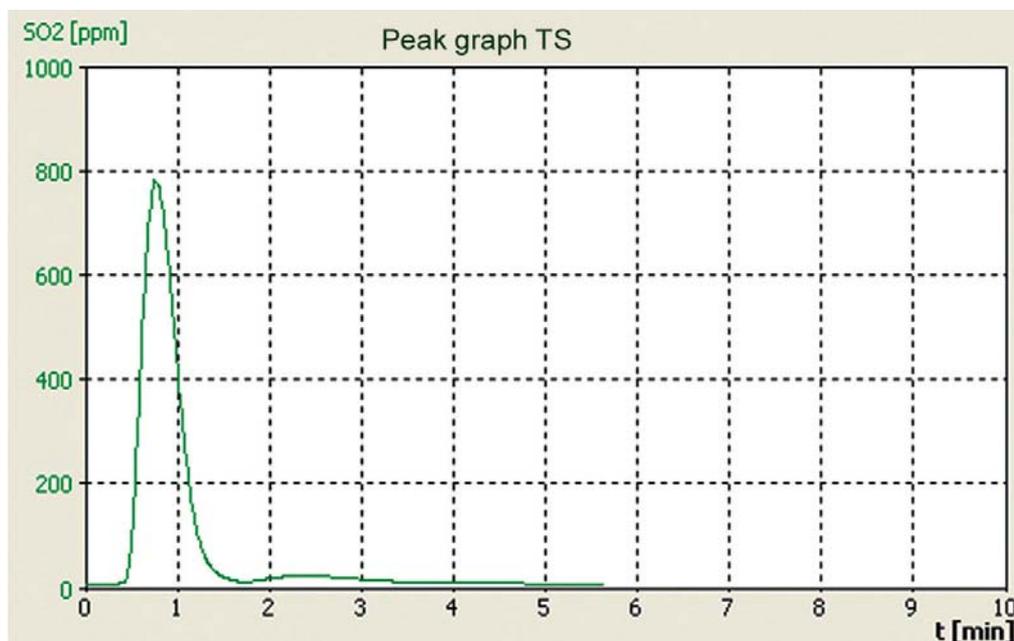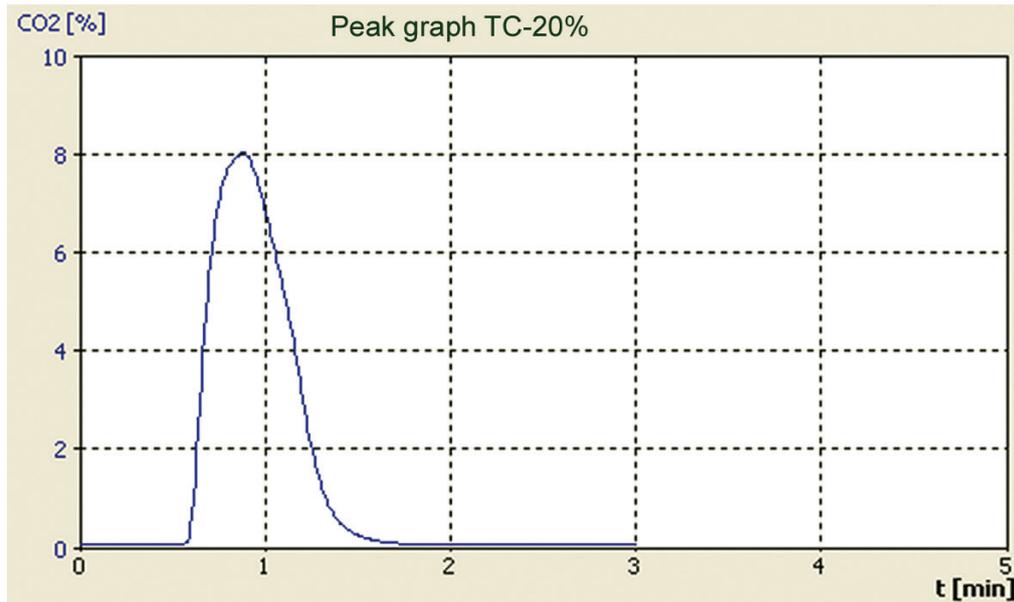Reference: Lit_EA_NSCL_01_09_e | ILM 09/2009 | GRO

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Figure 2: Measurement curves of the simultaneous carbon and sulfur determination of a derived fuel

Samples 6-10 are liquids with very low element contents. Because of this, the multi EA® 5000, an elemental analyzer optimized for the determination of trace contents, was used. Sulfur, nitrogen and carbon contents were determined simultaneously, saving time. The determination of the chlorine content occurred sequentially in the same analysis cycle. The used sample volumes were between 20 and 100 µl.

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No.	Sample	TC ± RSD	TS ± RSD	TN ± RSD	TCl ± RSD
6	Biodiesel_1	76.2 wt-% ± 0.3%	2.98 ppm ± 0.7%	13.5 ppm ± 1.7%	161 ppb ± 1.1%
7	Biodiesel_2	76.2 wt-% ± 0.3%	0.93 ppm ± 0.9%	2.01 ppm ± 2.3%	< 100 ppb
8	Bioethanol_1	52.3 wt-% ± 0.1%	728 ppb ± 1.8%	48.0 ppb ± 14.2%	< 100 ppb
9	Bioethanol_2	52.3 wt-% ± 0.1%	1120 ppb ± 1.4%	58.9 ppb ± 11.2%	560 ppb ± 11.2%
10	DF blend	85.4 wt-% ± 0.2%	5.12 ppm ± 1.5%	1.31 ppm ± 2.1%	267 ppb ± 6.4%

Table 3: Multi-element analysis of various liquid biofuels and their blends

For the analyzed high-purity end products biodiesel and bioethanol and their blends, only trace concentrations of the tested elements, except for carbon, were detected.
Figure 3 is representative of the measurement curves of a biodiesel.
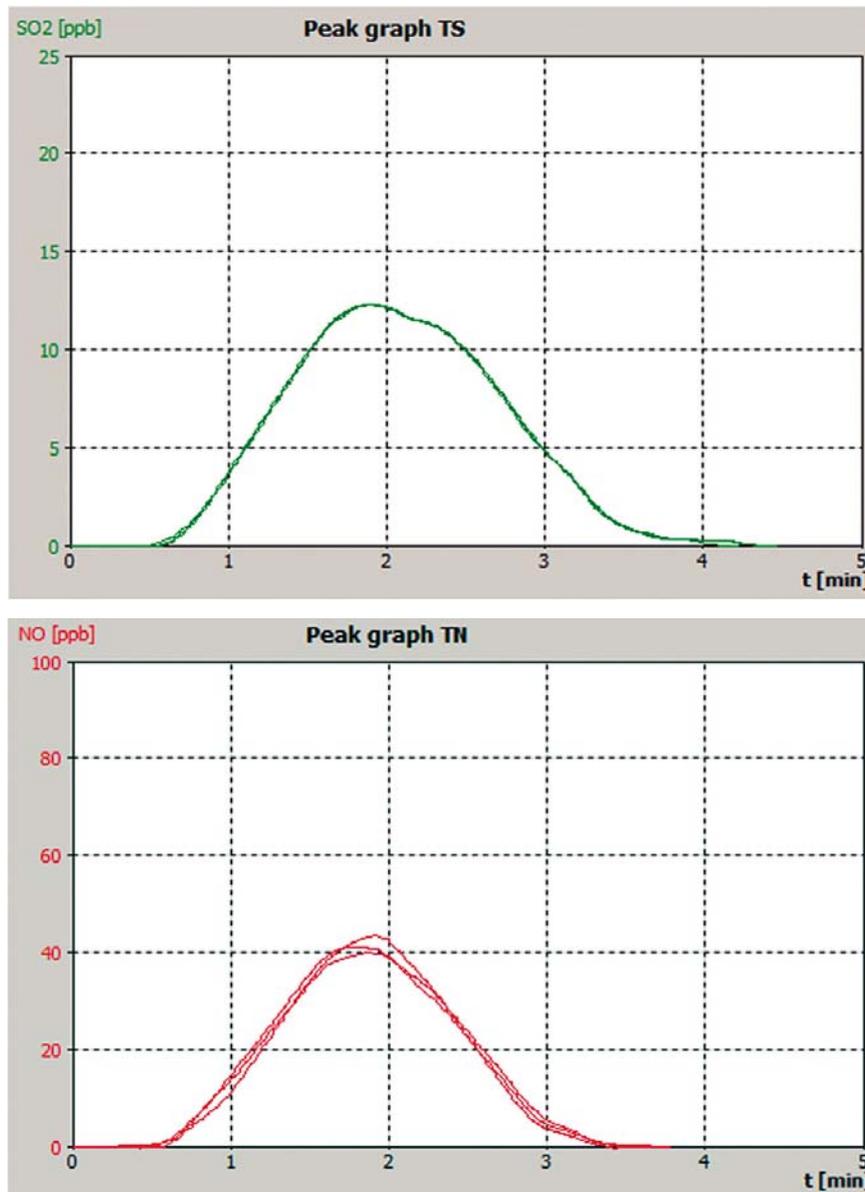

Figure 3: Measurement curves of the multi-element analysis of a biodiesel sample

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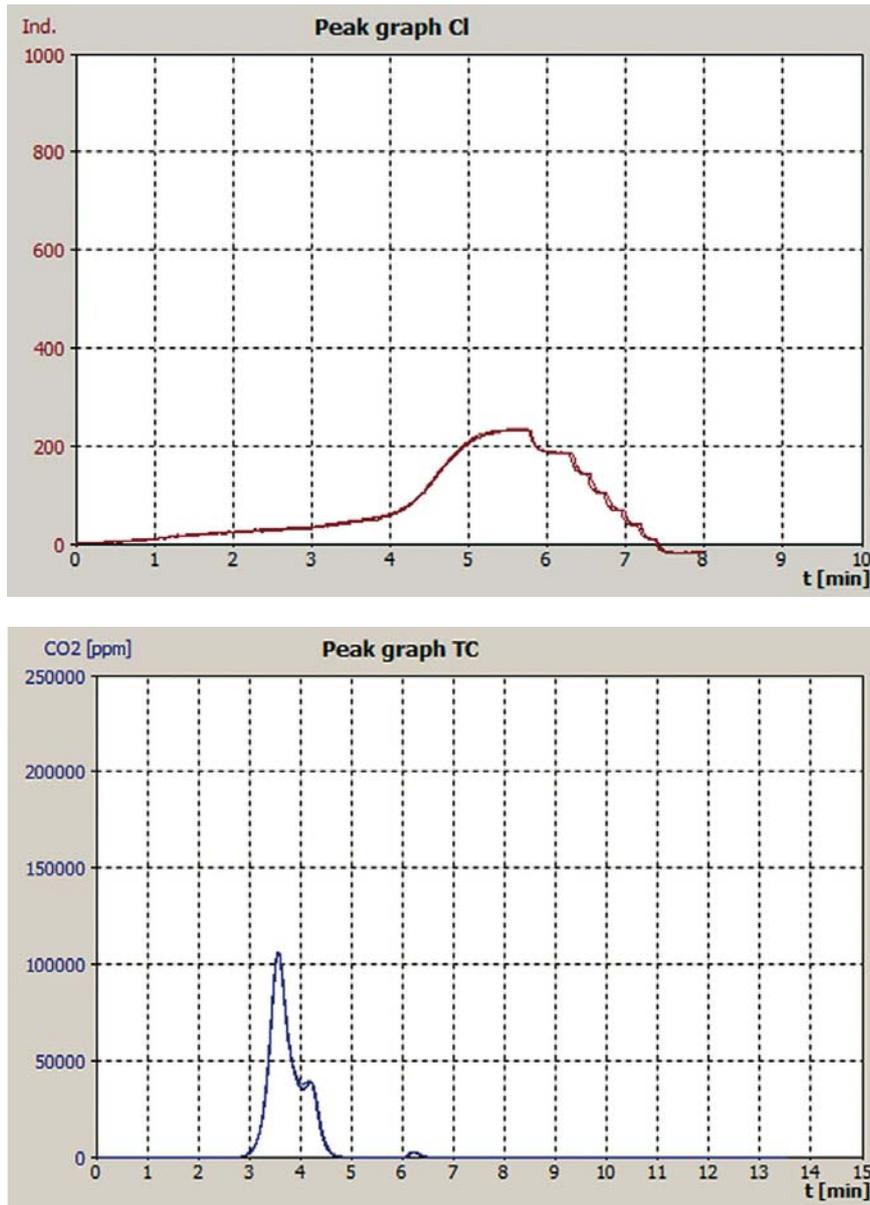Reference: Lit_EA_NSCL_01_09_e | ILM 09/2009 | GRO

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Figure 3: Measurement curves of the multi-element analysis of a biodiesel sample

The carbon content of the analyzed samples was, determined by their organic origin, between 52 – 85 wt-%.

The final examination of the results shows that the analysis systems of the multi EA® series are perfectly matched to the special features of the particular matrix and the various concentration ranges.

Furthermore, because of the comprehensive method packages and flame sensor technology, the time-consuming, and often error-prone, creation of methods and optimization of process parameters is no longer necessary.

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Summary

Biomass is a renewable, organic supplier of raw material. With the use of various chemical and biochemical procedures, fuels and energy sources for the production of heat are created from it. This type of use requires the fulfillment of legal requirements that are defined in standards such as ASTM D 6751, DIN EN 14214 or DIN EN 15376. The percentage of undesirable nitrogen, sulfur and chlorine-containing hydrocarbons, from which environmentally hazardous compounds (NO_x, SO_2 and HX) are produced during combustion processes, varies depending on the raw materials used for production.

Too high contents of these elements also negatively effect the further processing of intermediate stages and end products, for example, through reactor corrosion and contamination of expensive catalysts. In order to prevent this at the outset, the precise and fast determination of the elements sulfur, nitrogen and chlorine is of prime importance.

For this, the elemental analyzers of the multi EA$^®$ series offer a solution for every matrix.

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