



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

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 (CO₂ 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, sulphur 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.

Because of the matrix-optimised combustion processes, a threefold determination is normally sufficient.

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 analysed 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 sulphur, 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 optimised, 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.

INSTRUMENTATION

Analysis technique

All measurements with elemental analysers of the multi EA® series (Figure 1) were conducted with the following configuration:

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 sulphur 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; and
- 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; and
- Microcoulometric chlorine module – for the determination of chlorine content.

SAMPLE MEASUREMENT

The samples were directly analysed without pre-treatment with the multi EA® 5000 or the multi EA® 4000. The introduction and conveyance of the samples occurred automatically.

The determination of the sulphur, 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 sulphur, 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 optimises the combustion process, thereby enabling a fast, safe and complete reaction, even with difficult sample matrices.

The measurements of the gaseous reaction products (CO₂, SO₂, NOx and HX) formed during combustion were recorded after the test gas drying using the detection principles listed in Table 1.

Because of the matrix-optimised combustion processes, a threefold determination is normally sufficient.

Calibration

For the determination of sulphur and carbon content at macro level, the elemental analyser 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 (Table 1).

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

Table 1: Used detection systems and calibration substances.

Element	System	Detection	Calibration substance	Range
sulphur	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%
sulphur	multi EA® 4000	NDIR	Carbon 0.65% S abs.	15 µg – 8 mg S
Carbon	multi EA® 4000	NDIR	Carbon 78.8% C	10 µg – 500 mg C
Chlorine	multi EA® 4000	Coulometric	---	1 µg – 20 mg Cl abs.



Figure 1. a) The elemental analysis systems of the multi EA® series. b) Solid autosampler FPG 48.

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RESULTS AND DISCUSSION

The analysed 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 3g 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 summarised in Table 2.

Table 2: Multi-element analysis of various solid biomass samples and their secondary products.

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

** 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.



Figure 2. Measurement curves of the simultaneous carbon and sulphur determination of a derived fuel.

Samples 6 - 10 are liquids with very low element contents. Because of this, the multi EA[®] 5000, an elemental analyser optimised for the determination of trace contents, was used. Sulphur, 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.

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

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 ± 8.4%

For the analysed high-purity end products biodiesel and bioethanol and their blends, only trace concentrations of the tested elements, except for carbon, were detected.

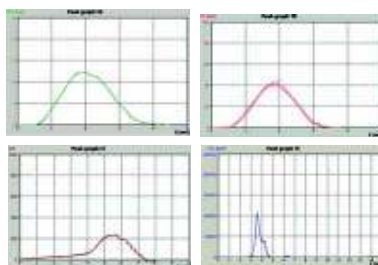


Figure 3. Measurement curves of the multi-element analysis of a biodiesel sample.

The carbon content of the analysed 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 optimisation of process parameters is no longer necessary.

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 fulfilment 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, sulphur and chlorine-containing hydrocarbons, from which environmentally hazardous compounds (NO_x, SO₂ 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 sulphur, nitrogen and chlorine is of prime importance.

For this, the elemental analysers of the multi EA[®] series offer a solution for every matrix.

Quick and Simple Starter Kits for Freeze Drying



The benchtop 'BTK' range of freeze dryers has been popular in universities and research laboratories for many years due to its ease of use, flexibility and extensive range of accessories. But when starting out in freeze drying the number of options can seem daunting. To help simplify the process Biopharma have put together four packages of the most popular sets. These systems come complete with all the necessary adapters and connections to get started – the only other thing that's required is a vacuum pump, which we are able to supply if one is not available.

The packages on offer are: BT2KES - a great starter system, flexible, cost-conscious and easy to use; BT4KXL - a system for those who need a bit more out of their freeze dryer, with a larger capacity manifold and colder condenser; BT4KZL - an ultra-low -103°C condenser and a stainless steel 'vertical' manifold, this is for processing non-aqueous solutions; and BT6KEL - this system has been put together for those who need to process larger volumes, with a 9 litre condenser and extra shelving.

Offering these units in packages also means Biopharma can cut costs, meaning savings for customers typically in the region of 2-3%.

BTKs are commonly used in universities and research laboratories for applications as diverse as agricultural research, biotechnology, food science and pharmacology.

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Outperforming Pumps

Lambda has developed peristaltic pumps (PRECIFLOW series), which combine exceptional properties with very compact size. A specially developed tubing compression system, placed in an asymmetrical pump head of large diameter, handles the tubing with great care. This offers advantages in flow rate regularity and provides long lifetime for the tubing. Since it also works well with low cost silicone tubing, the pump finally saves more money than it initially costs.

Visualisation of the pump activity in controlled systems like bioreactors by means of an incorporated integrator brings an excellent new possibility to follow culture growth and other process parameters. Lambda pumps are real workhorses, otherwise they could never give a five years warranty.



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