Challenge
Quantitative digestion of biofuel samples and their precursors without soot formation in the shortest measurement time.

Solution
Time- and matrix-optimized combustion using flame sensor technique and optimization of process parameters.

Intended audience
Laboratories and companies in the biofuel and renewable energy sector, producers of biofuels and feedstocks, R&D and quality control labs monitoring N, S, and Cl in bio-based fuels and intermediates.

Elemental analysis for N/S/Cl determination in biofuels and their precursors

Introduction

New methods for the production of alternative fuels are a growing field of interest. Technologies based on fermentation of starch and sugar, and the trans-esterification or hydrocracking of plant and animal oil, delivering so-called first generation biofuels, are already well established but linked to limited resources for ethical and ecological reasons. Another promising approach consists of processes based on the conversion of cellulose-rich biomass and waste (second generation biofuels). With the use of biogenic materials for fuel production, it is important to monitor the inherently high amount of harmful nitrogen, sulfur and chlorine-containing hydrocarbons that results. This is not only due to the adherence of given regulations and legal limits (Tier 1 to 4), but also to avoid negative effects on the production process and environment. Therefore, a strict monitoring of the feedstocks, intermediates, and final products is crucial. The origins of such matrices are just as different as their digestion behavior. A quantitative combustion of all sample components is the precondition for correct elemental analysis. In the past this was a time-consuming challenge, requiring experience in developing specific boat programs for each sample matrix. In addition, there was frequent need for maintenance intervention and repeated measurements due to soot formation and contamination of the analyzer. The slightest changes in the process, different matrix composition or other sample quantity affected the results' correctness.

To overcome this, the flame sensor technology was developed to automatically optimize the combustion process to the specific needs of any matrix type, quantity and composition. With the effective soot prevention, the maintenance effort is reduced to a minimum.

Materials and methods

The different biofuels and precursors were analyzed for nitrogen, sulfur and chlorine contents using the multi-elemental analyzer multi EA 5100. Equipped with HiPerSens detection systems, it covers a wide and linear operation range from lowest ppb to wt%.

Samples and reagents

Six samples (feed materials, intermediates and final products) were analyzed, as well as standard materials, to check the performance of the analyzer.

The analyzed sample matrices are a representative spectrum from the field of biofuel production. Samples 1, 2, 4 are feed stock and process materials with high viscosity and high element contents. The final products (samples 3, 5, 6) are different biofuels. They are light volatile, have a low viscosity and contain the elements of interest just in the trace level as undesired impurities.

Sample preparation

Using the multi EA 5100 in horizontal mode in combination with the flame sensor technology allows for a direct analysis of the samples without sample preparation. The flame sensor creates ideal digestion conditions for any organic sample matrix. Just one single method for solids or liquids is enough to analyze the full spectrum of matrices, independent of their viscosity, volatility, and combustibility.

Calibration

Liquid calibration standards based on 2,4,6-trichlorphenol (Cl), dibenzothiophene (S) and pyridine (N) in isooctane were used to calibrate the analysis system in the appropriate concentration ranges.

Instrumentation

A multi EA 5100 equipped with HiPerSens CLD, UVFD and coulometric detection for the determination of nitrogen, sulfur and chlorine was used in horizontal operation mode. For the automated sample introduction and transfer into the analyzer the system was equipped with an automatic boat drive with flame sensor technology and the MMS multi matrix sampler. The flame sensor ensures a trouble-free and matrix-optimized transfer and combustion of the different materials.

For the determination of chlorine sample volumes of 100 µL were used, and for nitrogen and sulfur 40 µL were used. The sample digestion was carried out by efficient catalyst-free high temperature combustion in a quartz tube. This process is controlled and adapted fully automatically to the special needs of every matrix component by the flame sensor technology. This ensures matrix-independent, optimal results in the shortest possible time. The process is split into two phases. In the first process phase, evaporation of volatile sample components in an inert gas stream, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere, takes place. In the second phase the heavier, nonvolatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. Here, the flame sensor ensures a uniform evaporation of exactly the amount of sample that can be completely oxidized by the available amount of oxygen. For this purpose the resulting combustion flame is monitored in real time. The registered flame values are used to calculate an optimum digestion program for each matrix, including a sufficient number of waiting points, minimized waiting times, and maximized analysis speed. This allows for a fully automated adjustment of the process to the specific requirements of the individual components, thus optimizing the quality of analysis and its duration. The dried gaseous reaction products were transferred into the relevant detection systems – for sulfur, UV fluorescence, and for nitrogen, chemoluminescence. The detection of chlorine was carried out by means of microcoulometric titration.

The implemented Auto-Protection System guarantees the highest operational safety (particle and aerosol trap) and a complete transfer (no condensation loss) of the formed HCl into the high sensitive cell. Afterwards the determination of the chlorine content is carried out by means of a microcoulometric titration. The multi EA 5100 enables a detection limit of 50 µg/L Cl. Depending on the cell type used, direct analysis of Cl contents up to 10 wt% is also possible.

Method parameters

Standard method settings for horizontal operation stored in the method library are applied. The parameter settings for the combustion process are summarized in table 1.

Evaluation parameters

Standard method settings from the method library are applied. The parameter settings for the different detection systems are summarized in table 2.

Table 1: Process parameters

Parameter	Specification
Furnace temperature	1050 °C
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Draw up	2 µL/s
Injection	3 µL/s

Table 2: Detection parameters

Parameter	Specification	Parameter	Specification Cl
Max. integration time	800 s	Max. integration time	1200 s
Start (N)	1.9 ppb	Threshold value	300 cts
Threshold (N)	2.0 ppb	Max. drift	100 cts/s
Start (S)	1.0 ppb	Threshold	25 cts
Threshold (S)	1.1 ppb	Cell temperature	23 °C
Stability	7	Titration delay	30 s

Results and discussion

The examined samples are a representative spectrum from the field of biofuel production, from feed materials to intermediates to ultra-pure fuels. The results given in Table 3 are averages of three replicate analyses.

Table 3: Results of the N/S/Cl determination

Measurement	TS ± RSD	TN ± RSD	TCl ± RSD
BCO* (crop plants)	0.40 wt% ± 0.42%	0.41 wt% ± 0.62%	23.4 ppm ± 3.32%
Corn oil	20.3 ppm ± 1.92%	54.2 ppm ± 0.18%	8.82 ppm ± 1.10%
Biodiesel (from corn oil)	0.87 ppm ± 2.83%	2.00 ppm ± 2.30%	<< 0.10 ppm
Crude tall oil	0.36 wt% ± 0.61%	99.9 ppm ± 2.89%	8.36 ppm ± 3.32%
B-t-L** (from tall oil)	5.33 ppm ± 1.57%	0.38 ppm ± 2.57%	<< 0.10 ppm (< LOD)
Bio ethanol (from cellulose)	0.73 ppm ± 1.83%	0.06 ppm ± 11.2%	0.56 ppm ± 11.2%
Standard 1.44 ppm N/S/Cl	1.42 ppm ± 1.28%	1.39 ppm ± 2.21%	1.47 ppm ± 1.83%

* BCO = bio crude oil, ** B-t-L = bio mass to liquid

Due to the matrix-optimized combustion a threefold determination is sufficient to achieve results within 3% RSD. This is remarkably affecting the sample processing time and thereby generating a higher sample throughput. The analysis results received and their reproducibility depict the high quality of the digestion process. The proper performance of the analysis system was approved by analyzing standard materials for the determination of nitrogen, sulfur and chlorine (see Table 3). Typical measuring curves are depicted for the crude tall oil exemplarily in Figures 1 a-c.

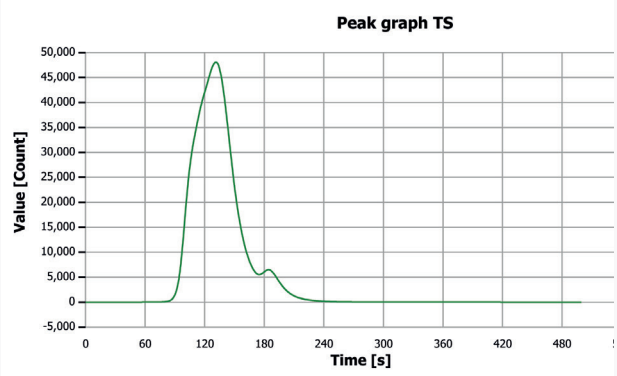

Figure 1 a: TS measuring curve for crude tall oil

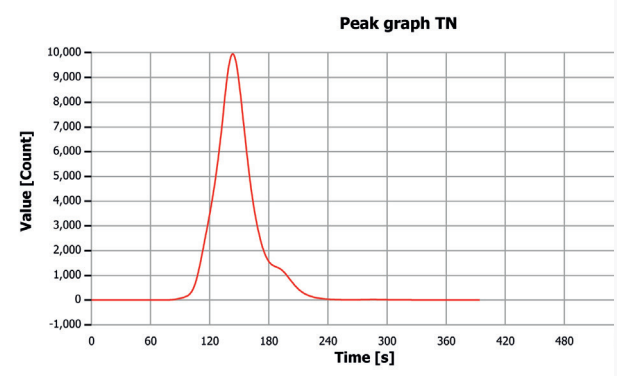

Figure 1 b: TN measuring curve for crude tall oil

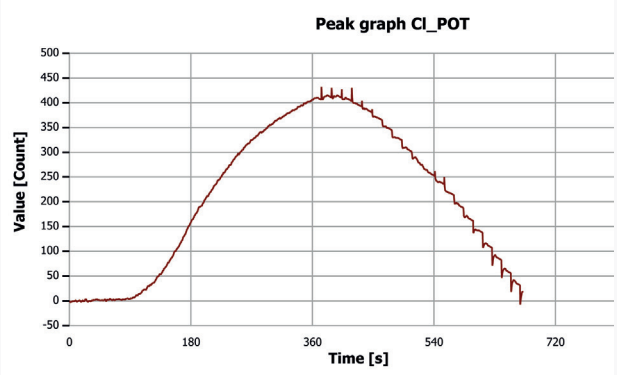

Figure 1 c: TCl measuring curve for crude tall oil

Summary

The multi EA 5100 with flame sensor technology facilitates time- and matrix-optimized decomposition, as this is crucial for the fast and reliable analysis of challenging matrices such as pure biofuels and their precursors. Without any effort of developing specific boat programs for each sample a maximum efficiency is ensured with the minimum need for maintenance.

Further optimization of measurement times can be done by decreasing the sample quantities for highly concentrated sample matrices. The same process and detection parameters can be applied.
The used HiPerSens detection systems for nitrogen, sulfur, and chlorine enable the the analysis of samples in the widest possible concentration range without additional time-consuming pretreatment. This reduces sample processing time effectively.

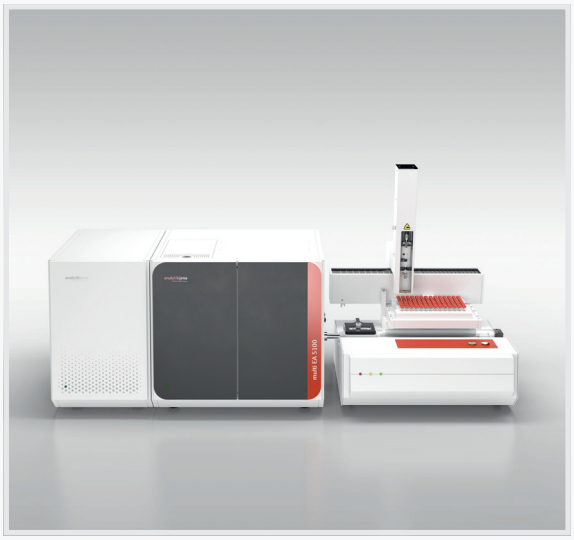

Figure 2: multi EA 5100 with MMS and ABD

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100	450-300.011	Elemental analyzer for determination of sulfur, nitrogen, carbon
C/N/S High-performance drier kit	450-300.012	Efficient reaction gas drying for CNS analysis
S module	450-300.021	Extension for sulfur determination by UV-fluorescence detection
N module	450-300.022	Extension for nitrogen determination by chemiluminescence detection
Cl module	450-300.023	Extension for chlorine determination by coulometric titration
Extension kit Cl high sensitive	450-300.024	Extension kit high sensitive for Cl module
MMS – Multi Matrix sampler	450-300.030	Autosampler for liquids and solids
Liquids kit for MMS	450-300.033	Extension kit for MMS for dosing of liquids
multiWin software	450-011.803	Control and evaluation software, incl. method library

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.2 · Author: AnGr
en · 05/2026
© Analytik Jena GmbH+Co. KG | Pictures ©: Pixabay/Couleur