

Challenge
Ultra-trace analysis - Ensuring reliable results in accordance with ASTM D4629 for bio-based fuels of diverse source materials.

Solution
Fast and optimized combustion process for reliable and reproducible ultra-trace analysis independent of the type of the biofuel.

Intended audience
Laboratories and companies in the energy sector, biofuel producers, refineries, quality control labs monitoring ultra-trace nitrogen in bio-based fuels and intermediates.

Total nitrogen determination in bio-based fuels according to ASTM D4629 – standard test method for trace nitrogen in liquid hydrocarbons by syringe/inlet oxidative combustion and chemiluminescence detection

Introduction

The production of alternative fuels becomes increasingly popular, as they provide a way to respond to both the growing demand for energy and the goal to reduce carbon emissions. In addition to technologies based on the fermentation of starch and sugar, and the transesterification or hydrocracking of plant and animal oil (first generation biofuels), processes based on the conversion of cellulose-rich biomass and waste appear to be promising (second generation biofuels). With the use of biogenic materials for fuel production, their inherently high content of harmful hydrocarbons containing nitrogen, sulfur and chlorine has to be monitored. This is not only due to the adherence of given regulations and legal limits (Tier I–IV), but also to avoid negative effects on the production process, such as catalyst poisoning, and the environment. Even lowest levels of nitrogen compounds can seriously affect the performance and service life of catalysts, hence their ratio must be kept as low as possible. The desired TN content is far below 1 ppm, in general it should be around 100 ppb N. For this reason, a strict monitoring of the intermediate and final products is inevitable.

In ultra-trace analysis many factors influence the quality of analysis and thereby of course the final result. Besides the sensitivity of the detection system used, factors like the cleanliness of the apparatus used (system blank), the skills of the responsible operator (method development and adaptation to each sample matrix), the quality and suitability of the calibration used and, of course, the combustion quality (enabling sharp peak modulation) are highly important.

To eliminate or minimize all these possible error sources, a fast and catalyst-free high-temperature combustion in vertical operation mode and the use of the extremely

sensitive HiPerSens detection technology is required. This eliminates matrix-related method optimization which often leads to a confusing multitude of methods. Thanks to a quartz pyrolyzer, even matrices containing traces of heavier components can be digested completely without soot formation. This reduces the maintenance effort to a minimum.

Materials and methods

The different bio-based fuels were analyzed for their nitrogen content by using a compEAct N elemental analyzer. Equipped with the HiPerSens detection system, it enables determination of the smallest traces as low as 0.6 ng N abs.

The analyses have been run in vertical operation mode. All samples were dosed directly into the evaporation zone of the quartz glass combustion tube. This process was carried out fully automatically by means of a LS 2 high-throughput liquids autosampler. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1050 °C. In the first process phase, evaporation of volatile sample components in an inert gas stream takes place, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier, nonvolatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. Thereby the quartz pyrolyzer ensures a uniform evaporation, modulates the combustion process, and prevents incomplete combustion. This establishes the best conditions for a reproducible and fast ultra-trace analysis. Afterwards, reaction gases were dried and transferred into the HiPerSens chemiluminiscence detector.

Sample preparation

The analyzed sample matrices are a representative spectrum from the field of bio-based fuels. Samples 1–4 are different end products (bio-based fuels). They are light volatile, have a low viscosity, and contain TN in the ultra-trace level. The samples were analyzed directly without a sample preparation step.

Calibration

Liquid calibration standards based on pyridine in isooctane were used to calibrate the analysis system. For evaluation of the gained measurement results the calibration range 1 (ultra-trace) was used. Figure 2 shows the calibration curve for the CLD detector. The calibration was checked with different concentrated standards.

calibration range	1
measurement range [µg]	0.0004 - 0.04
measurement range [AU]	167 - 14,851
k_0	-27.68
k_1	366,811.9
coefficient of determination, R^2	0.99867
calculation volume, V_{Cal} [µl]	40
calculation density, ρ_{Cal} [-]	-
detection limit [µg/l]	14.33
quantification limit [µg/l]	52.16
method standard deviation [µg/l]	13.81
method coefficient of variation [%]	6.06
daily factor	0.918

Figure 1: Calibration range 1 – ultra-trace

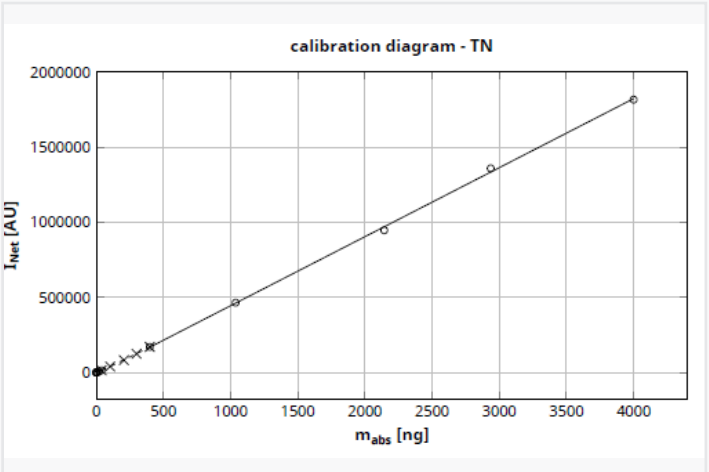


Figure 2: Wide-range calibration curve of the HiPerSens detector

Instrumentation

A compEAct N equipped with CLD detection for the determination of nitrogen was used. For the automated sample introduction and transfer into the analyzer the system was equipped with the LS 2 high-throughput liquids sampler.
For the determination in the ultra-trace range, sample volumes of 40 µL were used.

The sample digestion is carried out by efficient catalyst-free high-temperature combustion in a quartz tube. The process is split into two phases. In the first phase evaporation of light components and pyrolysis of the heavier components takes place within an inert argon atmosphere. The resulting gaseous products are converted in the pure oxygen atmosphere of the combustion zone. In the second phase the system switches completely to oxygen and the remaining components are combusted quantitatively.
The implemented Auto-Protection System guarantees highest operational safety (particle and aerosol trap) and a complete transfer of the formed NOx into the CLD. The compEAct N enables a detection limit as low as 15 µg/L N.

Method parameters

From the compEAct's integrated method library module, the standard method ASTM D4629 was used for all analyses. The following table summarizes the parameter settings for the combustion process.

Evaluation parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 1: Process parameters compEAct

Parameter	Specification
Furnace temperature	1050 °C
Second combustion	60 s
Ar flow (first phase)	150 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	150 mL/min
Draw up	2 µL/s
Injection	0.5 µL/s

Table 2: Detection parameters CLD

Parameter	Specification NS
Max. integration time	300 s
Start (N)	1 cts
Stop (N)	1 cts

Results and discussion

The examined samples are a representative spectrum from the field of biofuel. The results given in Table 3 are averages of three replicate analyses.

Table 3: Results of the TN analysis

Measurement	TN	SD
Biodiesel (corn oil)	0.87 ppm	± 0.02 ppm
B-t-L** (tall oil)	5.33 ppm	± 0.08 ppm
Bioethanol (cellulose)	0.18 ppm	< 0.01 ppm
Bio-based diesel	0.34 ppm	± 0.02 ppm
Standard 0.5 mg/L N	0.5 mg/L	± 0.01 mg/L
Standard 0.05 mg/L N	0.05 mg/L	± 0.01 mg/L

** B-t-L = bio mass to liquid fuel

Due to the optimal process conditions a threefold determination is generally sufficient to reach results within 3 % RSD. This is significantly affecting the sample processing time and thereby generates a higher sample throughput. The obtained analysis results and their reproducibility depict the high quality of the sample combustion. The proper performance of the analysis system was confirmed by analyzing standard materials with known N contents (see Table 3).

Typical measuring curves for samples and standards are depicted in Figures 3–6.

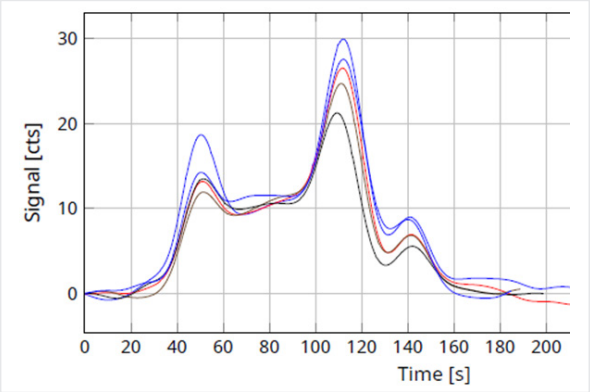


Figure 3: TN measuring curves for bio-based diesel fuel

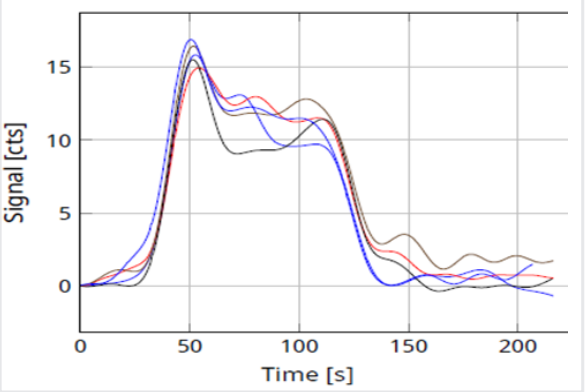


Figure 4: TN measuring curves for bioethanol

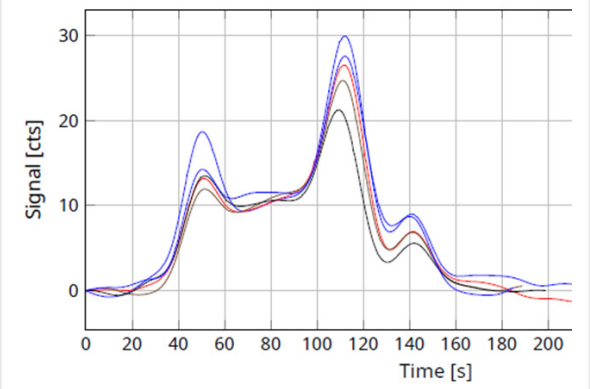


Figure 5: TN measuring curves for standard 0.05 µg/L N

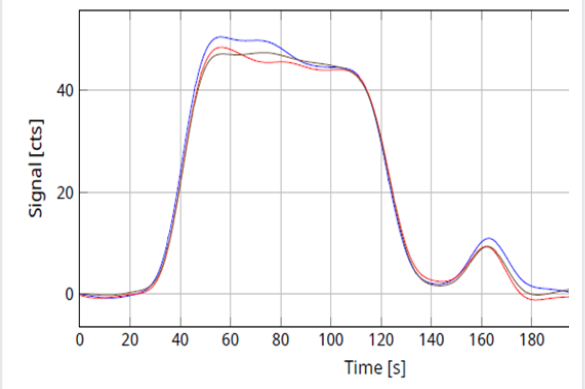


Figure 6: TN measuring curves for standard 0.5 µg/L N

Summary

The compEAct together with the LS 2 autosampler provides a fast and reliable solution for the precise determination of ultra-low TN contents in bio-based fuels. Thanks to the highly sensitive HiPerSens CLD, even smallest differences in the ppb range can be distinguished exactly. The optimal sample digestion and the efficient Auto-Protection system enable an excellent reproducibility. A high sample throughput is easily achieved using the LS 2 liquids sampler. If needed, the analysis system can be extended for the determination of pressurized gases and LPG by adding the suited sampling system.

Further time optimization can be achieved by decreasing the sample quantities for highly concentrated sample matrices. The same process and detection parameters can be applied.

The HiPerSens detection system used for nitrogen allows analyzing samples in the widest possible concentration. That also positively affects the processing time of samples.



Figure 7: compEAct N with LS sampler

Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

Article	Article number	Description
compEAct N	450-300.003	Analyzer for the determination of nitrogen in liquids and gases
LS 2	450-900.451	Autosampler for liquids
EAvolution software	450-011.300	Control and evaluation software

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.
Trademark notice: The brand names of the third-party products specified in the application note are usually registered trademarks of the respective companies or organizations.

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 1.1 · Author: AnGr
en · 06/2026
© Analytik Jena GmbH+Co. KG |
Picture p. 1 ©: Adobe Stock/Patchladda (AI generated)