Determination of Trace Nitrogen Contents in Different Types of Fuels and Fuel Blends According to ASTM D4629 resp. DIN 51444

Challenge

Fast and easy analysis of widely varying nitrogen contents in different types of diesel fuel according to industry standards.

Solution

Reliable results, independent of TN concentration or digestion characteristics, in very short time using compEAct N and the LS 2 liquids sampler.

Introduction

Diesel is a mixture of various hydrocarbons that is produced during the fractionated distillation of crude oil. Its boiling interval is in the range of 150 to 390° C. Diesel is used mainly as fuel for automobiles. It can contain traces of organically bound chlorine, sulfur and nitrogen originating either from natural sources or from additives. During combustion of the fuel, these compounds form environmental pollutants. As these pollutants are hazardous to the human health and the environment, their content (N, S, Cl) should be kept as small as possible. To ensure the product quality and adhere to legal limit values a permanent quality control is essential.

The compEAct N is an analysis system which was specifically optimized for the fast and trouble-free determination of nitrogen contents in a wide concentration range. Combining catalyst-free high-temperature combustion and highly sensitive HiPerSens® detection it allows the detection of nitrogen at concentrations ranging from 15 µg/l up to 10,000 mg/l with one and the same device.

analytikjena
An Endress+Hauser Company

Materials and Methods

Samples and Reagents

- Different fuel samples
- Isooctane (C_8H_{18}), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- Pyridine (C_5H_5N), GR for analysis (Merck Art.-No.: 1.09728.0100)
- Calibration standard kit Nitrogen (0–25 mg/l) (Analytik Jena, Art.-No.: 402-889.069)

Sample Preparation

The samples are light volatile, have a low viscosity, and contain TN in the ultra-trace level. That is why a pretreatment step was redundant. The samples were analyzed directly.

Calibration

Prior to the actual determination, the system was calibrated using nitrogen standard solutions based on pyridine (N) in isooctane in the range of 0 to 2000 µg/kg. Figure 1 and 2 depict typical calibration curves and performance parameters.

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

Fig.1: Calibration range 1 – ultra-trace

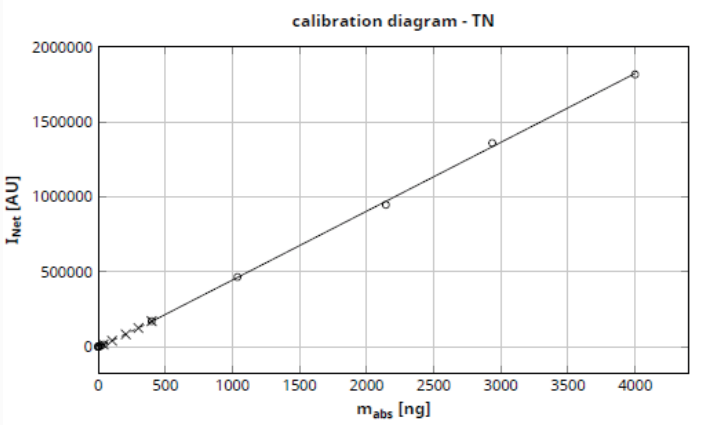

Fig.2: Wide-range calibration curve of the HiPerSens detector

The calibration was checked with different concentrated standards.

Instrumentation

The measurements were performed using a compEAct N, equipped with HiPerSens CLD detection for the determination of nitrogen. Sample introduction was carried out fully automatically by means of the LS 2 liquids sampler to ensure a high sample throughput.

The analyses have been run in vertical operation mode. The samples were dosed directly into the evaporation zone of the quartz glass combustion tube. This process took place fully automatically by means of the 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. The implemented Auto-Protection System guarantees highest operational safety (particle and aerosol trap) and a complete transfer of the formed NOx into the chemoluminescence detector after a sufficient drying of the reaction gases. The compEAct N enables a detection limit of as low as 15 µg/l N.

Method Parameters

The standard method ASTM D4629 from the ASTM method module was used for all analyses. The following table summarizes the parameter settings for the combustion process.

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

Evaluation Parameters

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

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 fuel production. The results given in Table 3 are averages of three replicate analyses of samples and test standards. For all samples and standards an injection volume of 40 µl was used. Figures 3–6 show typical measuring curves for selected samples as well as for one standard.

Table 3: Results of the total nitrogen determination in different fuels

Measurement	TN	SD
Diesel (automotive, DK)	0.87 ppm	± 0.02 ppm
UL-Diesel (UL-DK)	7.77 ppm	± 0.04 ppm
Bio Diesel (2nd generation, B-t-L)	0.22 ppm	< 0.01 ppm
Diesel + 7 % FAME	2.53 ppm	± 0.04 ppm
Diesel (Marine Gasoil)	28.7 ppm	± 0.71 ppm
Regular Gasoline (OK)	2.24 ppm	± 0.12 ppm
Light Gasoline	0.14 ppm	< 0.01 ppm
Jet Fuel A	9.17 ppm	± 0.04 ppm
Kerosene	3.65 ppm	< 0.01 ppm
TN Standard (c = 0.07ppm)	0.07 ppm	< 0.01 ppm
TN Standard (c = 0.72ppm)	0.72 ppm	± 0.03 ppm
TN Standard (c = 36 ppm)	36.2 ppm	± 0.09 ppm

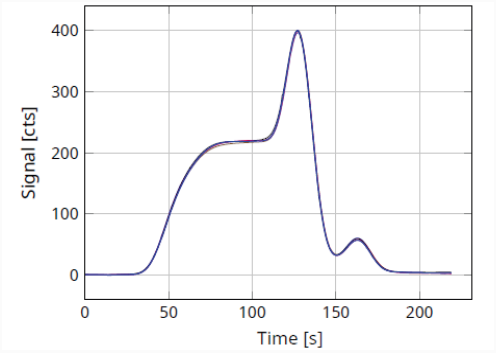

Fig. 3: TN analysis curve for sample "Kerosene"

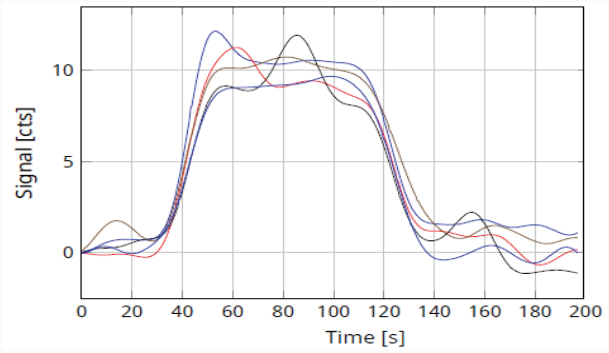

Fig. 4: TN analysis curve for sample "Light Gasoline"

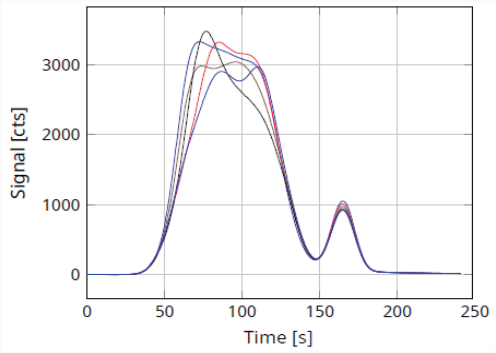

Fig. 5: TN analysis curve for sample "Marine Gasoil"

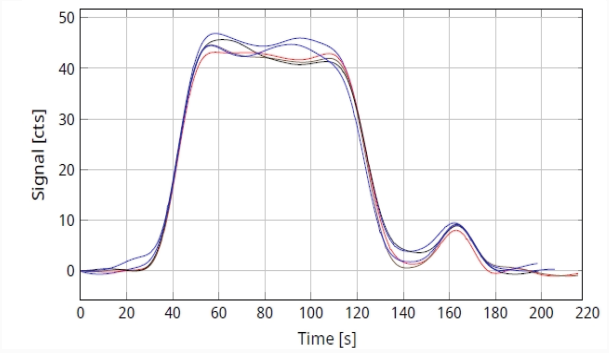

Fig. 6: TN analysis curve for standard "0.72 ppm N"

Due to the optimal process conditions a threefold determination is generally sufficient to reach results within 3 % RSD. This is remarkably affecting the sample processing time and thereby generates a higher sample throughput. The analysis results received 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).

Conclusion

The compEAct N is extremely well suited for the measurement of widely varying nitrogen contents in versatile fuel samples (e.g., diesel, gasoline, kerosene, bio diesel). The detector, with its unique HiPerSens® technology, achieves a measuring range of up to 10,000 mg/l starting at a limit of detection as low as 15 µg/l of nitrogen.

The optimal sample digestion and the efficient Auto-Protection system enable excellent reproducibility, independent of TN concentration or digestion characteristics and composition of the analyzed fuel (e.g., FAME, color additives etc.). A high sample throughput is easily achieved by using the LS 2 liquids sampler.

The sample volume can be reduced to 10 to 20 µl to save further analysis time. Thanks to compEAct's sensitivity, this is sufficient to gain reliable results in very short time. For analysis of gaseous fuels and LPG, the analysis system can be extended by adding the suited sampling system.

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