Determination of Trace Nitrogen in Liquid Petroleum Hydrocarbons by Oxidative Combustion and Chemiluminescence Detection According to ASTM D4629 resp. DIN 51444

Challenge

Fast and easy analysis of widely varying nitrogen contents in different types of fuels, related products, and process streams according to industry standards.

Solution

Reliable results, independent of TN concentration or digestion characteristics, in short time using the multi EA 5100 combined with the MMS – a multi-matrix sampling system.

Introduction

Refinery samples like fuels (diesel, platformer, etc.) are mixtures of various hydrocarbons that are produced during the fractionated distillation of crude oil. Their boiling intervals are mainly in the range of 150 to 390 °C. In general they are used as fuel for automobiles or as combustibles. They 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 low as possible. Another aspect is their effect on the performance and life time of catalysts used in several process steps. A too high content of these undesired elements can remarkably affect the quality of the products as well as the activity of the catalyst (poisoning). To ensure the product quality and adhere to legal limit values a permanent quality control is essential.

The multi EA 5100 is specifically optimized for the fast and trouble-free determination of nitrogen contents in a wide concentration range. Combining catalyst-free high-temperature combustion and effective gas purification and drying with the highly sensitive HiPerSens detection, it allows the detection of nitrogen at concentrations ranging from 10 µg/L up to 10,000 mg/L with one and the same device.

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Materials and Methods

Samples and Reagents

Different refinery samples (diesel, gasoline, platformer, etc.) have been analyzed.

- 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)
- Extended standard kit for calibration and test nitrogen (0–25 mg/L) (Analytik Jena, Art.-No.: 402-889.076)

Sample Preparation

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

Calibration

Prior to the determination, the system was calibrated using nitrogen standard solutions based on pyridine (N) in isooctane. Figure 1 depicts a typical calibration curve with performance parameters.
The calibration was checked with different concentrated standards (see Table 3).

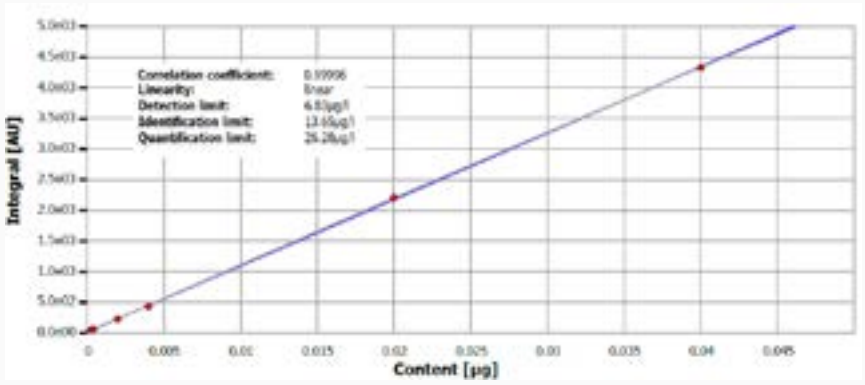

Figure 1: TN calibration, ultra-trace range, curve including statistics

Instrumentation

The measurements were performed using a multi EA 5100, equipped with HiPerSens CLD detection for the determination of nitrogen. Sample introduction was carried out fully automatically by means of the MMS multi matrix sampler equipped with liquids 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 equipped with a quartz pyrolyzer. This process took place fully automatically by means of the 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 analysis even for TN contents as low as ultra-traces. The Auto-Protection system of the multi EA 5100 and the high-performance dryer guarantee highest operational safety (particle and aerosol trap), sufficient drying, and a complete transfer of the formed NOx into the CLD. Thus it is possible to reach a detection limit of as low as 10 µg/L N.

Figure 2: multi EA 5100 with MMS sampler

Method Parameters

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

Table 1: Process parameters in vertical mode

Parameter	Specification
Furnace temperature	1050 °C
Second combustion	60 s
Ar flow (first phase)	100 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	100 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	240 s
Start	1.9 ppb
Stop	2.0 ppb
Stability	7

Results and Discussion

The examined samples are a representative spectrum from the field of refinery quality and process control. 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 3–7 show typical measuring curves for selected samples as well as for one standard.

Table 3: Results of the total nitrogen determination in different refinery samples and standards

Measurement	TN	SD
Platformer	0.03 mg/L	< 0.01 mg/L
C8 (HC mix)	0.04 mg/L	< 0.01 mg/L
Raffinate	0.04 mg/L	< 0.01 mg/L
Gasoil	1.38 mg/L	< 0.01 mg/L
Diesel (DK)	2.14 mg/L	< 0.01 mg/L
Gasoline (OK)	5.17 mg/L	± 0.05 mg/L
Jet fuel A	6.48 mg/L	± 0.04 mg/L
Heating oil (HEL)	177 mg/L	± 0.97 mg/L
TN Standard (c = 0.10 mg/L)	0.10 mg/L	< 0.01 mg/L
TN Standard (c = 5.00 mg/L)	5.03 mg/L	± 0.02 mg/L
TN Standard (c = 50.0 mg/L)	50.0 mg/L	± 0.10 mg/L

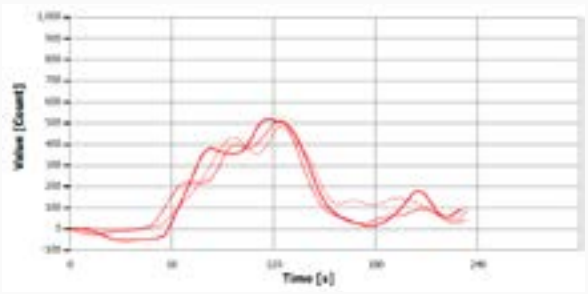

Figure 3: Analysis curve of "C8 (HC Mix)"

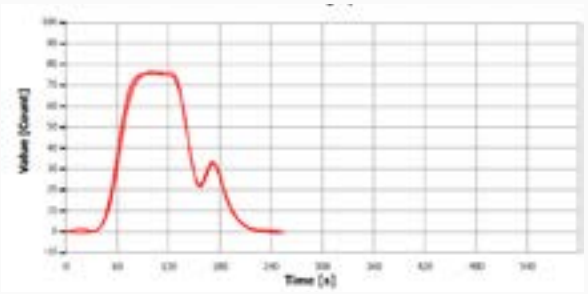

Figure 4: Analysis curve of "diesel (DK)"

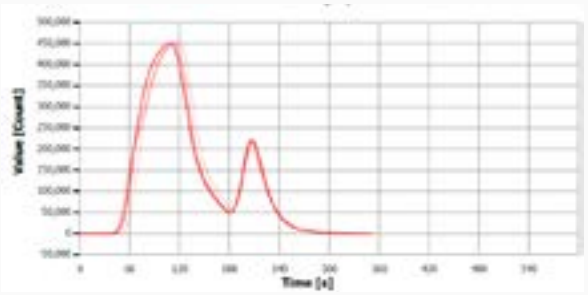

Figure 5: Analysis curve of "heating oil (HEL)"

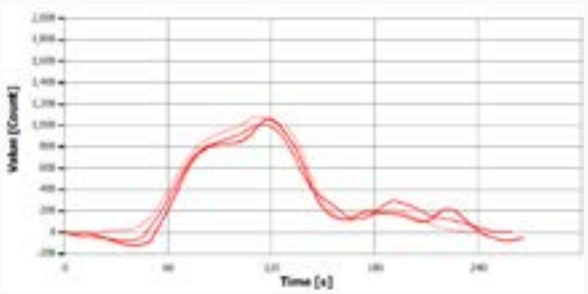

Figure 6: Analysis curve of "TN standard 0.1 mg/L"

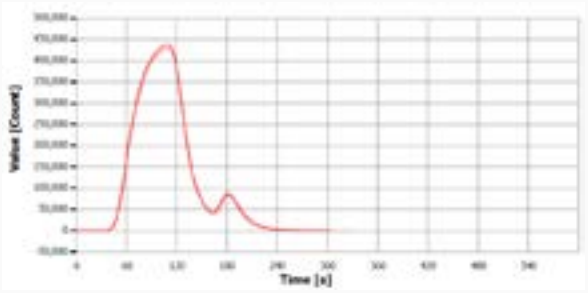

Figure 7: Analysis curve of "TN standard 50 mg/L"

Due to the optimal process conditions a threefold determination is generally sufficient to achieve 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 multi EA 5100 is extremely well suited for the measurement of widely varying nitrogen contents in versatile refinery 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 10 µg/L of nitrogen.

The optimal sample digestion and reaction gas treatment (guaranteed with the Auto-Protection system) enable excellent reproducibility, independent of TN concentration or digestion characteristics and composition of the analyzed matrix (e.g., FAME, color additives, etc.). A high sample throughput is easily achieved by using the MMS sampler with 112 positions for liquids. For lower throughput demands manual introduction of the samples by means of an autoinjector type AI resp. AI-EA is possible alternatively. If needed, the system can be extended for the analysis of other matrix types like gases and solids, or the determination of additional elements and parameters (e.g., sulfur, chlorine, carbon, TOC, AOX, EOX) by just adding the suitable sampling or detection system.

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