Determination of Nitrogen Contents in Petroleum Products by Boat-Inlet and Chemiluminescence Detection According to ASTM D5762

Challenge

Fast, reliable analysis of varying nitrogen contents in refinery products with matrix robustness and quantitative combustion independent of composition and element content.

Solution

Optimized high-temperature combustion with flame sensor technology and HiPerSens CLD detection for concentration-independent TN determination.

Introduction

Refinery samples are mixtures of various hydrocarbons (aliphatic, aromatic, polycyclic, etc.) resulting from the process of fractionated distillation of crude oil. Their boiling intervals, viscosities and combustion behavior vary in the same wide range. This makes it quite difficult to ensure equivalent analysis results for all matrix types. To avoid matrix effects like too low results or incomplete combustion, analysis in horizontal mode with boat inlet is the only suitable approach. Compared to vertical operation, the horizontal mode is disliked by many operators due to the remarkably increased analysis times and the necessity to create optimized combustion resp. boat programs for each matrix type and quantity. The quality of measurements is thus often a compromise between analysis time, desired sample throughput (analysis speed) and the dispersion of the measurement values.

Besides sulfur and chlorine, nitrogen is another important parameter to be monitored. For process and quality control widely varying TN contents have to be determined. While the focus during the refining process is mainly on TN traces, which can poison catalysts and result in undesired byproducts, product control and analysis of feed materials has to cover a wider concentration range. Contents up to the wt% range are common for matrices like crude oil, HC feeds, vacuum residues, but also for high-performance lube and engine oils.

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The multi EA 5100 is specifically optimized for the fast and trouble-free analysis of widely varying TN contents in challenging matrices in horizontal mode. Combining catalyst-free high-temperature combustion and effective gas purification and drying with the highly sensitive HiPerSens CLD, it allows the direct detection of nitrogen at concentrations ranging up to 10,000 mg/L with one and the same device.

Materials and Methods

Samples and Reagents

Different refinery and related samples (heating oil, gas oil, lube oil, 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)
- Calibration standard kits Nitrogen (Analytik Jena, Art.-No.: 402-889.075, 402-889.162, 402-889.165)

Sample Preparation

The samples were analyzed directly in case their viscosities were < 10 cSt and the element contents were within the operation range of the analyzer. Other samples were diluted with either isooctane or o-xylene to adapt the element content to the operation range resp. to enable comfortable sample supply by means of the MMS liquids sampler.

Calibration

Liquid calibration standards based on pyridine (N) in isooctane were used to calibrate the analysis system in a wide concentration range. Matrix-related calibration strategies were not required as the combustion is optimized and interfering components are eliminated before detection.
The calibration was checked with different concentrated standards.

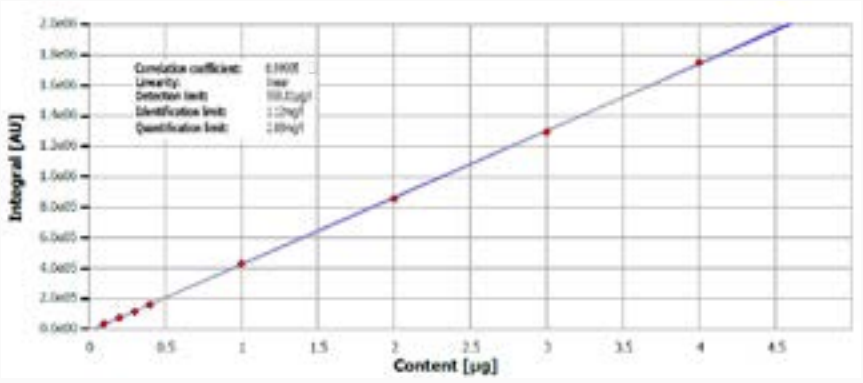

Figure 1: Examplary calibration for TN upper range, curve including statistics

Instrumentation

The measurements were performed using a multi EA 5100, equipped with HiPerSens chemiluminescence detection for the determination of nitrogen. Sample introduction was carried out fully automatically using the MMS multi matrix sampler equipped with liquids kit in combination with the ABD, an automatic boat drive with cooled sample introduction zone. This ensures a high sample throughput and best analysis results, even for samples with higher viscosity or complex composition.

The analyses have been run in horizontal operation mode. Therefore the samples were dosed directly into a quartz sample boat, installaed inside the ABD, by means of the MMS in liquids mode. After sample injection the ABD is fully automatically transferring the loaded boat into the hot zone of the combustion tube.

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 and pyrolysis of the heavier sample components takes place in an inert gas stream. This is followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier,

Figure 2: multi EA 5100 with ABD and MMS in horizontal operation mode

nonvolatile sample components resp. formed pyrolysis products are quantitatively oxidized in pure oxygen. Thereby the flame sensor technology ensures a uniform evaporation and quantitative combustion for any component of the sample matrix. Incomplete combustion, system contamination and thereby caused low quality of analysis results (too low, scattering) is prevented effectively. This establishes the best conditions for the analysis of any matrix type, even unknown ones, independent of the introduced quantity. Horizontal operation is especially recommended for unknown samples, high element contents, vigorously reacting or inhomogeneous materials (residue, polymers, etc.), but of course it is also suited for any other easy-to-handle sample with lower element contents. The implemented Auto-Protection system guarantees highest operational safety, including a particle and aerosol trap, and a complete transfer of the formed NO_x into the CLD after a sufficient drying of the reaction gases. The multi EA 5100 enables a detection limit of as low as 10 µg/L N.

Method Parameters

An approved method from the method library of the multi EA 5100 was used for all measurements. It is suitable for analysis of liquids and samples with increased viscosity or boiling points above 400 °C. The horizontal mode with flame sensor control ensures best analysis results in the shortest time without increasing maintenance effort. The syringeability can be enabled by a sufficient dilution with a suitable solvent (e.g., xylene) to enable a higher processing speed for samples which are too viscous for syringe inlet, or a wide-bore needle could be used. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100 in horizontal mode with flame sensor technology

Parameter	Specification
Furnace temperature	1050 °C
Cooling time (boat)	240 s
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 volume	40 µL
Injection	3 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
Max. integration time	600 s
Start	1.9 ppb
Stop	2.0 ppb
Stability	7

Results and Discussion

The analyzed samples are process intermediates and final products from refineries and petrochemical industry. The results given in Table 3 are averages of three replicate analyses of samples and test standards. For all samples resp. their dilutions and the test standards an injection volume of 40 µL was used.

Table 3: Results of the total nitrogen determination in different refinery samples and standards by means of double furnace technology

Measurement	TN	SD	Dilution
Diesel oil	57.0 mg/L	± 0.52 mg/L	-
Heating oil C	257 mg/L	± 1.51 mg/L	-
HCC feed	1.38 g/kg	< 0.01 mg/kg	1 in 116
Coker oil	1.40 g/kg	< 0.01 mg/kg	1 in 122
Vacuum oil	5.37 g/kg	± 0.05 mg/kg	1 in 100
TN Standard (c = 5.00 mg/L)	5.00 mg/L	± 0.10 mg/L	-
TN Standard (c = 1,000 mg/L)	999 mg/L	± 0.92 mg/L	-

Figures 3–6 show typical measuring curves for selected samples resp. standards.

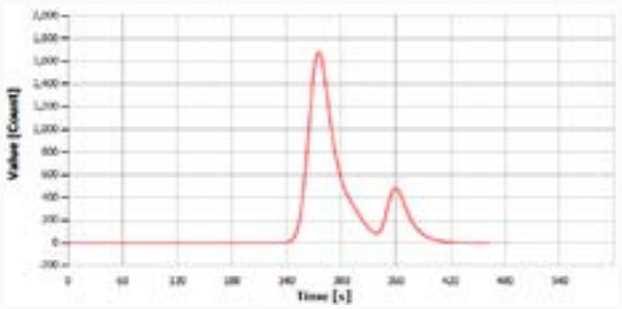

Figure 3: Analysis curve of "HCC feed" (dilution)

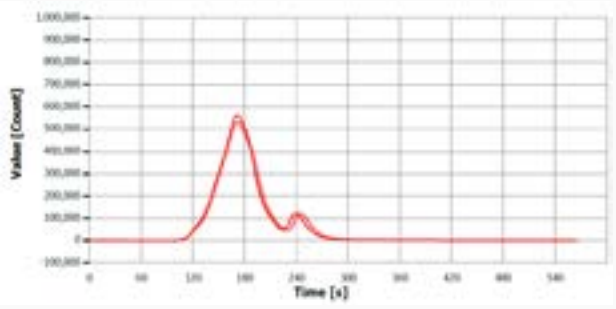

Figure 4: Analysis curve of "Diesel oil"

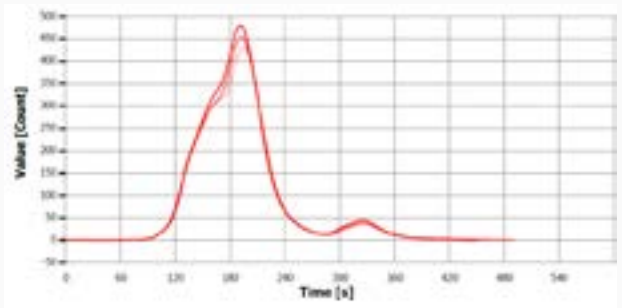

Figure 5: Analysis curve of "TN standard 5 mg/L"

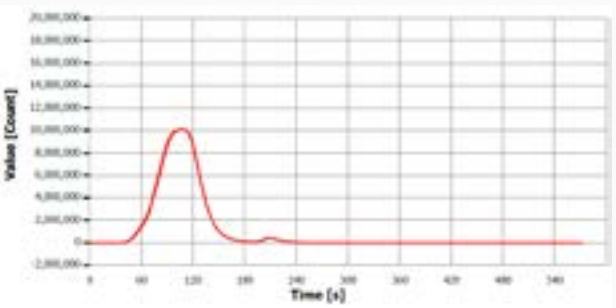

Figure 6: Analysis curve of "TN standard 1,000 mg/L"

Due to the matrix-optimized combustion in general a threefold determination is sufficient to achieve results far below 3% RSD. This remarkably affects the sample processing time and allows for a higher sample throughput. The analysis results received and their reproducibility prove the performance of the digestion process. The overall performance of the analysis system was validated by analyzing standard materials with known nitrogen contents, results are given in Table 3.

If desired, further time-wise optimization can be achieved by decreasing the sample quantities for higher concentrated sample matrices. The same process and detection parameters can be applied.

Conclusion

The multi EA 5100 together with the ABD provides a fast and reliable solution for the precise determination of widely varying nitrogen contents even in challenging samples. Thanks to the flame sensor technology best results can be achieved for any matrix in the shortest possible time, independent of their nitrogen content and combustion properties. This simplifies daily routine work and helps to siginificantly increase sample throughput while reducing operation and maintenance effort.

Thanks to the HiPerSens technology, a measuring range of up to 10,000 mg/L starting at a limit of detection as low as 30 µg/L of nitrogen can be achieved easily. The optimal sample digestion and the efficient Auto-Protection system, including a high-capacity membrane drier, enable excellent reproducibility, independent of the TN concentration or digestion characteristics and composition of the analyzed sample matrix. A high sample throughput is easily achieved by using the MMS liquids sampler with 112 positions, which is suitable for vertical as well as horizontal sample introduction techniques. For lower throughput demands manual introduction of the samples by means of boat injection (ABD) is possible alternatively.

If needed, the analysis 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 suited sampling or detection system.

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