Determination of Ultra Low Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection According to ASTM D7184

Challenge

Fast, sensitive and reliable analysis of nitrogen contents in the ultra-trace range in different types of liquid aliphatic and aromatic hydrocarbons and their mixtures.

Solution

Optimized vertical combustion combined with HiPerSens chemiluminescence detection for concentration-independent TN determination.

Introduction

Liquid hydrocarbons play an important role in the refinery processes, the petrochemical, chemical and polymer industry, either as raw materials, process intermediates, or as end products. Regardless of their source or their further use, they all have in common that they need to be ultrapure. Undesired components like sulfur, nitrogen or chlorine compounds affect the production process and the quality of the final products, even if they occur only in the smallest traces.

Besides sulfur, nitrogen impurities are also known to negatively affect the performance and economic life of used catalyst materials (poisoning). The formation of unwanted by-products and a decreased product quality is an additional problem. To prevent this, the TN content has to be kept as low as possible, preferably below 100 µg/L, making a close nitrogen monitoring essential in process and quality control labs. High-temperature combustion in combination with chemiluminescence detection is the most effective method for this monitoring.

The multi EA 5100 is an analysis system which has been specifically optimized for this challenging task. Combining high-temperature combustion, a high-performance reaction gas dryer, and sensitive HiPerSens detection, it allows the determination of nitrogen traces as low as 10 µg/L.

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Materials and Methods

Samples and Reagents

- Different aliphatic and aromatic hydrocarbons and their mixes (e.g., benzene, isooctane, BTX)

- 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 calibration standard kit Nitrogen (0.05–25 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 level. This made a pretreatment step 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 ng to 45 ng N. Figure 1 depicts typical calibration curves and performance parameters for ultra-trace applications.
The calibration was checked with different concentrated standards.

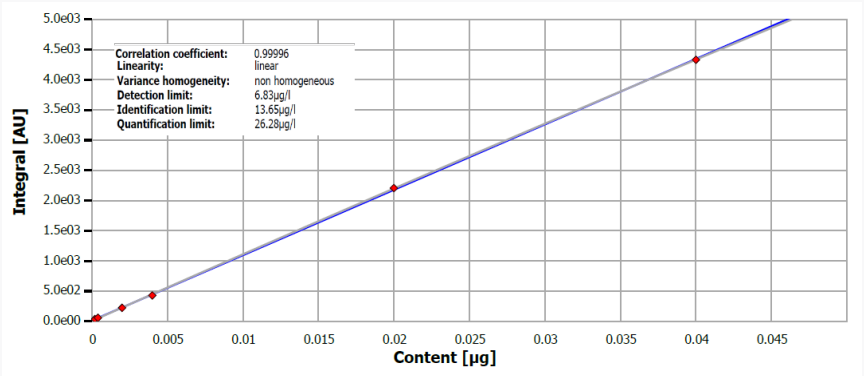

Figure 1: Example TN calibration for the ultra-trace range, curve including statistics

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 to ensure a maximum 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 MMS multi matrix sampler equipped with liquids kit. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1050 °C.

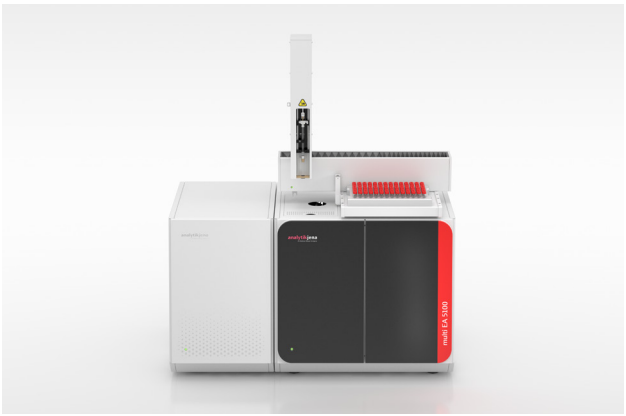

Figure 2: multi EA 5100 with MMS in vertical operation mode

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 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

The standard method ASTM D7184 from the method library of the analyzer's multiWin software was used for all analyses. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100

Parameter	Specification
Operation mode	vertical
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 volume	40 µL
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
Max. integration time	300 s
Start	0.2 ppb
Stop	0.5 ppb
Stability	7

Results and Discussion

The examined samples are a representative spectrum of hydrocarbons from refinery applications, the petrochemical and chemical industry as well as from polymer 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 resp. standards.

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

Measurement	TN	SD
Isooctane	42.6 ppb	± 5.60 ppb
Cumene	13.3 µg/L	< 1 µg/L
Benzene	536 µg/kg	± 6.55 µg/kg
Toluene	36.0 µg/L	± 2.85 µg/L
Naphtha	38.3 µg/L	± 3.13 µg/L
TN Standard (c = 100 µg/L)	98.5 µg/L	± 1.70 µg/L
TN Standard (c = 50 µg/L)	49.9 µg/L	< 1 µg/L

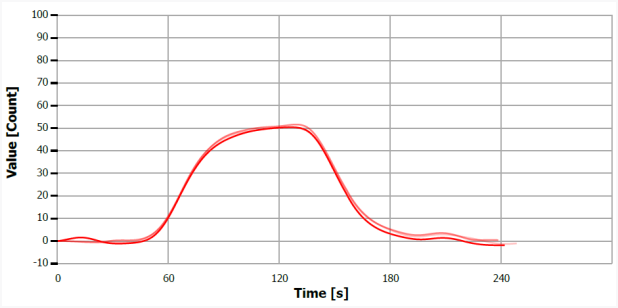

Figure 3: Analysis curve of "Benzene"

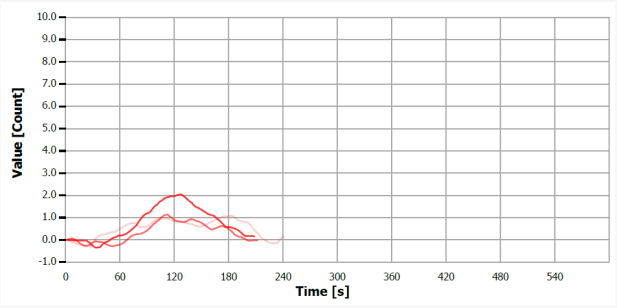

Figure 4: Analysis curve of "Isooctane"

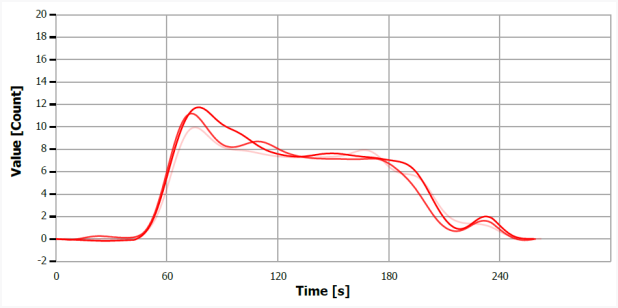

Figure 5: Analysis curve of "TN standard 100 µg/L"

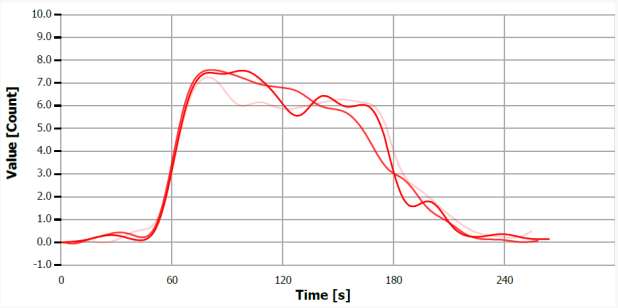

Figure 6: Analysis curve of "TN standard 50 µg/L"

Due to the optimal process conditions a three- to fivefold determination, with injection volumes of 40 µL per replicate analysis, is generally sufficient to reach satisfying results for ultra-trace applications. This is remarkably affecting the sample processing time and thereby generates a higher sample throughput. Utilization of huge injection volumes is unnecessary. 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 nitrogen contents (see Table 3).

Conclusion

The multi EA 5100 is extremely well suited for the measurement of widely varying nitrogen contents in manifold aliphatic and aromatic hydrocarbons and their mixes (e.g., naphtha, toluene, benzene, ethanol). The detector, with its unique HiPerSens technology and highly efficient reaction gas drying, achieves a measuring range of up to 10,000 mg/L starting at a limit of detection as low as 10 µg/L N.

The optimal sample digestion and the efficient Auto-Protection system enable excellent reproducibility, independent of the TN concentration or digestion characteristics and composition of the sample analyzed. A high sample throughput is easily achieved by using the MMS autosampler. For lower throughput requirements an autoinjector is available.

The analyzer can easily be extended to the analysis of other matrix types like gases and solids resp. the determination of sulfur, carbon or chlorine contents by just adding one of the available matrix-optimized sampling systems or detection modules.

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