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

Introduction

Liquid aliphatic and aromatic hydrocarbons play an important role in refining processes, in 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 ultra-pure. This means that they have to be free of undesired compounds, as these could affect the production process and the quality of the final products.

Impurities such as nitrogen-containing compounds not only affect the performance and economic life of catalysts used in the production process (catalyst poisoning), but also form unwanted by-products and thereby decrease the quality of the end products. Therefore their content has to be kept as low as possible, preferably below 100 ppb. To make this possible, the exact knowledge of the present nitrogen (TN) is required. Combustion-based elemental analysis coupled with a pressure-reduced chemiluminescence detector is the only method that has proven to be suitable for this challenging task.

The compEAct N is an analysis system which has been specifically optimized for the fast and trouble-free determination of nitrogen contents in the ultra-trace range. Combining catalyst-free high-temperature combustion and highly sensitive

Challenge

Fast and reliable analysis of N 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.

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HiPerSens detection, it allows the determination of nitrogen at concentrations ranging from 15 µg/l up to 10,000 mg/l with one and the same device and method.

Materials and Methods
Samples and Reagents
- Different aliphatic and aromatic hydrocarbons and their mixes (e.g. benzene, isooctane, naphtha)
- 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 (0–25 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 to 4,000 ng N. Figure 1 and 2 depict typical calibration curves and performance parameters for ultra-trace applications.

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

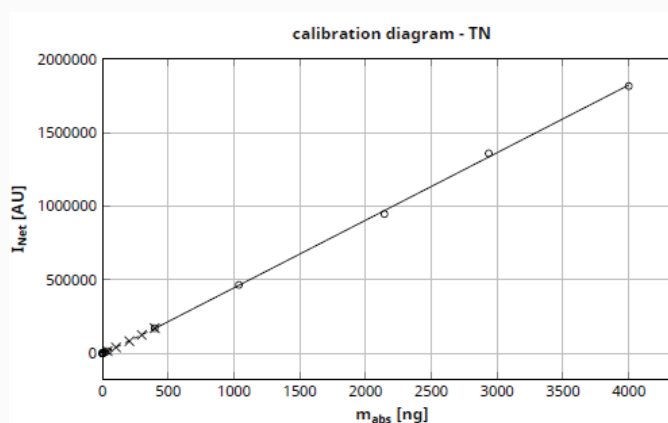Fig.1: TN calibration for ultra-trace range

Fig.2: Wide-range calibration curve of the HiPerSens CLD 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 using 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 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 CLD 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 D7184 from the method library of compEAct's EAvolution software was used for all analyses. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters compEAct N

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 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	1 cts
Stop	1 cts

Results and Discussion

The examined samples are a representative spectrum of hydrocarbons from refinery applications, the petrochemical and chemical industry as well as in 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 TN analysis

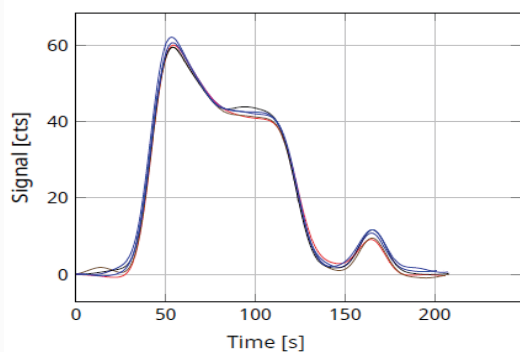| Measurement	TN	SD
Isooctane	42.6 ppb	± 5.60 ppb
Xylene (mix of isomers)	53.6 ppb	± 5.23 ppb
Benzene	59.8 ppb	± 1.08 ppb
Toluene	572 ppb	± 3.95 ppb
Ethanol	173 ppb	± 6.29 ppb
Cumene	119 ppb	± 3.74 ppb
Naphtha	489 ppb	± 5.92 ppb
TN Standard (c = 725 ppb)	726 ppb	± 16.3 ppb
TN Standard (c = 73.2 ppb)	72.4 ppb	< 1 ppb

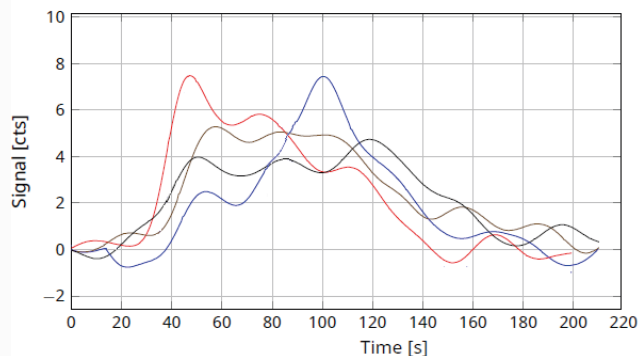Fig. 3: TN analysis curve for sample "Toluene"

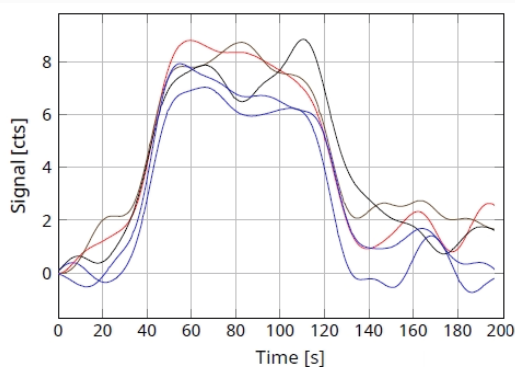Fig. 4: TN analysis curve for sample "Isooctane"

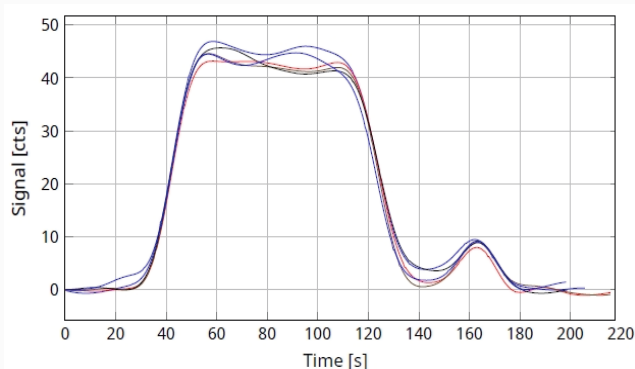Fig. 5: TN analysis curve for TN standard "73.2 ppb N"

Fig. 6: TN analysis curve for TN standard "725 ppb N"

Due to the optimal process conditions a three- to fivefold determination, with injection volumes between 20 and 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. 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 aliphatic and aromatic hydrocarbons and their mixes (e.g., naphtha, toluene, benzene, ethanol). 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 the TN concentration or digestion characteristics and composition of the sample analyzed. A high sample throughput is easily achieved by using the LS 2 liquids sampler.

The analyzer can easily be extended to include the analysis of gaseous and liquefied pressurized hydrocarbons by adding one of the available application-optimized sample supply systems