Challenge
Analysis of trace concentrations of total nitrogen (TN) in highly volatile hydrocarbons.

Solution
Fast, sensitive, and reliable analysis in vertical combustion mode with HiPerSens chemiluminescence detection using a cooled sampler according to UOP 981.

Analysis of Trace Nitrogen in Highly Volatile Liquid Hydrocarbons by Oxidative Combustion with Chemiluminescence Detection According to UOP 981

Introduction

Highly volatile hydrocarbons are frequent samples in the chemical industry, whether as solvents in the laboratory, in the production process, or in quality control as final products. The highest demands are often placed on the purity of the solvents. Very low analytical detection limits are required to reliably determine these ultra-trace nitrogen concentrations. Petrochemistry is another area in which highly volatile hydrocarbons with nitrogen contents in a wider range, e.g., light naphtha, play a role.

The challenge in analyzing very volatile samples is that they can easily evaporate. Thus, if happening during sample taking and introduction, it remarkably affects repeatability and correctness of analytical results. Another risk is a far too fast evaporation when being introduced to the combustion system. This can easily result in uncontrolled, incomplete combustion, formation of soot, and other undesired effects. To prevent this, intelligent strategies are needed for sample supply and sample digestion. The UOP 981 provides a standard operating procedure for such samples, using a temperature-controlled sampler set to 15 °C for sample dosing.

With the multi EA 5100, Analytik Jena offers a flexible elemental analyzer that has been optimized specifically for this demanding task. By combining high-temperature combustion, a high-performance reaction gas dryer, and the sensitive HiPerSens detection, it enables the determination of trace nitrogen with detection limits of 10 µg/L. In addition, a temperature-controlled autosampler MMS-T is utilized, which can be used for both cooled and heated sample supply.

In the UOP 981, an injection volume of 80 µL is recommended to achieve the necessary sensitivity. However, due to the very sensitive and stable chemiluminescence detector, an injection volume of 40 µL is sufficient on the multi EA 5100, saving valuable analysis time and sample volume. Thus, a higher sample throughput is possible with comparable results.

Materials and Methods

Samples and reagents

- Different highly volatile hydrocarbons (e.g., hexane, petroleum ether, 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 (0.05–25 mg/L) (Analytik Jena, Art.-No.: 402-889.076)

Sample preparation

The samples are highly volatile, have a low viscosity, and contain TN in the ultra-trace level. This made a pretreatment step redundant. The samples were analyzed directly. In addition, three samples were spiked with approximately 250 µg/L TN standard for quality control.

Calibration

Prior to the actual determination, the system was calibrated using nitrogen standard solutions based on pyridine (N) in isooctane. Figure 1 depicts a typical calibration curve and the performance parameters for ultra-trace applications.

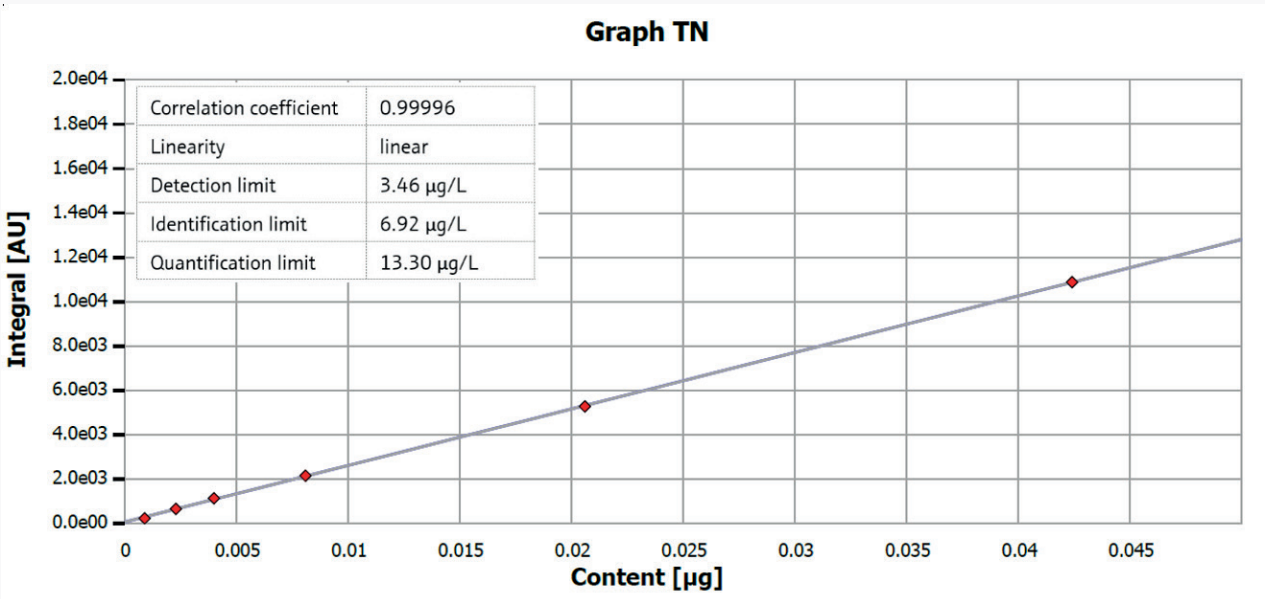

Figure 1: Calibration curve and statistics for the determination of ultra-trace concentrations of TN (80 µL, acc. UOP 981)

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 a cooled MMS-T autosampler set to 15 °C to prevent vaporization of the samples while ensuring a maximum sample throughput.

The analyses have been run in vertical operation mode. The cooled samples were dosed directly into the evaporation zone of the quartz glass combustion tube by aid of a cooled syringe. This process took place fully automatically by means of the MMS-T. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1,050 °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, if present, 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 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 following table summarizes the method parameter settings for the combustion process. As specified in the UOP 981 norm, an injection volume of 80 µL was used. However, measurements with 40 µL injection volume were also performed for comparison.

Table 1: Process parameters multi EA 5100

Parameter	Specification
Operation mode	Vertical
Furnace temperature	1,050° C
2nd combustion	60 s
Ar flow (1st phase)	100 mL/min
O_2 main flow	200 mL/min
O_2 flow (2nd phase)	100 mL/min
Draw up	2 µL/s
Injection volume	40 µL or 80 µL
Injection	0.3 µL/s

Evaluation parameters

The following table summarizes the method parameter settings for the detection.

Table 2: Detection parameters CLD

Parameter	Specification
Max. integration time	600 s
Start	0.5 cts
Stop	0.5 cts
Stability	7

Results and Discussion

Table 3 shows the results for volatile hydrocarbons. TN concentrations ranged from 9 to 153 µg/L and were thus in the ultra-trace range. For quality control, three samples were spiked with approximately 250 µg/L TN standard and the recoveries were determined. These were 95–100%, indicating the accuracy of the analyses. The UOP 981 standard specifies an injection volume of 80 µL. For comparison, the standard was also measured with 40 µL injection volume. The result shows that on the multi EA 5100, an injection volume of 40 µL is sufficient to obtain the same results as with an injection volume of 80 µL. This allows for a shorter measurement time and thus a higher sample throughput to be achieved.

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

Sample	Volume [µL]	TN ± SD [µg/L]	Spike recovery [%]
n-hexane	80	34 ± 2	n.a.
n-hexane + 253 µg/L TN standard	80	240 ± 12	95
Petroleum ether boiling range 30–50 °C	80	9 ± 7	n.a.
Petroleum ether boiling range 30–50 °C + 295 µg/L TN standard	80	296 ± 7	100
Light naphtha	80	153 ± 14	n.a.
257 µg/L TN standard in isooctane	80	271 ± 2	105
257 µg/L TN standard in isooctane	40	257 ± 6	100

The following figures show typical measurement curves of the individual samples and standards. The TN concentrations measured for the unspiked samples are close to the detection limit of the analyis technique (10 µg/L N). This is characteristic for ultra-pure hydrocarbons. The petroleum ether sample, with a gained concentration value of 9 µg/L, is even below the limit of detection, which is also reflected by the deviation of the replicate analysis. This sample can be presumed as nitrogen-free.

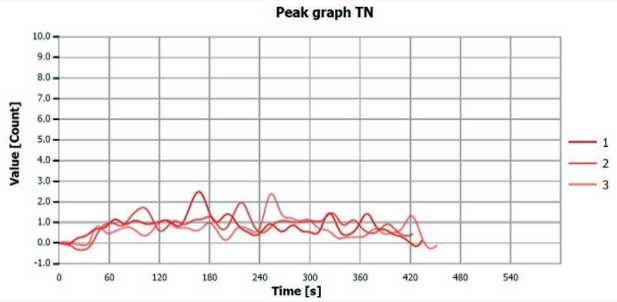

Figure 2: Measuring curve of "hexane"

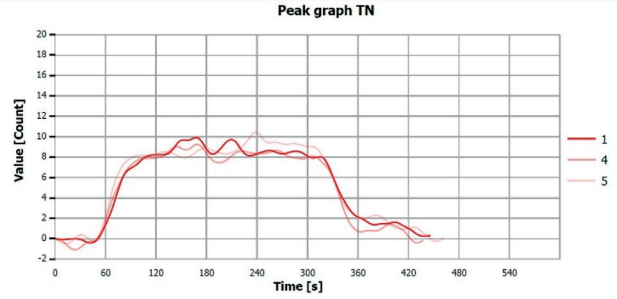

Figure 3: Measuring curve of "hexane with 253 µg/L N standard"

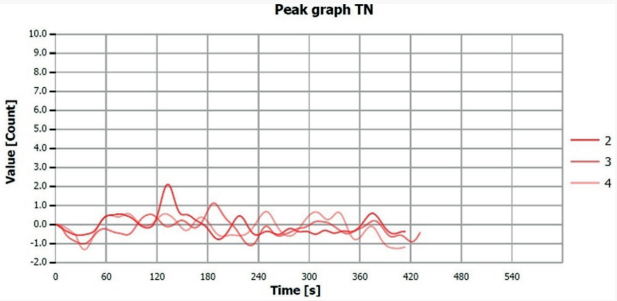

Figure 4: Measuring curve of "petroleum ether boiling range 30–50 °C"

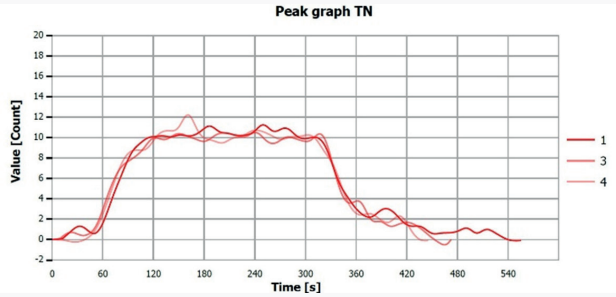

Figure 5: Measuring curve of "petroleum ether boiling range 30–50 °C with 295 µg/L N standard"

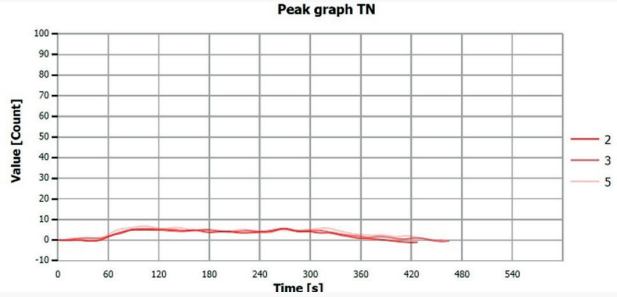

Figure 6: Measuring curve of "light naphtha"

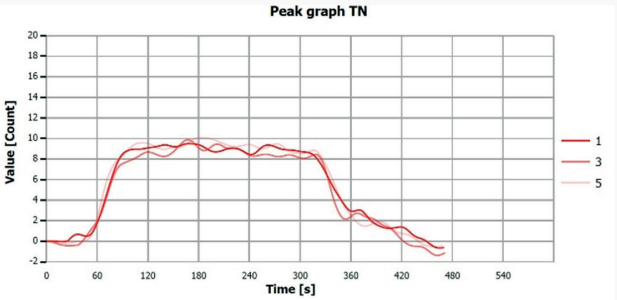

Figure 7: Measuring curve of "standard 257 µg/L N" with 80 µL injection volume

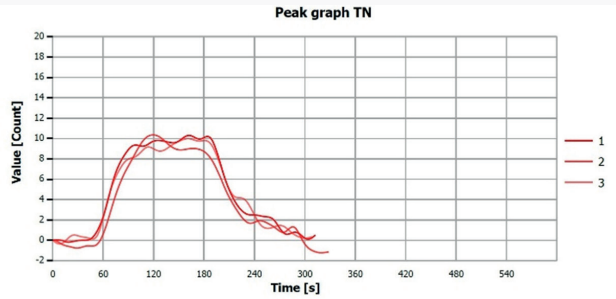

Figure 8: Measuring curve of "standard 257 µg/L N" with 40 µL injection volume

Conclusion

The multi EA 5100 N is very well suited for measuring ultra-trace levels of nitrogen in highly volatile hydrocarbons (e.g., petroleum ether, short-chain n-alkanes, or light naphtha). The temperature-controlled autosampler prevents evaporation of the highly volatile samples and thus guarantees stable and reproducible measuring conditions even at high sample throughput. Optimal sample combustion and the efficient Auto-Protection system enable excellent reproducibility, regardless of the TN concentration and the composition of the analyzed sample. The chemiluminescence detector with its unique HiPerSens technology and the highly efficient reaction gas drying enable a detection limit as low as 10 µg/L N. Due to the very sensitive and stable detector, an injection volume of 40 µL is sufficient on the multi EA 5100 to meet the requirements of UOP 981. This results in a shorter measuring time and thus a higher sample throughput compared to an analysis with the 80 µL injection volume recommended in the norm. The multi EA 5100 can easily be extended for the analysis of other matrix types such as gases or solids by adding one of the matrix-optimized sample supply systems. Just as easily, another detection module can be added for the determination of sulfur, carbon, or chlorine contents.

Figure 9: multi EA 5100

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