Challenge
Analysis of trace concentrations of total sulfur (TS) in highly volatile hydrocarbons.

Solution
Fast, sensitive, and reliable analysis in vertical combustion mode with HiPerSens UV fluorescence detection using a cooled sampler according to UOP 987 method A.

Analysis of Low Trace Sulfur in Highly Volatile Liquid Hydrocarbons by Oxidative Combustion and UV Fluorescence According to UOP 987 Method A

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 end 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 concentrations. Petrochemistry is another area in which highly volatile hydrocarbons, e.g., light naphtha, play a role, but here the sulfur contents to be analyzed vary widely.

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 987 method A 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 such a demanding task. By combining high-temperature combustion, a high-performance reaction gas dryer, and the highly sensitive HiPerSens detection, it enables the determination of ultra-trace sulfur contents, as low as 5 µg/L. In addition, a temperature-controlled autosampler MMS-T is used, which can be used for both cooled and heated sample supply.

In the UOP 987 method A, an injection volume of 80 µL is recommended to achieve the necessary sensitivity. However, due to the very sensitive and stable UV fluorescence 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.

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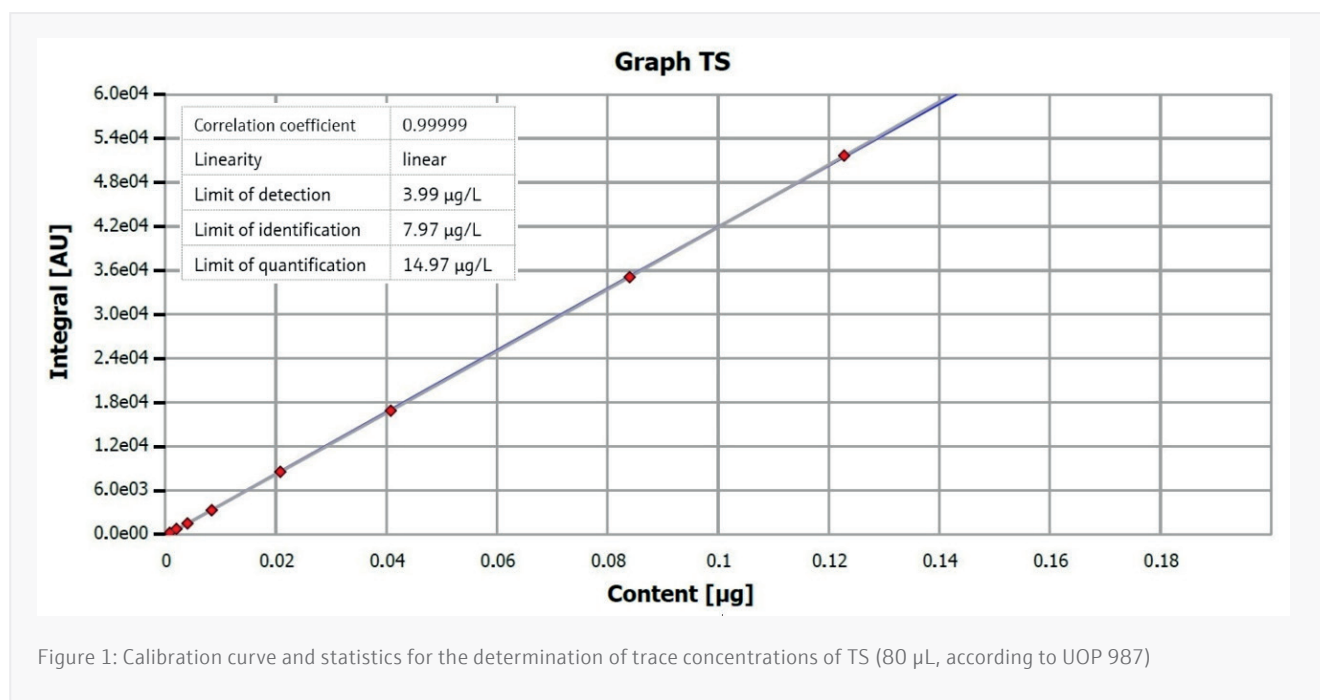
Materials and Methods

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)
- Dibenzothiophene ($C_{12}H_8S$), GR for synthesis (Merck Art.-No.: 8.20409.0025)
- Extended calibration standard kit sulfur (0.05–10 mg/L) (Analytik Jena, Art.-No.: 402-889.061)

Sample preparation

The samples are highly volatile, have a low viscosity, and contain TS 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 TS standard for quality control.

Calibration

Prior to the actual determination, the system was calibrated using sulfur standard solutions based on dibenzothiophene (S) 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 trace concentrations of TS (80 µL, according to UOP 987)

Instrumentation

The measurements were performed using a multi EA 5100 elemental analyzer, equipped with HiPerSens UV fluorescence detection (UVFD) for the determination of sulfur. Sample introduction was carried out fully automatically by a cooled MMS-T autosampler set to 15 ℃, 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 ℃. 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, if present, 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 SO_2 into the UVFD, after a sufficient drying of the reaction gases. The multi EA 5100 enables a detection limit of as low as 5 µg/L absolute.

Method parameters

The following table summarizes the method parameter settings for the combustion process. As specified in the UOP 987 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 ℃
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 UVFD

Parameter	Specification
Max. integration time	600 s
Start	0.2 cts
Stop	0.2 cts
Stability	7

Results and Discussion

Table 3 shows the results for various volatile hydrocarbons. TS concentrations ranged from 10 to 344 µg/L and were thus in the ultra-trace range. As expected, the light naphtha had a much higher sulfur concentration of 174 mg/L, which is typical for such matrix. For quality control, the three samples were spiked with approximately 262 µg/L TS standard and the recoveries were determined. These were 97–107%, indicating the accuracy of the analyses. The UOP 987 method A specifies an injection volume of 80 µL. For comparison, a sample (petroleum ether boiling range 40–60 ℃) and a standard were also measured with 40 µL injection volume. The results show that on the multi EA 5100, an injection volume of 40 µL is sufficient to obtain the same results as with 80 µL, with the advantage of a remarkably shorter analysis time. This allows a higher sample throughput.

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

Sample	Volume [µL]	TS ± SD [µg/L]	Spike recovery [%]
n-hexane	80	10 ± 0.5	n.a.
n-hexane + 255 µg/L TS standard	80	255 ± 4	100
Petroleum ether boiling range 30–50 ℃	80	344 ± 4	n.a.
Petroleum ether boiling range 30–50 ℃ + 260 µg/L TS standard	80	605 ± 3	97
Petroleum ether boiling range 40–60 ℃	80	24 ± 0.6	n.a.
Petroleum ether boiling range 40–60 ℃ + 242 µg/L TS standard	80	256 ± 3	106
Petroleum ether boiling range 40–60 ℃ + 242 µg/L TS standard	40	250 ± 4	103
Light naphtha	80	174 ± 1 mg/L	n.a.
262 µg/L TS standard in isooctane	80	280 ± 1	107
262 µg/L TS standard in isooctane	40	279 ± 0.5	106

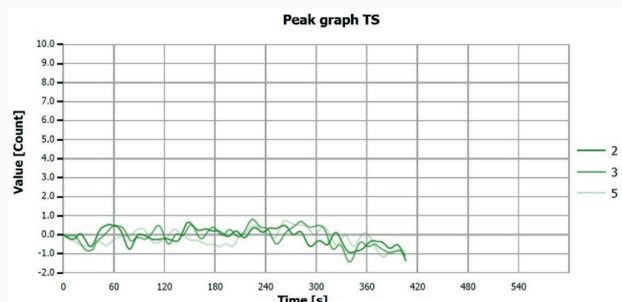The following figures show typical measurement curves of the individual samples and standards.

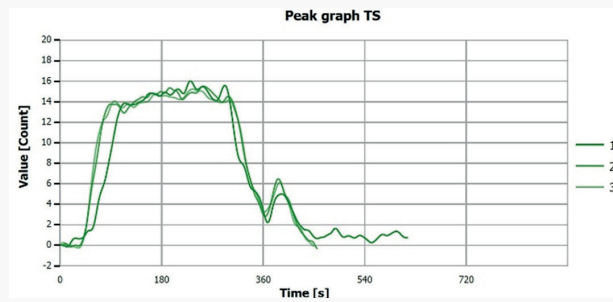Figure 2: Measuring curve of "hexane"

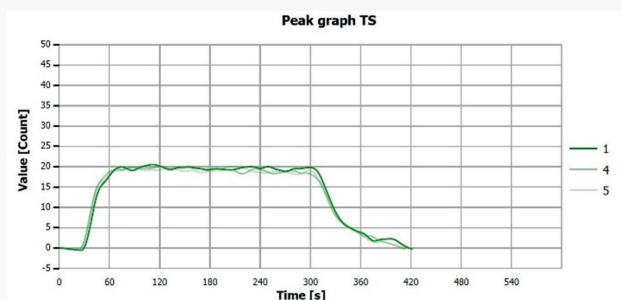Figure 3: Measuring curve of "hexane with 255 µg/L TS standard"

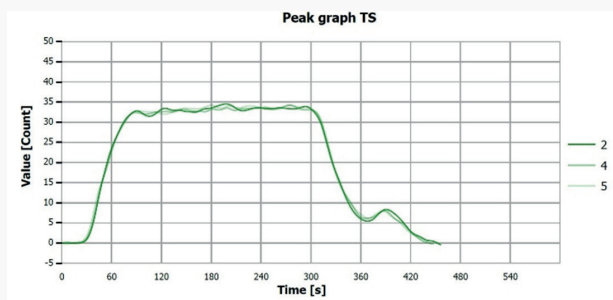Figure 4: Measuring curve of "petroleum ether boiling range 30–50 °C"

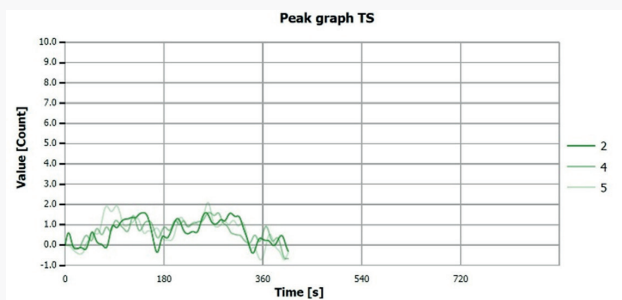Figure 5: Measuring curve of "petroleum ether boiling range 30–50 °C with 260 µg/L TS standard"

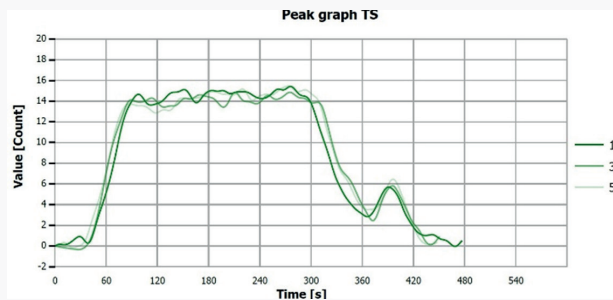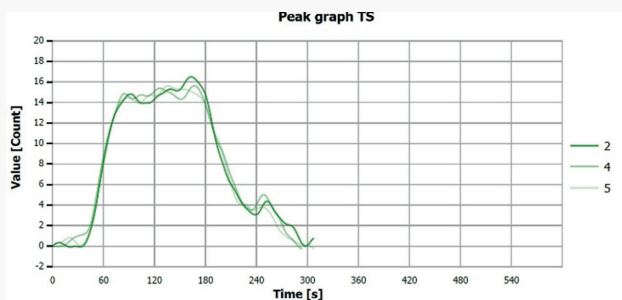Figure 6: Measuring curve of "petroleum ether boiling range 40–60 °C" with 80 µL injection volume

Figure 7: Measuring curve of "petroleum ether boiling range 40–60 °C with 242 µg/L TS standard" with 80 µL injection volume

Figure 8: Measuring curve of "petroleum ether boiling range 40–60 °C with 242 µg/L TS standard" with 40 µL injection volume
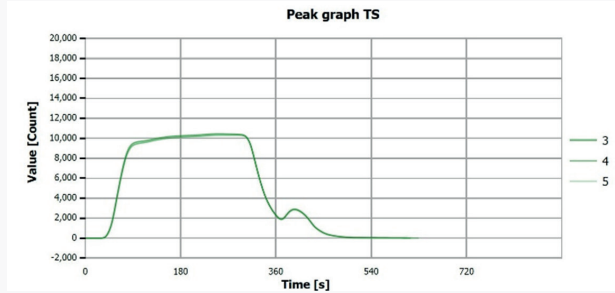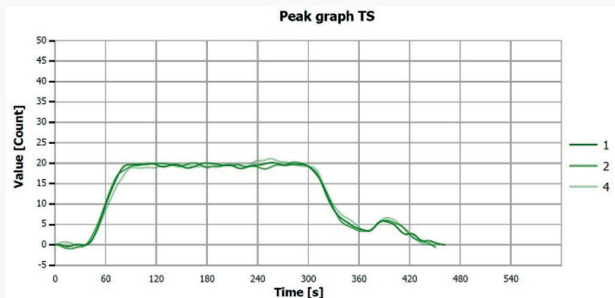
Figure 9: Measuring curve of "light naphtha"

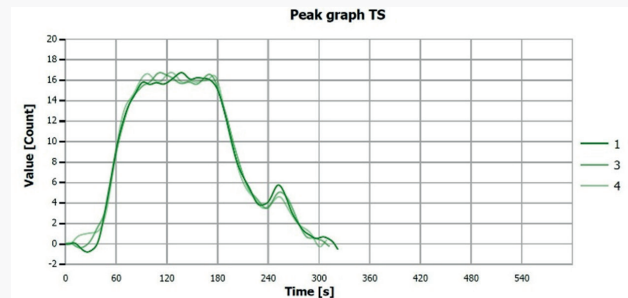Figure 10: Measuring curve of "standard 262 µg/L TS" with 80 µL injection volume

Figure 11: Measuring curve of "standard 262 µg/L TS" with 40 µL injection volume

Conclusion

The multi EA 5100 is very well suited for measuring trace levels of sulfur 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 results even at high sample throughput. Optimal sample combustion and the efficient Auto-Protection system enable excellent reproducibility, regardless of the TS concentration and the composition of the analyzed sample. The UV fluorescence detector with its unique HiPerSens technology and the highly efficient reaction gas drying enable a detection limit of only 5 µg/L S. 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 the UOP 987 norm. 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 easy, another detection module can be added for the determination of nitrogen, carbon, or chlorine contents.
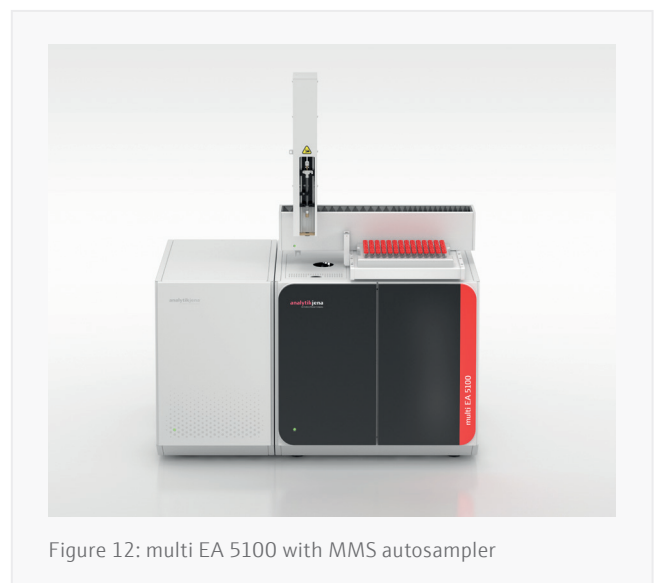

Figure 12: multi EA 5100 with MMS autosampler