Challenge

Fast, sensitive and reliable analysis of sulfur 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 UV fluorescence detection for concentration-independent TS determination.

Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by UV Fluorescence according to ASTM D7183

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 negatively affect the production process and the quality of the final products even if they occur only in the smallest traces.

Especially sulfur impurities are known to affect the performance and service life of the used catalyst materials (poisoning). The formation of unwanted by-products and a decreased product quality are additional problems. To prevent that, the TS content has to be kept as low as possible, preferably below 100 µg/L, making a close sulfur monitoring essential in process and quality control labs. Hence, high-temperature combustion in combination with UV fluorescence detection is the most effective method.

The multi EA 5100 is an analysis system specifically optimized for this challenging task. Combining high-temperature combustion, a high-performance reaction gas dryer, and sensitive HiPerSens detection, it allows for the determination of sulfur traces as low as 5 µg/L.

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Materials and Methods

Samples and Reagents

Different aliphatic and aromatic hydrocarbons and their mixes (e.g., toluene, isooctane, etc.) have been analyzed.

- 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 light volatile, have a low viscosity, and contain TS 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 sulfur standard solutions based on dibenzothiophene (S) in isooctane. Figure 1 depicts a typical calibration curve and the performance parameters for ultra-trace applications.
The calibration was checked with different concentrated standards.

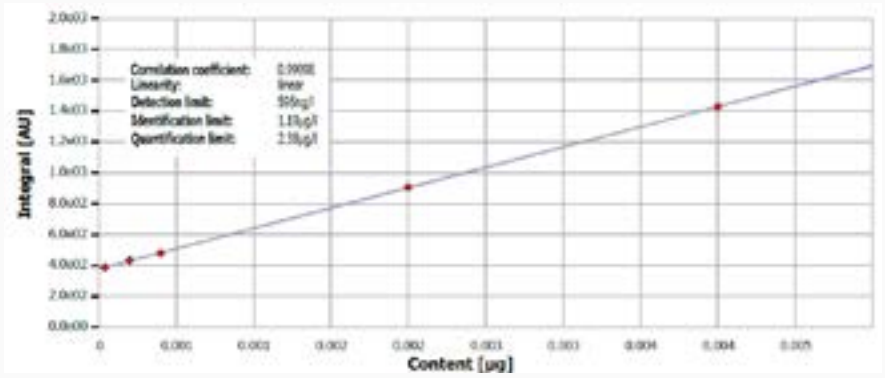

Figure 1: Example of a TS calibration for the ultra-trace range, curve including statistics

Instrumentation

The measurements were performed using a multi EA 5100, equipped with HiPerSens UV fluorescence detection for the determination of sulfur. 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 in liquids mode. 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, controls 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 (particle and aerosol trap) in combination with a high-performance reaction gas drying, guarantees highest operational safety and a complete transfer of the formed SO_2 into the UVFD without adsorption or condensation losses. The multi EA 5100 enables a detection limit as low as 5 µg/L S.

Figure 2: multi EA 5100 with MMS in vertical mode

Method Parameters

The standard method ASTM D7183 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
Furnace 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 UVFD

Parameter	Specification
Max. integration time	240 s
Start	1.0 ppb
Stop	1.1 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 sulfur determination in different refinery samples and standards

Measurement	TS	SD
Isooctane	24.4 µg/L	± 0.12 µg/L
Xylene (mix of isomers)	228 µg/L	± 4.87 µg/L
BTX mix	155 µg/kg	± 12.4 µg/kg
Toluene	19.0 µg/L	± 2.24 µg/L
TS Standard (c = 500 µg/L)	501 µg/L	± 8.73 µg/L
TS Standard (c = 50 µg/L)	51.0 µg/L	± 1.85 µg/L

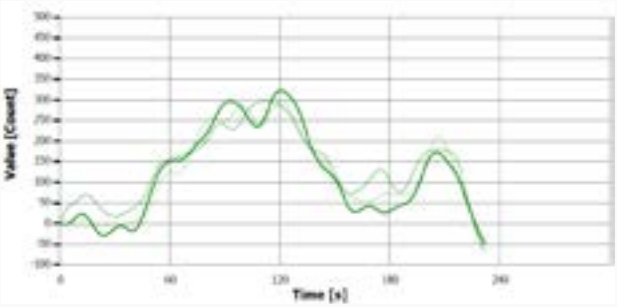

Figure 3: Analysis curve of "BTX mix"

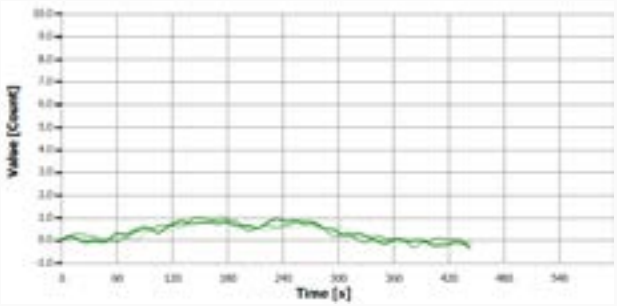

Figure 4: Analysis curve of "Isooctane"

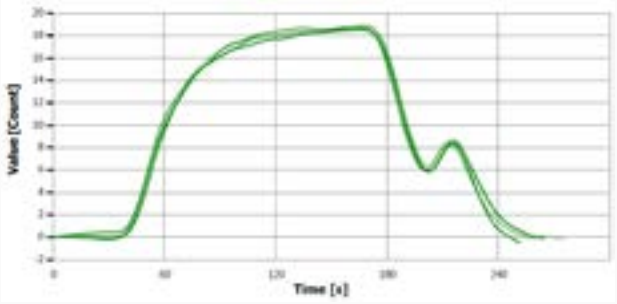

Figure 5: Analysis curve of "TS standard 500 µg/L"

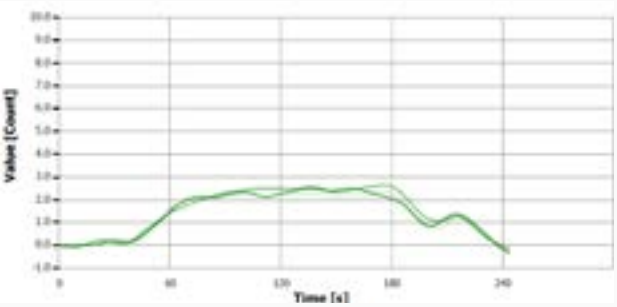

Figure 6: Analysis curve of "TS standard 50 µg/L"

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 and time-consuming strategies like trap and release are redundant. The analysis results received and their reproducibility show the high quality of the sample combustion. The proper performance of the analysis system was confirmed by analyzing standard materials with known sulfur contents (see Table 3).

Conclusion

The multi EA 5100 is extremely well suited for the measurement of ultra-trace sulfur concentrations in versatile aliphatic and aromatic hydrocarbons and their mixes (e.g., naphtha, toluene, xylene, acetone). The detector, with its HiPerSens technology, achieves a measuring range of up to 10,000 mg/L starting at a limit of detection as low as 5 µg/L of sulfur.

The optimal sample digestion and the efficient Auto-Protection system, including a high-capacity dryer, enable excellent reproducibility, independent of the TS concentration or digestion characteristics and composition of the sample matrix analyzed. A high sample throughput is easily achieved by using the MMS liquids sampler. For lower throughput demands an autoinjector can be used alternatively. If required, the analyzer can be extended easily to include the analysis of solids and gases by adding a matrix-optimized sampling system resp. the determination of nitrogen, carbon or chlorine contents by adding one of the optional detection modules.

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