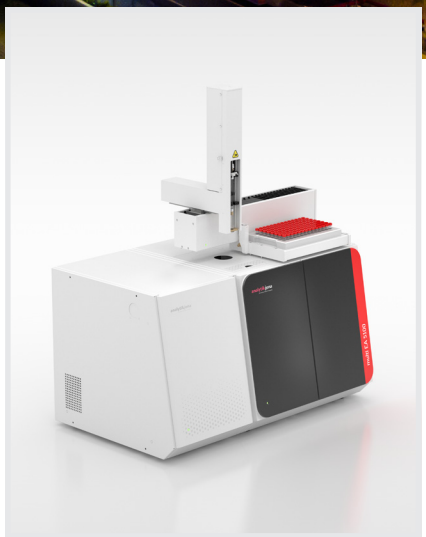

Ultra-sensitive High-throughput TS Analysis in Light Hydrocarbons, Spark Ignition Engine Fuel, and Diesel Engine Fuel by UV Fluorescence according to ASTM D5453 – Vertical Approach

Challenge

Reliable and fast analysis of widely varying sulfur contents in fuels and related refinery matrices. Sensitive, ultra-trace analysis, sample pre-treatment-for higher contents, different matrix-related methods required.

Solution

Vertical combustion with double furnace technology, HiPerSens UVFD for concentration-independent TS determination.

Introduction

The determination of total sulfur (TS) by means of combustion-coupled UV-fluorescence detection is an integral part of the daily routine in the process and quality control of refineries, derived fuels production, and many other labs dealing with control and legal limit checking of fuels and related matrices. No matter if analyzing process streams, additives, or ultra-pure end products, it is crucial to gain information about the sulfur content in the shortest possible time. This is to avoid undesirable effects such as catalyst poisoning, low product quality, or exceeding legal limits. The fact that fewer and fewer lab technicians are analyzing an ever-increasing number of samples, especially when it comes to trace and ultra-trace applications, leads to an enormous pressure on performance in terms of reliability of the results and the processing time. Delayed or incorrect results significantly influence the company's performance and profitability. Where time is money, a technique ensuring the fastest possible yet reliable analyses is a crucial precondition.

The vertical approach, with direct injection into the combustion tube, offers a more than twice increased throughput speed compared to the horizontal mode with boat inlet for sample supply. Besides this, the mode is characterized by minimum process blank and generation of significant peaks even in ultra-trace analysis. All this makes the vertical operation very attractive. Nevertheless there

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are limitations, it is only applicable for sample matrices with boiling points up to 400 °C and viscosities below 10 cSt. The multi EA 5100 with its double furnace technology allows for efficient combustion for any type of matrix while optimizing the analysis time.

Materials and Methods

Samples and Reagents

Different fuels and related samples (diesel, gasoline, kerosene, HEL, 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)
- Standard kits for calibration and test (Analytik Jena, Art.-No.: 402-889.164, 402-889.167, 402-889.061)

Sample Preparation

All samples had low viscosities (< 10 cSt) and boiling intervals below 400 °C. A pretreatment step was not necessary, as they were perfectly suited for the direct injection by means of a µL-syringe. Due to its very small process blank and sharp peak modulation, the vertical operation is especially recommended for analysis of sulfur contents in the trace and ultra-trace range.

Calibration

Liquid calibration standards based on dibenzothiophene (S) in isooctane were used to calibrate the analysis system in a wide concentration range. Matrix-related calibration strategies were not required as the combustion is optimized and interfering components are eliminated before detection. The calibration was checked with different concentrated standards.

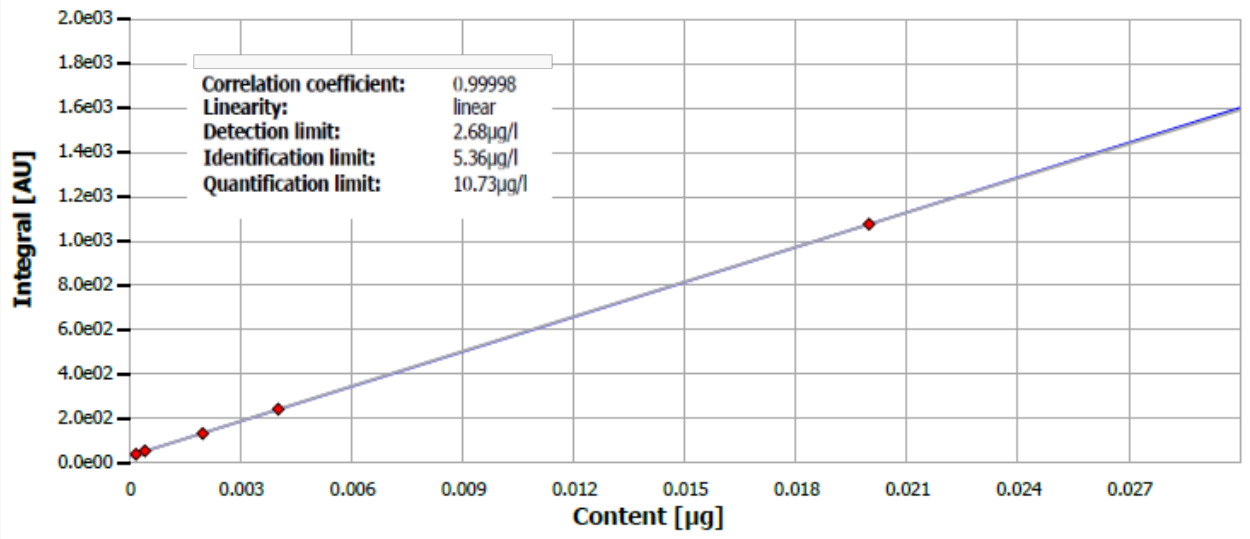

Figure 1: Example calibration for TS ultra-trace range, curve including statistics

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 using the MMS multi matrix sampler equipped with liquids kit to ensure a high sample throughput.

The analyses have been run in vertical operation mode, which is especially suited for precise and fast determination of trace contents. Thanks to an extremely low process blank and the sharp modulation of the generated peaks, even quantities in the lowest ppb-range deliver significant peaks.

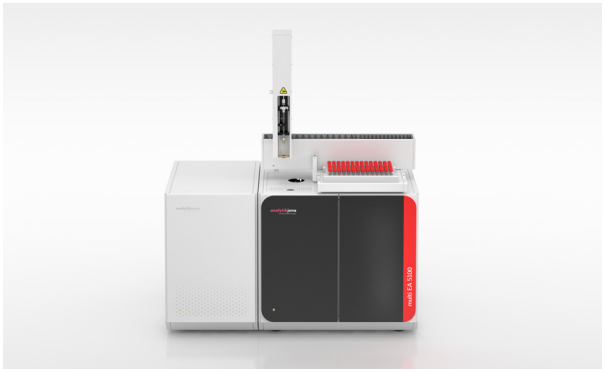

Figure 2: multi EA 5100 with MMS in vertical operation mode

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. 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 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 analysis. The implemented Auto-Protection System guarantees highest operational safety, including a particle and aerosol trap, and a complete transfer of the formed SO_2 into the ultraviolet fluorescence detector (UVFD) after a sufficient drying of the reaction gases. The multi EA 5100 enables a detection limit of as low as 5 µg/L S.

Method Parameters

The method *ASTM D5453-V* from the method library of multi EA 5100 was used for all measurements. It is suitable for analysis of liquid samples with viscosities ≤10 cSt and boiling points ≤ 400 °C. For any other sample, e.g., liquids that are highly viscous, contain particles, or have boiling points above 400 °C, the horizontal operation mode should be applied to ensure best analysis results at minimum maintenance effort. The following table summarizes the parameter settings for the vertical combustion process with double furnace.

Table 1: Process parameters multi EA 5100 in vertical mode with quartz pyrolyzer

Parameter	Specification
Furnace temperature	1,050 °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

The standard method settings applied are summarized in the following table.

Table 2: Detection parameters UVFD – vertical mode

Parameter	Specification
Max. integration time	240 s
Start	1.0 ppb
Stop	1.1 ppb
Stability	7

Results and Discussion

The analyzed samples are a representative spectrum of fuels, their blends and other related process streams. 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.

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

Measurement	TS	SD
Raffinate	0.08 mg/L	± 0.01 mg/L
C8 hydrocarbons	0.13 mg/L	± 0.01 mg/L
Reformer	0.19 mg/L	± 0.02 mg/L
Platformer	0.40 mg/L	< 0.01 mg/L
Heavy gasoline	0.60 mg/L	< 0.01 mg/L
Light gasoline	0.96 mg/L	± 0.02 mg/L
Gasoline-1	1.92 mg/L	± 0.02 mg/L
Kerosene	2.32 mg/L	± 0.03 mg/L
Diesel oil (dark)	3.56 mg/L	± 0.03 mg/L
Diesel (car fuel)	4.09 mg/L	± 0.02 mg/L
Gasoline-2	5.50 mg/L	± 0.02 mg/L
Jet A	6.17 mg/L	± 0.03 mg/L
Diesel (marine fuel)	10.2 mg/L	± 0.30 mg/L
Heating oil extra light (HEL)	94.2 mg/L	± 0.10 mg/L
TS Standard (c = 0.10 mg/L)	0.10 mg/L	< 0.01 mg/L
TS Standard (c = 1.00 mg/L)	0.99 mg/L	< 0.01 mg/L
TS Standard (c = 10.0 mg/L)	10.0 mg/L	< 0.01 mg/L
TS Standard (c = 100 mg/L)	100 mg/L	± 0.61 mg/L

Figures 3–7 show typical measuring curves for selected samples resp. standards.

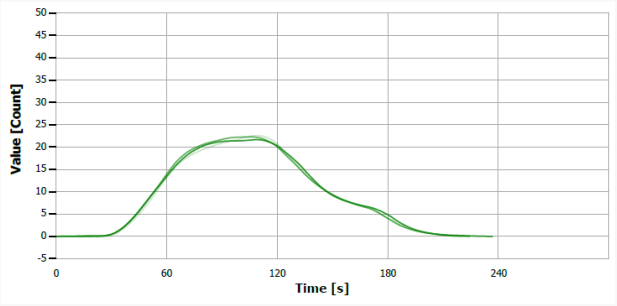

Figure 3: Analysis curve of "gasoline-1"

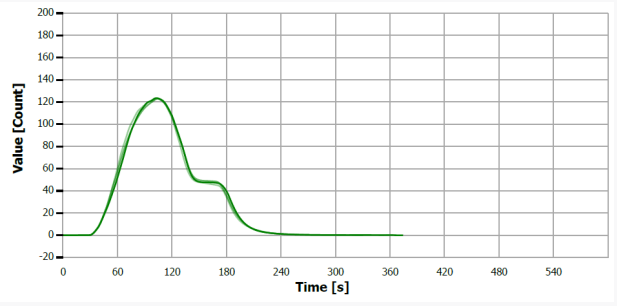

Figure 4: Analysis curve of "diesel (marine fuel)"

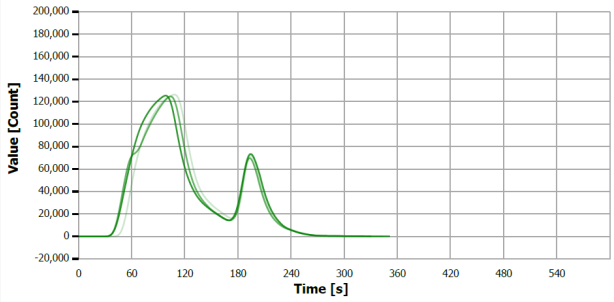

Figure 5: Analysis curve of "heating oil (HEL)"

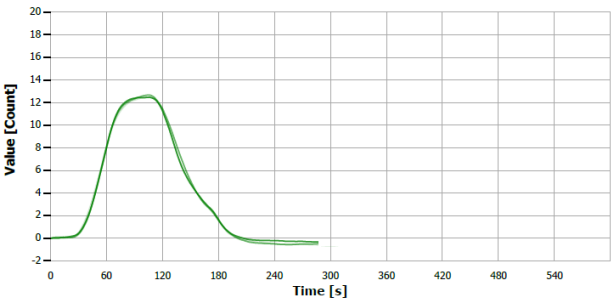

Figure 6: Analysis curve of "TS standard 1.00 mg/L"

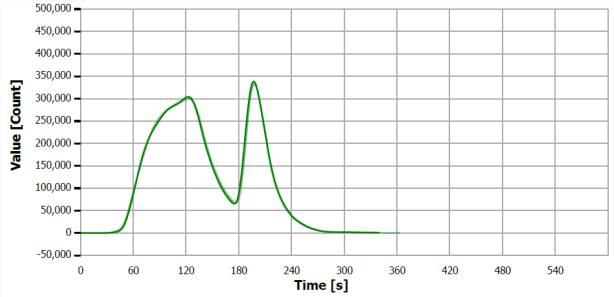

Figure 7: Analysis curve of "TS standard 100 mg/L"

Due to the matrix-optimized combustion in general a two- to threefold determination is sufficient for high element contents to achieve reliable results below 3% RSD. This remarkably affects the sample processing time and allows for a higher sample throughput. The analysis results received and their reproducibility prove the performance of the digestion process. The overall performance of the analysis system was validated by analyzing standard materials with known sulfur contents, results are given in Table 3.

Conclusion

The multi EA 5100 together with the MMS in liquids mode provides a fast and reliable solution for the precise determination of widely varying sulfur contents. Thanks to the double furnace technology best results can be achieved for any matrix in the shortest possible time, independent of its sulfur content and combustion properties. The furnace mode can easily be adapted to generate best analysis conditions for the special needs of each sample matrix and concentration level. Change-over from vertical to horizontal combustion mode and vice versa takes less than 10 minutes. This simplifies daily routine work and helps to remarkably increase sample throughput while reducing operation and maintenance effort.

Thanks to the unique HiPerSens technology, a measuring range of up to 10,000 mg/L starting at a limit of detection as low as 5 µg/L of sulfur can be easily achieved. The optimal sample digestion and the efficient Auto-Protection System, including a high capacity membrane dryer, enable excellent reproducibility. A high sample throughput is easily achieved using the MMS autosampler with 112 position liquid trays. For lower throughput demands an autoinjector AI or AI-EA can be used alternatively.

If needed, the analysis system can be extended for the analysis of other matrix types like gases and solids, or the determination of additional elements and parameters (e.g., nitrogen, chlorine, carbon, TOC, AOX, EOX) by just adding the suited sampling or detection system.

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