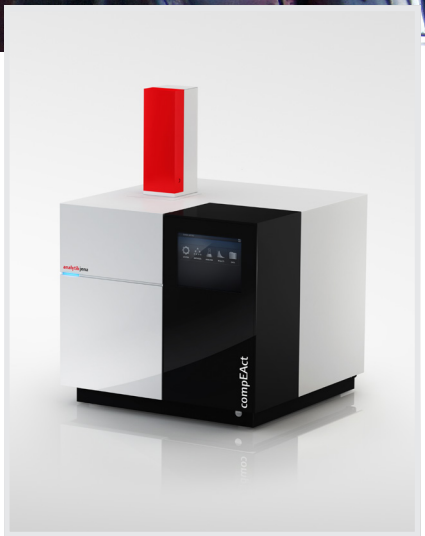

Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel and Diesel Engine Fuel by Ultraviolet Fluorescence according to ASTM D5453

Challenge

Fast, sensitive and reliable analysis of widely varying sulfur contents in different types of liquid fuels, combustibles and related matrices.

Solution

Optimized vertical combustion combined with HiPerSens UV fluorescence detection 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 feeds, process streams, additives, or ultrapure end products, it is a must to have information about the sulfur content in the shortest possible time. This is to avoid undesirable effects such as catalyst poisoning, corrosion of installation parts, low product quality, or exceeding legal limits. Therefore the sulfur content of many different samples of the production process has to be determined in close intervals. This and the fact that fewer and fewer lab technicians are analyzing an ever-increasing number of samples, some of which are challenging, leads to an enormous pressure on performance in terms of time and reliability of the measurement values. Delayed or incorrect results significantly influence performance and profitability of the laboratory. Where time is money, a technique which ensures fast and reliable analyses independent of matrix effects and operator skills is urgently needed.

The compEAct S is an analysis system which has been specifically optimized for the fast and trouble-free determination of sulfur contents in an impressively wide

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concentration range. It allows the determination of sulfur at concentrations ranging from 5 µg/l up to 10,000 mg/l with one and the same device and the same analysis method.

Materials and Methods

Samples and Reagents

- Different fuels and related samples (diesel, gasoline, kerosene, 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 kit for calibration and test of compEAct S (Analytik Jena, Art.-No.: 402-889.309)

Sample Preparation

The samples were analyzed directly. No sample preparation was required.

Calibration

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

calibration range	**1**
measurement range [µg]	0 - 0.2
measurement range [AU]	91 - 79,514
k_0	-40.38
k_1	397,642.5
coefficient of determination, R^2	0.99999
calculation volume, V_{Cal} [µl]	20
calculation density, ρ_{Cal} [-]	-
detection limit [µg/l]	20.7
quantification limit [µg/l]	80.55
method standard deviation [µg/l]	13.57
method coefficient of variation [%]	0.49
linearity	linear

Fig.1: TS calibration for ultra-trace range

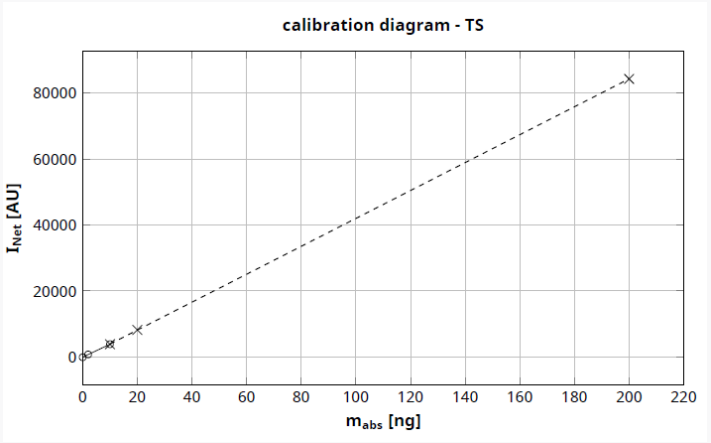

Fig.2: Wide-range calibration curve of the HiPerSens UVF detector

The calibration was checked with different concentrated standards.

Instrumentation

The measurements were performed using a compEAct S, equipped with HiPerSens UV fluorescence detection for the determination of sulfur. 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 SO_2 into the UVFD after a sufficient drying of the reaction gases. The compEAct S enables a detection limit of as low as 5 µg/l S.

Method Parameters

The standard method ASTM D5453 from the method library of compEAct's EAvolution software was used for all measurements. It is suitable for direct analysis of liquid samples with viscosities ≤ 10 cSt (syringeable liquids) and boiling points ≤ 400 °C. For liquids with slightly increased viscosity values, but still boiling ≤ 400 °C, a sufficient dilution (e.g., with xylene) can be applied to enable syringeability and analysis. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters compEAct S

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 UVFD

Parameter	Specification
Max. integration time	300 s
Start	1 cts
Stop	1 cts

Results and Discussion

The analyzed samples are a representative spectrum of crude oil-based and bio-based fuels and blends of both. 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 TS analysis

Measurement	TS	SD
Raffinate	122 ppb	± 1.15 ppb
Naphtha (light)	632 ppb	± 3.27 ppb
Gasoline E 10	55.7 ppb	± 3.95 ppb
UL Diesel (car)	1.25 ppm	± 0.02 ppm
Diesel+7 % FAME	9.30 ppm	± 0.11 ppm
Bio-ethanol	195 ppb	± 6.13 ppb
Bio-based diesel (B-t-L)	144 ppb	< 0.01 ppb
Kerosene	9.90 ppm	± 0.03 ppm
Jet A	14.1 ppm	± 0.02 ppm
Ship diesel (yellow)	19.5 ppm	± 0.23 ppm
Heating oil extra light (HEL)	107 ppm	± 0.99 ppm
TS Standard (c = 145 ppm)	145 ppm	± 0.48 ppm
TS Standard (c = 14.5 ppm)	14.4 ppm	< 0.01 ppm
TS Standard (c = 1.45 ppm)	1.45 ppm	< 0.01 ppm
TS Standard (c = 145 ppb)	144 ppb	± 2.13 ppb

Figures 3–8 show typical measuring curves for selected samples resp. standards.

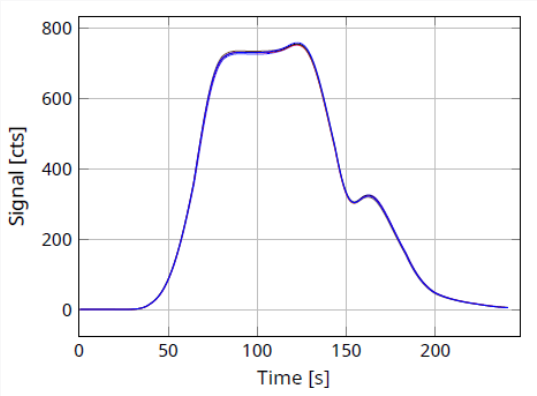

Fig. 3: TS analysis curve for sample "Jet A"

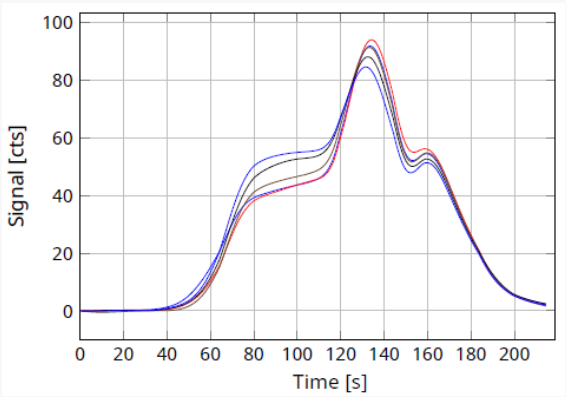

Fig. 4: TS analysis curve for sample "UL diesel"

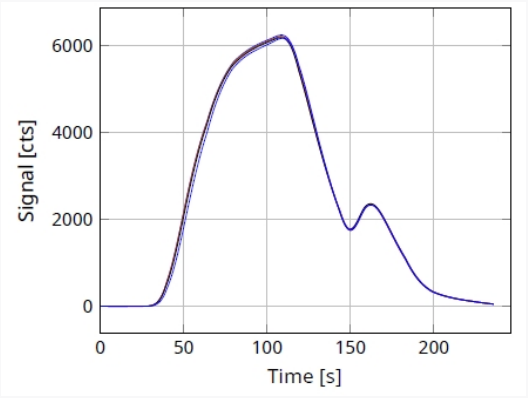

Fig. 5: TS analysis curve for sample "Heating oil - HEL"

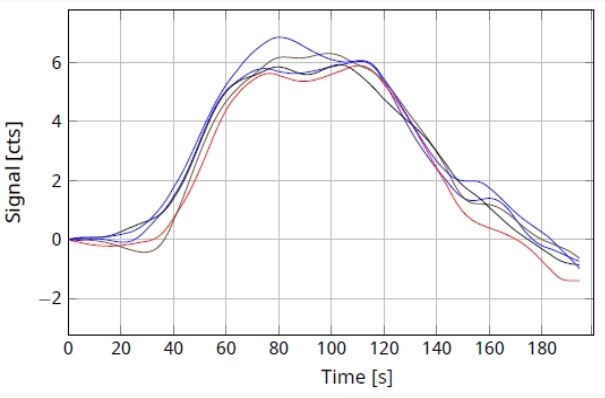

Fig. 6: TS analysis curve for sample "Raffinate"

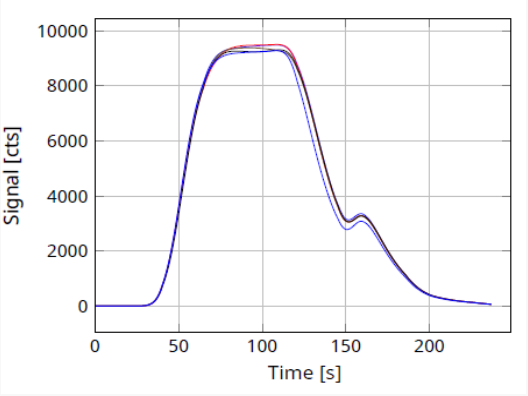

Fig. 7: TS analysis curve for TS standard "145 ppm S"

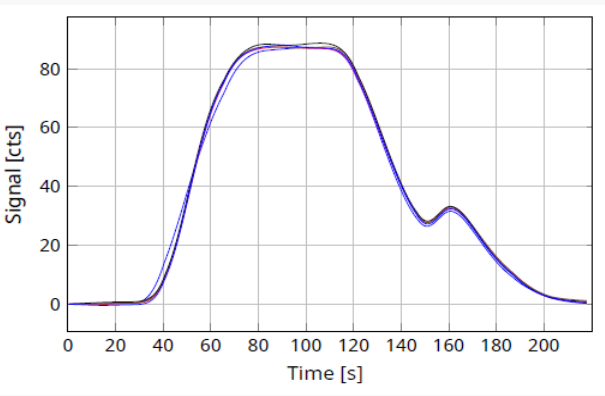

Fig. 8: TS analysis curve for TS standard "1.45 ppm S"

Due to the matrix-optimized combustion a threefold determination is generally sufficient to achieve results far below 3 % RSD. This remarkably affects the sample processing time and allows 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, the results are given in Table 3.

If desired, further time optimization can be achieved by decreasing the sample quantities for higher concentrated sample matrices. The same process and detection parameters can be applied.

Conclusion

Together with the LS 2 liquids sampler, the compEAct S provides a fast and reliable solution for the precise determination of widely varying sulfur contents in different fuels and related matrices from refinery applications in the daily routine. The system can handle the samples no matter if they are crude oil-based or generated from renewable energy sources (e.g., sugar, cellulose) or mixtures of both.

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 reached easily. The optimal sample digestion and the efficient Auto-Protection system, including a high capacity membrane dryer, enable excellent reproducibility, independent of the TS concentration or digestion characteristics and composition of the analyzed sample matrix. A high sample throughput is easily achieved by using the LS 2 liquids sampler. For lower throughput demands the LS 1 liquids sampler resp. the AI autoinjector can be used. If needed, the analysis system can be extended for the determination of TS in gaseous or liquefied pressurized fuels (e.g., CNG, LPG) by just adding the suited sampling system.

References

Groebel, A., "Productivity Boost in Sulfur (UVFD) Routine Analysis". PIN, 08/09 2017, page 8-9

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

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