Matrix-independent TS Determination in Light Hydrocarbons, Spark Ignition Engine Fuel, and Diesel Engine Fuel by UV Fluorescence according to ASTM D5453 – Horizontal Approach

Challenge

Fast, reliable analysis of refinery samples with varying sulfur contents and properties. Matrix robustness and quantitative combustion independent of the sample's combustion behavior.

Solution

Optimized horizontal combustion with double furnace technology and 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 feeds (e.g., crude oil), process streams (e.g., higher vacuum fractions) and residues (e.g., bottomers), or the end products (e.g., diesel), 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, corrosion of installation parts, low product quality, and exceeding legal limits. Therefore the sulfur content has to be determined in close intervals. Also the fact that fewer and fewer experienced lab technicians have to analyze an ever-increasing number of samples leads to high pressure on performance in terms of reliable results and fast processing time. In contrast to easily processed fuels, others are challenging and require an additional sample pretreatment, combustion in horizontal mode with boat inlet, and the adaptation of crucial process parameters. These tasks require time and experienced operators. The smallest mistake in method optimization will not only affect the quality of results, but also lead to remarkably increased maintenance effort and cost. Delayed or incorrect results significantly influence the company's performance and profitability. Where time is money, a technique ensuring fast and reliable analyses independent of matrix properties and operator skills is urgently needed.

The multi EA 5100 with its double furnace technology enables optimal conditions for any type of matrix. Soot formation, incomplete or uncontrolled combustion, and deflagration can be avoided easily using the horizontal mode with flame sensor technology.

Materials and Methods

Samples and Reagents

Different fuels and related samples (diesel, gasoline, heating oil, 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)
- Sulfur standard kits for calibration and test (Analytik Jena, Art.-No.: 402-889.164, 402-889.167, 402-889.061)

Sample Preparation

The samples were analyzed directly. Therefore the horizontal operation mode was used to enable a direct introduction without the necessity for a prior sample pretreatment step (e.g., dilution to decrease concentration and/or viscosity). This clearly saves time and cost while eliminating a major error source.

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.

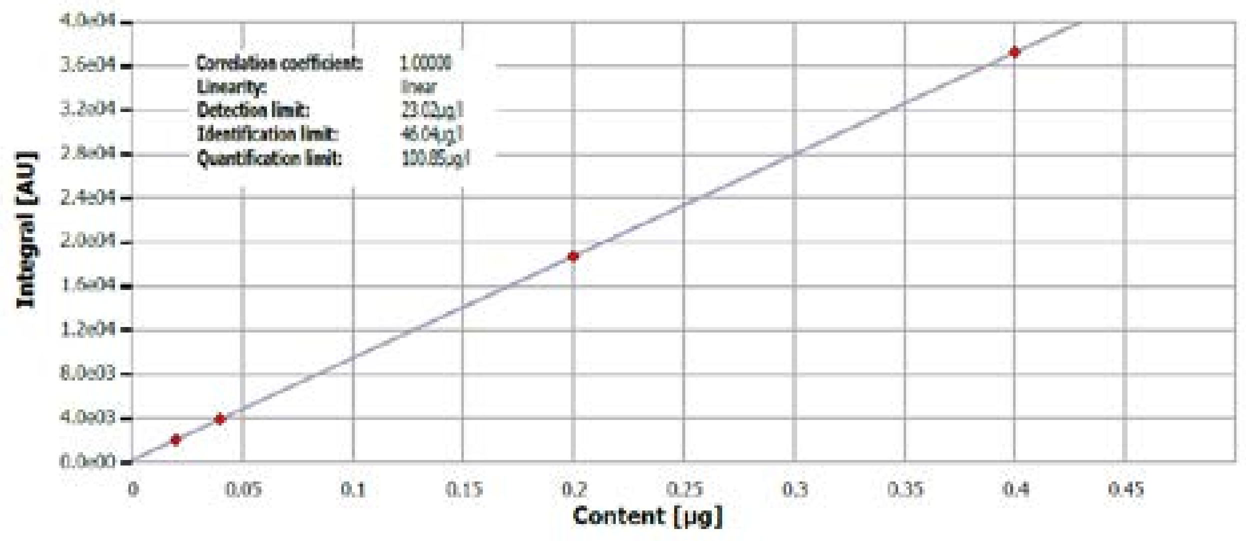

Figure 1: Example calibration for TS middle range, curve including statistics

Instrumentation

The measurements were performed using a horizontally configured 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 in combination with the ABD, an automatic boat drive equipped with the flame sensor technology. This ensures a high sample throughput and best analysis results, even for samples with higher viscosity or complex composition.

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

The analyses have been run in horizontal operation mode. Therefore the MMS in liquids mode was used to directly dose the samples into a quartz sample boat which was placed inside the automatic boat drive (ABD). After sample injection the ABD fully automatically transfers the loaded boat into the hot zone of the combustion tube.

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 and pyrolysis of the heavier sample components takes place in an inert gas stream. This is followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier, nonvolatile sample components resp. formed pyrolysis products are quantitatively oxidized in pure oxygen. This way the flame sensor technology ensures a uniform evaporation and quantitative combustion for any component of the sample matrix. Incomplete combustion, system contamination and thus caused low quality of analysis results (too low, scattering) is effectively prevented. This establishes the best conditions for analysis of any matrix type, even for untreated vacuum gas oil, distillation residues, engine oil or crude oil, independent of the introduced sample quantity. The horizontal operation mode is especially recommended for unknown samples, high element contents, vigorously reacting or inhomogeneous materials (residue, polymers, etc.). Still it is also suited for any other easy-to-process samples with lower element contents. 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 UVFD after a sufficient drying of the reaction gases. The multi EA 5100 enables the direct analysis of sulfur contents up to 10,000 mg/L.

Method Parameters

The method *ASTM D5453-H* from the method library of multi EA 5100 was used for all measurements. It is suitable for analysis of liquids, also for those with high viscosity, or boiling points above 400 °C. In this case only the horizontal mode can ensure reliable analysis results in the shortest possible time without increasing maintenance efforts. To enable a higher processing speed for samples which are too viscous for syringe inlet, the syringeability can be enabled by a sufficient dilution with a suitable solvent (e.g., xylene) or by using a wide-bore needle. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100 in horizontal mode with flame sensor technology

Parameter	Specification
Furnace temperature	1,050 °C
Cooling time (boat)	240 s
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Draw up	2 µL/s
Injection volume	40 µL
Injection	3 µL/s

Evaluation Parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 2: Detection parameters UVFD – horizontal mode

Parameter	Specification
Max. integration time	360 s
Start	1.0 ppb
Stop	1.1 ppb
Stability	7

Results and Discussion

The analyzed samples are a representative spectrum of crude oil-based fuels and other relevant process streams and products. 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 refinery samples and standards

Measurement	TS	SD
BTX (hydrocarbon mix)	0.06 mg/L	± 0.01 mg/L
Diesel (fuel)	8.86 mg/L	± 0.01 mg/L
Gasoline (OK)	9.87 mg/L	± 0.05 mg/L
Itermediate-1	14.2 mg/L	± 0.14 mg/L
Diesel oil	37.5 mg/L	± 0.09 mg/L
Heating oil (HEL)	92.3 mg/L	± 0.50 mg/L
TS Standard (c = 0.10 mg/L)	0.10 mg/L	± 0.02 mg/L
TS Standard (c = 50.0 mg/L)	50.5 mg/L	± 0.15 mg/L

Figures 3 – 6 show typical measuring curves for selected samples resp. standards.

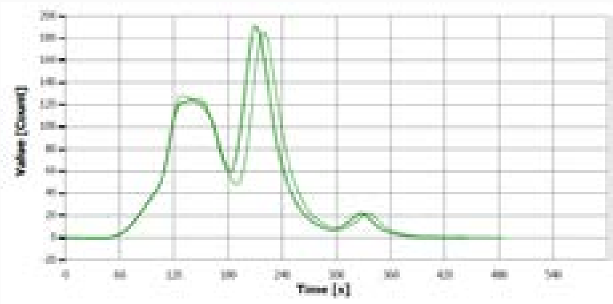

Figure 3: Analysis curve of "gasoline (OK)"

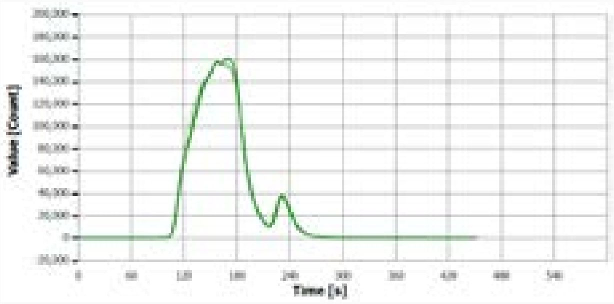

Figure 4: Analysis curve of "heating oil (HEL)"

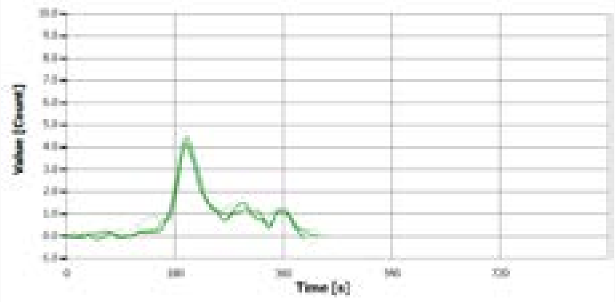

Figure 5: Analysis curve of “TS standard 0.10 mg/L”

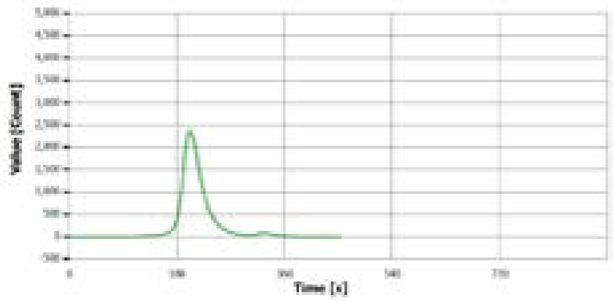

Figure 6: Analysis curve of “TS standard 50.0 mg/L”

Due to the matrix-optimized combustion in general a threefold determination is sufficient to achieve results far 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.

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

Conclusion

The multi EA 5100 with flame sensor technology provides a fast and reliable solution for the precise determination of widely varying sulfur contents, even in the most challenging sample. Thanks to the fully automatically optimized digestion process and the quantitative combustion, best results can be achieved for any matrix, independent of their properties, and in the shortest possible time. 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 in liquids mode with 112 positions, which is suited for vertical as well as horizontal sample supply techniques. For lower throughput demands manual introduction of the samples by means of boat injection (ABD) is possible 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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