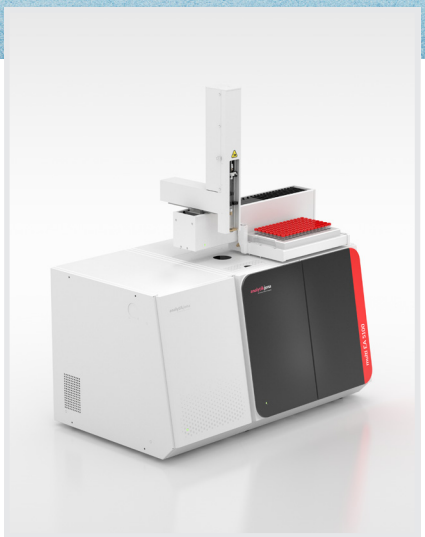

Challenge

Analysis of S traces within presence of higher TN concentrations caused by addition of performance improving agents (cetane improver)

Solution

S determination using Micro Plasma Optimization and UV fluorescence detection

Diesel Fuels and Fuel Additives – Interference-free Determination of Sulfur Traces by UV Fluorescence Detection with MPO according to ASTM D5453

Introduction

The fast and correct determination of total sulfur is an integral part of process and quality control in refineries. The most reliable method to do this is combustion of the sample followed by UV fluorescence detection of the produced SO_2.

Independent of the sulfur content, the majority of matrices can be analyzed with excellent results. But some of them give too high sulfur readings due to the presence of interfering components, such as nitrogen compounds. This effect is caused by a cross-sensitivity to NO, which fluoresces in the same wavelength range as SO_2. Depending on the nitrogen content of the sample, this can lead to too high results of approx. 0.6%–2% of the TN content on the TS result. As an example, for a matrix, with 500 ppm TN, the TS value will be falsified by approximately 3–10 ppm.

Refinery products contain a multitude of additives, amongst them cetane improvers. They are used to improve the ignitability (cetane number) of fuels. For this purpose compounds containing nitrogen, such as amyl nitrate, cyclohexyl nitrite, triethylene glycol dinitrate, 2-ethoxyethyl nitrate, or 2-ethylhexyl nitrate, have proven to be especially suitable and cost efficient. Besides the positive effect on the ignition characteristics these substances also lead to increased nitrogen contents in the final product.

analytikjena
An Endress+Hauser Company

Depending on the amount of cetane improver this can have a significant influence on the sulfur determination. This is a serious problem, considering the fact that some fuels already have an "actual" TS content close to the specified maximum limit of 15 ppm resp. 10 ppm (ASTM D4814, D6751//DIN EN 590, DIN EN 14214). If the sulfur content is analyzed after the add-on of such additives the result can be higher than allowed. The fuel exceeds the specified threshold (e.g. ULSD, grade S15) and does no longer comply with the requirements. This means that a time and cost intensive "after treatment" is required (e.g. blending with a more pure fuel). However, these unnecessary costs and efforts can easily be avoided by using interference-free working detection techniques.

While conventional sulfur analyzers fail in presence of nitrogen-containing additives, the patented Micro Plasma Optimization (= MPO) technology overcomes this problem. Correct TS readings are achieved, regardless of the composition of the test matrix. This is realized by the conversion of interfering components into harmless species by means of direct ionization of the reaction gas stream.

Samples and Reagents

Sample Preparation

All provided samples were light volatile liquids with normal viscosity. No further treatment was required.

Calibration

The calibration of the multi EA 5100 was carried out by different concentrated liquid standards (0–100 ppm), based on dibenzothiophene in iso-octane.

Instrumentation

The multi EA 5100 equipped with HiPerSens UV Fluorescence detector and Micro Plasma Optimizer (MPO) covers a unique wide measurement range from ultra-trace contents (5 ppb) up to the weight percent range (1 wt%). The flexible adaptation of the sample volume (1–100 µL), based on the expected sulfur content, allows the operator to benefit from high precision combined with short analysis times. The innovative MPO technology renders interfering nitrogen compounds harmless. This enables a correct and precise determination even for the smallest sulfur contents.

The optimization of the digestion process was carried out using the double furnace technology. To guarantee highest precision, the combustion process is adapted perfectly to the special requirements of the sample matrix to be examined. Dosing of the samples was performed fully automatically by means of the multi matrix sampler MMS in liquids mode. For each sample a volume of 40 µL was injected into the evaporation zone of the combustion tube. The sample digestion was carried out in a biphasic combustion process at 1050 °C with a surplus of oxygen. The generated reaction gas was dried and purified, before the included SO_2 was quantified by means of an UV-fluorescence detector, equipped with MPO module. By direct ionization of the reaction gas, the MPO converts all interfering compounds into harmless species. No additional auxiliary materials (catalysts) or auxiliary gases (NO, O_2) are required. Thanks to the excellent reproducibility, a triplicate analysis was sufficient to achieve reliable results.

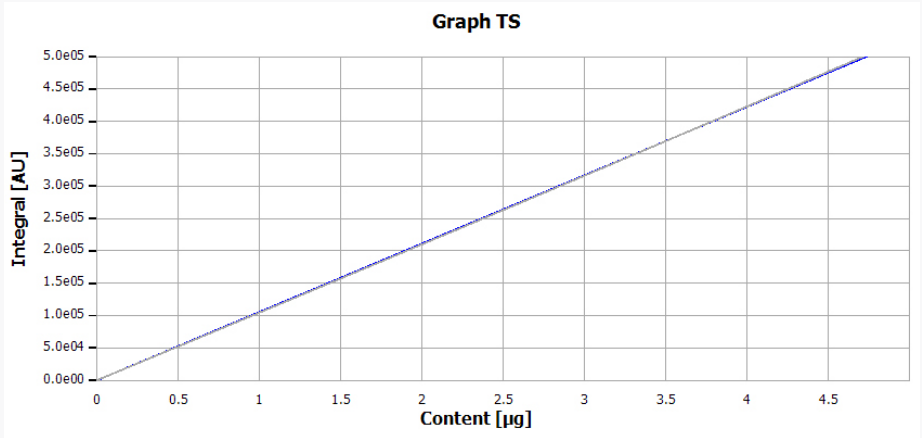

Figure 1: Calibration curve for the determination of sulfur

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 with an increased content of nitrogen. Table 1 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 results for the TS determination without and with the utilization of the MPO technology are summarized in Table 3. The samples were analyzed in both modi to depict the interfering effect of the N-containing additives resp. to show the efficiency of the MPO technology. In addition also the amount of interfering nitrogen was quantified by means of a chemoluminescence detector (CLD). The corresponding TS analysis curves are shown in Figure 2–6.

Table 3: Results of the sulfur determination with and without utilization of MPO technology.

Sample	Micro Plasma Optimization		TN Interference
	inactive	active	
	TS ± RSD	TS ± RSD	TN ± RSD
Diesel fuel 1	185 ppb ± 3.41 %	190 ppb ± 2.38 %	373 ppb ± 2.93 %
Diesel fuel 2	10.5 ppm ± 0.24 %	9.8 ppm ± 1.18 %	73 ppm ± 0.13 %
Additive solution	12.3 mg/L ± 1.88 %	6.87 mg/L ± 1.99 %	563 mg/L ± 0.16 %
Standard 100 mg/L N	1.03 mg/L ± 1.67 %	22.4 µg/L ± 4.81 %	100 mg/L ± 0.56 %
Mix standard 100 mg/L N + 1.00 mg/L S	1.93 mg/L ± 0.85 %	1.02 mg/L ± 0.13 %	100 mg/L ± 0.33 %

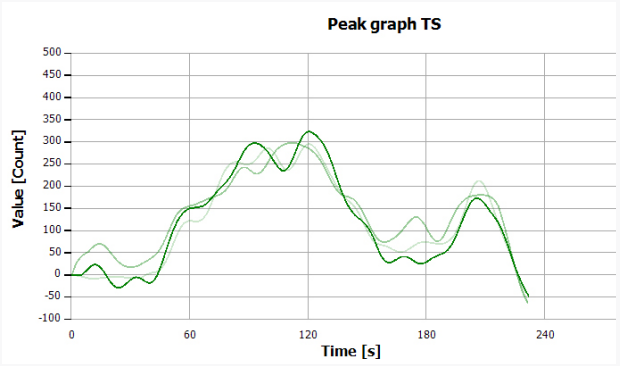

Figure 2: TS determination of "diesel fuel 1" with MPO

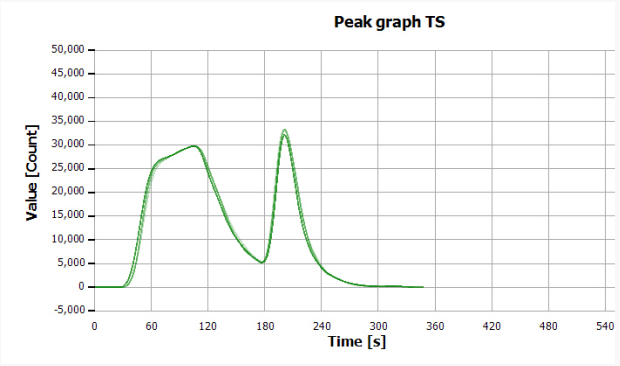

Figure 3: TS determination of "diesel fuel 2" with MPO

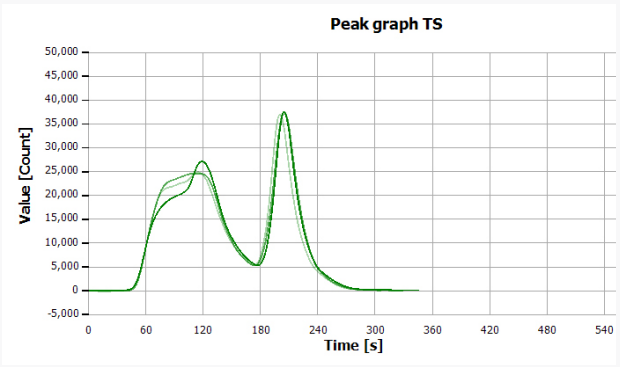

Figure 4: TS determination of "additive solution" with MPO

For samples (diesel fuel 1) which only contain nitrogen in the ultra-trace range (e.g. from natural sources), the results gained with and without usage of the MPO technology are identic.
When analyzing samples (diesel fuel 2, additive solution) containing higher TN quantities caused by addition of performance improving agents (e.g. cetane improver), the advantage of the MPO technology is clearly visible. Depending on the nitrogen content, more or less significant differences between the two detection technologies occur. The UV-fluorescence without MPO delivers too high measurements for sulfur determination due to cross-sensitivity for nitrogen monoxide. The correct, "actual" TS contents of these matrices can only be determined by using the MPO technology.

The efficiency of this technique is clearly displayed by analysis of the mix standard, which consists of exactly 1 mg/L S in presence of 100 mg/L N. When being analyzed by the classic UV-fluorescence without MPO (Figure 5), the TS results are falsified, too high due to the present 100 mg/L TN. When being analyzed by means of UVF with the MPO technique (Figure 6), the same sample delivers the real sulfur content.

Conclusion

The multi EA 5100 with Micro Plasma Optimizer guarantees correct results when measuring sulfur traces in presence of high nitrogen quantities. This is especially important in quality control of diesel fuels and related matrices, containing additives. Of course the application possibilities of this technology are not limited to petrochemical applications. It can be used for all

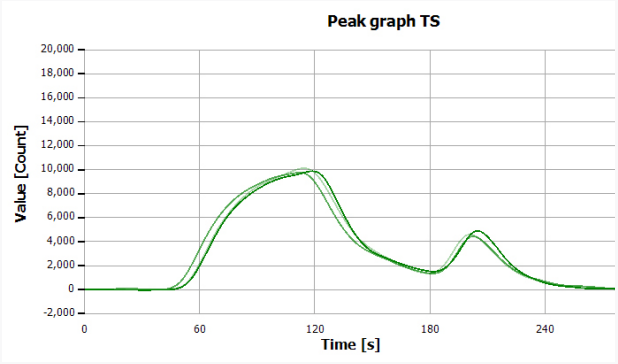

Figure 5: TS determination of the "mix standard" (a.) without MPO

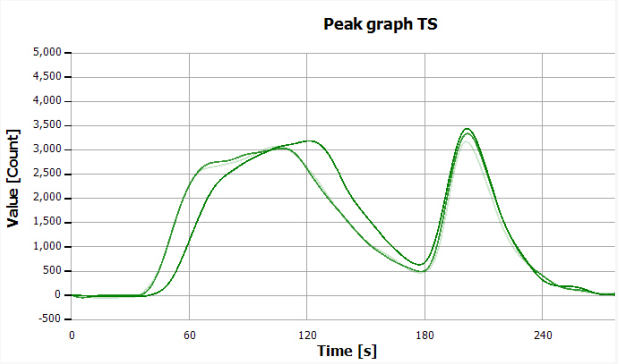

Figure 6: TS determination of the "mix standard" (b.) with MPO

organic solids (e.g. polymers, fats), liquids (e.g. hydraulic oil, lubricating oil), and gases/LPG when the correct sulfur content has to be determined in the presence of increased nitrogen concentrations.
The multi EA 5100 can be upgraded with suitable accessory modules for automatic determination of Nitrogen (TN), Chlorine (TX) and Carbon (TC) in solid, liquid, gaseous and LPG sample matrices.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

en · 02/2020
© Analytik Jena GmbH+Co. KG | Picture p.1 ©: iStock/MR1805