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

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 SO₂.

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 SO₂. 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.
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.

**Instrumentation**
The multi EA® 5000 S 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 5000 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 SO₂ 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, O₂) are required. Thanks to the excellent reproducibility, a triplicate analysis was sufficient to achieve reliable results.

**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® 5000 S was carried out by different concentrated liquid standards (0 – 100 ppm), based on dibenzothiophene in iso-octane.

![Graph TS](image-url)
Results and Discussion

The results for the TS determination without and with the utilization of the MPO technology are summarized in table 1. 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 1: Results of the sulfur determination with and without utilization of MPO technology.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micro Plasma Optimization</th>
<th>TN Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>inactive</td>
<td>active</td>
</tr>
<tr>
<td></td>
<td>TS ± RSD</td>
<td>TS ± RSD</td>
</tr>
<tr>
<td>Diesel fuel 1</td>
<td>185 ppb ± 3.41 %</td>
<td>190 ppb ± 2.38 %</td>
</tr>
<tr>
<td>Diesel fuel 2</td>
<td>10.5 ppm ± 0.24 %</td>
<td>9.8 ppm ± 1.18 %</td>
</tr>
<tr>
<td>Additive solution</td>
<td>12.3 mg/l ± 1.88 %</td>
<td>6.87 mg/l ± 1.99%</td>
</tr>
<tr>
<td>Standard 100 mg/l N</td>
<td>1.03 mg/l ± 1.67 %</td>
<td>22.4 µg/l ± 4.81%</td>
</tr>
<tr>
<td>Mix standard 100 mg/l N + 1.00 mg/l S</td>
<td>1.93 mg/l ± 0.85 %</td>
<td>1.02 mg/l ± 0.13 %</td>
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</tbody>
</table>

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 identical.

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® 5000 S 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 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® 5000 S 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.