Application Note: 42114

Sulfur Analysis in Nitrogen contained refinery samples using TS 4000 Total Sulfur analyzer with TTS technology

Key Words

- Diesel fuels
- Pulsed UV-Fluorescence
- Total Sulfur
- TTS Technology

Introduction

Managing the Total Sulfur content in basic and finished refinery products is highly important to increase the productivity and efficiency of the processes within those refinery operations. The life time of specific catalyst materials used within the refinery operation is very much dependent on the sulfur content of the typical process stream. An accurate and reliable sulfur content determination is required in order to optimize the blending capabilities, save enormous amounts of money and increase up-time of the refinery operation.

The production of low sulfur diesel fuels (ULSD) also includes the use of cetane improver to boost the cetane number. Cetane Improver is often called 2-ethylhexyl-nitrate (2-EHN).

The ASTM D5453 method is the current reference method for the analysis of total sulfur content in petroleum products by oxidative UV-Fluorescence detection technique. This method also describes the interference
of nitrogen components which may affect the total sulfur reading. In order to overcome this interference Thermo Fisher Scientific developed a new patented True Total Sulfur (TTS) technology, which neutralizes these interferences, and incorporated it into the newly designed TS 4000 Total Sulfur Analyzer.

This application note describes the use of the TS 4000 for the analysis of Total Sulfur in petroleum products using Cetane Improvers.

Principle of operation

The TS 4000 Total Sulfur Analyzer includes a temperature controlled automatic sample introduction module for both syringe and boat introduction supported by the Thermo Scientific NeXYZ liquids autosampler. For this application the syringe injection technique is used with the Liquids Module. The syringe drive injects the samples at a constant rate into the Liquids Module, where the liquid will evaporate at 500°C. The carrier gas leads the evaporated sample into the dual zone high temperature furnace supported with a quartz combustion tube. The combustion process ensures the complete oxidation of the sample into mainly CO_2 and water in an oxygen-rich environment. After the combustion stage, the formed gases are conditioned by a Perma Pure dryer and the dry gas (which includes SO_2) flows through the TTS technology-based reaction chamber before entering the pulsed UV-Fluorescence detector. The UV-F detector unit consists of a pulsed UV-lamp for the excitation of SO_2 (SO_2*) and a photomultiplier tube (PMT), which detects the light emitted by SO_2* returning to its ground stage. The Automatic Gain Control (AGC) ensures a constant energy level of the UV-lamp for excellent long term stability and so reducing the need for re-calibration.

Analysis

The TS 4000 was calibrated with seven calibration standards under the conditions as shown Table 1. Table 2 shows the calibration standards and diesel fuel sample set. The standards were measured to demonstrate the linearity of the system. After calibration a diesel fuel sample, which is spiked with Cetane Improver, is analyzed to show the independency and accuracy of the TS 4000 when using TTS technology. The results of these tests are presented below.

Argon injection	100 mL/min
Oxygen injection	100 mL/min
Oxygen Combustion	300 mL/min
TTS flow	40 mL/min
Furnace temperature I	1000°C
Furnace temperature II	1000°C
Inlet temperature	500°C
Injection speed	1 uL/sec
Injection volume	100 uL

Table 1: System settings of TS 4000

Cal standards	Diesel sample with added Cetane Improver
Blank	Diesel sample
0,1 ppm	Diesel + 500 ppm CI
0,5 ppm	Diesel + 1000 ppm CI
1 ppm	Diesle + 1500 ppm CI
5 ppm	Diesel + 2000 ppm CI
10 ppm	Diesel + 2500 ppm CI
25 ppm	
50 ppm	

Table 2: Calibration standards and Diesel sample set with Cetane Improver additions

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Results

The standards used for the calibration are measured within the mid range of the UV-Fluorescence detector. Table 4 shows the mean values of the measurements with use of Cetane Improver (CI) additions.

Cal standards	Area counts	Sulfur Conc(mg/kg)	RSD (%)
Blank	216	0,08	8,6
0,1 ppm	336	0,17	0,4
0,5 ppm	1264	0,52	3,9
1 ppm	2670	1,04	4,9
5 ppm	12776	4,98	2,1
10 ppm	24670	9,96	3,2
25 ppm	65622	25,3	3,0
50 ppm	131720	49,9	1,4

Table 3: Calibration data for TS 4000 mid range operation

Sample	Sulfur Concentration (mg/kg)	RSD (%)
Diesel sample	4,85	0,55
Diesel + 500 ppm CI	4,87	0,73
Diesel + 1000 ppm CI	4,89	0,58
Diesle + 1500 ppm CI	4,94	0,74
Diesel + 2000 ppm CI	4,96	0,83
Diesel + 2500 ppm CI	4,99	0,72

Table 4: Sulfur measurements of sample with CI

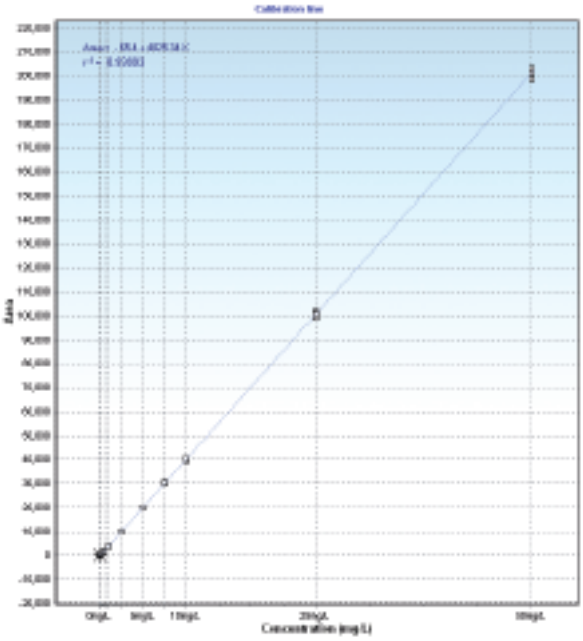

Figure 1: Calibration line TS 4000 0 – 50 ppm (line 0-50)

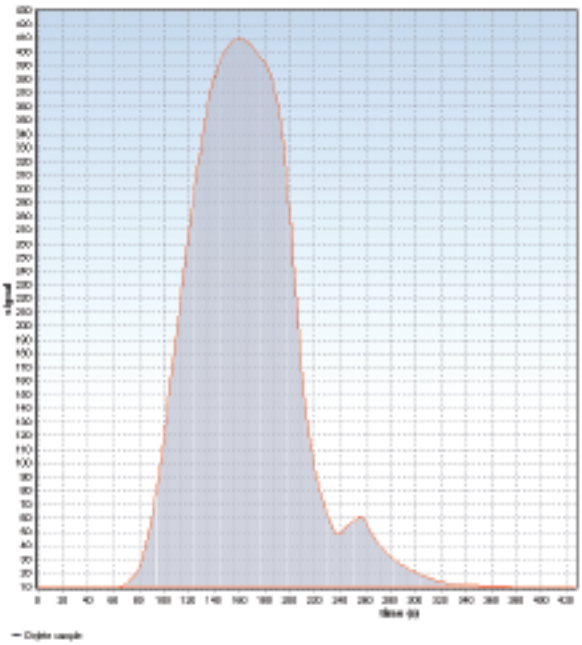

Figure 2: Measurement curve 10 ppm sulfur standard (std 10ppm)

Discussion

The ASTM D5453 method describes how nitrogen containing samples will contribute approximately 2% to a false positive signal. This means that in the case of samples containing 100 ppm nitrogen it can increase the maximum sulfur reading up by 2 ppm. The use of our newly developed TTS technology incorporated within the TS 4000 Total Sulfur analyzer eliminated this effect completely.

The reproducibility and linearity results for the calibration standards show RSDs smaller than 5%. Table 4 shows the superior performance of the TS 4000 solution when it comes to interference free operation with the implementation of TTS technology.

Conclusion

The newly developed Thermo Scientific TS 4000 Total Sulfur analyzer significantly improves refinery efficiency and blending capabilities using superior sulfur measurement technology. The TTS technology based UV-Fluorescence Total Sulfur analyzer can easily be adapted for those refinery operations which make use of Cetane Improvers, but also for processes where high nitrogen contained samples are involved.

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