



Combining UV-Fluorescence Detection and True Total Sulphur Technology for Improved Refinery Efficiency

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Managing the Total Sulphur content in basic and finished refinery products is highly important to increase the productivity and efficiency of the processes employed within refinery operations. The lifetime of specific catalyst materials used within the refinery process is very much dependent on the sulphur content of the typical process stream. An accurate and reliable sulphur content determination is required in order to optimize the blending capabilities and increase uptime of the refinery operation, thereby saving enormous amounts of money. The production of low sulphur diesel fuels (ULSD) involves the use of a cetane improver, which helps to boost the cetane number. The cetane improver is often called 2-ethylhexyl-nitrate (2-EHN) and it is capable of considerably increasing engine power.

Introduction

The ASTM D5453 method is the current reference method for the analysis of total sulphur content in petroleum products by oxidative UV-Fluorescence (UV-F) detection technique. UV-Fluorescence is the preferred technique for total sulphur analysis. XRF can also be used for such an analysis but the presence of Carbon (C) and Oxygen (O), especially in bio-ethanol fuel, will influence the analysis triggering the need for correction factors. In terms of sensitivity, most XRF systems can go down to 10 ppm with a precision of 10 +/- 1 ppm whereas the UV-F technique does have a precision level of 10 ppm +/- 0.2 ppm.

Combustion combined with UV-F has been used for many years for accurate and fast analysis of sulphur in a variety of organic products. During the combustion stage of the process, the sample is combusted into its oxides. The combustion gases are conditioned and led into the detector where Sulphur Dioxide (SO₂) is excited using a flash UV light source. When the molecule relaxes into its ground state, the emitted light can be detected. The emission wavelength of SO₂ is spread over a range, unlike some other elements that have specific spectral lines. The filter placed in front of the photomultiplier is chosen in the area where SO₂ is emitted. Within that spectral area, Nitric Oxide (NO) also has one band at its emission in NO + hv1 → NO* → NO + hv2, partly contributing to the signal which could lead to a positive false sulphur concentration. NO is formed at 1000 °C from organic nitrogen products. Eliminating nitrogen interference is important, especially in refineries in order to obtain a reliable total sulphur reading and optimize the refinery process.

In order to overcome the nitrogen interference, Thermo Fisher Scientific has developed a new patent pending True Total Sulphur (TTS) technology, which neutralizes these interferences. TTS technology is the only technique available, capable of introducing NO during the combustion process and completely eliminating the nitrogen interference, but also to improve the SO₂ yield performance. The new technology has been incorporated into the newly designed Thermo Scientific TS 4000 Total Sulphur analyzer. This article describes the use of the TS 4000 Total Sulphur analyzer for the analysis of Total Sulphur in petroleum products using cetane improvers.

Principle of Operation

The TS 4000 Total Sulphur 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 was used with a liquids autosampler. For this application, the syringe injection technique was used with a liquids introduction module. The syringe drive injected the samples at a constant rate into the liquids introduction module, where liquids evaporate at 500°C. The carrier gas led the evaporated sample into the dual zone high

temperature furnace supported with a quartz combustion tube. The combustion process, in an oxygen rich environment, ensured that a complete oxidation of the sample into mainly SO₂ and other products like CO₂ and water was obtained. Following the combustion stage, the formed gases were conditioned by a Perma Pure dryer and the dry gas (which included SO₂) was then processed through the TTS technology based reaction chamber before entering the pulsed UV-Fluorescence detector.

Method

The TS 4000 Total Sulphur analyzer complies with the ASTM D5453, D6667, D7183 and ISO 2084-6 standards and is therefore suitable for determination of the sulphur levels of a wide range of petroleum and hydrocarbon products in the range of 0.02 mg/kg to 10.000 mg/kg.

Sample Introduction

The liquids introduction module provides users with the capability to introduce samples either manually or automatically. A controlled injection speed and/or sample introduction ensures high precision and superb reproducibility in pyrolysis. The liquids autosampler incorporates a 180-sample position tray for unattended analysis of multiple sample introductions. All variables in sampling are performed easily.

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

Combustion

The TS 4000 Total Sulphur analyzer is fitted with a dual-zone furnace and equipped with a Ni/Cr/Ni thermocouple and a quartz combustion tube for enhanced combustion performance. The temperature is adjustable up to 1250°C. The key advantage of this combustion tube principle is the combustion capacity avoiding soot formation and yet enabling high injection speed with accuracy and less downtime.

Conditioning

Water affects the operation of the UV-Fluorescence detector. Therefore, a Perma Pure scrubber was placed

between the furnace and the reaction chamber in order to remove the water vapor from the gas stream. A glass fiber will ensure that small combustion particles will stay away from entering the detector part of the analyzer.

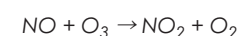
Detection

Sulphur

The dried gas stream was carried into the fluorescence chamber, which consists of a pulsed UV-lamp for the excitation of SO₂ and a photomultiplier tube (PMT), which detects the light emitted by SO₂ returning to its ground state. The automatic Gain Control (AGC) ensures a constant energy level of the UV-Lamp for excellent long term stability, thus reducing the need for re-calibration.

True Total Sulphur Technique

Even an optimized TS-UV detector can detect nitrogen as NO, which emits at the same wavelength range as SO₂. According to ASTM 5453, up to 0.5% of the nitrogen concentration in the sample is measured as sulphur. By ensuring that the NO → NO₂ reaction is outside the detector, the interference of this reaction is eliminated:



Therefore, all signal measured is from the SO₂ reaction.

When using ozone to eliminate the NO interference in samples with high nitrogen concentrations calibrated with standards without any nitrogen content, there is still a visible increase in the sulphur result. Therefore, a constant high amount of NO is added before the sample enters the furnace. The significant higher amount of NO "protects" the SO₂ molecule.

At higher nitrogen levels, the NO works as a yield improver, thus increasing the overall yield of SO₂ in the sample. When sulphur is combusted into its oxide within an oxygen rich environment, the achievable yield of SO₂ is approximately 90%. Although the exact process in the furnace is not known, there are indications that oxygen radicals can cause the conversion of SO₂ into SO₃.



Because the TS-UV detector is not SO₃-sensible, the recovery of the sulphur standard is decreased. Thus, the effect of variation between samples is eliminated and the analyses become matrix independent.

The TS 4000 combines the two principles described above to enable accurate low level sulphur analyses in samples with high concentrations of nitrogen.

Analysis

The TS 4000 was calibrated with seven calibration standards under the conditions detailed in 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 that had been spiked with a cetane improver was analyzed to demonstrate the independency and accuracy of the TS 4000 when using the TTS technology. The results of these tests are presented below.

Cal standards	Area counts	Sulphur Conc (mg/kg)
Blank	216	0.08
0,1 ppm	336	0.17
0,5 ppm	1264	0.52
1 ppm	2670	1.04
5 ppm	12776	4.98
10 ppm	24670	9.96
25 ppm	65622	25.3
50 ppm	131720	49.9

Table 2 Calibration data for TS 4000 mid range operation

Results

The standards used for the calibration were measured within the range of the UV-Fluorescence detector. Table 3 shows the mean values of the measurements following the addition of a cetane improver.

Discussion

The ASTM D5453 method specifies that nitrogen-containing samples contribute approximately 2% to a false positive signal. This means that in the case of samples containing 100ppm nitrogen, it can increase the maximum sulphur reading up by 2ppm. The use of the newly developed TTS technology incorporated in the TS 4000 Total Sulphur analyzer eliminated this effect completely. The reproducibility and linearity results for the calibration standards demonstrated RSDs smaller than 2%. Table 3 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 TS 4000 Total Sulphur analyzer significantly improves refinery efficiency and blending

capabilities using superior sulphur measurement technology. The TTS technology based UV-Fluorescence Total Sulphur 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.

Sample	Sulphur Concentration (mg/kg)	RSD (%)
Diesel sample	7.35	0.62
Diesel + 500 ppm CI	7.38	0.71
Diesel + 1000 ppm CI	7.36	0.59
Diesel + 1500 ppm CI	7.35	0.68
Diesel + 2000 ppm CI	7.37	0.70
Diesel + 2500 ppm CI	7.36	0.63

Table 3. Sulphur measurements of sample with Cetane Improver

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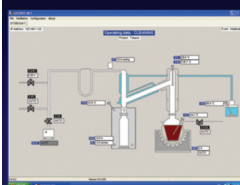
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