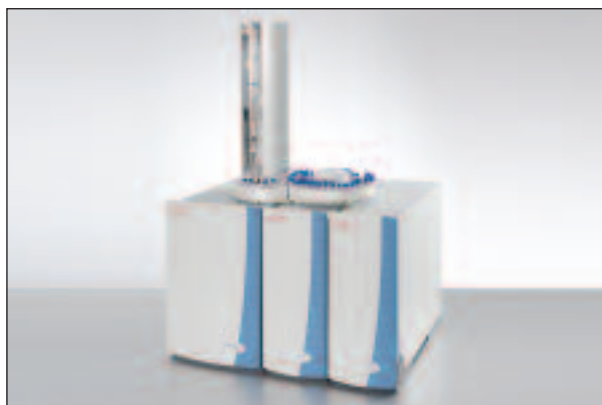


Total Sulfur analysis in petroleum products according to ASTM D5453

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Introduction



The Total Sulfur content is an important analysis when undertaking process/quality control analyses and for ensuring the compositional specifications in finished petrochemical products are met. For example, Sulfur components in process feeds may damage the catalyst performance in refinery processes, thus lowering the refinery efficiency and consequently its profitability. Additionally, Total Sulfur content in products like automotive fuels is subjected to restriction by local and international laws and must therefore be monitored using reliable technology and methodology.

The American Standardization of Testing Methods (ASTM) published the ASTM D5453 method specifically for the petroleum industry, covering the determination of the total sulfur content in liquid petroleum products by ultraviolet fluorescence detection. It is applicable for liquid hydrocarbons with a boiling point in the approximate range of 25 to 400 °C like naphtha, distillates, ethanol, gasoline, and diesel/biodiesel blends with sulfur content in the range of 1 to 10000 mg/kg (ppm).

The Thermo Scientific TITAN 4000 total sulfur configuration is ideal for the determination of total sulfur, particularly in liquid hydrocarbon samples as noted under the ASTM D5453 methodology. Furthermore, the technological advances made with the TITAN 4000™ allow liquid samples with any boiling point range to be injected into the unique sample injection system, providing the sample is within the appropriate viscosity range. This application note describes the use of the TITAN 4000 for adherence to the ASTM D5453 method.

Principle of operation

The Thermo Scientific TITAN 4000 incorporates an automatic syringe driven liquid introduction device, combustion oven, gas conditioning and sulfur detection module system.

The TITAN 4000 TS-UVF analyzer configuration includes a unique designed injection port as standard, which is maintained at 70 °C. This is in order to prevent any blockage of the injection needle due to formation of cracking products. The liquid sample is sprayed into the high temperature dual-zone combustion oven fitted with a robust quartz combustion tube. The patent-pending injection port and combustion tube require only oxygen, and ensure complete oxidation of the sample into mainly CO₂ and water in an oxygen-rich environment.

The sulfur components are oxidized into SO₂ (sulfur dioxide). Water and interferences (if any) are removed by the conditioning stage, which involves a permeable membrane dryer tube. The dried and clean gas with SO₂ is led to the detector module which contains a pulsed UV lamp for the excitation of SO₂ (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 and to reduce the need for frequent lamp calibration.

Analysis

The TITAN 4000 was calibrated with two sets of calibration standards as suggested by ASTM D5453 under the conditions as shown in table 1. The resultant calibration curves can be seen in Figures 1 and 2. The standards are measured to demonstrate the linearity of the analyzer.

Parameter	Setting
Injection temperature	70 °C
Furnace 1 temperature	1000 °C
Furnace 2 temperature	1000 °C
Injection speed	1 uL/sec
Injection volume	25 uL
Gasflow oxygen	800 mL/min

Table 1: System settings

Key Words

- TITAN 4000
- ASTM D5453
- Petroleum products
- Sulfur

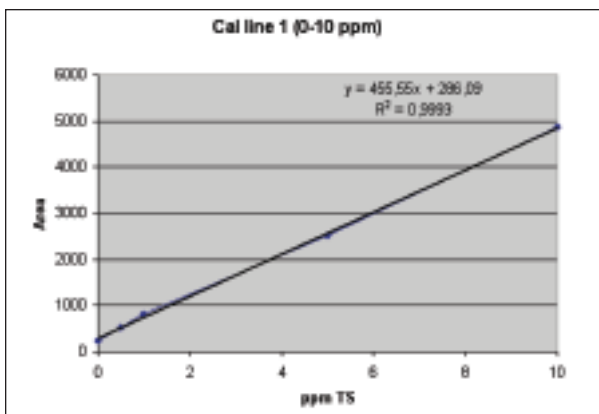


Figure 1: Calibration line 0 – 10 ppm TS (blank, 0,5; 1,0; 5 and 10 mg S/L)

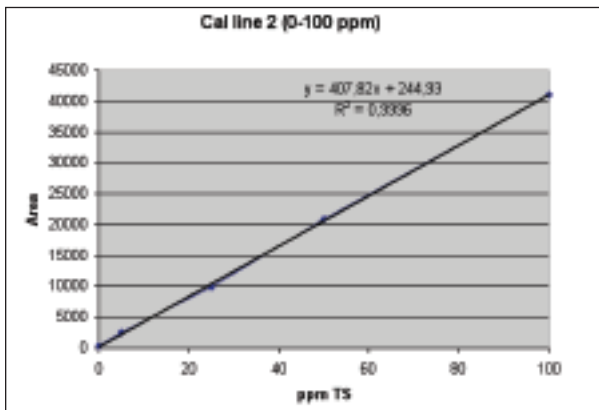


Figure 2: Calibration line 0 – 100 ppm TS (blank; 5; 25; 50 and 100 mg S/L)

After running the calibration lines a set of ULSD (Ultra-Low Sulfur Diesel) and ethanol samples were each analyzed four times to show the repeatability of the TITAN 4000 whilst demonstrating compliance with ASTM D5453. The standards used for the calibration were prepared by diluting a standard stock solution of 1000 mg dibutyl sulfide in isoctane.

Results

Sample	ASTM RR Average (mg S/kg)	Total Sulfur (mg S/kg)	TITAN 4000 RSD (%)
ULSD 1	10.9	10.5	1.2
ULSD 2	4.63	4.83	2.1
ULSD 3	5.28	5.38	1.7
ULSD 4	7.66	7.70	2.0
ULSD 5	10.86	10.60	1.3
Ethanol	3.49	3.42	1.9

ASTM RR = Official reported Total Sulfur concentration in mg/kg by ASTM D5453 Round Robin test.
 Total Sulfur = average total sulfur concentration determined by TITAN 4000.
 RSD = relative standard deviation in %.

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Conclusion

Advanced injection and combustion technologies combined with UV-Fluorescence detection in the Thermo Scientific TITAN 4000 total sulfur configuration provide accurate linear ultra low sulfur analysis in petrochemical products with excellent repeatability in full compliance with the ASTM D5453 test method. Furthermore, with analysis times of less than two minutes the TITAN 4000 increases laboratory productivity significantly.

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