Dependable Ultra Low Sulphur Analysis According to ASTM D5453 Using Advanced Ultraviolet Fluorescence Technology

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High concentration of sulphur in basic and finished petrochemical products has a negative impact on the refinery process, health and the environment. The life time of specific process catalysts used in petroleum and chemical refining is very much dependent on the trace amounts of sulphur-bearing materials contained in the feedstocks. In addition, when automotive fuels containing high levels of sulphur are burned, sulphur dioxide (SO_2) gases are formed causing a range of health issues including breathing difficulties in people with asthma, respiratory illness, worsening of existing heart disease, visibility impairment as well as environmental issues such as acid rain[1]. Furthermore, in order to limit environmental impact, regulations regarding the Sulphur content in automotive fuels specify ever lower allowable levels.

In response, the US Environmental Protection Agency (EPA) has implemented an Ultra Low Sulphur Diesel (ULSD) fuel program to reduce emissions from diesel-powered vehicles[2]. Under these regulations, a minimum of 80% of the diesel fuel produced for highway vehicles must be ULSD with a maximum sulphur content of 15 ppm, while the remaining 20% may be low sulphur diesel fuel (LSD) with maximum sulphur content of 500 ppm. However, from June 1, 2010 onwards, all highway diesel fuel must be ULSD. The same tendency on sulphur specification applies to other automotive fuels like gasoline and biodiesel.

Accurate and reliable ultra low sulphur content determination is required in order to optimise the life time of catalysts, saving enormous amounts of money, increase up-time of the refinery operations and comply with the strict EPA regulations. Traditionally determination of Sulphur by combustion techniques have limitations regarding the boiling point range of the sample. This is mainly caused by the applied introduction technique.

The American Standardisation of Testing Methods (ASTM) has introduced the D5453 standard[3] specifying the use of ultraviolet fluorescence (UV-F) for the determination of total sulphur in light hydrocarbons, spark ignition engine fuel, diesel engine fuel and engine oil.

ASTM D5453

The ASTM D5453 test method can be used to determine the sulphur content both in process feeds and in finished products. It covers the analysis of total sulphur in liquid hydrocarbons containing less than 0.35 % (m/m) of halogen(s) and boiling in the range from approximately 25 to 400°C, with viscosities between 0.2 and 20 cSt (mm^2/S) at room temperature. Three separate precision inter-laboratory studies (ILS) and three other investigations have determined that the ASTM D5453 test method is applicable to naphtha, distillates, engine oil, ethanol, fatty acid methyl ester (FAME) and engine fuel such as gasoline, oxygen enriched gasoline, diesel, biodiesel, diesel/biodiesel blends and jet fuel. Samples containing 1.0 to 8000 mg/kg of total sulphur can be analysed.

Thermo Fisher Scientific has developed an advanced total sulphur analyser to facilitate easy, efficient and cost-effective compliance with the ASTM D5453 test method.

Technological Advancements

The newly designed Thermo Scientific TITAN 4000 total sulphur analyser is equipped with a unique and patent-pending sample injection system and combustion tube. Together, these innovations provide unsurpassed analysis times and a significantly larger application range.

The modular design of the analyser enables easy exchange between modules, limiting the need to troubleshoot and repair a module onsite. Additionally, an additional detector module can be added to the system at a later stage. Due to dedicated gas connectors that establish multiple gas paths between the adjacent individual analyser modules, exchanging modules is extremely easy and the need for glass connectors is eliminated.

To cater for sample applications within the scope of the ASTM D5453 method, the new technology incorporates a unique injection port which is maintained at 70°C allowing the injection of liquid samples within any boiling point range provided it is within the appropriate viscosity range. Even very heavy products can be injected as long as they can be dissolved in a solvent. Keeping the needle and the injector at the lowest possible temperature helps prevent any blockage of the injection needle when analysing viscous samples or higher boiling point components. The injection port works by nebulising the sample with the Oxygen gas flow, eliminating the need for an inert carrier gas. The device's design enables complete sample introduction into the inner combustion tube and optimal mixing with oxygen *(Figure 1)*.

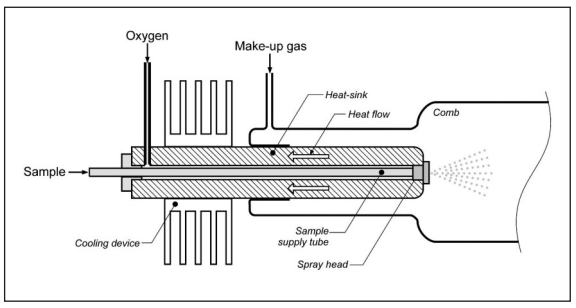

Figure 1: Simplified layout of the spray injector

A further advancement integrated in the new technology is a folded turbo combustion tube comprising a primary compartment and a turbo compartment which is folded back over the outside of the primary compartment and includes a number of separate tube shaped cavities *(Figure 2)*.

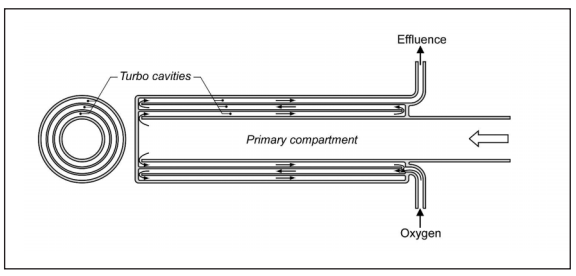

Figure 2: Simplified cross section of the folded turbo tube

The innovative folded turbo combustion tube operation is based on the high level laminar plug flow principle while it employs nine static mixers in the cavities of the turbo compartment to facilitate superior mixing performance. Gas flows are directed in both vertical directions through the consecutive cavities. The exit of the final cavity is located on the same side as the entrance of the combustion tube, enabling the inlet and the outlet of the tube to be located on its top side whereas the bottom part of the tube remains closed.

An additional differentiating parameter of the new technology compared with traditional configurations is that the required make-up gas flow is provided by the oxygen supply and regulated using a Pressure Control Valve (PCV). The PCV is designed to quickly cope with decreasing or rising pressure by adding or reducing extra oxygen flow. The make-up gas flow runs through a flow exchange module (FEM) where it is measured.

Principle of Operation

To commence the analysis, liquid samples are sprayed into the high temperature dual zone combustion oven fitted with the folded turbo combustion tube. The injection port and combustion tube require only oxygen and ensure complete oxidation of the sample into mainly CO_2 and water in an oxygen-rich environment. Sulphur components are oxidised into SO_2 while water is removed by the conditioning stage to a level below the dewpoint, which involves a permeable membrane dryer tube. The dried and clean gas with SO_2 is led to the Total Sulphur Pulsed-UV-Fluorescence (TS-UVF) detector module consisting 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 state. The Automatic Gain Control (AGC) ensures a constant energy level of the UV lamp for excellent long term stability.

An experiment was developed to demonstrate the capability of the new technology for precise and dependable determination of ultra low sulphur content in liquid petroleum in compliance with the ASTM D5453 standard.

Experimental

For this application, the Thermo Scientific TITAN 4000 total sulphur analyser was calibrated using three calibration standard sets as suggested by the ASTM D5453 method. The conditions employed throughout the analysis are detailed in Table 1. The calibration standards were prepared by diluting a standard stock solution of 1000 mg dibutyl sulfide in xylene. Every standard was subsequently measured four times to demonstrate the repeatability of the analyser.

Parameter	Setting
Injection temperature	70°C
Furnace 1 temperature	1000°C
Furnace 2 temperature	1000°C
Injection speed	1 µL/sec
Injection volume	25 µL
Gasflow oxygen for combustion	600 ml/min

Table 1. System settings

After running a calibration curve, a set of ULSD and ethanol samples were analyzed four times to demonstrate the repeatability, application coverage and ASTM D5453 compliance of the TITAN 4000 *(Table 2)*.

Sample	ASTM RR Average[1] (mg S/kg)	Total Sulphur[2] (mg S/kg)	TITAN 4000 RSD3 (%)
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	10.9	10.6	1.3
Ethanol	3.49	3.42	1.9

Table 2. Analytical results

Results

Analytical results were compared to the ASTM D5453 standards as these originated through the ASTM round robin tests whereby samples were sent to 200 laboratories for analysis and calculation of the mean results.

1. ASTM RR represents the official reported total sulphur concentration in mg/kg by ASTM D5453 round robin test.
2. Total Sulphur is the average total sulphur concentration determined by TITAN 4000.
3. RSD stands for relative standard deviation in %

Conclusion

Managing the ultra low sulphur content in basic and finished petrochemical products is highly important in order to increase the productivity and efficiency of refinery operations and comply with stringent US EPA legislation. Advanced ultraviolet fluorescence detection combined with new injection and combustion technologies on the Thermo Scientific TITAN 4000 total sulphur analyser allow for accurate linear ultra low sulphur analysis in petrochemical products with excellent repeatability and in full compliance with the ASTM D5453 test method.

For more information about the new Thermo Scientific TITAN 4000 Total Nitrogen/Sulphur analyzer, please visit the Thermo Scientific booth 303 at Gulf Coast Conference, Galveston, Texas.

Alternatively, please call +1 800-532-4752, email analyze@thermofisher.com or visit:www.thermo.com/titan4000

References

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