Application Note: 420042

Total Sulfur in Hydrocarbons Determination according to ASTM D5453 using the TS 3000

Key Words

- Total Sulfur
- ASTM D5453
- Fuel
- Hydrocarbons
- Oil
- Ultraviolet fluorescence

Introduction

Sulfur in combustion fuels is one of the major causes of acid rain. For this reasons many countries around the world have defined regulation to control the Sulfur content in fuels for combustion engines and power plants. In 2005 the maximum Sulfur content in fuels was set for many countries at a level of 10 mg Sulfur per kilogram fuel (10 ppm). It is also to be expected that the maximum Sulfur content in fuels for other countries will be set to the same level or may be even lower.

Cracking and reforming processes strongly depend on catalysts. These catalysts are sensitive to impurities like Sulfur. It is of great interest to minimize the Sulfur content in the feedstock of these processes to protect the catalysts from being poisoned. Poisoned catalysts lower product quality and yield and must be regenerated or replaced eventually. These effects endanger the profitability of the process.

The ASTM D 5453 describes the method to determine the Total Sulfur content in a range of 1 to 8,000 ppm in process feeds, half-products and finished products boiling in a range from approximately 25 to 400 °C.

Thermo Electron Corporation designed the TS 3000 analyzer for determination of Sulfur by UV-fluorescence specifically for engine oils, fuels and light hydrocarbons like gases, liquids, liquefied gases and even solids. This application note describes the use of the TS 3000 according to the ASTM D5453 method.

Principle

The sample is combusted at high temperature and in an oxygen-rich environment by direct injection. The Sulfur is oxidized to Sulfur Dioxide. The combustion gases are dried and transported to the UV-fluorescence detector (figure 1).

There are several introduction modules for specific applications. The operator can easily swap an introduction module for another, making the TS 3000 multifunctional. For this application the liquids module is used. The syringe drive injects the samples at a constant rate into the introduction module, where the liquid samples with boiling points up to 450 °C can evaporate (up to 400 °C is required according this ASTM method). The carrier gas leads the gaseous sample into the high temperature dual zone combustion oven. The patented combustion tube in the oven ensures complete oxidation of the sample into mainly CO_2 and water in an oxygen-rich environment. The Sulfur is oxidized into SO_2. Water and interferences, if any, are removed by the conditioning step. The dried and clean gas with SO_2 is led to the detector unit. The detector unit consists of a pulsating UV lamp for the excitation of SO_2 (SO_2*) and a photo multiplier tube (PMT), which detects the light emitted by SO_2* returning to its ground state. The Automatic Gain Control ensures a constant energy level of the UV-lamp for excellent long term stability, reducing the need for calibration.

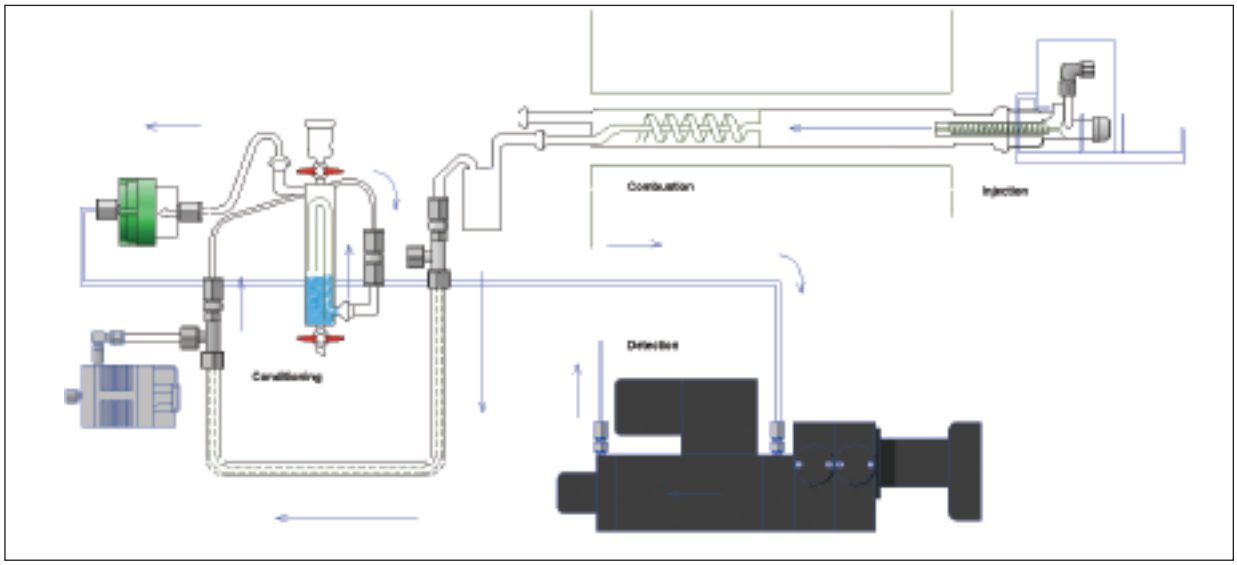

Figure 1: Schematic flow of the TS 3000

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Analysis

The TS 3000 is calibrated with three calibration standard sets as suggested by the ASTM method under the conditions as shown in table 1. ASTM D5453 suggests calibration ranges 0.5 to 10 mg/L, 5 to 100 mg/L and 100 to 1000 mg/L. Narrower ranges may be used, if desired. To illustrate the dynamic range of the TS 3000 we chose the calibration ranges as shown in table 2. The calibration solutions for curve III are prepared by diluting a standard stock solution of 10,000 mg/L thiophene in xylene and for curve I and curve II by diluting a 1,000 mg/L thiophene in xylene. Every solution is measured 3 times to test the repeatability.

Oxygen injection	300 mL/min
Argon injection	100 mL/min
Oxygen combustion	100 mL/min
Furnace temperature I	1000 °C
Furnace temperature II	1000 °C
Inlet temperature	500 °C
Injection speed	0.2 - 1 µL /sec
Sample volume	20 - 100 µL

Table 1: System settings

CURVE I SULFUR IN mg/kg	CURVE II SULFUR IN mg/kg	CURVE III SULFUR IN mg/kg
0.5	5	1000
1.0	25	2000
2.5	50	5000
5.0	100	
10.0	150	
	250	
Injection speed 1 µL /sec	Injection speed 1 µL /sec	Injection speed 0.2 µL /sec
injection volume 100 µL	injection volume 20 µL	injection volume 20 µL

Table 2: Calibration ranges

Results

The calibration data for curve I, II and II are listed in table 3, table 4, table 5 respectively.

	MEAN AREA	RSD (%)
Std 0.5	756	0.66
Std 1.0	1702	0.54
Std 2.5	4046	0.65
Std 5.0	7475	2.00
Std 10.0	14821	2.00

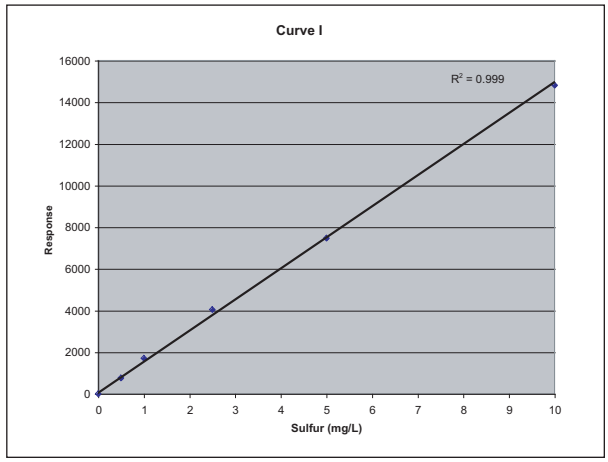
Table 3: Calibration data for curve I

	MEAN AREA	RSD (%)
Std 5	349	0.90
Std 25	1780	0.28
Std 50	3576	0.63
Std 100	7345	0.64
Std 150	10589	1.78
Std 250	17456	1.63

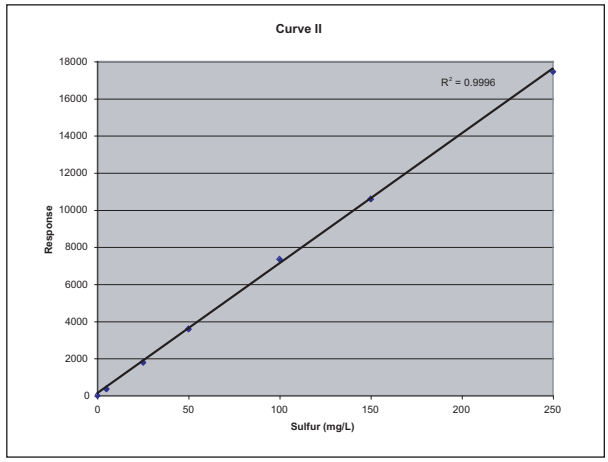
Table 4: Calibration data for curve II

	MEAN AREA	RSD (%)
Std 1,000	23142	1.44
Std 2,000	42268	1.77
Std 5,000	97649	4.25

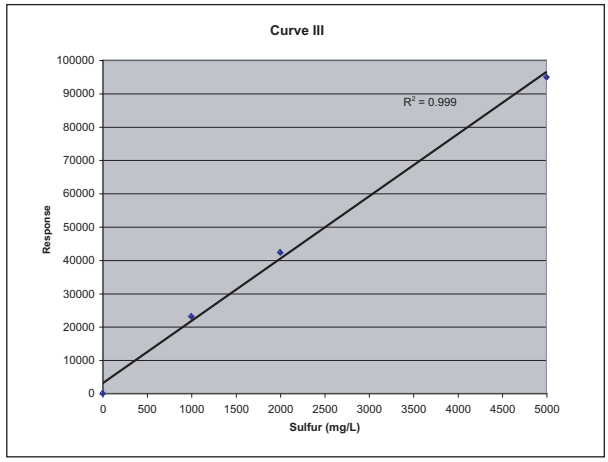
Table 5: Calibration data for curve III



Graph 1: Calibration curve I



Graph 2: Calibration curve II



Graph 3: Calibration curve III

Discussion

Although in ASTM D5453 is stated that the calibration curves should be linear there is no specification for the linearity. We assume a correlation coefficient better than 0.995 is considered as linear. Under this assumption the TS 3000 exceeds the minimum required linearity.

In ASTM D5453 a mathematical repeatability test is defined as:

Less than 400 mg/kg : $r = 0.1788X^{0.75}$ (1)

Greater than 400 mg/kg : $r = 0.02902X$ (2)

X is the average of the results being compared.

The difference between two test results may not exceed the r-value in more than one case in 20.

CONCENTRATION (mg/L S)	Δ_{max} (mg/L)	r
0.5	0.006	0.1
1.0	0.01	0.2
2.5	0.04	0.4
5.0	0.2	0.6
10.0	0.4	1.0
25	0.1	1.9
50	0.6	3.4
100	1.4	5.8
150	0.4	7.6
250	1.6	11.2
500	9.6	13.4
1000	22	77.2
2000	21	64.7
5000	70	166.9

Table 6: Repeatability

For every measurement the repeatability of the two replicates giving the largest difference are calculated with equation (1) or (2). Results of these calculations are listed in table 6. The difference of the two measurements are also listed in table 6. The differences of the measurements are never larger than the r-values as listed in table 6. The repeatability of the TS 3000 exceeds the repeatability requirements for ASTM D5453.

Conclusions

Thermo's Total Sulfur TS 3000 analyzer complies with method ASTM D5453 on measuring principle, linearity and repeatability. Data shows that the TS 3000 can even exceed the minimum requirements on linearity, dynamic range and repeatability. Laboratories using the TS 3000 can benefit from a broader dynamic range by needing less calibration points to define the calibration curve. The broader dynamic range also means less chance of out-of-range samples and reduces the need for diluting the samples. The repeatability of the TS 3000 offers more confidence in the results and minimizes the need for re-measuring the samples, saving time and improving the productivity of the laboratory.

The scope of method ASTM D5453 standard specifies the method for determination of total sulfur in fossil fuels containing 1 mg/kg to 8,000 mg/kg. For total sulfur analysis at lower concentrations the application note "Ultra low-level analysis of Total Nitrogen and Total Sulfur in hydrocarbons with the TN/TS 3000 analyzer" (AN42035) is available. It illustrates the performance of the TS 3000 analyzer at ultra low concentrations down to 25 µg/kg.

The method of sample treatment described in this publication should be performed only by a competent chemist or technician trained in the use of safe techniques in analytical chemistry. Users should acquaint themselves with particular hazards which may be incurred when toxic materials are being analyzed and handled in the instruments, and the instrument must be used in accordance with the operating and safety instructions given in the Operators manual.

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