TRACE LEVEL TOTAL SULFUR DETERMINATION ACCORDING TO ASTM D5453

A COMPREHENSIVE STUDY ON THE 0.1 TO 1 MG/KG RANGE

Trace Elemental analyzers and ASTM D5453

The need for trace level Sulfur analysis by elemental combustion analyzers is growing. The method appears to be used more in Hydrocarbon products such as Benzene, Toluene, and recently developed renewable fuels like VGO or HEFA diesel(blends). Currently ASTM D5453 doesn't allow reporting Total Sulfur below 1.0 mg/kg and lacks direction on how to analyze at trace levels down to 0.1 mg/kg.

This article describes an extensive test setup to venture the requirements for our analytical combustion equipment to reach low-level quantification levels in the range of 0.1 to 10 mg/kg for Total Sulfur according to the ASTM D5453 method.

Detection of Total Sulfur – UV-Fluorescence

When organic Sulfur components are combusted in the high-temperature furnace, the following reaction takes place:

$R - S + O_2 \rightarrow SO_2 + H_2O + CO_2$

After complete sample oxidation, the combustion gas is conditioned by removing water vapor and particles. The conditioned gas stream containing the Sulfur Dioxide (SO_2) molecules is transferred to the reaction chamber. The Xenon flashed UV lamp will excite the Sulfur Dioxide molecules to SO_2* at specific wavelengths and due to the unstable character of SO_2* it will relax back to SO_2 instantly. The released energy will be emitted in the form of light and will be detected by the Photomultiplier Tube (PMT). The amount of light emitted equals the total amount of SO_2 (Total Sulfur) present in the sample.

Detection:

$SO_2 + hv_2 \rightarrow SO_2$*

SO_2* $\rightarrow SO_2 + hv_2$

Trace level study setup

For this study, a variety of different configurations was used. All configurations will run the same standards and samples. The following analyzers have been used to perform the analysis of TS and TN at trace level:

Xplorer TN/TS - Horizontal furnace setup

Sample introduction:

o Boat introduction

o Liquid module: direct injection

Autosamplers:

o Archie

o XLS-30

Xplorer-V TN/TS - Vertical furnace setup

Sample introduction:

o Xpro-V Liquid inlet: direct injection

Autosamplers:

o Integrated LS-26

Experimental setup and system parameters

For the horizontal sample introduction, all samples and standards were introduced by either direct liquid injection (Archie and XLS-30) or boat introduction (Archie). For the vertical injections, the integrated liquid autosampler (LS-26) of the Xplorer-V was utilized.

For calibration of the analyzers, two different solvents were used based on Xylene or Iso-Octane, to verify the applicability of these solvents. After each calibration, a series of different matrices were injected to check the variation in injection volumes and solvent variations on the recovery. The following table shows the variation of the several injection configurations tested:

Table 1: Overview of variation of different injection configurations and samples

Analyzer model	Sample introduction	Auto sampling systems	Injection Volume (µ=l)	Calibration Matrix	Calibration range (mg/kg)	Sample Matrix
Xplorer NS	Boat introduction	Archie	30	Iso-Octane	0,1 to 10	Gasoil CRM
Xplorer-V NS	Direct Liquid injection	XLS-30	50	Xylene		Gasoline CRM
		Internal LS-26	100			Naphtha CRM
						Biodiesel B100 CRM

System parameters applied:

The following method parameters were applied to the variations of calibration lines and sample injections:

Table 2: Overview of method parameters per configuration

Parameter settings	*Xplorer*-V TN/TS	*Xplorer* TN/TS	*Xplorer TN/TS boat introduction*
Oxygen Flow	400 mL/min	300 mL/min	300 mL/min
Argon Flow	100 mL/min	100 mL/min	100 mL/min
Inlet cleaning time	10 seconds	100 mL/min	100 mL/min
Furnace Temperature I	800 °C	1000 °C	750 °C
Furnace Temperature II	1050 °C	1050 °C	1050 °C
Internal System Temperature	32 °C	36 °C	36 °C
Liquid module Temperature	n/a	500 °C	n/a
Injection Speed	1 µL/s to 1.3 µL/s	1 µL/s	5 µL/s
Injection Volume	Between 10 µL and 100 µL	Between 10 µL and 100 µL	30 µL
Boat introduction speed	n/a	n/a	Custom – optimized for trace level

Evaluation of results:

Depending on the injection volume and speed for each configuration, the analyzer was calibrated with a set of Xylene standards and a set of Iso-octane standards from 0.1 mg/kg to 10 mg/kg. Resulting in a total of 21 calibration lines. Evaluation of the calibration lines and the sample results were based on:

o The coefficient for determination of the calibration lines (how well a fit is applicable).

o The RSD values on the lowest injection point of the calibration curve at 0.1 mg/kg.

o Recovery of the sample CRM.

o The RSD values of the sample matrices.

Calibration

Standards used for calibration were made from Dibutyl Sulfide (S) in Iso-Octane or Xylene. The Xplorer analyzers are calibrated in the range of 0,1-10 mg/kg. All calibration points have been corrected for the average blank area count. After running all the individual calibration lines and corresponding samples the following overview was extracted:

Table 3: Overview of various calibration lines for TS 0,1 – 10 mg/kg

Analyzer	Sample Introduction	Injection volume / speed	Calibration line solvent	R2 of calibration line	RSD (%) @ 0,1 mg/kg (N=5)
Xplorer NS	Boat introduction	30 µL + 5,0 µL/S	Iso-Octane	0,99998	4,3
			Xylene	0,99977	4,5
Xplorer NS	Liquids module + Archie	30 µL + 1,0 µL/S	Iso-Octane	0,99994	12,7
			Xylene	0,99995	14,0
		50 µL + 1,0 µL/S	Iso-Octane	0,99925	4,9
			Xylene	0,99996	4,7
		100 µL + 1,0 µL/S	Iso-Octane	0,99943	3,9
			Xylene	0,99999	3,7
Xplorer NS	Liquids module XLS-30	30 µL + 1,0 µL/S	Iso-Octane	0,99978	10,4
			Xylene	0,99977	6,6
		50 µL + 1,0 µL/S	Iso-Octane	0,99921	4,7
			Xylene	0,99997	4,0
		100 µL + 1,0 µL/S	Iso-Octane	0,99978	4,5
			Xylene	0,99997	3,7
Xplorer-V NS	Xpro-V Inlet	30 µL + 1,3 µL/S	Iso-Octane	0,99997	8,0
			Xylene	0,99995	8,4
		30 µL + 1,0 µL/S	Iso-Octane	0,99997	6,6
			Xylene	0,99958	7,0
		50 µL + 1,0 µL/S	Iso-Octane	0,99962	3,7
			Xylene	0,99999	3,0
		100 µL + 1,0 µL/S	Iso-Octane	0,99997	3,3
			Xylene	0,99998	1,5

Table 4: Sample matrix injections and final results overview

Analyzer	Sample Introduction	Injection volume / speed	Standard Matrix	Gasoil CRM Average mg/kg (N=5)	RSD (%)	Naphtha CRM Average mg/kg (N=5)	RSD (%)	Biodiesel CRM Average mg/kg (N=5)	RSD (%)	Gasoline CRM Average mg/kg (N=5)	RSD (%)	Points
Xplorer NS	Boat introduction	30 µL + 5,0 µL/S	Iso-Octane	4,4	0,5	0,49	0,4	0,27	3,5	5,0	0,6	7
			Xylene	5,0	0,5	0,52	0,5	0,26	4,0	5,4	0,6	10
Xplorer NS	Liquids module + Archie	30 µL + 1,0 µL/S	Iso-Octane	4,6	3,2	0,37	13,7	0,07	17,0	4,2	2,1	4
			Xylene	4,3	1,3	0,56	5,9	0,25	12,5	4,5	2,4	5
		50 µL + 1,0 µL/S	Iso-Octane	5,2	1,6	0,54	4,1	0,34	3,7	5,0	1,4	9
			Xylene	4,6	0,7	0,48	3,9	0,22	5,2	4,3	2,8	7
		100 µL + 1,0 µL/S	Iso-Octane	5,2	0,6	0,55	1,5	0,30	4,3	5,0	1,2	9
			Xylene	4,8	0,5	0,51	4,4	0,24	2,2	4,5	1,7	8
Xplorer NS	Liquids module XLS-30	30 µL + 1,0 µL/S	Iso-Octane	3,2	3,5	0,23	14,2	0,27	13,3	3,54	0,51	3
			Xylene	3,7	6,5	0,50	10,7	0,34	10,1	5,02	2,32	6
		50 µL + 1,0 µL/S	Iso-Octane	4,9	3,2	0,34	7,4	0,28	4,3	4,73	2,36	6
			Xylene	4,6	0,7	0,37	7,5	0,28	2,9	4,37	1,23	6
		100 µL + 1,0 µL/S	Iso-Octane	5,0	1,4	0,56	4,0	0,31	2,4	5,15	1,91	10
			Xylene	4,7	1,7	0,52	4,4	0,25	2,9	4,97	1,07	10
Xplorer-V NS	Xpro-V Inlet	30 µL + 1,3 µL/S	Iso-Octane	4,1	1,1	0,54	2,4	0,22	1,9	4,9	1,9	7
			Xylene	4,3	2,2	0,58	2,5	0,23	4,7	5,3	3,1	6
		30 µL + 1,0 µL/S	Iso-Octane	4,2	1,2	0,55	4,4	0,24	3,6	5,1	2,3	7
			Xylene	4,3	0,4	0,58	1,9	0,23	4,0	5,2	2,4	7
		50 µL + 1,0 µL/S	Iso-Octane	4,7	0,3	0,56	2,3	0,26	4,1	5,3	1,7	10
			Xylene	4,8	0,4	0,57	2,0	0,24	3,5	5,3	1,7	9
		100 µL + 1,0 µL/S	Iso-Octane	4,8	0,2	0,56	1,0	0,24	2,5	5,2	1,2	10
			Xylene	4,9	0,4	0,56	1,1	0,24	3,7	5,3	0,8	10

In order to evaluate the results from the different configurations on their performance in the trace range, the results were awarded with a point-based system. Points were awarded based on a set of criteria. The more points that were earned the better the performance was in the trace range. Each independent end result on variations were awarded based on the following criteria:

o R2 of designated calibration line >0.999 = 1 point

o RSD on 0.1 mg/ kg calibration injection (n=5) <5.0 = 1 point

o Recovery of the sample CRM between 95% and 105% = 1 point per sample matrix

o Gasoil CRM limits: Expected 4,80 mg/kg (limits are 4,56 to 5,04 mg/kg)

o Naphtha CRM limits: Expected 0.53 mg/kg (limits are 0.50 to 56 mg/kg)

o Biodiesel CRM limits: Expected 0.25 mg/kg (limits are 0.24 to 0.26 mg/kg)

o Gasoline CRM limits: Expected 5.20 mg/kg (limits are 4.94 to 5.46 mg/kg)

o RSD on the end value of sample matrix <5.0 = 1 point per sample matrix

A maximum of 10 points could be earned in total. A score of 8 points was set as the minimum to apply for applicability for trace level determination of Total Sulfur at levels ranging from 0.1 – 1.0 mg/kg. The complete overview of all the results including the total earned points can be viewed in the table results.

Results

In table 4 an overview of the results can be found, this table shows per analyzer depending on both the sample introduction type and injection volume the results of the analyzed CRM samples using a calibration line made in Iso-octane or Xylene matrix. The results are rounded according to ASTM D5453 including the RSD value measured over five injections. The last column shows the sum of total points earned for that individual configuration.

Summary of the application

Sample volume:

Looking at the complete overview there is a clear downtrend in the variation of RSD results with the increase of the sample volume. This applies to both sample injections and the low-level calibration level of 0.1 mg/kg for the Total Sulfur standard.

Iso-Octane VS Xylene:

The effect of using Iso-Octane or Xylene as solvent results in the following noticed effects:

- Injections of Xylene-based standards give a more stable baseline view and show higher response factors at the lower level concentration injections compared to standards that are made in Iso-Octane solvent.

- Using Iso-Octane as a solvent basis for the calibration line standards results in peak splitting when the boat application is used and higher concentration levels are injected.

- Xylene gives a higher blank injection for Total Sulfur compared to Iso-Octane but still within acceptable ranges.

- Iso-Octane gives higher Total Nitrogen blanks, this is not lined out in the scope of this application note but could contribute when Total N is also valuable.

Most effects mentioned above are likely caused by the fact that Iso-Octane contains far more CH3 molecules compared to Xylene, which can form more H_2O during combustion and an excess of O_2. The lower boiling point of Iso-Octane results in the peak splitting with boat application which makes it harder to integrate.

Boat introduction VS direct liquid injection:

Both a direct liquid injection and boat introduction setup are applicable for trace level determinations. The usage of a boat introduction generates acceptable results but has a longer analysis time and lower response factor. The best results are achieved by injection of high sample volumes, the boat application is limited to sample size injections of a max 30 µL.

Example peaks and overlays – best analyzer setups

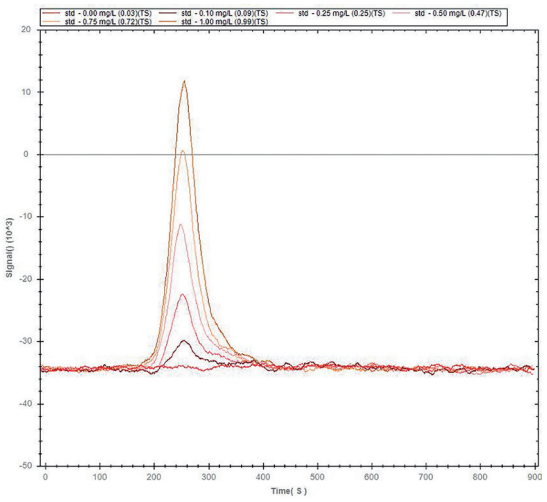

Figure 1: Xplorer TN/TS with boat drive overlay of calibration levels 0.1 - 1.0 mg/kg

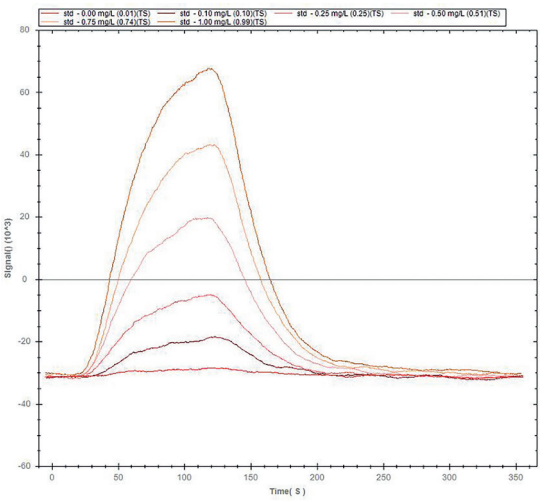

Figure 2: Xplorer TN/TS liquids module overlay calibration levels 0.1 - 1.0 mg/kg

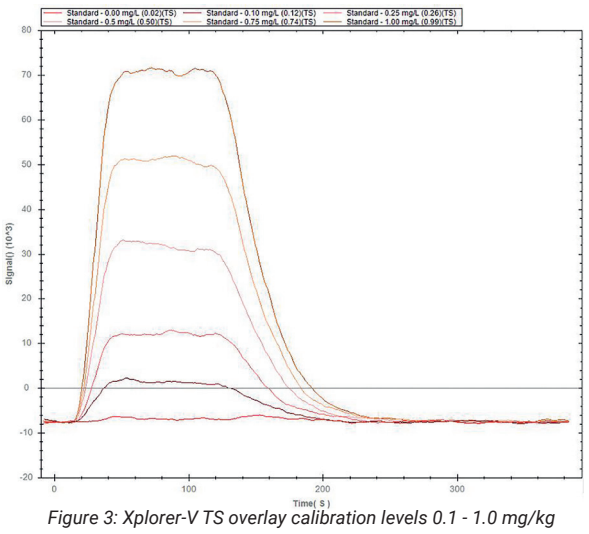

Figure 3: Xplorer-V TS overlay calibration levels 0.1 - 1.0 mg/kg

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