PAC | Application Note

Determination of Total Sulfur in Gasoline by UVF according to ASTM D5453 / TIER 3.

- Rapid and Accurate Determination of Total Sulfur
- Fully Automated Injection and Combustion system
- Repeatability & Accuracy: EPA TIER 3 compliancy

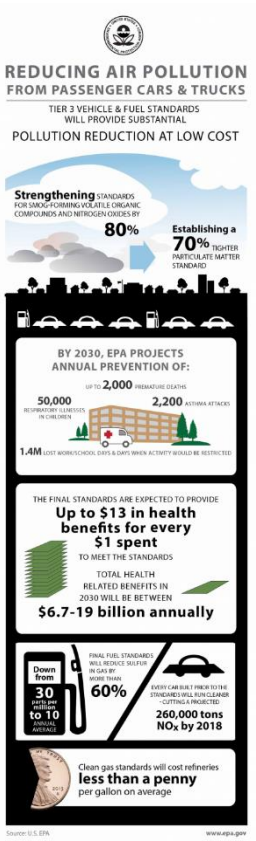
Keywords: ASTM D5453, ElemeNtS, Sulfur, UVF, Gasoline, TIER 3

INTRODUCTION

Sulfur is a natural component in crude oil that will be present in gasoline and diesel as well, unless it is removed during the production process. Sulfur in gasoline and diesel contributes to air pollution, so lowering the Sulfur content in these products contributes to the reduction of air pollution and further control of emissions.

The U.S. Environmental Protection Agency ("EPA"), has a program in place to reduce air pollution from passenger cars & trucks. This so-called **"TIER 3 vehicle & fuel standards"** program will provide a substantial pollution reduction. By strengthening older programs one wants to reduce smog forming volatile organic compounds and nitrogen oxides by 80%.

With this, the EPA claims that the introduction of the TIER 3 program by 2030 has resulted in an annual prevention of 2,000 early deaths, 2,200 asthma attacks and up to 50,000 respiratory diseases in children. The total health benefits are between $6.7 - 19 billion dollars annually. The proposed reductions in Sulfur for petrol will immediately lead to a reduction in emissions and health benefits of the existing fleet and will support overall air quality over time.



EPA TIER 3 REQUIREMENTS

The TIER 3 program, which has come into effect per January 1st, 2017 for all major gasoline producers and importers, incorporates a performance based Analytical Test Method Approach. This means a measurement system based upon established performance criteria for accuracy and precision with use of analytical test methods. It is a measurement system used by laboratories to demonstrate that a particular analytical test method is acceptable for demonstrating compliance. The criteria are specified in e-CFR document title 40, part 80, subpart D & paragraph 80.47, see next page.

Precision	Accuracy
The maximum allowable standard deviation computed from the results of a minimum of 20 tests made over 20 days (tests may be arranged into no fewer than five batches of four or fewer tests each, with only one such batch allowed per day over the minimum of 20 days) on samples using good laboratory practices taken from a single homogeneous commercially available gasoline must be less than or equal to 1.5 times the repeatability "r" divided by 2.77, where "r" equals the ASTM repeatability of ASTM D7039. The 20 results must be a series of tests with a sequential record of analysis and no omissions.	*(i) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric Sulfur standard in the range of 1-10 ppm, say 10 ppm, shall not differ from the accepted reference value (ARV) of the standard by more than 0.70 ppm Sulfur (0.75 * Maximum STDEV for the tested level);* *(ii) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric Sulfur standard in the range of 10-20 ppm, say 20 ppm, shall not differ from the ARV of the standard by more than 1.02 ppm Sulfur (0.75 * Maximum STDEV for the tested level);*

ASTM D5453 MEASURING PRINCIPLE

ASTM D5453 is an established test method for the determination of total Sulfur in liquid hydrocarbons containing 1.0 to 8000 mg/kg total Sulfur, boiling in the range from approximately 25°C to 400 °C and with viscosities between approximately 0.2 and 20 cSt (mm^2/S) at room temperature.

A hydrocarbon liquid sample is directly injected, by a fully automated liquid sampler, into a high temperature, dual temperature zone combustion tube where the sample is vaporized and combusted. The released Sulfur is oxidized to Sulfur dioxide (SO_2) in an oxygen rich atmosphere.

$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O$$

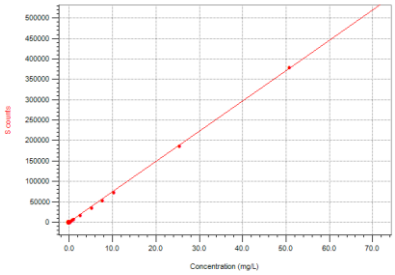
A stream of inert gas (helium or argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are excited by the absorption of energy of a UV source and emit light (fluorescence) while they relax to a stable state.

$$SO_2 + hv_{ex} \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + hv_{em}$$

A Photomultiplier tube measures the emitted light and convert it to an electrical signal.

The response signal is integrated to calculate the area. The Sulfur concentration of an unknown product is calculated using the linear regression function of the concentration of standard mixtures versus integrated area.



VALIDATION

The system and methodology of the **Antek ElemeNtS** total Sulfur analyzer is thoroughly tested for response linearity, precision and accuracy, to validate its performance according to ASTM D5453 and TIER 3 regulations.

CALIBRATION

A calibration curve is composed using dibenzothiophene in i-octane standards. Each calibration solution and blank (i-octane) is measured three times. The average response of the blank injections is subtracted from each calibration standard response conform method. Although the ElemeNtS system is linear in response in the range from 0 – 1000 mg/L, a separate calibration curve has been created in a typical gasoline range (0-25 mg/L).

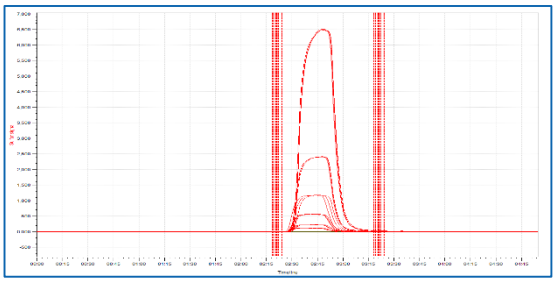


Figure 1: Overlay 0 – 25 mg/L (n=3)

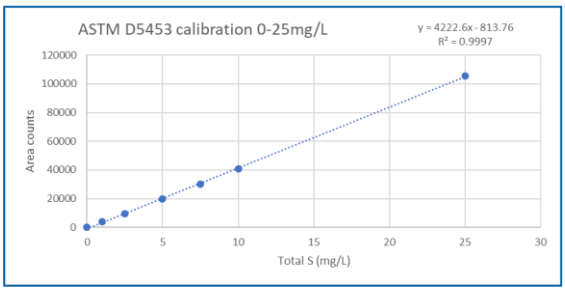


Figure 2: Calibration curve covering typical Gasoline range of ASTM D5453

PRECISION

To calculate the precision, various Sulfur containing samples (obtained from an Inter Laboratory test) were analysed over a period of > 20 days. The standard deviation for all samples is calculated and compared to the maximum allowable value. This maximum allowable value is calculated as: 1.5 * ($r_{ASTM\ D7039}$) / 2.77
The system meets TIER 3 specifications if Δ Stdev ≤ Max. Stdev. See below examples:

Table 1: TIER 3 precision test result for various samples (Gasoline & Diesel)

	Diesel B7	Reformulated Gasoline	Diesel B7			Gasoline ≈5 ppm	Gasoline ≈10 ppm	Gasoline ≈15 ppm
Day 1	9.38	5.78	10.52		Day 1	4.81	9.86	15.13
Day 2	9.24	5.70	10.43		Day 2	4.80	10.05	15.27
Day 3	9.22	5.80	10.41		Day 3	4.80	10.05	15.37
Day 4	9.19	5.50	10.42		Day 4	4.84	10.03	15.32
Day 5	9.19	5.49	10.33		Day 5	4.74	9.79	14.99
Day 6	9.16	5.54	10.44		Day 6	4.77	9.93	15.34
Day 6	9.34	5.74	10.53		Day 6	4.74	9.77	14.94
Day 8	9.29	5.58	10.41		Day 8	4.79	9.96	15.18
Day 9	9.63	5.72	10.49		Day 9	4.80	9.93	15.09
Day 10	9.35	5.67	10.65		Day 10	4.86	10.02	15.22
Day 11	9.15	5.53	10.48		Day 11	4.77	9.88	15.18
Day 12	9.26	5.12	10.33		Day 12	4.82	9.94	15.28
Day 13	9.41	5.52	10.51		Day 13	4.75	9.81	15.08
Day 14	9.18	5.57	10.54		Day 14	4.79	9.95	15.23
Day 15	9.33	5.50	10.39		Day 15	4.79	9.96	15.21
Day 16	9.27	5.74	10.51		Day 16	4.82	9.99	15.24
Day 17	9.31	5.77	10.49		Day 17	4.72	9.89	15.14
Day 18	9.30	5.78	10.47		Day 18	4.78	9.93	15.24
Day 19	9.24	5.43	10.46		Day 19	4.74	9.93	15.06
Day 20	9.28	5.43	10.44		Day 20	4.81	9.94	15.22
					Day 21	4.65	9.72	14.96
					Day 22	4.70	9.80	14.93
					Day 23	4.70	9.92	14.11
					Day 24	4.80	9.98	15.18
					Day 25	4.85	9.94	15.30
Average	9.29	5.60	10.46			4.78	9.91	15.16
Standard Deviation	**0.108**	**0.168**	**0.075**			**0.049**	**0.092**	**0.129**
RSD	1.16%	3.00%	0.72%			1.04%	0.93%	0.85%
max Standard Deviation 1.5 * ($r_{ASTM\ D7039}$) /2.77)	**0.902**	**0.686**	**0.962**			**0.630**	**0.934**	**1.175**

Table 2: TIER 3 precision test results summary

PRECISION			
Sample	**Max Standard Deviation Method**	**Measured Standard Deviation**	**Result**
Diesel B7	0.902	0.111	✔
Reformulated Gasoline	0.686	0.168	✔
Diesel B7	0.962	0.075	✔
Gasoline ≈5 mg/kg	0.630	0.047	✔
Gasoline ≈10 mg/kg	0.934	0.090	✔
Gasoline ≈15 mg/kg	1.175	0.121	✔

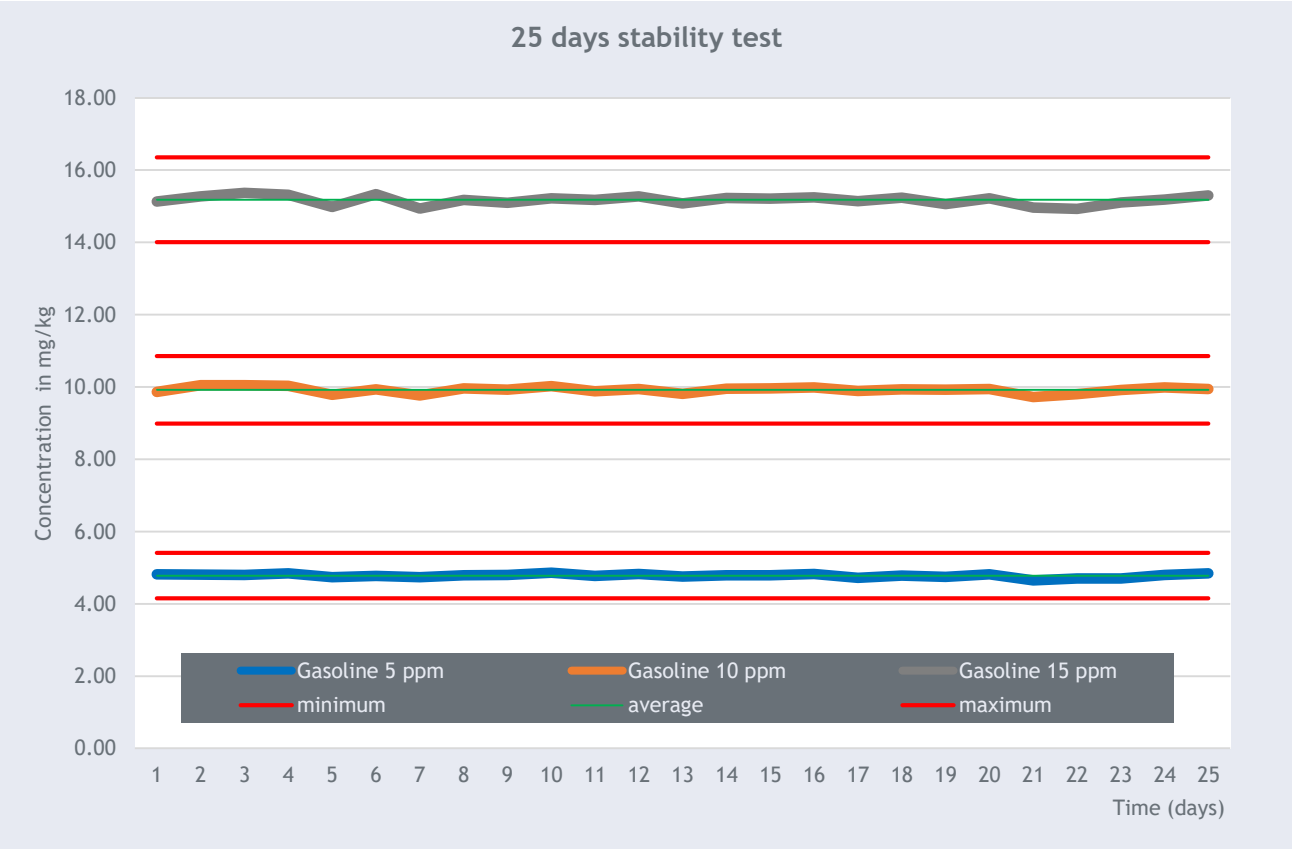


Figure 3: QC chart for Gasoline sample

ACCURACY

For accuracy determination three tests have been performed covering both the "low range" (~10 ppm) and the "high range" (~20 ppm) according §80.47 (b) (2)):

Average of at least 10 continuous tests performed on a commercially available gravimetric Sulfur standard; testing within two ranges is required:

- *In the range of 1-10 mg/kg shall not differ from the ARV of the standard by more than 0.75 * Maximum STDEV for the level being tested*
- *In the range of 10-20 mg/kg shall not differ from the ARV of the standard by more than 0.75 * Maximum STDEV for the level being tested*

Table 3: *TIER 3 Accuracy test result for three gasoline samples*

	Analysis results	Δ vs target		Analysis results	Δ vs target		Analysis results	Δ vs target
1	4.89	-0.11		9.86	-0.14		14.89	-0.11
2	4.94	-0.06		9.80	-0.20		14.94	-0.06
3	5.00	0.00		9.94	-0.06		14.99	-0.01
4	4.93	-0.07		10.02	0.02		15.01	0.01
5	5.01	0.00		9.89	-0.11		14.97	-0.04
6	4.99	-0.01		9.88	-0.12		15.10	0.10
7	4.98	-0.02		9.90	-0.10		15.03	0.03
8	4.99	-0.01		9.93	-0.07		15.05	0.05
9	4.98	-0.02		10.01	0.01		15.01	0.01
10	4.99	-0.01		9.92	-0.08		15.06	0.05
Mean	**4.97**	**-0.030**		**9.91**	**-0.085**		**15.00**	**0.004**
Target value	5.00			10.00			15.00	
Standard Deviation	0.036			0.066			0.060	
Max StDev 1.5 * ($r_{ASTM\ D7039}$) /2.77	0.643			0.934			1.168	
Accuracy (0.75 * Max StDev)	**0.483**			**0.701**			**0.876**	
Δ vs target	**-0.030**			**-0.085**			**0.004**	

Table 4: *TIER 3 Accuracy test result summary*

ACCURACY			
Sample	Max Accuracy limit	Average deviation	Result
ASI standard 5.0 mg/kg	0.483	0.030	✔
ASI standard 10.0 mg/kg	0.701	0.085	✔
ASI standard 15.0 mg/kg	0.876	0.004	✔

CONCLUSION

TIER 3 “20-day stability and accuracy tests” are performed to confirm if the Antek ElemeNtS complies with the minimum requirements as stated by the EPA. The performance is checked by comparing the ElemeNtS test results with the requirements that are needed to meet the regulation of Sulfur in gasoline measurements according to the TIER 3 program (§ 80.47).

The system complies with both precision and accuracy criteria for approval for the absolute fuel parameter of gasoline Sulfur.

Antek's lab instruments provide reliable, precise elemental analysis for total nitrogen and Sulfur, speciated nitrogen and Sulfur, fluoride, chloride, and bromide. Antek products are recognized by global regulating bodies, leading scientific research institutions, and process laboratories as the instrument of choice for selective multi-element detection.