

Determination of Total Sulfur in ECA Marine Fuel according to ASTM D5453; EPA/MARPOL annex VI; D2622 correlation

- Easy Maintenance with Automated Leak Tests and Maintenance door
- Safety as a Priority with Automatic Gas Shutoff and Furnace Cooldown
- Rapid and Accurate Determination of Chemically bound Sulfur
- Fully Automated Injection and Combustion system
- Repeatability and Precision meeting EPA/MARPOL requirements



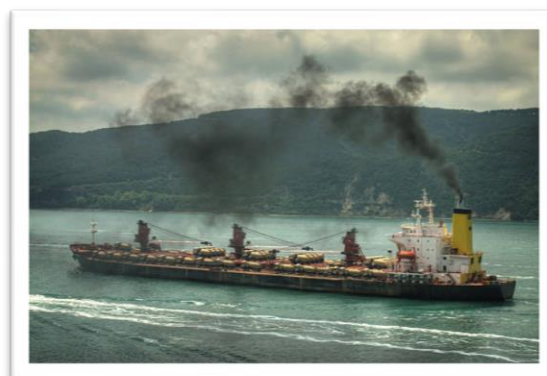
Keywords: Sulfur, D5453, UVF, EPA, MARPOL, ECA, D2622, ElemeNtS

Introduction:

Sulfur is a natural component in crude oil that will be present in marine fuel oil and gasoil, unless it is removed during the production process. Sulfur in fuels 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 regulations in place to reduce air pollution from marine vessels as part of its participation in the International Convention for the Prevention of Pollution from Ships (MARPOL). These regulations are described in 40 CFR Part 80 – Subpart I. Inside the Emissions Control Areas (ECA), a maximum of 1,000 ppm Sulfur is permitted. Outside of these areas a global limit of 0.50% is set in place since International Maritime Organization (IMO) 2020 went into effect.

The ECAs are sea areas in which stricter controls for airborne emissions are enforced. They were established with Annex VI of the MARPOL protocol. Sulfur limits for these ECAs went from 1.50% before 2010, to 1.00% between 2010-2015 and down till 0.10% from 2015 on. Ships sailing in these waters must use a compliant fuel or use an equivalent approved method, such as SOx scrubbers.



In the document 40 CFR Part 80, the regulations pertaining to ECA marine fuel are laid out. One of the regulations is about the approval of test methods, with the criteria listed in the table:

“(2) Approval of test methods approved by voluntary consensus-based standards bodies. Beginning January 1, 2016, any test method approved by a voluntary consensus-based standards body, such as the ASTM International or the International Organization for Standardization (ISO), shall be approved as a test method for determining the sulfur content of diesel fuel if it meets the applicable accuracy and precision criteria under § 80.584. These records must be kept by the facility for a period of five years.”

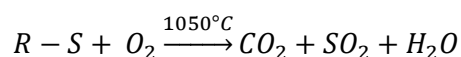
Precision	Accuracy
<p><i>For ECA marine fuel subject to the 1,000 ppm sulfur standard of § 80.510(k), of a standard deviation less than 18.07 ppm, computed from the results of a minimum of 20 tests made over 20 days (tests may be arranged into no fewer than five batches of four or fewer tests each, with only one such batch allowed per day over the minimum of 20 days) on samples taken from a single homogeneous commercially available diesel fuel with a sulfur content in the range of 700-1,000 ppm. The 20 results must be a series of tests with a sequential record of the analyses and no omissions. A laboratory facility may exclude a given sample or test result only if the exclusion is for a valid reason under good laboratory practices and it maintains records regarding the sample and test results and the reason for excluding them.</i></p>	<p><i>(3) For ECA marine fuel subject to the 1,000-ppm sulfur standard of § 80.510(k):</i></p> <ul style="list-style-type: none"> <i>(i) The arithmetic average of a continuous series of at least 10 tests performed on a commercially available gravimetric sulfur standard in the range of 300-400 ppm sulfur shall not differ from the ARV of that standard by more than 13.55 ppm sulfur;</i> <i>(ii) The arithmetic average of a continuous series of at least 10 tests performed on a commercially available gravimetric sulfur standard in the range of 900-1,000 ppm sulfur shall not differ from the ARV of that standard by more than 13.55 ppm sulfur; and</i> <i>(iii) In applying the tests of paragraphs (b)(3)(i) and (ii) of this section, individual test results shall be compensated for any known chemical interferences.</i>

It is therefore necessary to demonstrate the performance of an analyzer to approve it for the determination of sulfur in marine fuel used within ECA's. The Antek ElemeNtS complies with, and even outperforms, the requirements set out by the EPA, making it an excellent alternative for traditional methods of sulfur determination in marine fuels.

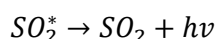
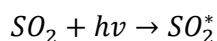
Measuring principle

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 (mm²/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 (SO₂) in an oxygen rich atmosphere.



A stream of inert gas (helium or argon) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here the SO₂ molecules are excited by the absorption of energy of a UV source and emitting light (fluorescence) while it relaxes to a stable state.



A Photomultiplier tube measures the emitted light and converts it into 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.



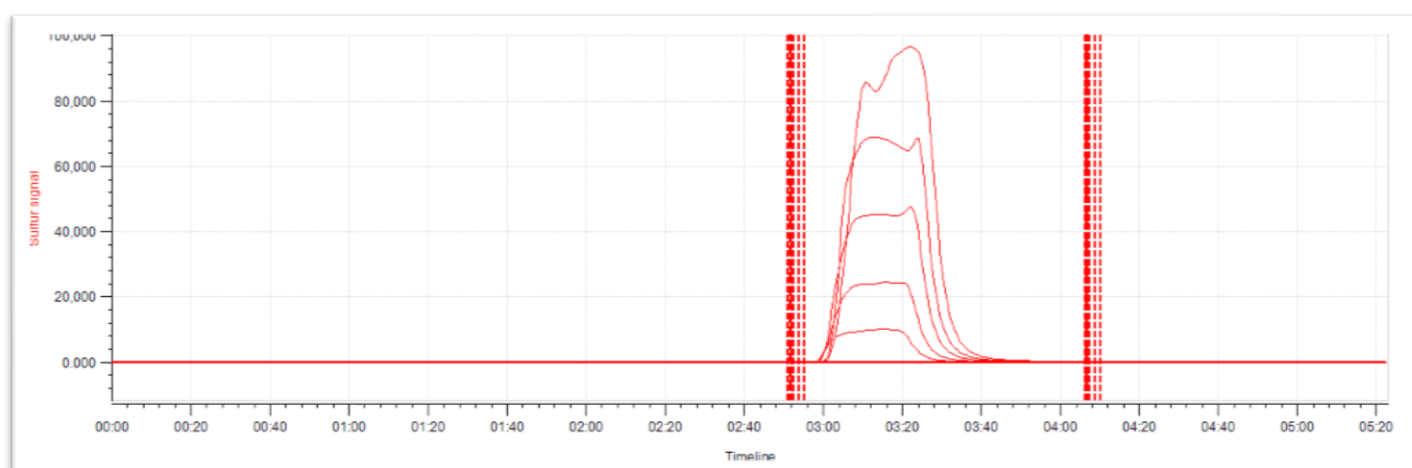
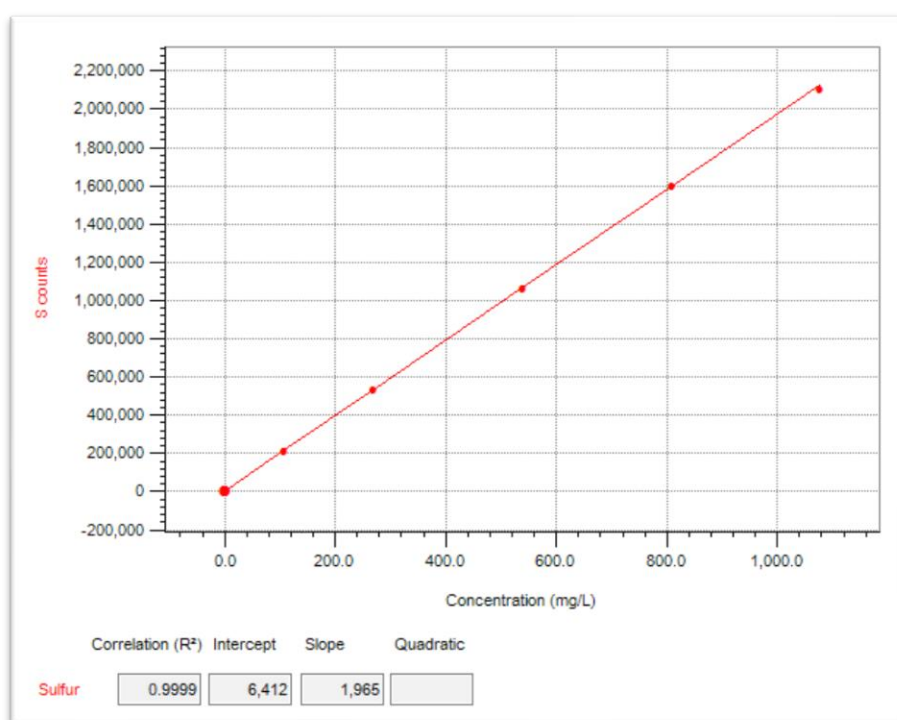
Validation

The Antek ElemeNtS total sulfur analyzer system and methodology is rigorously tested for response linearity, precision and accuracy, to validate its performance according to ASTM D5453 and the 40 CFR part 80 regulations.

Calibration

A calibration curve is constructed using dibenzothiophene in iso-octane standards. Each calibration solution and blank is measured three times. The average response of the blank injections is subtracted from each calibration standard response conform method. The ElemeNtS is linear in the complete range required for ECA marine fuel (0-1000 mg/L)

Sulfur 0-1000 mg/L	
Conc. mg/L	Area
0	71
108	217848
269	539140
539	1069362
808	1602318
1077	2113741
Slope	
	1965
Intercept	
	6412
Correlation	
	0.9999

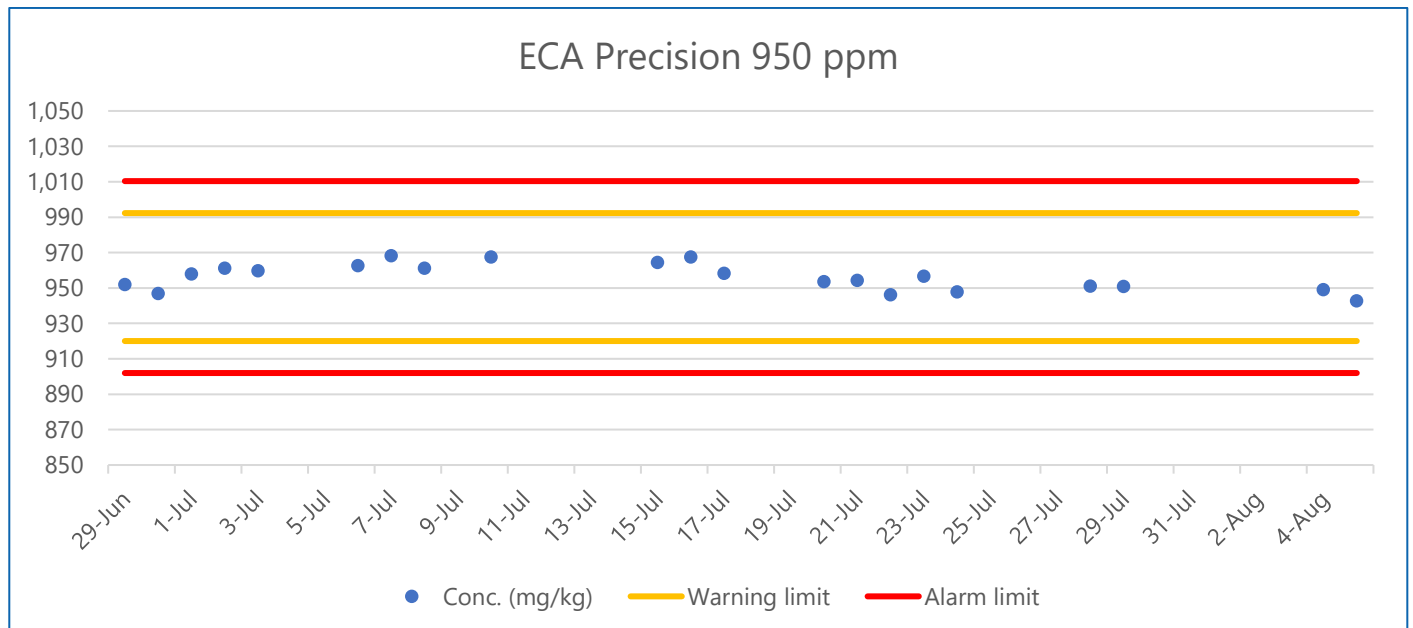


Precision

To conform to the precision statement of 40 CFR part 80, it is necessary to analyze a gasoil sample of 700-1000 mg/kg at least 20 times over the course of at least 20 days. In this case, a 950 mg/kg gasoil sample was measured 21 times over the course of 21 days.

The standard deviation obtained for this test should be less than 18.07. The ElemeNtS conforms to this requirement with a standard deviation of 7.60.

ECA Precision 950 ppm			
Date	Counts	Conc. (mg/L)	Conc. (mg/kg)
29/Jun	1,561,328	791.3	952.0
30/Jun	1,552,976	787.0	946.9
01/Jul	1,570,901	796.2	957.9
02/Jul	1,576,354	798.9	961.2
03/Jul	1,573,981	797.7	959.7
06/Jul	1,578,598	800.1	962.6
07/Jul	1,587,786	804.8	968.2
08/Jul	1,576,301	798.9	961.2
10/Jul	1,586,642	804.2	967.5
15/Jul	1,581,732	801.7	964.5
16/Jul	1,586,589	804.2	967.5
17/Jul	1,571,706	796.6	958.4
20/Jul	1,563,949	792.6	953.6
21/Jul	1,564,941	793.1	954.2
22/Jul	1,551,737	786.4	946.1
23/Jul	1,569,007	795.2	956.7
24/Jul	1,554,514	787.8	947.8
28/Jul	1,559,727	790.5	951.0
29/Jul	1,559,440	790.3	950.8
04/Aug	1,556,418	788.8	949.0
05/Aug	1,546,103	783.6	942.7
Average	1,568,130	794.8	956.2
Std. dev.	12411	6.32	7.60
Max Std. dev.			18.07

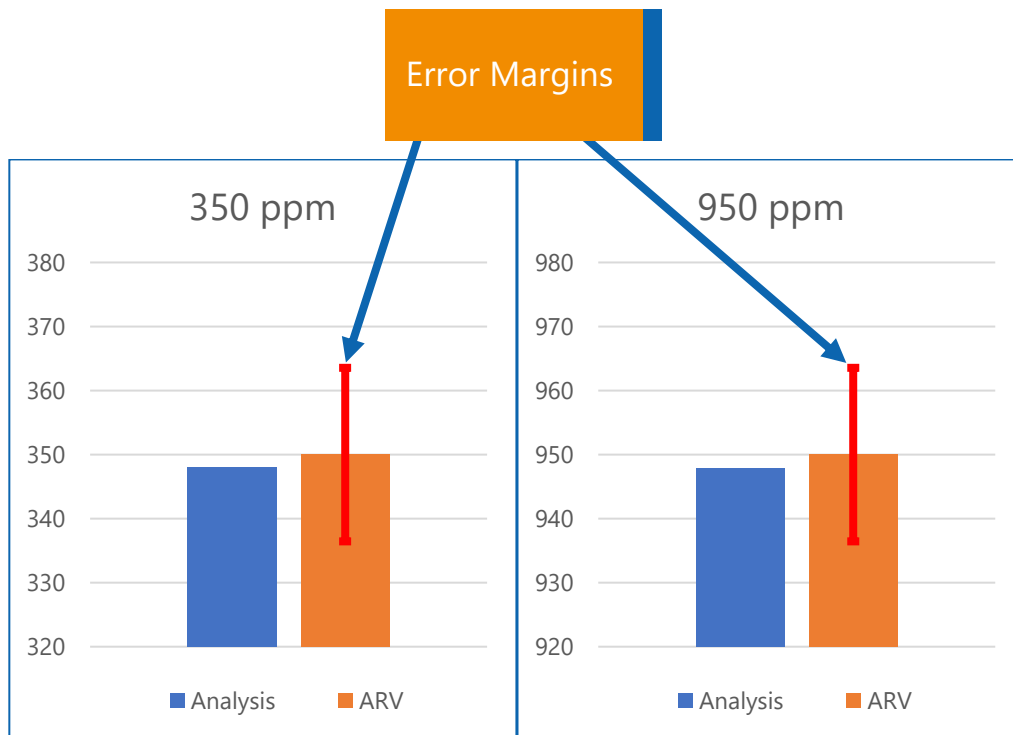


Accuracy

To validate the accuracy, conform the requirements, two gasoil standards are to be measured 10 times. One with a concentration of 300-400 ppm and another of 900-1000 ppm sulfur. In this analysis the two standards were 350 mg/kg and 950 mg/kg sulfur.

ECA Accuracy 350 ppm			
Injection	Counts	Conc. (mg/L)	Conc. (mg/kg)
1	576,316	290.0	348.9
2	575,573	289.6	348.5
3	575,634	289.7	348.5
4	576,000	289.9	348.7
5	574,854	289.3	348.0
6	574,436	289.1	347.8
7	574,568	289.1	347.9
8	573,749	288.7	347.4
9	574,083	288.9	347.6
10	572,868	288.3	346.8
Average	574,808	289.3	348.0
ARV			350.0
Difference			-2.00
Allowed			13.55

ECA Accuracy 950 ppm			
Injection	Counts	Conc. (mg/L)	Conc. (mg/kg)
1	1,559,638	790.4	951.0
2	1,559,929	790.6	951.1
3	1,559,404	790.3	950.8
4	1,556,925	789.1	949.3
5	1,555,677	788.4	948.5
6	1,553,101	787.1	947.0
7	1,552,010	786.6	946.3
8	1,550,762	785.9	945.5
9	1,549,878	785.5	945.0
10	1,547,819	784.4	943.7
Average	1,554,514	787.8	947.8
ARV			950.0
Difference			-2.17
Allowed			13.55



The ElemeNtS conforms to the maximum allowable difference, with 2.00 and 2.17 respectively, where 13.55 is allowed. This demonstrates the ElemeNtS's outstanding accuracy.

Conclusion

The results demonstrate that the ElemeNtS analyzer is a powerful tool, that meets and exceeds the requirements of both ASTM D5453 and EPA/MARPOL. Linearity is excellent, with a correlation coefficient of 0.9999 over the concentration range of the method. Superb accuracy and precision exceed the performance criteria of 40 CFR part 80.

In addition to the analytical performance, the ElemeNtS has several other distinct advantages. Each analyzer is factory tested and comes with a start-up kit, allowing for fast commissioning. High degree of automation with the 749 ALS and short analysis times of 5 minutes, enable large sample throughput. The 10" touchscreen can be used to fully control the instrument during daily use. Automated leak testing and the front maintenance door allow easy maintenance, making sure the analyzer maintains its superior performance. The safety features build into the ElemeNtS prevents hazardous situations and protects employees and assets from injuries and damage.

Please contact your local PAC representative for more information or a quote. We can provide both (online) demonstrations and the analysis of your samples, so you can observe the performance of the best sulfur and nitrogen analyzer on the market yourself.