Determination of Total Sulfur in Biofuels, from Feedstock to End-product according to ASTM D5453

- Analyze the Complete Scope of Biofuels with the Horizontal ElemeNtS
- No Need for Oxygen Corrections as with X-Ray Technology
- Interference-free Determination Using the Nitrogen Interference Kit
- Repeatability and Precision Meeting ASTM D5453 Requirements

Keywords: Sulfur, Biofuels, UVF, Feedstock, Diesel, D5453, ElemeNtS

Introduction:

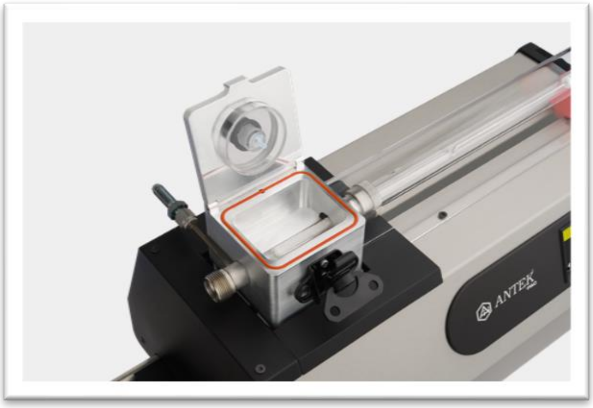
Sulfur is a natural component in both crude oil and biobased feedstocks that will be present in diesel and gasoline unless it is removed during the production process. Sulfur in fuels contributes to air pollution, so lowering the Sulfur content in these products contributes to the reduction of air pollution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

Hydrotreatment or hydrocracking is a process used after the pretreatment steps to upgrade the bio feedstocks into biofuels. This process not only converts the relatively large and complex molecules into molecules of the size and boiling point range of conventional fuels, but it is also used for the removal of heteroatoms including Sulfur (S) and Nitrogen (N). The analysis of these species in the feedstocks is used to control the treatment process and determine content in the final product. Final product testing is required for eventual product release.

In general, the first generation of biofuels derived from vegetable oils contain low concentrations of Sulfur. Second generation biofuel feedstocks can come from many different sources, such as animal fats and used cooking oil, and can have widely ranging Sulfur concentrations. To optimize the process and ensure end-product compliancy, it is very important to obtain analytically correct results. The many different feedstocks and products can complicate the analysis, as a single analyzer might not be able to easily handle samples that are solid, liquid, or gaseous without any extra sample preparation.

Measuring principle

Liquid samples are injected, by a fully automated liquid sampler, into a sample boat. Solid samples are weighed into this sample boat and placed on the boat carrier. The sample boat is then introduced into the combustion tube at a controlled speed. The combustion tube is heated by a furnace to 1050°C. The Sulfur bound components are 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) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here the SO_2 molecules are excited by the absorption of energy of a UV source and emitting light (fluorescence) while it relaxes to a stable state.

$$SO_2 + hv \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + hv$$

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.

Horizontal ElemeNtS

In 2018 PAC successfully introduced the Antek ElemeNtS for total Sulfur and Nitrogen analyses in liquids and gases. The standard method requirement of a boat-inlet introduction, as well as the ability to analyze viscous liquids and solid samples, have led to the development of the horizontal configuration of the ElemeNtS platform.

The horizontal ElemeNtS offers the same benefits as the vertical configuration. The ability to use the 749 ALS for high liquid sample throughput and the use of the PAC Accura for accurate gas and LPG injection. The 10″ touchscreen on the front offers full control of the instrument in addition to the automated vacuum and pressure tests for easy leak detection. The front maintenance door allows easy access to the consumables, eliminating the need to access the back of the instrument. In addition, the vertical and horizontal configurations share about 90% of their parts, eliminating the need for different stocks of spare parts and consumables.

Analytically the horizontal ElemeNtS is very similar to its vertical counterpart. It has a wide linear dynamic range of up to 10^4 for Sulfur, allowing for a single calibration curve of 0.1-1000 ppm. The working range is up to 1% mass. Its superb repeatability and excellent precision ensure it meets requirements. Each instrument is factory tested with round-robin samples, covering the range of products as defined in the method scope, and compared to the accepted reference value (ARV). The limit of detection is calculated according to ISO11843 and is <100 ppb for the horizontal ElemeNtS.

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.

Calibration

Two calibration curves were constructed to cover the complete range of samples. One for liquids, using dibenzothiophene in iso-octane standards, from 0 to 100 mg/L Sulfur, and another for solids using polymer standards from 1 to 500 mg/kg Sulfur. Results are displayed in tables 1 and 2.

The method editor in the IRIS software allows the technician to shorten or lengthen the calibration, depending on the concentration of the sample. Because of this option, only 1 method with corresponding calibration is necessary to quantify a wide range of samples with different concentrations of Sulfur.

Table 1: Liquid calibration

Sulfur 0-100 mg/L	
Conc. mg/L	**Area**
0	145
0.5	1684
1.0	3245
2.5	7954
5.0	16730
7.5	25170
10	33872
25	85957
50	172503
75	260795
100	345322
Slope	3465
Intercept	-419
Correlation	1.0000

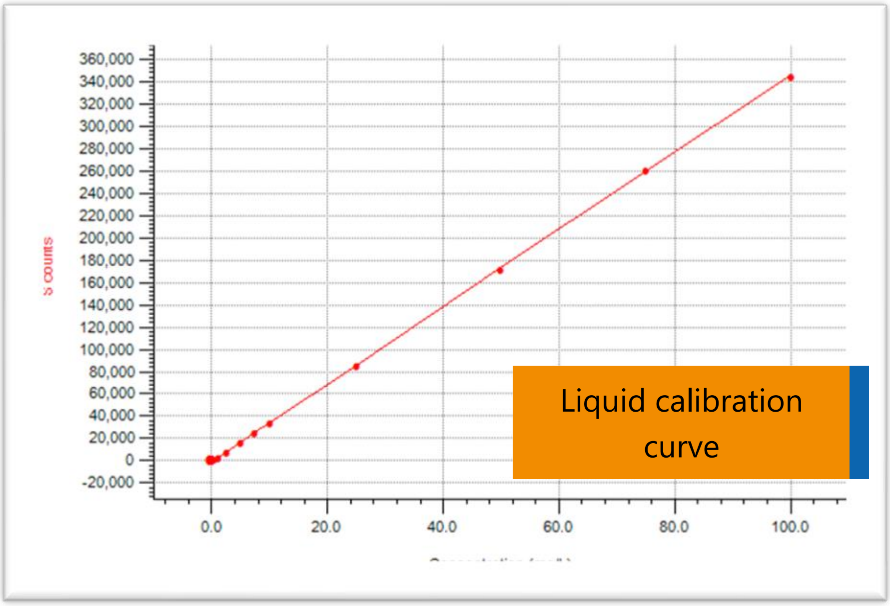
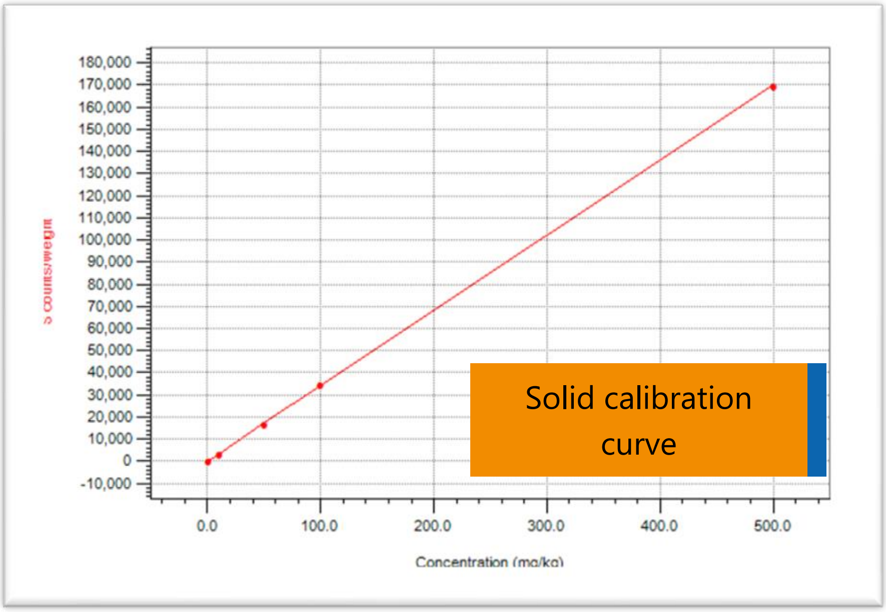


Table 2: Solid calibration

Sulfur 1-500 mg/kg	
Conc. mg/L	**Area/mg**
1	561
10	3234
50	17016
100	34881
500	169926
Slope	340
Intercept	225
Correlation	1.0000



Feedstock

Several biofuel feedstock samples ranging from first-generation feedstock such as palm oil, to second generation feedstock such as used cooking oil and waste animal fat are analyzed. The 2 used cooking oils were analyzed with the 749 autosampler, the palm oil heated and injected as a liquid as well. The solid samples (2 animal fats) were weighed into the sample boat (~20mg) and placed on the boat carrier before analysis.

Samples were analyzed at least three times, with two samples analyzed 10 times in a row to determine the repeatability standard deviation. This repeatability is compared to the ASTM D5453 repeatability although, strictly taken, solid samples are not included in its scope. Results are displayed in tables 3 and 4.

Table 3: Feedstock results

Feedstock results		
Sample name	**Conc. (mg/kg)**	**RSD %**
Used cooking oil 1	60.8	0.2
Used cooking oil 2	38.8	0.7
Palm Oil	24.0	0.4
Animal fat 1	6.46	1.9
Animal fat 2	113	1.2

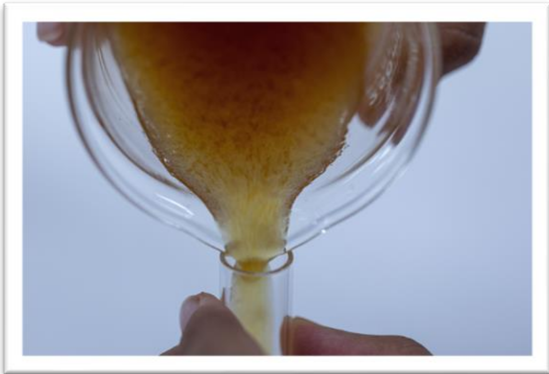
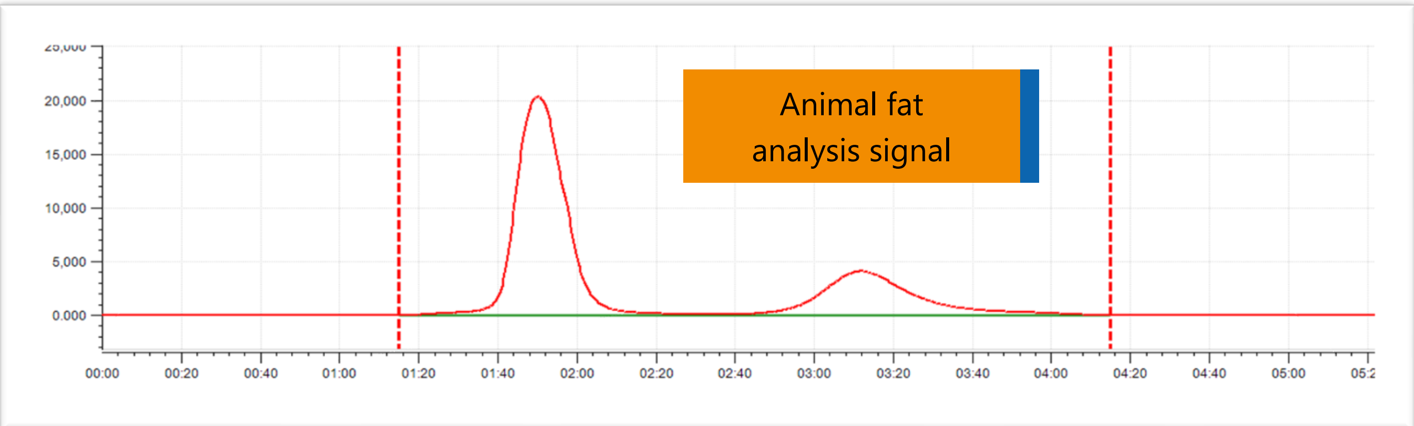


Table 4: Feedstock repeatability

Feedstock repeatability		
Injection	**Palm Oil**	**Animal Fat 2**
1	24.02	114.9
2	24.09	113.2
3	23.84	114.2
4	23.98	111.6
5	24.09	113.9
6	24.14	111.7
7	24.03	110.3
8	23.91	113.9
9	23.86	113.1
10	23.99	113.2
Average	23.99	113.0
Standard deviation	0.101	1.394
r (Analysis)	0.28	3.86
r (D5453)	1.94	6.20



Intermediates

There are several ways that biofuel feedstocks can be converted to a usable state:

- First generation biofuel feedstocks, like palm oil, are commonly trans esterified to produce fatty acid methyl ester (FAME), which can then be blended into traditional petroleum diesel.
- Hydrocracking is also commonly used to obtain hydrotreated vegetable oil (HVO), which has chemical properties very similar to normal diesel.
- Crops such as corn and sugar cane are used to produce ethanol through fermentation, which can be blended into gasoline.

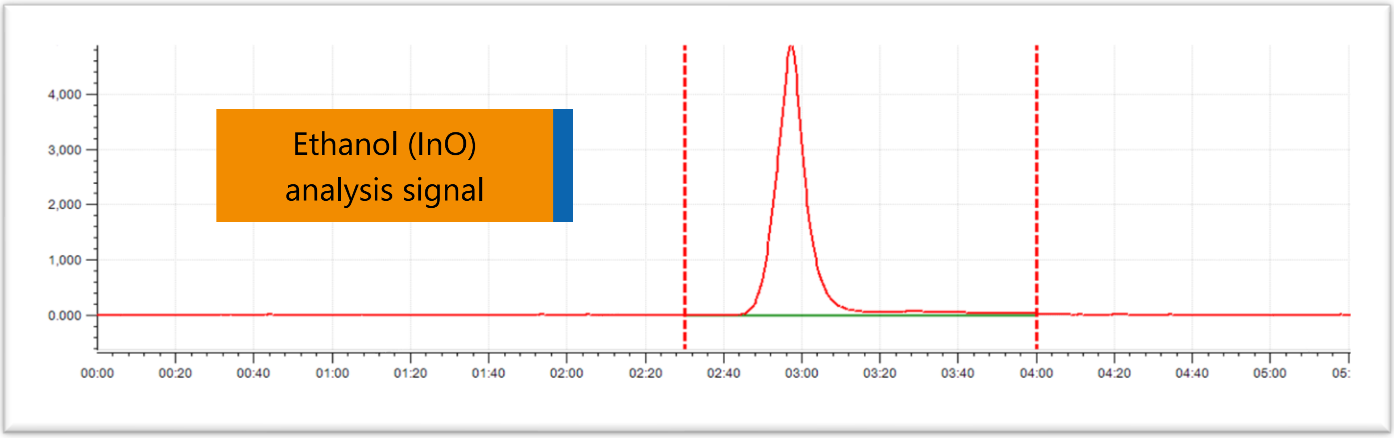
The samples analyzed are all liquid, as can be expected for material that is to be blended into diesel or gasoline. Three FAME's derived from used cooking oil (UCO), palm oil (PO) and animal fat (AF) were analyzed as well as two ethanol samples. The ethanol samples were spiked with either an organic (Org) or an inorganic (InO) Sulfur compound and the recovery determined. Results are displayed in tables 5 and 6.

Table 5: Intermediates results

Intermediates results		
Sample name	**Conc. (mg/kg)**	**RSD %**
FAME (UCO)	12.0	1.1
FAME (PO)	2.09	3.0
FAME (AF)	14.3	0.9
EtOH (Org)	10.0	0.4
EtOH (InO)	10.8	1.4

Table 6: Ethanol precision

Ethanol precision				
Sample name	**Target (mg/kg)**	**Conc. (mg/kg)**	**Δ (mg/kg)**	**D5453 R/√2**
EtOH (Org)	10.0	10.1	0.08	3.3
EtOH (InO)	11.1	10.8	0.29	3.5



End-products

Because of government regulations and tax incentives, the proportion of biofuels in the total energy consumption is rising. An example is the EU Directive on Renewable Energy. This directive sets targets for its member states and includes the proportion of energy used in the transport sector to be at least 10% biofuels by 2020. Gasoline with 10% ethanol (E10) and diesel with 7% FAME (B7) are widely available in the EU consequently.

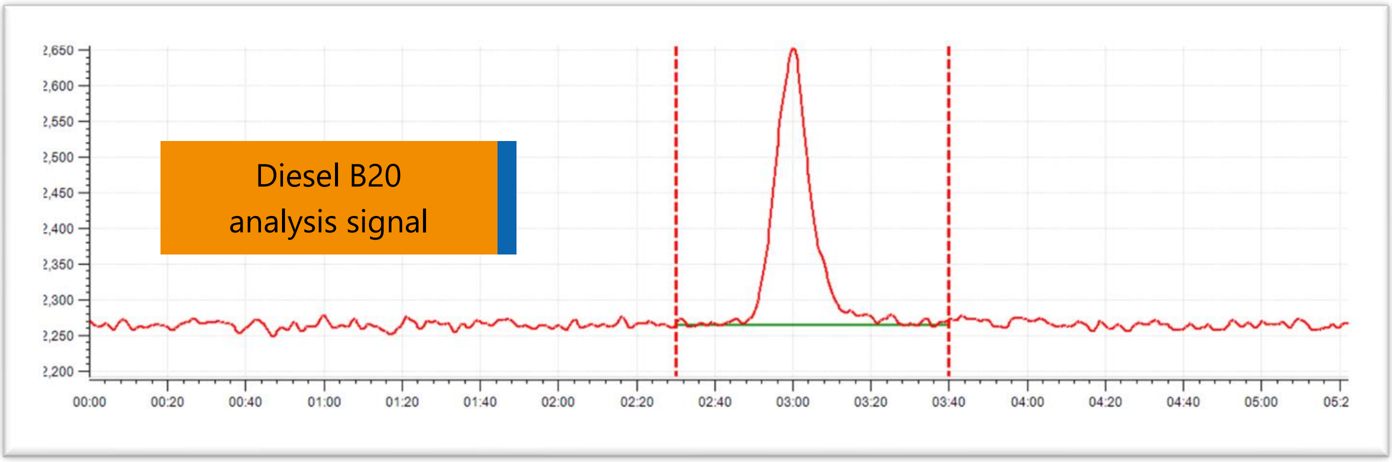
In this study, three different biodiesel blends (B7, B20 and B30) and two different ethanol/gasoline blends (E5 and E85) are analyzed by injecting 3 times. The B7 and both gasoline blends have verified concentrations derived from a performance testing program (PTP). The concentration found in this study is compared to the verified concentration using the ASTM D5453 reproducibility.

Table 7: End-product results

End-product results		
Sample name	**Conc. (mg/kg)**	**RSD %**
Diesel B7	9.84	1.0
Diesel B20	1.32	1.9
Diesel B30	1.22	1.2
Gasoline E5	5.12	2.5
Gasoline E85	1.79	2.3

Table 8: End-product precision

End-product precision				
Sample name	**Target (mg/kg)**	**Conc. (mg/kg)**	**Δ (mg/kg)**	**D5453 R/√2**
Diesel B7	9.64	9.84	0.20	3.20
Gasoline E5	4.42	5.12	0.70	1.87
Gasoline E85	1.72	1.79	0.07	0.88



Conclusion

The results demonstrate that the ElemeNtS analyzer is a powerful tool, that meets and exceeds the requirements of both ASTM D5453 and todays biofuel market. Linearity is excellent, with a correlation coefficient of 1.0000 over the concentration range of both liquid and solid calibrations. Very good repeatability for both liquid and solid sample analyses, better than the typical method repeatability. Precision is superb and well exceeding ASTM D5453 reproducibility, assuring the result is correct.

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 boat inlet drive (BID) giving 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.

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