Determination of Sulfur in Food using Combustion UV-Fluorescence with the horizontal EleмeNtS

- Boat-inlet drive suitable for edible oils, grains, and legumes
- Analysis time of 5 minutes for all matrices
- Minimal to no sample preparation required
- Excellent repeatability and precision when analyzing food

Keywords: Food, UV-Fluorescence, Combustion, boat-inlet, ElemeNtS

Introduction:

Sulfur is an essential element for all life, and therefore always present in biological materials like food. Several amino acids and vitamins contain sulfur in their structure. Sulfur is needed for biochemical functioning and is an elemental macronutrient for all living organisms. Many fertilizers contain sulfur, as plants need it for the formation of chlorophyll among others. Because it is such an important element, food producers or farmers want to know the concentration of it in their foods or plants.

A commonly used method for the determination of sulfur in a wide array of sample matrices is combustion UV-fluorescence. This method has a long history in the petrochemical and pharmaceutical industries. It is standardized in many standard test methods, such as ASTM D5453 and ISO 20846.

The sample, either a liquid or a solid, is introduced into a sample boat. This sample boat is then inserted into the combustion tube at a controlled speed. The combustion tube is heated by a furnace to a temperature of 1050°C. The sulfur bound components are vaporized and combusted, the released sulfur is oxidized to sulfur dioxide in an oxygen rich atmosphere.

$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O \qquad SO_2 + hv \rightarrow SO_2^* \qquad SO_2^* \rightarrow SO_2 + hv$$

A stream of inert gas (argon or helium) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here, a UV-lamp shines light of a specific wavelength on the molecules which are thereby converted to an excited state. It emits light (Fluorescence) upon falling back to the ground state.

A photomultiplier tube measures the emitted light and converts it into an electronic signal. This response signal is integrated to calculate the area. The sulfur concentration of an unknown sample is calculated using the linear regression function of the concentration 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. It is especially suited to the wide array of matrices that is encountered when analyzing food.

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 the requirements of standard test methods like ASTM D5453. 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).

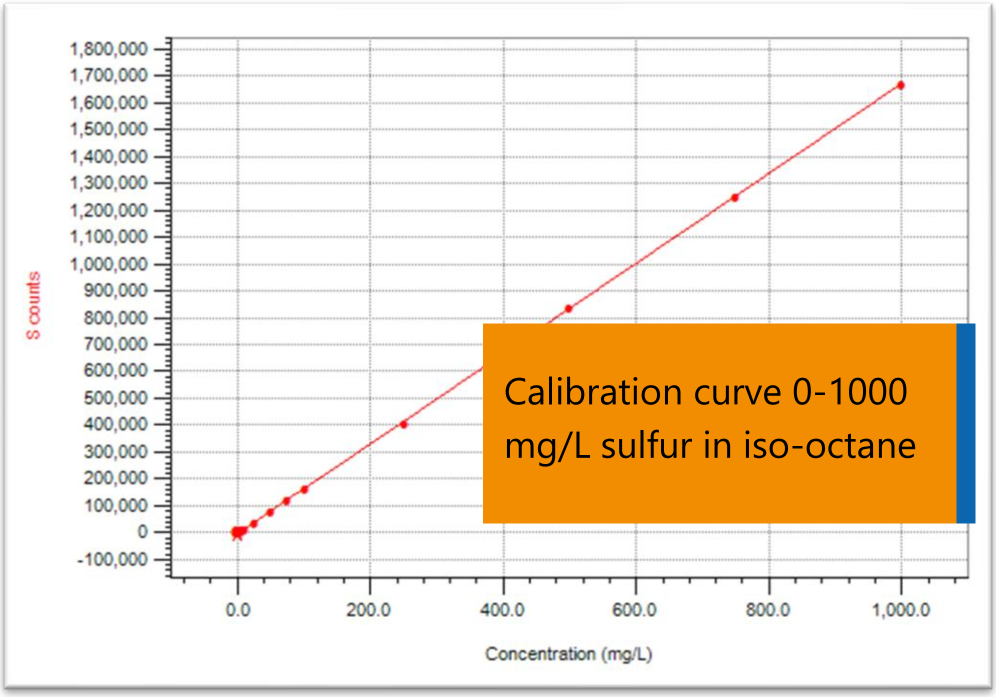
The limit of detection is calculated according to ISO 11843 and is <100 ppb for the horizontal ElemeNtS. The vertical configuration is preferred when analyzing ultra-trace samples.

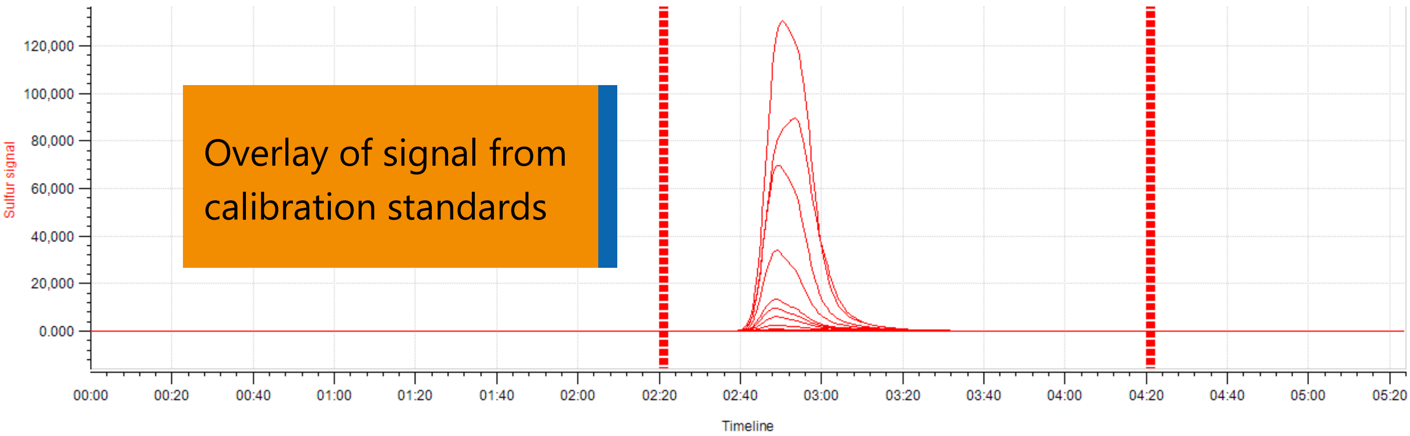
Calibration

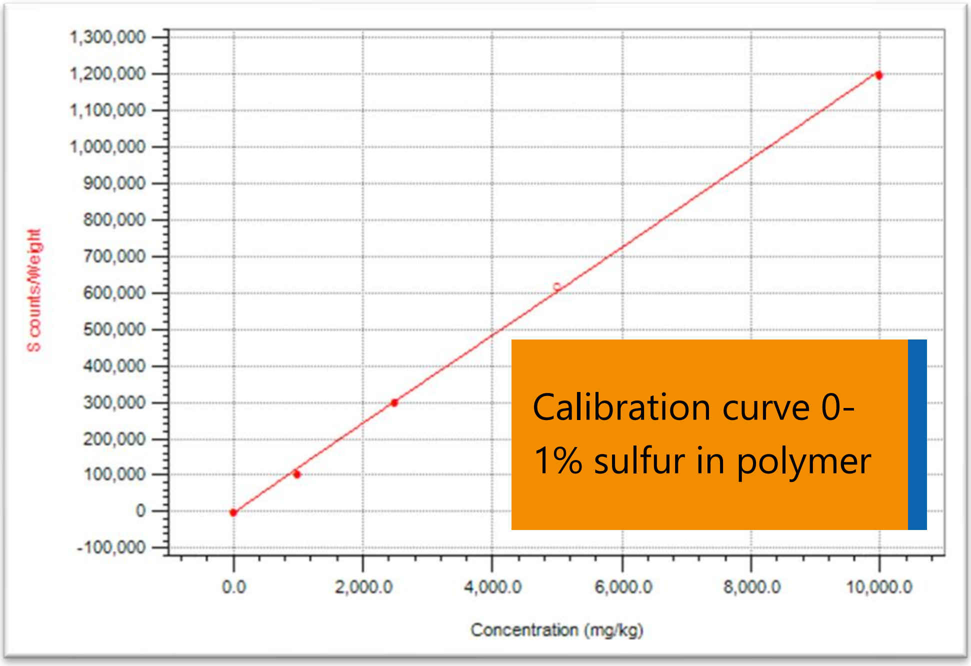
Good calibration is important to obtain correct results. In this case the ElemeNtS was calibrated twice, one liquid calibration using iso-octane standards from 0-1000 mg/L. The other calibration was for solids using polymer standards ranging from 0-1% sulfur.

Combustion UV fluorescence suffers less from matrix effects as some competitive techniques do. Therefore, it is not necessary to calibrate in the same matrix as the samples. Still, it is advisable that the calibrant and sample should match as much as possible. In the case of the solid calibration, a matching calibrant was not found and instead a polymer standard was used.

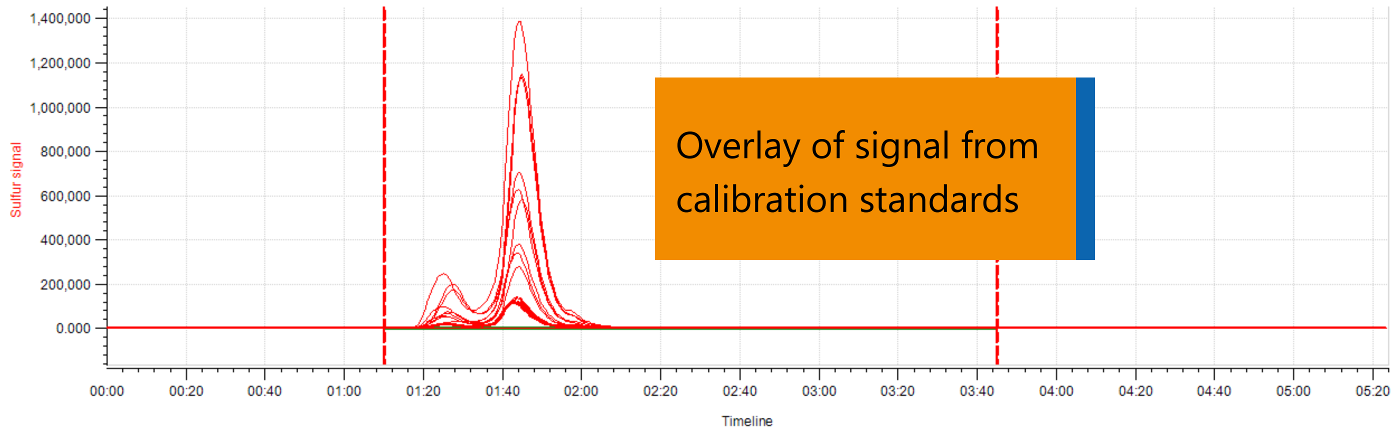
Calibration line 0-1000 mg/L	
Concentration S (mg/L)	**S counts**
0	43
1	1559
2.5	3969
5	7862
7.5	11997
10	14805
25	38314
50	82064
75	124059
100	166291
250	407703
500	842501
750	1251661
1000	1672960
Intercept	**-1506**
Slope	**1674**
R2	**1.0000**







Solids cal. 0-10000 mg/kg	
Concentration S (mg/kg)	**S counts/mg**
0	-2
1000	106244
2500	304128
5000	620933
10000	1201830
Intercept	**-1487**
Slope	**121**
R2	**0.9994**



The correlation coefficient for both the liquid and solid calibrations exceed 0.999. This indicates a very linear calibration curve and demonstrates the large working range of the ElemeNtS, which is up to 1% mass.

Results

To determine the suitability of the ElemeNtS for the analysis of food, different samples were analyzed. These samples were mustard oil, coconut oil, soybean meal and wheat flour. The mustard oil was measured pure, the coconut oil was heated before analysis to liquefy, whilst the soybean meal and wheat flour were measured as a solid.

Food samples results						
Sample	**S counts**	**S counts / mg**	**Conc. S mg/L**	**~D15**	**Conc. S mg/kg**	**RSD %**
Coconut oil	22708	-	14.47	0.92	**15.7**	0.6
Mustard oil	596446	-	357.2	0.97	**368**	0.2
Soybean meal	5296335	832323	-	-	**6885**	1.7
Wheat flour	2423121	210233	-	-	**1748**	1.9

The results show a very nice RSD for both the liquid and solid samples. The solid samples have an RSD that's a bit higher than the liquid samples, this is probably caused by weighing errors.

Repeatability

To validate the repeatability of the ElemeNtS analyzer, two samples were injected 10 times each. The repeatability standard deviation is then calculated and multiplied by 2.77 to obtain the repeatability r. This repeatability is then compared to the repeatability of ASTM D5453.

Repeatability		
Injection	**Coconut**	**Mustard**
1	14.52	356.6
2	14.49	356.4
3	14.30	357.6
4	14.48	357.6
5	14.40	357.8
6	14.41	357.2
7	14.61	358.1
8	14.46	357.3
9	14.42	356.2
10	14.56	357.5
Average	**14.47**	**357.2**
Std. dev.	**0.09**	**0.64**
r	**0.24**	**1.78**
$r_{(D5453)}$	**1.3**	**14.7**
Std. dev. (D5453)	**0.48**	**5.30**

Repeatability obtained is well within the limits specified by ASTM D5453. This demonstrates that the ElemeNtS is a very repeatable analyzer.

Conclusion

The results demonstrate that the ElemeNtS analyzer is a powerful tool, that meets and exceeds the requirements of ASTM D5453. Even though the scope of ASTM D5453 does not include food, compliance to its precision and bias is a good indicator of performance. The correlation coefficient of the calibration curves exceeds 0.999, indicating a very linear calibration curve. The obtained RSD for all samples is below 2%, and the repeatability is also well within the limits described by D5453. It can be concluded that the ElemeNtS is a very suitable instrument for the analysis of sulfur in food.

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, enables 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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