**PAC**

# Determination of Sulfur in Polymers by Boat-inlet Combustion and UV-fluorescence

- Horizontal ElemeNtS allows highly accurate analysis

- Repeatable introduction with the boat-inlet drive (BID)

- Protection of the optics against accidental sooting with the particle filter

- Fast analysis times: 5 minutes for both liquids and solids, shorter for gases

- Safety as a priority with automatic gas shutoff and furnace cooldown
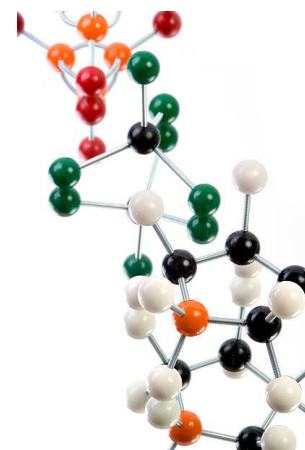
**Keywords**: Sulfur, polymers, UV-fluorescence, boat-inlet, ElemeNtS

## Introduction:

Polymers are substances consisting of very large molecules, composed of many repeating subunits. In the petrochemical industry, polymers most often are synthetic plastics. Some common examples of these plastics include polyethylene (PE), polypropylene (PP) and polystyrene (PS). They have a wide array of applications such as packaging, tires, insulation and many more.

Plastics often contain additives to make it more flexible, durable or fire-resistant. Examples of additives are plasticizers, fillers and stabilizers. Determining the concentration of additive in polymers is very important, as the desired effect depends on this. Some of these additives contain sulfur and therefore the concentration of additives can be derived from the concentration of sulfur.

Combustion UV-fluorescence is an established technique to determine the sulfur concentration in a wide variety of matrices. There are established standard test methods, such as ASTM D6667 for determination of sulfur in gas and LPG, or ASTM D5453 for sulfur determination in liquids. These methods are used to conform with both environmental regulations and product specifications. There is no established standard test method for the determination of sulfur in polymers. But the combustion UV-fluorescence technique can still be used for it.

## 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.

## Measuring principle

About 20 mg of solid polymer sample is inserted by boat-inlet drive, into a high temperature combustion tube where the sample is vaporized and combusted. The released sulfur is oxidized to sulfur dioxide ($SO_2$) in an oxygen rich atmosphere.

$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O$$
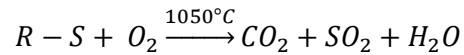
A stream of inert gas (helium or argon) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here the $SO_2$ molecules are excited by the absorption of energy of a UV source and emitting light (fluorescence) while it relaxes to a stable state.

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

$$SO_2^* \rightarrow SO_2 + hv$$
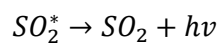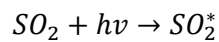
A photomultiplier tube measures the emitted light and converts it into an electrical signal.

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 samples versus integrated area.
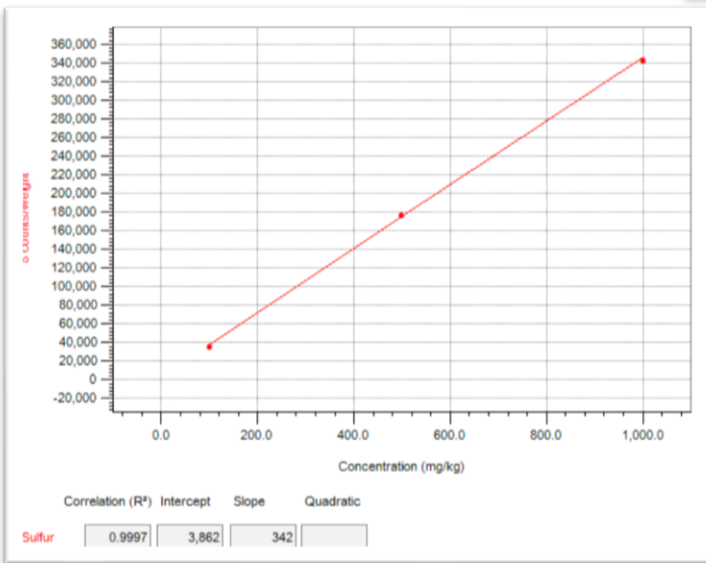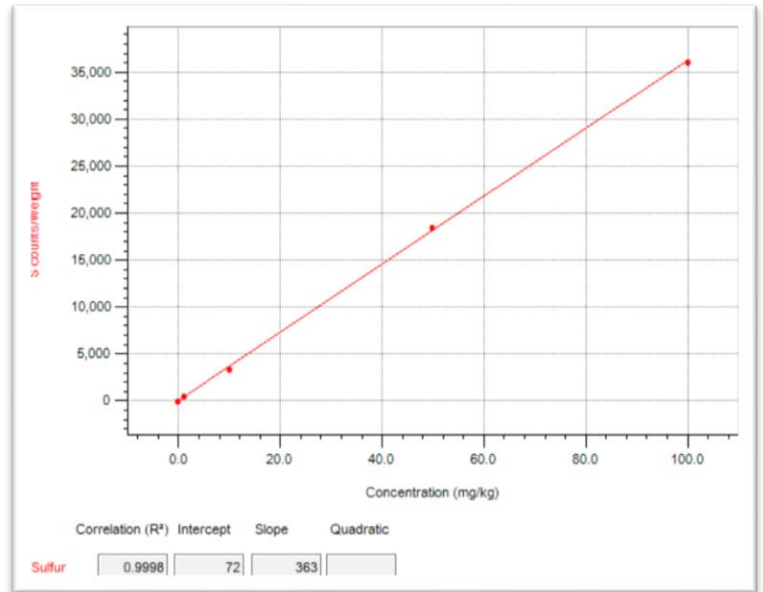
## Validation

The horizontal ElemeNtS total nitrogen analyzer system and methodology are rigorously tested for linear response, recovery, precision and repeatability to validate its performance.

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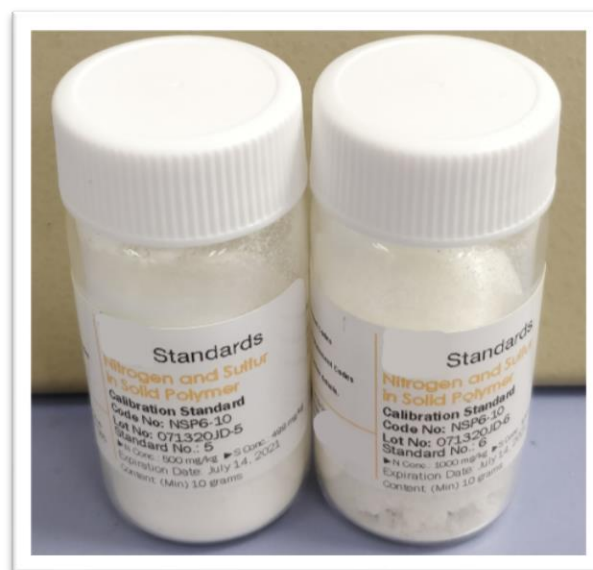
## Calibration

The ElemeNtS is calibrated using sulfur in polymer standards. Although the ElemeNtS is linear from 0.1-1000 mg/kg, two curves are prepared for optimum precision. One curve from 0-100 mg/kg and one curve from 100-1000 mg/kg.

| Solids 0-100 mg/kg | |
|---|---|
| Conc. mg/kg | Counts/mg |
| 0 | 13 |
| 1 | 568 |
| 10 | 3452 |
| 50 | 18500 |
| 100 | 36205 |
| | |
| Slope | 363 |
| Intercept | 72 |
| Correlation | 0.9998 |



| Correlation (R²) | Intercept | Slope | Quadratic |
|---|---|---|---|
| Sulfur | 0.9998 | 72 | 363 | |



| Correlation (R²) | Intercept | Slope | Quadratic |
|---|---|---|---|
| Sulfur | 0.9997 | 3,862 | 342 | |

| Solids 100-1000 mg/kg | |
|---|---|
| Conc. mg/kg | Counts/mg |
| 100 | 36205 |
| 500 | 177956 |
| 1000 | 344039 |
| | |
| Slope | 342 |
| Intercept | 3862 |
| Correlation | 0.9997 |
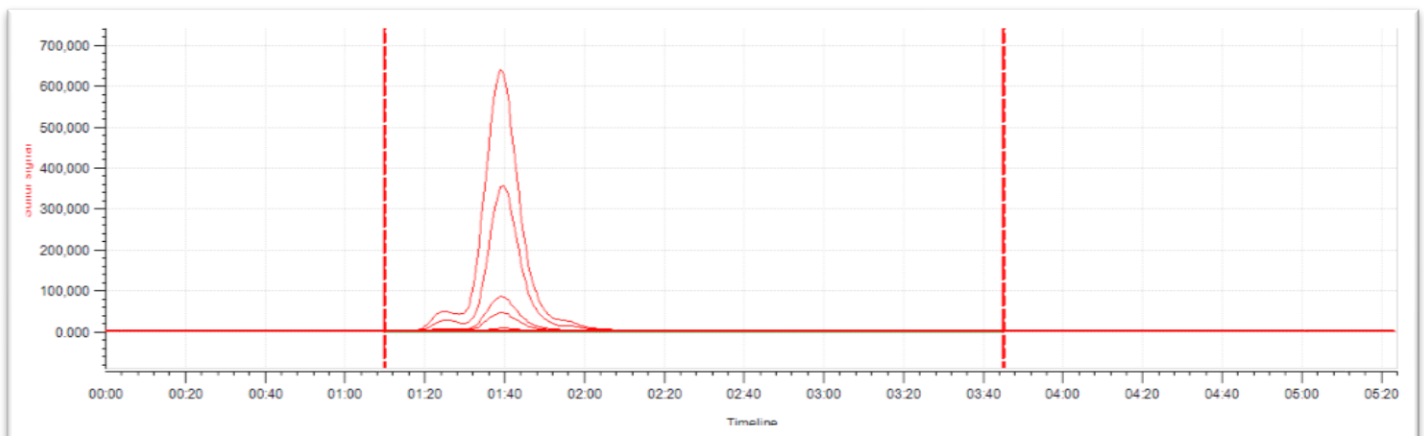
# Recovery and precision

To validate recovery and precision, two certified reference materials (CRM) are analyzed. These reference samples are ERM-EC680K and ERM-EC681K, which are manufactured by the Institute for Reference Materials and Measurements under the directorate of the European Commission's Joint Research Centre. Quantification of the samples was done using the appropriate calibration curve. The maximum allowed difference is obtained by an Inter Laboratory Study (ILS), using ICP-AES, IC and ID-TIMS.

| ERM Recovery and precision | | | | | |
|---|---|---|---|---|---|
| Sample name | Counts/mg | Conc. (mg/kg) | Target (mg/kg) | Δ Analysis (mg/kg) | Δ Allowed (mg/kg) |
| ERM-EC680K | 27215 | 74.86 | 74 | 0.86 | 4 |
| ERM-EC681K | 212207 | 614.0 | 630 | -16.0 | 40 |
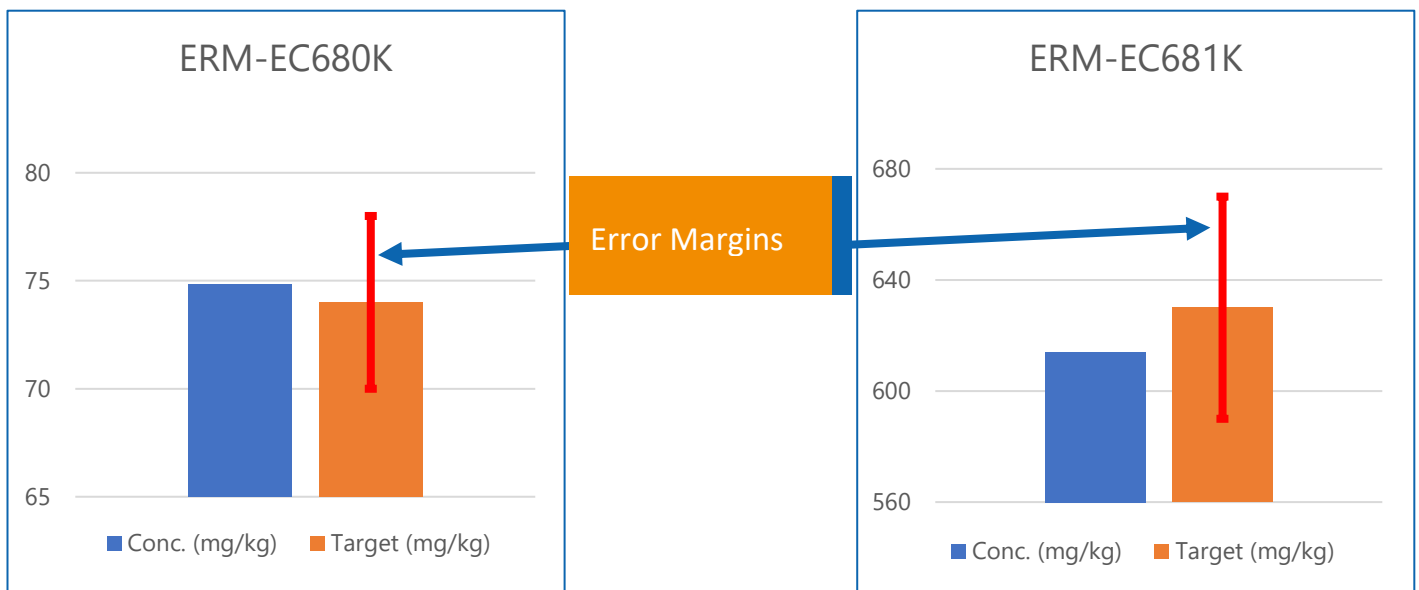


The quantified concentration is very close to the reference value. The observed deviation is less than the allowed difference derived from the ILS. The results can thus be labeled as significantly equal to the reference value.

## Repeatability

To validate the repeatability of the ElemeNtS analyzer, the reference materials were analyzed 10 consecutive times. The repeatability (r) was then calculated using the obtained standard deviation and compared to the method repeatability of ASTM D5453. Although this method does not include polymers in its scope, it is a good indication of the system performance.

The repeatability obtained during this analysis is well within the method repeatability of D5453.
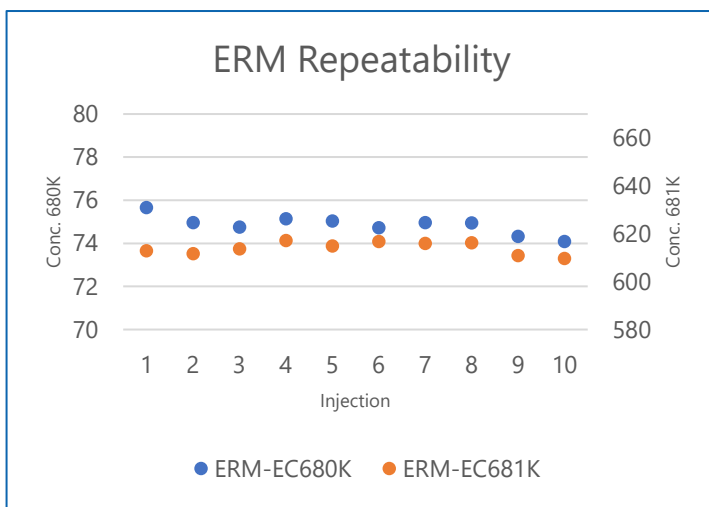
| ERM Repeatability | | |
|---|---|---|
| **Injection** | **ERM-EC680K** | **ERM-EC681K** |
| **1** | 75.66 | 612.9 |
| **2** | 74.96 | 611.7 |
| **3** | 74.76 | 613.7 |
| **4** | 75.14 | 617.1 |
| **5** | 75.04 | 614.9 |
| **6** | 74.73 | 616.7 |
| **7** | 74.96 | 616.0 |
| **8** | 74.94 | 616.2 |
| **9** | 74.32 | 610.9 |
| **10** | 74.08 | 609.7 |
| | | |
| **Average** | 74.86 | 614.0 |
| **Std. Dev.** | 0.436 | 2.624 |
| **Repeatability (r)** | 1.21 | 7.27 |
| **Method Repeatability ($r_{D5453}$)** | 4.55 | 17.82 |

**ERM Repeatability**

## Conclusion

The results demonstrate that the Antek ElemeNtS is a powerful tool, that meets and even exceeds the requirements. It has an excellent linearity, with a correlation coefficient of higher than 0.999 over the concentration range. Recovery and precision are very good, with significantly correct results for the two samples analyzed. The ElemeNtS has unrivalled repeatability, with the results far exceeding the demands set by the (indicative) method.

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.