APPLICATION HIGHLIGHT:

Elemental Analysis of WPPO: Sulfur & Nitrogen by UVF & Chemiluminescence

Introduction:

In comparison to mechanical and biological technologies, plastic pyrolysis as part of a chemical recycling drew a great attention for its economic and environmental benefits. It can convert plastic waste into WPPO which can be used as a fuel or valuable raw petrochemical materials. A sample WPPO is shown in Figure 1.

Pyrolysis is a possible route to utilize non-biodegradable materials as several countries are struggling with managing plastic waste. Pyrolysis of mixed plastic waste generates 50% less CO2 compared to energy recovery i.e., incineration. In addition, pyrolysis oil has several aromatic and aliphatic chemical components. Those components are quite diverse in their chemical properties as they may be cyclic, saturated, non-saturated, having long carbon chains and containing different elements such as sulfur, nitrogen, and oxygen.

Analysis of the chemical elements in the WPPO is critical to value its environmental impacts. Sulfur and nitrogen can change the chemistry of the water by acidifying it and fertilize the soils. Consequently, it can negatively impact on the plants and the aquatic life. Moreover, sulfur and nitrogen can negatively impact oil refining processes by its corrosive effect and poisoning of the catalysts. Thus, it is of a great importance to quantify the sulfur and nitrogen content in the conventional and alternative energy sources.

Figure 1: WPPO sample.

Analysis Techniques:

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

The sample is introduced into a combustion tube which 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. 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 (see Figure 2a).

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

An often-used technique for the determination of nitrogen is based on the chemiluminescence principle. A well-known method based on this technique is ASTM D5762. The nitrogen bound components are vaporized and combusted as well, the released nitrogen is oxidized to nitrogen oxide (NO) in an oxygen rich atmosphere.

$$R - N + O_2 \xrightarrow{1050°C} CO_2 + NO + H_2O \qquad NO + O_3 \rightarrow NO_2^* + O_2 \qquad NO_2^* \rightarrow NO_2 + hv$$

Similar to sulfur, the reaction products are transferred to a reaction chamber by a stream of inert gas. In this reaction chamber, which is under a reduced pressure (using a build in vacuum pump), the NO molecules are converted to excited NO2* by the addition of ozone. It emits light (chemiluminescence) upon falling back to the ground state (see Figure 2b).

For both the sulfur and nitrogen a photomultiplier tube measures the emitted light and converts it into an electronic signal. This response signal is integrated to calculate the area. The nitrogen concentration of an unknown sample is calculated using the linear regression function of the concentration standard mixtures versus integrated area.

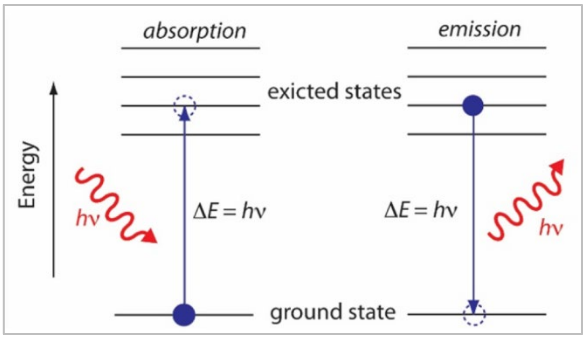

Figure 2a: UV fluorescence.

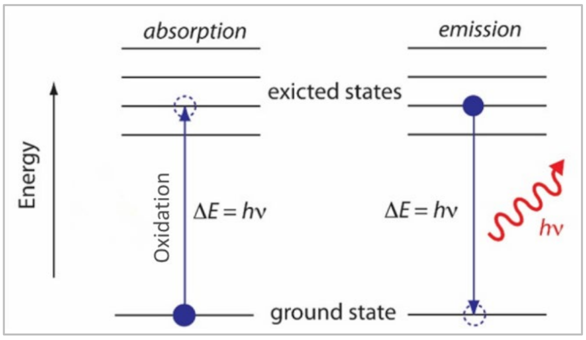

Figure 2b: Chemiluminescence.

Antek ElemeNtS

The Antek ElemeNtS is an analyzer for measuring the total sulfur (based on the UVF technology) and nitrogen content (based on the chemiluminescence technology) in various products. The system is capable of analyzing gases, liquids, and solid kind of products, for all kinds of industries, like oil and gas, petrochemical, pharmaceutical, foods, etc.

The analyzer is available in two configurations: vertical with a direct injection of the sample in a vertical mounted pyrotube, and a horizontal configuration where the sample is introduced in a horizontal type mounted pyrotube by means a boat. A certain amount of sample (can be liquid or solids), is introduced into a small ceramic boat. This sample boat is then inserted into the combustion tube at a controlled speed, using the boat-inlet-drive (BID).

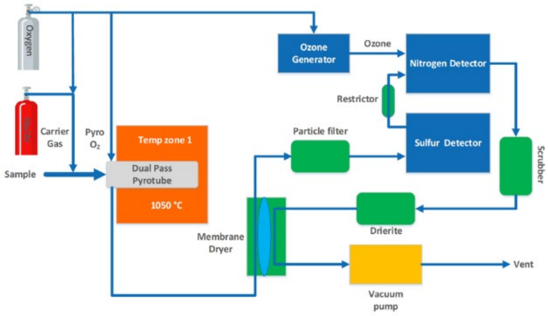

Figure 3: Simplifed Horizontal ElemeNtS system diagram.

Figure 4: Horizontal ElemeNtS system with Accura.

Analytically, the horizontal and vertical ElemeNtS are very similar. They both have a wide linear dynamic range of up to 104 for sulfur, allowing for a single calibration curve of 0.1-1000 ppm. The working range is up to 1% mass.

For the analysis of WPPO the horizontal configuration is preferred as it offers the flexibility of sample introduction by the BID. The product can be introduced into the boat in various ways, either as a liquid or weighed in if it is a solid or highly viscous product.

Calibration:

The Antek ElemeNtS was calibrated using iso-octane based standards from 0-1000mL concentrations.

Sample (mg/L)	N Count	S Count
Blank	282	69
1	1252	2748
2.5	2851	6883
5	5642	13942
7.5	8203	20979
10	11024	28119
25	27269	10043
50	54631	140017
75	80982	210651
100	108510	280586
250	261894	680884
500	508669	1354580
750	735514	2061659
1000	946308	2730294

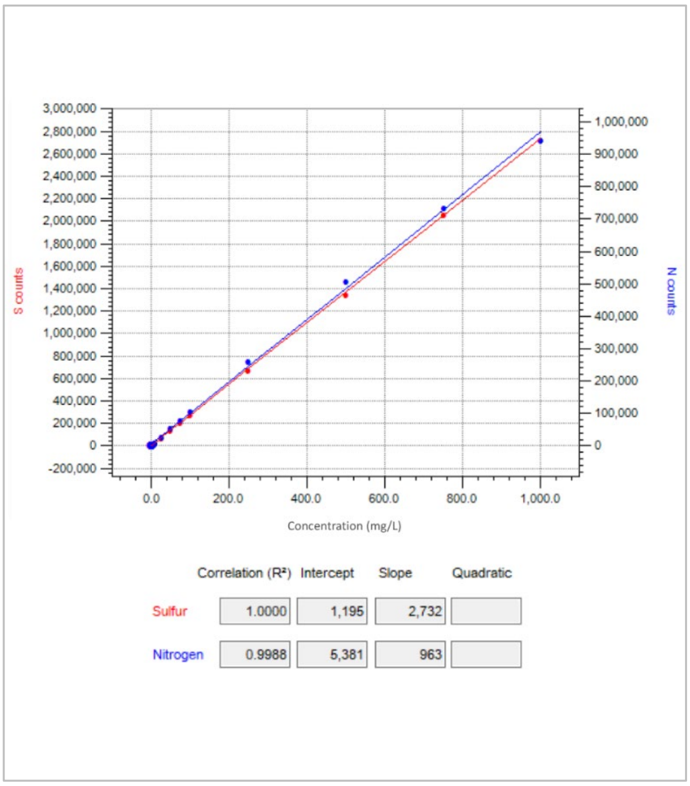

Figure 5: **Calibration line for 0-1000mg/L of sulfur and nitrogen in iso-octane based standards.**

The correlation (R^2) shows excellent results for sulfur and nitrogen calibration, as shown in Figure 5. It is 1 for sulfur measurements and 0.9988 for nitrogen.

Results:

A total of seven plastic WPPO samples were analyzed, and each sample was named and numbered to differentiate between them. A 10 µL of each sample was directly introduced in the boat of the BID without a need to dilute. Each sample was measured three times and the average of the three measurements is calculated by the PAC IRIS ElemeNtS software, as well as the repeatability (RSD's). Concentrations are reported in mg/L and mg/kg by taking into account the density of the samples as shown Table 1.

The PAC IRIS ElemeNtS software can also present an overlay of the analyzed samples, see Figure 6. The graph also clearly indicates a complete combustion of the product, which can be concluded from the peak shape and baseline.

Table 1: Summary results of seven different WPPOs.

Sample	S Count	N Count	S-RSD	N-RSD	Conc. S mg/L	Conc. N mg/L	Density kg/l	Conc. S mg/kg	Conc. N mg/kg
S1	363082	1488718	2.2	1.6	133	1538	0.8024	165	1916
S2	20389	366919	0.9	0.3	7	378	0.7594	9	496
S3	282559	680343	0.9	0.2	103	701	0.7819	132	897
S4	318369	689012	0.5	0.2	116	710	0.7852	148	904
S5	576065	135906	0.5	0.6	211	138	0.7755	271	177
S6	26376	266313	0.4	0.9	9	272	0.7737	12	352
S7	92999	660939	0.8	0.4	34	681	0.7887	43	863

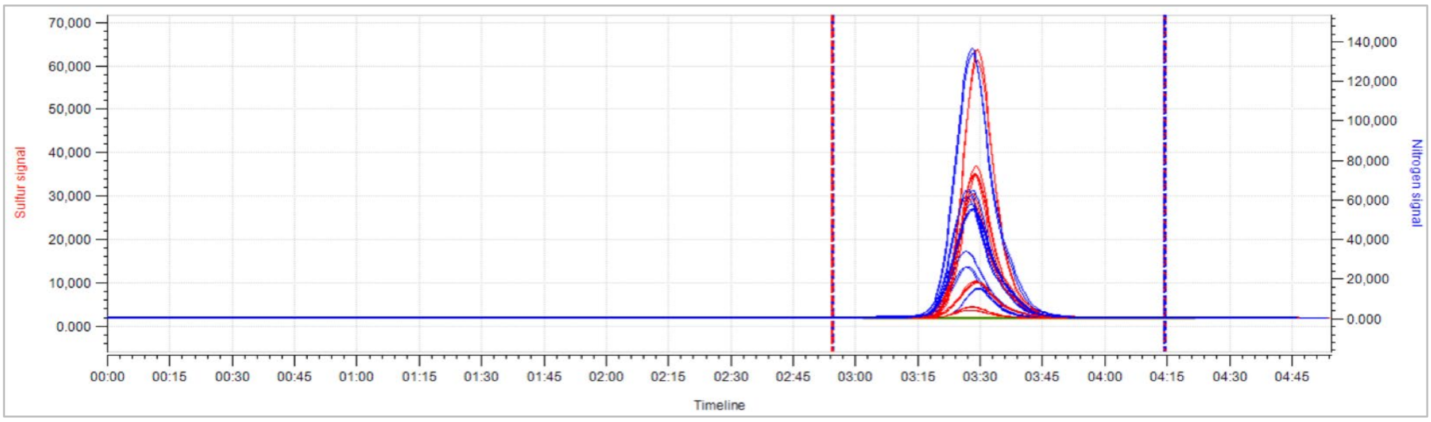

Figure 6: Signal overlay of various WPPO analysis.

The data in Table 1 implies that analyzed samples were determined to have sulfur (S) concentrations ranging from 9 to 271 mg/kg and nitrogen (N) concentrations from 177 to 1916 mg/kg, respectively. This suggests a need for further purification steps before their use as a fuel manufacturing or petrochemical feedstock purposes. In addition, the analysis shows the capability of Antek ElemeNtS on providing quite good repeatable results as RSDs for sulfur and nitrogen range from 0.2 to maximum 2.2%.

Conclusion:

The horizontal ElemeNtS analyzer is a powerful tool for the analysis of sulfur and nitrogen in sample matrices such as WPPO. The system is capable of analyzing the WPPO samples:

- In a wide concentration range
- Without sample pre-treatment
- With complete combustion
- In a short analysis time of 5 minutes
- With great repeatability

The linearity of the calibration curve is excellent with a correlation coefficient of 1 and 0.9988 for sulfur and nitrogen, respectively.

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