Productivity Boost in Sulphur (UVFD) Routine Analysis

The determination of total sulphur by means of combustion-coupled UV-fluorescence detection is an integral part of the daily routine in refineries and many other labs of related industries dealing with process and quality control. Independent of analysing feeds, process streams or ultra-pure final products, it is essential to have information about the "real" sulphur content in the shortest possible time.

This is to avoid any undesired effect like catalyst poisoning, corrosion of parts of installation, low quality of products, or exceeding legal limits. That's why the sulphur content of many different samples of the production process has to be determined in close intervals. This and the fact that fewer and fewer lab technicians analyse more and more, and in some cases challenging, samples is producing enormous pressure to deliver timely and reliable measurement values. Delayed or incorrect results significantly influence the performance and profitability of the company.

Where time is money, a technique that ensures fast and reliable analysis, independent of matrix effects and the operator's skills, is urgently needed.

Time pressure vs. reliability of results

In combustion-based organic elemental analysis, the very first step of the process – sample digestion – already determines the quality of the final result. Only a quantitative oxidation of all sample components can ensure trustable results. Sounds simple – but it isn't.

Petro-matrices can consist of several hundred compounds, including different aliphatic and aromatic hydrocarbons, alcohols, esters, nitrogen-containing additives, traces of sulphur-and halogen-containing impurities, and many others. As different as their chemical structure is their digestion behavior – evaporation, ignition etc. Only the complete oxidation of all matrix components can ensure a fast release of the required SO_2.

Depending on the furnace configuration used – vertical or horizontal mode – petro-matrices produce widely varying results. Regulatory bodies do not recommend the use of vertical mode for any matrices other than those with boiling point below 400 °C. This has a simple reason. Higher fractions mainly consist of compounds (long-chained, polyunsaturated or polycondensed structures), which cannot be evaporated under the given conditions. What happens, if this is attempted, is incomplete digestion with all its well-known facets – sticky pyrolysis residues, soot formation, increased system blank, instable base line and, last but not least, low-quality results. This normally makes the horizontal approach necessary, despite the drawbacks of remarkably longer processing times per analysis and the need for a skilled operator who is able to create an optimal program for the boat drive.

This is a dilemma! Either fast results, but with limited trustability and a remarkably increased maintenance effort, or reliable results, but with processing times that clearly reduce the lab's efficiency.

What is the best strategy?

The quartz-pyrolyzer is a valuable approach that benefits from the vertical advantages while avoiding its drawbacks. Even challenging samples (e.g. heavy diesel, pure plant oil) can be processed quickly, delivering correct results.

But there are much bigger challenges than the decomposition behavior of the sample matrix.

Especially in fuel analysis, undesired interferences endanger the correctness of results reporting. With the increasing utilization of nitrogen-containing additives (e.g. 2-ethylhexyl nitrate), the risk of exceeding the legal limit becomes a real threat. During combustion, such materials form NO and other oxides. Due to the positive cross-sensitivity of NO to UV fluorescence detection, the falsification of the measured sulphur content will be more or less significant. This effect is well documented in literature. Depending on the analyser type used, this results in 0.6 - 2 ppm of additional "false" TS per 100 ppm of "real" TN.

Considering that many fuels already have an actual TS content close to the specified limit of 10 ppm, this results in serious problems.

While a classic UV fluorescence analyser will give a falsified, excessively high result, the MPO technique enables reliable analysis without any extra effort. Compared to approaches like matrix-related calibration, utilization of N-based correction factors, or the usage of a trap and release separation system, which remarkably extends the analysis time, the MPO is clearly superior.

Meeting all challenges

A compEAct S[MPO] elemental analyser, equipped with new generation HiPerSens UVDF+ detection system and a LS 2 – liquids autosampler, was used for all tests.

The HiPerSens UVDF+ is including the patented Micro Plasma Optimizer (MPO), which ensures the correct sulphur analysis even in the presence of increased nitrogen content (e.g. diesel fuels with N-based cetane improver). A sample pretreatment, dilution of the higher concentrated samples or enrichment of the ultra-traces by trap and release technique, was not necessary due to the wide linear operation range of this detector. This ensures that the impact of operator mistakes will be lessened and the processing time of each sample will be remarkably shortened, independent of its concentration.

The MPO renders interfering nitrogen compounds harmless. This happens fully automatically as integral step of the analysis process.

Figure 1: compEAct S[MPO] with LS 2 liquids sampler and EAvolution software

The sample introduction was carried out fully automatically by means of the LS 2. For all samples, a volume of 10 μl was injected into the compEAct analyser. The quantitative combustion took place at 1050 °C.

To ensure a fast and complete digestion independent of the analysed sample matrix, a specially designed quartz glass reactor, including a quartz-pyrolyzer, was used.

The sophisticated management of process gases allows the lighter sample components to evaporate quickly and safely in a pure inert carrier gas atmosphere. Heavier components are pyrolyzed quickly and controlled on the active surface of the quartz-pyrolyzer. In this way, only the gaseous components can enter the combustion zone in the first stage of the process. In second stage, which immediately starts after injection was finished, the formed pyrolysis products as well as other heavier sample components, which were retained by the quartz-pyrolyzer, are digested quantitatively in presence of the sufficient amount of pure oxygen.

To avoid any undesired effect on long-term stability and sensitivity, the combustion gases were cleaned and dried sufficiently before entering the HiPerSens.

Before the formed SO_2 is detected by means of UV fluorescence,

the integrated MPO removes all interfering nitrogen compounds effectively. This is achieved with the assistance of powerful cold plasm ionization. The signal detected afterwards only represents the remaining SO_2.

Analysis Results

An advance of analysis the system was calibrated by means of standard solutions based on dibenzothiophene in iso-octane. Since combustion is optimal, matrix-related calibration strategies are redundant.

The seven samples examined (Table 1) are typical representatives of the wide spectra of petro-matrices. In general, three replicates were enough to gain trustable results.

Due to the optimal combustion, all samples could be processed in the same analysis sequence. This allows fast processing of most versatile matrices and in widely varying concentrations.
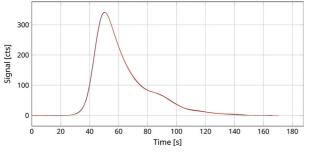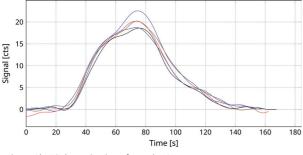

Figure 2a: TS determination of sample "5"

Figure 2b: TS determination of sample "2"

Table 1: Determination of sulphur contents with compEAct S^MPO

No.	Sample-ID	c_S	RSD
1	Gasoline	270 ppb	± 2.06%
2	Diesel (with 2-EHN)	7.27 ppm	± 2.10 %
3	Heating oil (HEL)	458 ppm	± 1.20 %
4	Heating oil (coker)	2,832 ppm	± 1.29 %
5	Diesel (high contents of bio-fuel)	5.33 ppm	± 0.75 %
6	FAME (pure)	1.59 ppm	± 1.96 %
7	Naphtha	47.4 ppb	± 13.4 %

Table 2: Comparison common Sulphur analyser vs. compEAct S^MPO

Sample-ID	compEAct S^MPO	Common analyser without MPO	c_S
"2" Diesel (with 2-EHN)	7.27 ppm	11.6 ppm	435 ppm

The high sensitivity of the HiPerSens detector enables minimal injection volumes and thus fast analysis results. Analysis times of approximately 3 min can be achieved for all analysed sample matrices, independent of their sulphur content.

Thanks to the MPO technology, the sulphur content can be determined free of "interference" and therefore correctly despite the increased nitrogen content of a sample. The results of sample No. 2 summarised in table 2 clearly demonstrate this.

Fast, reliable and matrix-independent

Whether they may be refineries or commercial analysis centers, modern routine laboratories require analysers that can be operated without any specialist knowledge, deliver reliable results in the shortest possible time, and require minimum human interactions at maximum sample throughput.

compEAct S^MPO is the ideal solution for demanding petro-applications and daily routine in such environments. With its on-the-point optimised vertical combustion and the wide linear operation range, combined with the advantages of the MPO technology, maximum productivity of the lab can be assured while operational effort is reduced to an absolute minimum.

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