



Total Sulphur Determination in Petro Industry and Refineries – Competitive, More Reliable and Faster than Ever Before

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The fast, reliable and cost-effective determination of sulphur impurities is an important task in the daily routine of quality control in refineries and petrochemical industry.

As described in crucial regulations like ASTM D7183, D5453, DIN 15486, 20846 and others, the most reliable method to do this is the thermal decomposition of samples followed by UV-fluorescence detection of the formed SO₂.

With conventional sulphur analysers, the time and effort required to achieve results can vary dependent on the sulphur content, digestion behaviour and composition of the sample matrix. Especially for the measurement of ultra-low and very high TS quantities, the process time can be remarkably extended. This affects the efficiency of the lab and thereby analysis costs.

Where time is money, better solutions are required! The multi EA[®] 5000 offers, independent of sulphur content, fast analysis – thanks to innovative HiPerSens detection.

Demand for fast sulphur analysis

During refining processes, even very low sulphur contaminations can poison the costly catalyst and thereby affect its effectiveness. Also the allowed quantity of TS in final products is strictly regulated by ASTM D 4814 and D 6751 as well as DIN EN 590 and 14214 must not be exceeded. That is why feed stocks, process streams and final products need to be monitored precisely to avoid problems.

Since the beginning, the determination of sulphur by UV-fluorescence technique has been approved as a valuable tool for process optimisation and quality control. Dependent on the process step, the sulphur contents to be determined can vary in a broad range, from a few ppb (e.g., raffinate) up to high ppm contents (e.g., intermediates).

In quality assurance every minute counts! This requires an analysis technique which enables a fast and correct sulphur determination independent of the concentration.

Instrumentation and analysis

An elemental analyser of the multi EA[®] series with an innovative HiPerSens detector was used for the examination of the samples. This UV-fluorescence detector is based on the intelligent wide-range principle, combining highest sensitivity with an impressively broad operation range (up to 10,000 ppm) and linearity. It can measure lowest contents (detection limit: 5 ppb S = 0.2 ng S absolute!) without difficulty or time-consuming enrichment procedures like trap and release.

Even for the presence of high TN contamination there is a strategy to gain correct results. As an option, the patented MPO technology renders interfering nitrogen compounds harmless.

The sulphur determination was carried out in a two-phase process at 1050°C. The samples were introduced by means of the multi matrix sampler MMS 5000.

In the first phase, the liquids are dosed directly into the evaporation zone of the multi purpose combustion tube. There evaporation and pyrolysis takes place in an inert gas stream. The resulting gaseous products are immediately oxidised in the oxygen-rich atmosphere of the combustion zone. This guarantees significant measurement peaks even for the smallest sulphur quantities. The second phase, which enables complete conversion of pyrolysis products, involves conditioning the analysis system by flushing it with pure oxygen. The benefit of this "self-cleaning step" becomes obvious when analysing sulphur contents below 500 ppb (ultra-traces). In this range, process blanks must be as small and stable as possible to gain reliable results.

The generated SO₂ is introduced to the HiPerSens detector after drying and purification. Thanks to its unique sensitivity and excellent reproducibility, there is no need for high injection volumes and many replicates. Generally, 2 or 3 analyses per sample are enough to gain reliable results.



Fig. 1: multi EA[®] 5000 with multi matrix sampler

Flexibility in calibration

The calibration of the system was carried out with liquid standards on the basis of dibenzothiophene in iso-octane. The flexible multiWin[®] software allows different strategies to ease calibration. Depending on the concentration range, the system can be calibrated with one single standard (Fig. 2b) and variable volumes (high contents), or with different standards (Fig. 2a) and fixed volumes (ultra-trace contents). There is no need to have many methods, one for each calibration range. Thanks to the intelligent multi-range principle, up to 5 different calibration ranges can be linked with one and the same method. Depending on the gained integral, the software fully automatically selects the suitable calibration to calculate the correct result. This simplifies laboratory routine and avoids the need for recalculation.

As a measure of quality and applicability, the multiWin[®] software calculates statistical data in compliance with DIN 32645 fully automatically.

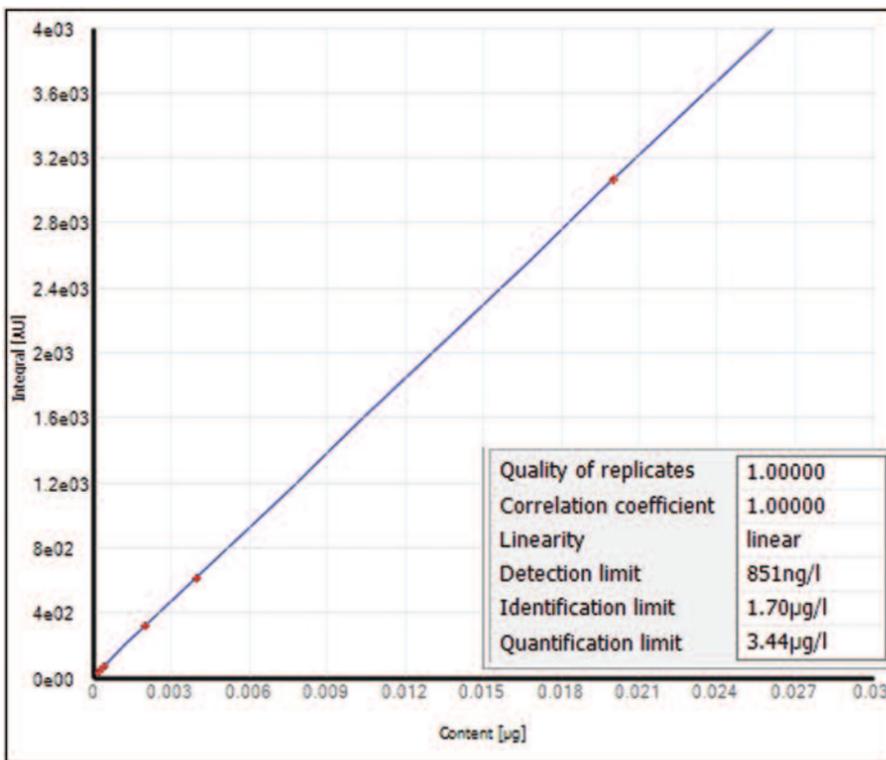


Fig. 2a: Calibration curve for ultra-trace contents

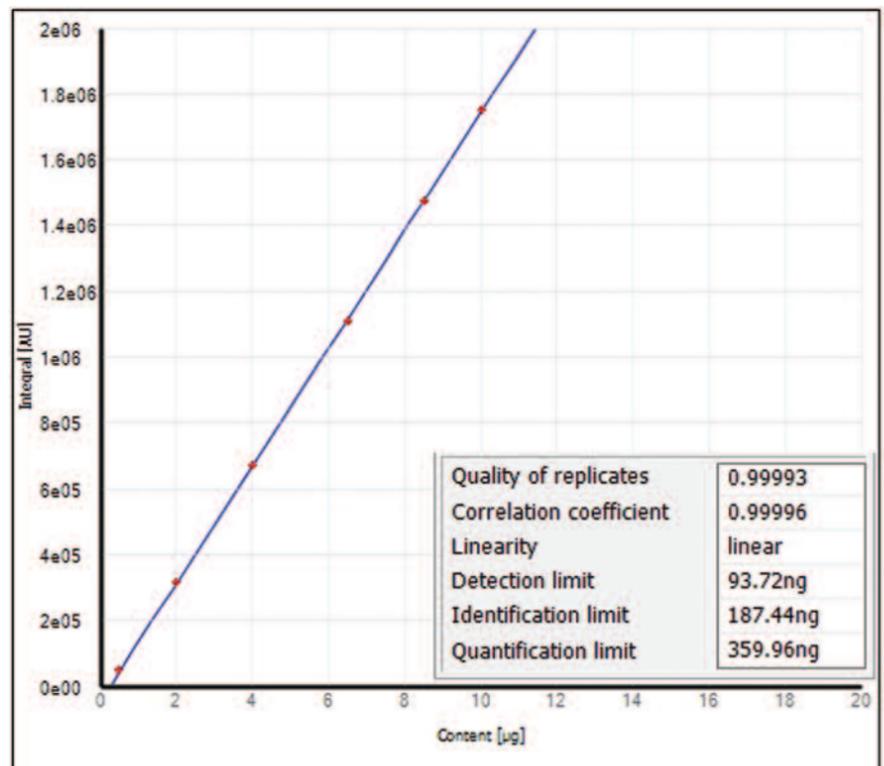


Fig. 2b: Calibration curve for high contents

Results

The examined samples are a representative spectrum of petrochemical matrices. The results of the sulphur determination of samples are summarised in table 1.

Table 1: Determination of the sulphur contents in petrochemical matrices

No.	Sample ID	TS	RSD
1	Raffinate	39.8 µg/l	11.3%
2	Naphtha	116 µg/l	0.36%
3	Gasoline	7.79 mg/l	1.38%
4	Jet fuel	1.91 mg/l	0.80%
5	Diesel fuel	1.61 mg/l	1.61%
6	Light heating oil (HEL)	106 mg/l	0.03%
7	Benzene	384 µg/l	1.79%

An analysis time of approximately 3 min can be reached for all analysed sample matrices independent of their sulphur content. Thanks to high precision of sampling and optimal combustion, normally 2 or 3 replicates are enough.

The impressive sensitivity of the HiPerSens detector allows the use of smallest sample quantities and thus short analysis times.

In addition, its wide operation range enables fast and comfortable analysis of high concentrated samples without the need of a time-consuming, costly dilution step.

Fast, reliable, economic – the three goals of high-throughput labs

While sulphur analysers which are still equipped with common UV-fluorescence detectors need significantly longer analysis times for the determination of very low sulphur contents (trap and release, multiple injection, extremely high sample volumes) or high sulphur contents (dilution), the multi EA® 5000 with its innovative and maintenance-free HiPerSens detector can make the job faster.

Integrated features such as Auto Protection, Self Check System, method library and automatic maintenance counter guarantee fast analysis, low downtime and extremely low running costs.

Extension modules like carbon, nitrogen and chlorine detectors or samplers for gases, LPG and solids enable the owner to benefit even more from his investment.

All these benefits turn the multi EA® 5000 into an analysis system which is ideally suited to meet the contemporary requirements of high-throughput analysis centers.

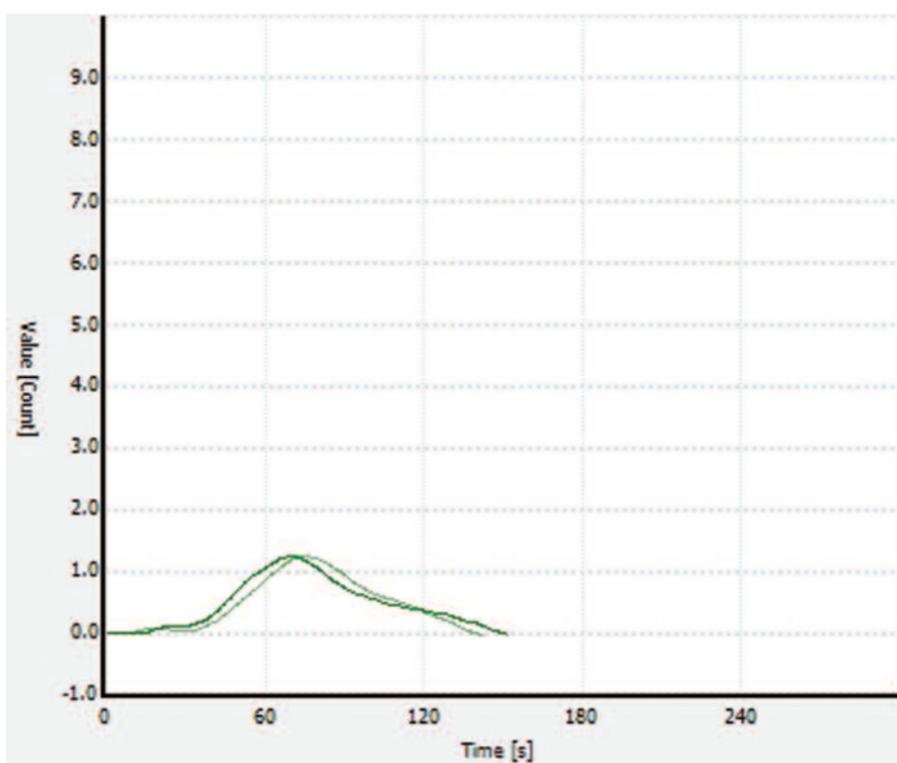


Fig. 3: TS determination of naphtha (ultra-trace content)

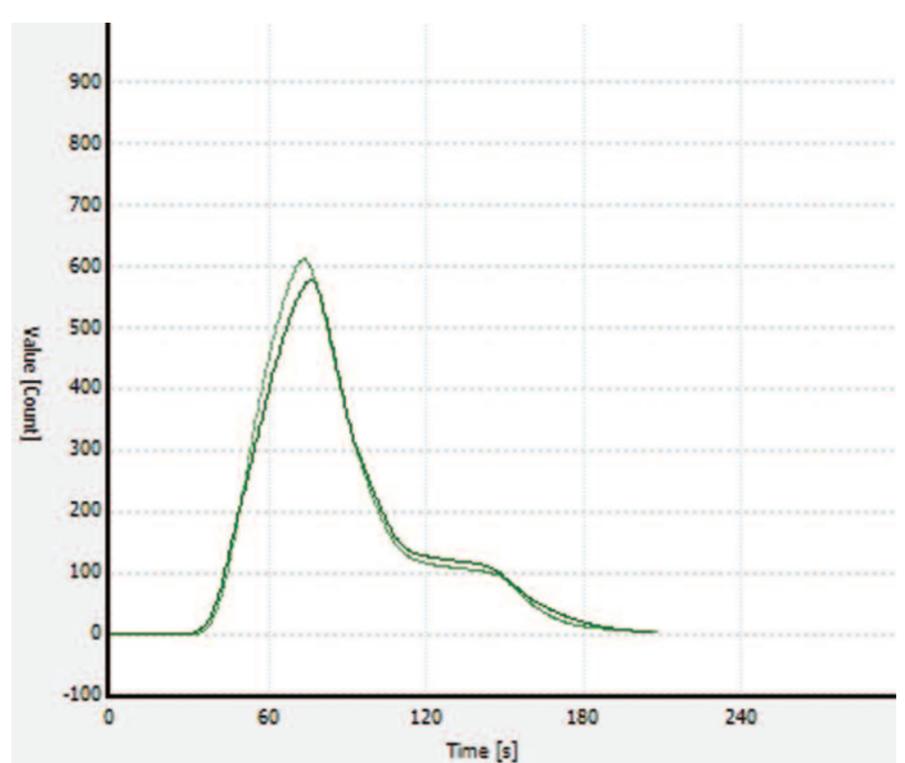


Fig. 4: TS determination of HEL (high content)

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