

Interference-free Sulphur Analysis in Fuels

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There is no question that fuels need to be monitored. During the combustion of carbon fuels, not only the carbon dioxide focused on in public discussions, but also other combustion products arise. In addition to various nitrogen oxides, sulphur oxides are of particular interest. If sulphurous organic substances are combusted, SO_2 is generated, provided there is sufficient oxygen supply. This compound acts as potent toxin, especially in the catalytic converters found in private cars in industrial nations. Furthermore, sulphuric acid (H_2SO_3) results from dissolving in water, one of the main causes of acid rain. Especially in Europe, this has caused multiple problems in nature and the environment, agriculture, as well as building damage during the 80s of the 20th century. Thus the intensive control of SO_2 entering the environment is of vital interest.

A major introduction of SO_2 is through the combustion of fossil fuels. Whereas large plants, such as power stations, often have flue gas desulphurisation equipment, the emission from smaller contributors, such as heating systems in houses or cars, must be controlled through the fuel itself. The limit values for sulphur content of fuels for transport were significantly reduced in recent years. In the year 2009 a 100 percent market penetration of sulphur-free fuel (< 10 ppm) was implemented in the European Union, and other industrial and industrialising nations are adapting to these limits. [1] Reductions for other fuel types are being planned. The sulphur content for maritime fuels in the North Sea and Baltic Sea, for example, as well as in the English Channel, is currently being reduced to 0.1% (presently 1.5). The same limit values will apply from that date onwards for the US and Canadian coasts. For the remaining EU waterways a limit of 0.5% (presently 4.5%) is being introduced. [2]

The safe monitoring of the sulphur content in various fuels is therefore a basic requirement for laboratories working in the various sectors of petrochemistry or refineries. For this purpose they also need a powerful analysis technology that can analyse both the end products and their raw materials. For the detection of SO_2 in combustion gases, detection using fluorescence induced by ultraviolet light has been proven to be successful. These UVF detectors have the advantage of measuring the SO_2 content in a flowing gas across a large measuring range. The advantage of UV fluorescence compared to other detection methods is its high sensitivity, longterm stability and high applicative flexibility. This is countered by the problem of cross-sensitivity to nitrogen monoxide (NO) which has a fluorescence within similar wavelengths.

Experimental

All measurements were performed using an elementary analyser from the multi EA® 5000 series. Dependent on the sample matrix and based on the double furnace option, a horizontal or vertical method could be used. The device also has an integrated gas box for controlling the gas supply as required.

For the horizontal method the multi EA® 5000 (fig. 1) was equipped with an automatic boat feeder. This controls, in combination with a flame sensor, the feed parameters autonomously and independently of the matrix and thus guarantees the complete conversion of the analytes. The combustion takes place in a two-zone combustion tube. During the first phase the analytes are pyrolysed in an argon atmosphere. These pyrolysis gases are passed to the second zone of the combustion tube where they are incinerated at 1050°C in a pure oxygen atmosphere. This produces SO_2 from sulphurous organic compounds in accordance with the following equation:



The analysis gases are passed to the UVFD module after drying and purifying.

The UV fluorescence detector used achieves a measuring range of max. 10,000 ppm and min. 5 ppb in sulphur without having to take recourse to rather lengthy procedures, such as "trap and release".

Quantification took place via a calibration using suitable standards. To this end di-benzo-thiophene was dissolved in ultrapure isooctane. From a 1000 ppm stock solution dilutions in isooctane of up to 50 ppb concentrations were prepared. To prepare a calibration graph, these standards were analysed using the same methods as for the subsequent analytes.

The different fuel types were supplied for combustion either vertically (highly volatile analytes) or horizontally dependent on their viscosity. In both methods the MMS5000 was used for automatic sample supply. Equipped with a syringe, it can dose these liquids. In combination with a gripper the samples can be handled as if they were solids. The control of the analyser and analysis of results took place using the device software.

Sulphur Detection in Fuels

An important requirement for analysis equipment in petrochemistry is the largest possible dynamic measuring range to allow for the analysis of both, raw or intermediate products, often heavy loads and end products with very low concentrations. Table 1 shows an example of this kind of analysis. Two production steps of bio diesel from wood oil were analysed. The raw product had an intensive colour and rather viscous consistency. It was analysed analogue to a solid in the horizontal mode. It was found that the concentration of sulphur in this raw material is rather high with 2400 ppm. The refined end product, on the other hand, a clear liquid of low viscosity, could be measured in a vertical furnace position. The sulphur content of less than 5.5 ppm is clearly below the statutory limit values, so that this product may be used as fuel additive or pure.

The high measuring range of the multi EA® 5000 permits the monitoring of the entire production process and can be used for different matrices arising.

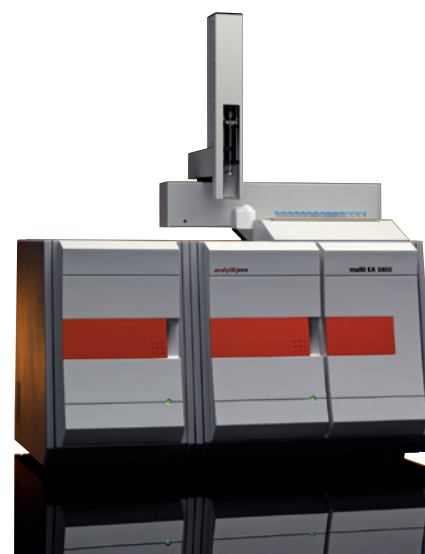


Figure 1: multi EA® 5000 by Analytik Jena

Table 1: Sulphur content of bio diesel from wood oil

Bio diesel (wood oil)	TS ± SD [ppm]
Raw material	2.430 ± 77.8
End product	5.43 ± 0.07

Different Refined Fuels

The following table shows the results for different fuel samples. The high precision of the results also means that a reliable result is available after only a few repeat measurements. All Diesel samples were measured horizontally as liquid in this case, the other samples vertically.

Table 2: Sulphur content in different refined fuels

Sample	TS ± SD [ppm]
Bio diesel A	2.98 ± 0.02
Bio diesel B	0.93 ± 0.01
Bio diesel C	0.86 ± 0.06
Bio diesel D	0.872 ± 0.02
Bio ethanol A	0.73 ± 0.01
Bio ethanol B	1.12 ± 0.02
Bio ethanol C	0.70 ± 0.01
Diesel A	1.61 ± 0.03
Diesel B	1.64 ± 0.02
Gasoline A	7.79 ± 0.11
Gasoline B	5.82 ± 0.02

Use of UVF Detectors with a Micro Plasma Optimiser (MPO)

When using UVF detectors, the already mentioned cross-sensitivity to NO can lead to distorted results. The fluorescence of NO tends to only have an intensity of 0.6 – 2% compared to the fluorescence intensity of SO₂, but in very nitrogen-rich samples with very low sulphur content this can cause problems. For example: 200 ppm nitrogen lead to a total sulphur result of 1 – 4 ppm. With the very low limit values for fuels the limit value may thus quickly be exceeded as a false positive result.

However, especially in modern fuels, nitrogen compounds are added to improve the combustion properties. Substances, such as amyl nitrate, cyclohexyl nitrite or tri-ethylene glycol nitrite make up to 5 %-wt, depending on the fuel. These so-called cetane improvers modify the ignitability and octane rating of petrol and diesel positively, but due to the increased nitrogen content ways must be found during the sulphur analysis using UVF detectors to eliminate this irrelevant content. This can be achieved by processing the analytes, e.g. by dilution with pure fuel. Or these expensive procedures are dispensed with and an interference-free detection method is used.

To measure samples with high nitrogen content, a UVF detector with the patented MPO technology was used. The MPO creates plasma in the gas flow that selectively oxidises NO to NO₂, so that the combustion products of the nitrogen compounds no longer display a specific fluorescence. This allows for the real sulphur content to be detected even if there is a large mass percentage of nitrogen in the sample, without the need for additional processing steps.

Table 3 shows the sulphur content of different fuels dependent on the activity of an MPO. The detected mass percentage of nitrogen for the respective sample is also stated. This was measured using a chemiluminescence detector (CDL) located after the UVF detector in an additional detector module within the measuring gas flow. The software permits the easy change-over from single element mode with the MPO enabled for sulphur to multiple element mode with the MPO disabled. It becomes apparent that at higher nitrogen concentrations the use of the MPO is useful to derive the true sulphur content.

Table 3: Sulphur content with and without MPO enabled and corresponding nitrogen concentrations

Sample	MPO on TS ± SD [ppm]	MPO off TS ± SD	TN ± SD
Diesel C	6.4 ± 0.07	6.7 ± 0.14	25.0 ± 0.01
Diesel D	9.8 ± 0.12	10.5 ± 0.02	73 ± 0.09
Gasoline C	7.5 ± 0.07	7.5 ± 0.03	5.3 ± 0.07
Gasoline D	11.9 ± 0.08	11.9 ± 0.07	3.0 ± 0.04

Summary

The examples above demonstrate that the multi EA® 5000 is ideally suited as a versatile sulphur analyser for the quick and simple monitoring of intermediate and end products. With its high measuring range and the flexibility of sample supply it permits the analysis of various matrices from highly viscous or solid to highly volatile material mixes. The use of an MPO further offers the option to perform reliable and specific analyses with the UVF detector used even where nitrogen content is high. The change-over from multiple element mode to single element mode is easily possible at any time, allowing the end user to adjust individually to the analytical problem faced.

The use of these methods is not only limited to fuels and their manufacture. There are many applications where a non-negligible amount of nitrogen is present in addition to sulphur in the analysis of organic matrices, such as polymers, grease, lubricants and oils for different uses as well as gases.

Sources

[1] <http://www.ifqc.org/Spotlight.aspx?Id=135> accessed 2014-05-13

[2] a) http://europa.eu/legislation_summaries/other/I21050_de.htm accessed 2014-05-13

[2] b) [http://www.imo.org/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-\(SOx\)-%E2%80%93-Regulation-14.aspx](http://www.imo.org/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-%E2%80%93-Regulation-14.aspx) accessed 2014-05-13

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New Partnership Challenges Traditional Sensing with Innovative Technologies for HP Processes

Servomex (USA), provider of continuous gas analysis solutions for the Hydrocarbon Processing (HP) and Natural Gas (NG) industries, has joined forces with H2scan, provider of accurate, tolerant and affordable hydrogen leak detection and process gas monitoring solutions, to provide complete light hydrocarbon measurement and analytical solutions to its HP and NG customers.

The new partnership completes Servomex's end-to-end offering for the innovative, multi component light hydrocarbon analyser and GC alternative the SERVOTOUGH SpectraScan by providing a more robust and reliable measurement of hydrogen in hydrocarbon gases, using a unique alternative technology to traditional thermal conductivity sensors. H2scan's hydrogen-specific sensing system is uniquely able to detect hydrogen against virtually any background gases without false readings or expensive support equipment required.

Rhys Jenkins, Market Sector Manager at Servomex, explains: "Unlike thermal conductivity sensors, the H2scan does not require significant application development for each mix of hydrocarbon gases, yet it exceeds industry standards. The combination of the two new and innovative technologies in the H2scan and SpectraScan is a head on challenge to traditional GC industry options for hydrocarbon sensing. The result is superior, yet simpler detection for HP and NG applications at considerably lower implementation and product lifetime costs for our customers."

The H2scan patented "Chip on a flex" technology provides a far more robust and reliable direct measurement of hydrogen than any thermal conductivity sensor, making it a natural collaborative partner for the SpectraScan "Tunable Filter Spectroscopy" optical sensor. As an out-of-the box solution, the H2scan is easily configurable alongside the SpectraScan and comes with customer support that matches Servomex's own customer-centric ethos.

Michael Nofal, Vice President Sales & Business Development at H2scan said: "Our hydrogen specific sensing systems based on a patented "Chip on a flex" technology have the ability to operate in real-time. This is important for the SERVOTOUGH SpectraScan which also operates in real time, unlike GC technologies which have a time lag. We also bring a host of benefits in terms of the lowest total cost of ownership, low maintenance and longer calibration intervals, simple system integration and installation and tolerance to harsh background contaminants."

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