



## Accurate Low Level Sulphur Measurement in Diesel with High Nitrogen Content Using UV Fluorescence

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### Finding a way to eliminate the nitrogen interference reveals not only true interference in the sulphur detector, but also an effect on the combustion of sulphur to sulphur dioxide.

#### Introduction

With the introduction of new regulations by the United States Environmental Protection Agency, the petroleum refining industry now meets strict limitations on the sulphur content of automotive diesel and gasoline. June 2006 marked the deadline by which most refiners had to meet a 15 parts per million (ppm) sulphur content limit for much of their diesel and gasoline production. ASTM method D5453, "The standard test method for determination of total sulphur in light hydrocarbons, motor fuels and motor oils by ultraviolet fluorescence" is a combusive UV Fluorescence technique used to quantify sulphur in gasoline and diesel fuel. It is a widely used analytical technique in the petroleum industry for measuring sulphur finished motor fuels.

Ultra-low sulphur diesels are already in use across much of Europe, and are expected to become a viable alternative to mainstream fuel in the United States by the year 2010. Although de-sulphurisation units are already in use in many refineries, they decrease the concentration of unsaturated hydrocarbon components, resulting in lower performing fuels. To achieve optimum performance levels from these low sulphur diesels, up to 1500 ppm nitrogen-containing compounds (cetane improvers) are added. The high amounts of nitrogen in samples nowadays result in a significant positive bias to the sulphur analysis results.

In a total sulphur ultra violet detector (TSUV), sulphur dioxide is excited using an ultraviolet (UV) light source. When the molecule relaxes into its ground state, the emitted light is detected. When the light beams are filtered sufficiently to a specific element, no interference is expected. However, the reality is that filters are not efficient enough and the elements have overlapping absorption spectra and overlapping emission spectra.

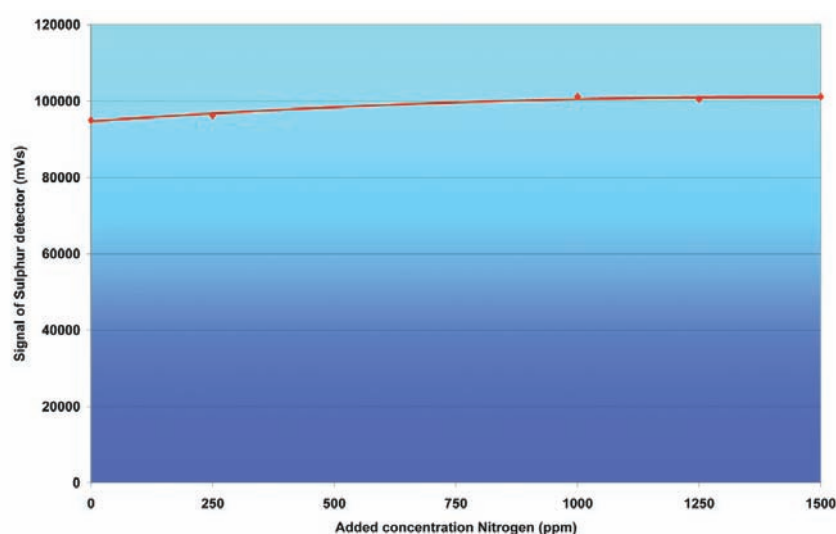
This article demonstrates a new patent pending method of solving nitrogen interferences using a UV-Fluorescence detection system (Thermo Fisher Scientific) for sulphur analysis.

#### Technology

Combustion and UV Fluorescence (UV-F) have been used for many years for accurate and fast analysis of low levels of sulphur in motor fuels. The combination of sensitivity, speed, ease of use, and low cost per analysis is unequalled by any alternative technique. However, UV-F detection is known to be limited due to the interference of nitric oxide (NO). High concentration levels of these nitrogen-containing compounds in the sample give a positive bias to the sulphur concentration measurement. One way to remedy this interference is to tune the UV-F detector, by using other excitation filters or detection filters but this does not completely eliminate the interference effect.

Even an optimised detector can detect nitrogen as NO which emits at the same wavelength as sulphur dioxide (SO<sub>2</sub>). Up to 0.5 % of the nitrogen concentration in the sample is measured as sulphur. Nitrogen as nitrogen dioxide (NO<sub>2</sub>) has a different absorption and emission spectra as NO and falls outside the cut-off bands of detector filters. Therefore, converting NO into NO<sub>2</sub> would solve the NO interference. The conversion of NO into NO<sub>2</sub> is done with ozone in the reaction:  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

When using ozone to eliminate the NO interference on the Total Sulphur analysers (Thermo Fisher Scientific), there is still an increase in the sulphur signal, as shown in Graph 1. A sample containing 250 ppm of sulphur is divided over 5 vials. To each vial a different known concentration of a nitrogen-containing compound is added, yielding samples containing 0, 250, 1000, 1250 and 1500 ppm of nitrogen.



Graph 1: Effect of nitrogen on the sulphur analysis using ozone

To validate the effectiveness of the ozone, another experiment was conducted. A sample containing no sulphur, but 100 ppm of nitrogen was analyzed with and without the ozone mixture. The interference of nitrogen to sulphur was 1.3 ppm when no ozone mixture was applied. By mixing the effluent with ozone before the detector, a value similar to a blank measurement is obtained. Even with adding additional NO to the furnace, the contribution of the NO signal to the sulphur signal has been reduced to virtually zero. Therefore, only sulphur emits inside the detector, as shown in table 1.

Table 1: Nitrogen interference using different analyzer set-up

	Measured Sulphur (ppm)
Standard method	1.3
Mixing Ozone after furnace	0.03
Additional NO in furnace and mixing ozone after furnace	0.02

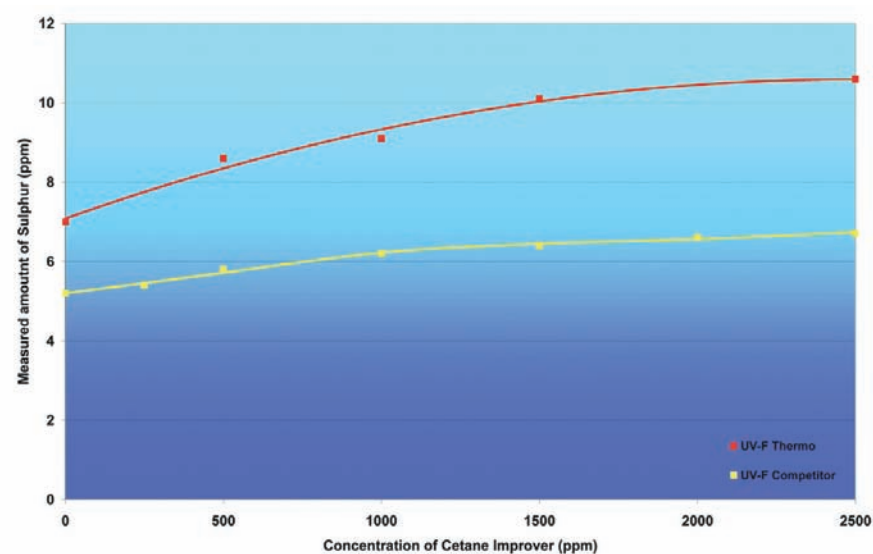
Therefore, the increase in signal as shown in graph 1 cannot be a contribution of NO to the TS signal, as the NO is completely eliminated. But, what is the cause of the increase of the sulphur signal at different nitrogen levels in the sample?

#### Experiment

Thermo Scientific Total Sulphur analysers are capable of detecting sulphur at extremely low levels in solid, viscous liquid, gas or liquefied gas samples and can be used for the determination of total sulphur in motor fuels and a wide variety of light and heavy hydrocarbons.

The TS 3000 and SphiNCX system (Thermo Fisher Scientific) incorporates a high-end pulsed ultraviolet (UV) fluorescence detector, which offers increased sensitivity, greater long-term stability and reduced operating costs when compared to continuous source UV-Fluorescence. With optional mass flow controllers for ease-of-use and reproducibility, the turbo combustion tube allows even demanding sample types to be analysed accurately and reliably.

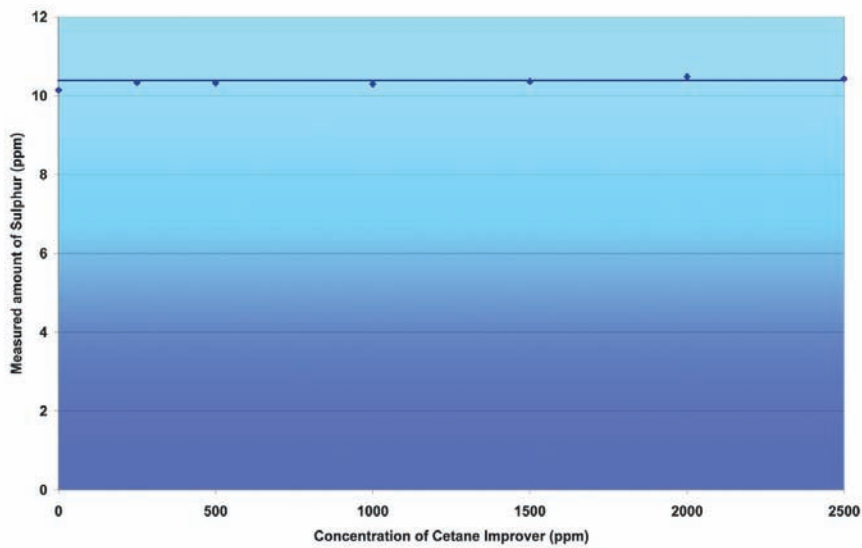
Graph 2 shows a sample range to which cetane improver has been added and measured on different systems.



Graph 2: Impact of the cetane improver concentration on the sulphur analysis

Graph 2 shows that the impact of any concentration of cetane improver on sulphur is minimized in the region of above 1500 ppm.

When sulphur is combusted into its oxides inside an oxygen rich environment, the achievable yield of SO<sub>2</sub> is approximately 90%. The yield is the proportion of the amount of sulphur originally contained in the sample that is actually converted into sulphur dioxide. Although the exact process that takes place inside the furnace is not yet known, there are indications that oxygen radicals can be the cause of the conversion of SO<sub>2</sub> into SO<sub>3</sub> (the UV-Fluorescence detector principle is not sensitive to SO<sub>3</sub>). At higher levels, the cetane improver works as a yield improver inside the furnace, which increases the overall yield of sulphur in the sample. With these samples, a greater quantity of sulphur dioxide for a given sample volume or mass will be produced, offering improved detection. Additionally, depending on the amount of yield improver used for a particular sample, it is possible to provide a consistently greater yield of sulphur dioxide from the sample than has been previously possible. Thus, the effect of the variation between samples is eliminated and the analyses become matrix independent.



Graph 3: Effect of concentration of cetane improver on sulphur measurement using new technology

Researchers at Thermo Fisher Scientific invented a process in which a defined amount of NO is added to the sulphur sample in the furnace inhibiting the formation of SO<sub>3</sub>, resulting in a higher yield combustion of SO<sub>2</sub>. Table 1 shows that the addition of NO into the furnace as a yield improver is fully eliminated by the ozone. Graph 3 shows that there is no effect of the concentration of the cetane improver in the sample on the result of the sulphur analysis.

### Conclusion

UV-Fluorescence detection for sulphur analysis is subject to interferences from NO. A well tuned detector may suppress the interference effect. Today's low level sulphur diesels contain high levels of nitrogen-containing compounds as cetane improver. Because of these high levels, even a well tuned UV-Fluorescence detector suffers from the interference of the nitrogen in the diesel. Adding ozone to the effluent to eliminate the NO reveals a parallel effect in the combustion furnace. Adding a defined amount of NO gas to the feed gas of the analyzer makes the combustion conditions in the furnace independent to the matrix. These two principles can be applied as an option to the Thermo Scientific TS 3000 and SphINX analyzers to enable accurate low level sulphur analyses in samples with high concentrations of nitrogen.

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### An XRF for all Requirements

Industry experts have come to expect superior performance from **Rigaku** (USA) wavelength dispersive X-ray fluorescence (WDXRF) spectrometers. Rigaku currently offers three benchtop WDXRF spectrometers: the Primini, the single-element Analysers, and the ZSXmini II. All represent a paradigm of providing outsized performance in small packages.

The new Primini benchtop spectrometer represents the next stage in the evolution of Rigaku's line of WDXRF instrumentation. Using just three crystals, the Primini is capable of analysis from F9 to U92 in a vacuum atmosphere. Since it is a WDXRF system, the Primini does not have the resolution problems typically associated with EDXRF instruments, nor does it suffer from a lack of light element sensitivity.

The Mini-Z series of benchtop WDXRF analysers are designed for analyzing specific element(s). Since the optics are configured to a particular element(s), this series allows for high precision and ease of analysis. The Sulphur Analyser, configured for analysis of S in fuel oil, gasoline, diesel, etc., meets the 15 ppm EPA regulation, and has a LLD (lower limit of detection) of 0.3 ppm. This instrument can also be configured as a Si or Al Analyser (e.g., for coated Si or Al on paper or plastic), an Ni Analyser (e.g., for Ni coating of plating) or a Zr Analyser (e.g., for Zr coating).

The ZSXmini II is an affordable, full range, easy-to-use, air-cooled, benchtop WDXRF spectrometer. A perfect choice for mobile laboratories, research or teaching applications, this low-cost instrument is capable of performing quantitative analysis under vacuum or helium without standards using the included advanced fundamental parameters software.

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### Trace Analysis of Sulphur and Nitrogen in Gasoline or Diesel



Trace Analysis of Sulphur and Nitrogen in Gasoline or Diesel is a major challenge for the oil related industries. Concentrations of these elements in petroleum products has an immediate influence on the environment or the production process. These days, special attention is paid to the drastic reduction of sulphur concentration in gasoline or diesel. The expectation of an adequate analysis method requires reliable results down to < 5 ppb for S.

**Elementar Analysensysteme GmbH's** (Germany) newly developed instrument vario Trace S/N combines two complete combustion detection channels in one instrument. This allows maximum detection for sulphur and nitrogen even in a combination instrument without any compromises.

A further key in trace analysis is the possibility to inject up to 80 µl of gasoline or 10 ml of propane within a few seconds only for an absolutely residue-free combustion. This serves for sharp and high peaks which are even further enhanced by means of the purge-and-trap-technique – as in the case of sulphur. The highly sensitive detection methods such as chemiluminescence and UV-fluorescence are used for this high performance automatic analyser which is also available for S or N analysis only. As an option, also the highly sensitive halogen analysis is possible.

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## Targeted Analytical Solutions Ultra Low Sulfur Analyzer

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