

Sulphur Analysis, a Downward Spiral of Detection Limits

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Sulphur in finished fuels has been the focus of interest for the last 50 years for advocates (environmentalists, governments, auto and engine manufacturers) of low Sulphur regulations. The environmental organisations and governments have imposed to reduce total Sulphur in finished fuels down to 10 parts per million (ppm) in gasoline and 50 ppm in the US and Europe, where improved engine designs require high quality fuels (high octane gasoline, high cetane diesel).

The permitted Sulphur levels are steadily being lowered from a level of about 330 mg/kg in gasoline and 500 mg/kg in diesel fuels to 30 and 15 mg/kg in gasoline and diesel, respectively, in 2006, and near zero by 2010.

The petroleum and petrochemical industries have their own challenge to meet with the norms and regulations and deal with the Sulphur products that are produced during refining processes.

As for product export and regulation, total Sulphur is of importance, for the refinery process however, only some individual Sulphur species are of importance. For many, the HydroDeSulphurisation (HDS) is the gold standard for removing Sulphur from fuels, The Claus process is the most significant gas Desulphurising process, recovering elemental Sulphur from gaseous hydrogen sulphide.

There are many analyses that are used to report total Sulphur in petroleum finished products and in feed stocks. Whereas some individual Sulphur species like hydrogen sulphide, mercaptanes and naphthenes are of importance and can be only be analysed using specific analysers. Sulphur combined into cycles of aromatic structure such as thiophenes, benzothiophenes, dibenzothiophenes and substituted dibenzothiophenes are more difficult to de-sulphurise and are more harmful for catalysts.

High concentrations of H₂S are often found in petroleum and natural gas and are of major concern during the drilling of oil wells. Employees as well as people in surrounding cities need to be protected against this hazardous gas.

H₂S is corrosive to steel and therefore is a potential cause of damage within the refinery process. Not only is the H₂S introduced into the process by the feed, but at several steps in the process H₂S may be formed. For example, hydro treating is used to de-sulphurise the feedstock, the Sulphur then being converted into H₂S.

Refineries therefore need to measure the H₂S content in the feedstock at several steps in the process.

1. Analysis methods

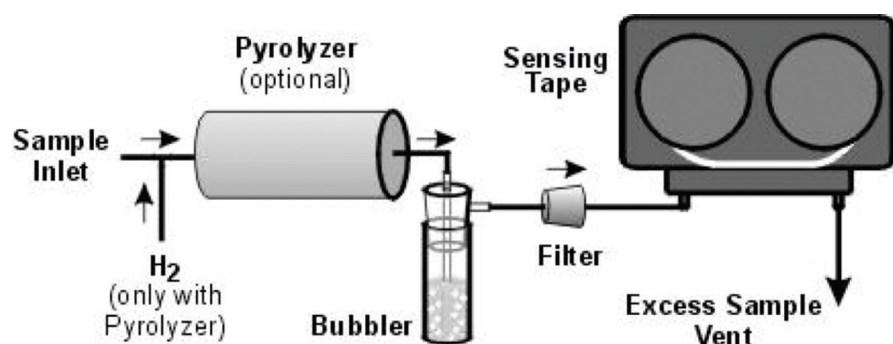
There are numerous methods for the determination of Sulphur in different petroleum products from ppb levels up to m% levels.

Giving the importance of measuring lower and lower concentrations of Sulphur in petroleum products, there are many methods and different technologies developed and modified. Reporting Sulphur results are for most refineries only standardised methods.

For Many decades the wet Chemistry method was D 129, Test Method for Sulphur in Petroleum Products (General Bomb Method), this method is now however less and less used. A widely used Sulphur analyser for gaseous samples is the Lead Acetate analyser.

a) Lead Acetate

The lead acetate tape method for the detection of hydrogen sulphide (H₂S) and Total Sulphur in gaseous streams is based on the established principle that H₂S reacts specifically with lead acetate to form a brown lead sulphide stain. The tape will begin to darken at a rate proportional to the concentration of H₂S in the sample stream.



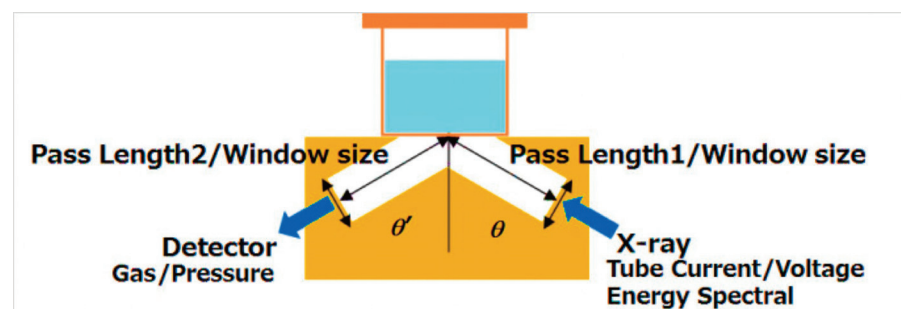
This method (ASTM D2420) is easy to use, but not precise and reliable like other available methods. Methyl mercaptan in the gas interferes with Hydrogen Sulphide results and lower detection limits of 4 ppm are not possible. A more advanced method to measure Sulphur in different petroleum products is ASTM D4045, Sulphur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry. Here all the Sulphur species are hydrogenised to Hydrogen Sulphide at high temperature and measured using lead acetate tap. This method is used to monitor and for the qualification of the Sulphur amount in the petroleum products rather than a quantification method.

b) X-RAY analysis of Sulphur

One of the most used methods for total Sulphur analysis is the X-ray fluorescence analyser. This analyser uses different technologies based on X-Ray.

One of the most commonly used X-Ray analyser is the Energy Dispersive X-Ray Fluorescence (EDXRF) according to ASTM D4294, ISO8754 using a Proportional Counter – A low background proportional counter is the key in a new EDXRF-based method to measure lower levels of Sulphur. This low background proportional counter suppresses the noise resulting in a lower detection limit compared to traditional proportional counters. The ASTM D4294 method has been modified in 2010 to meet with the new clean fuel specification. The limit of quantification was 150 ppm mass and has been lowered to 17 ppm mass total Sulphur.

(M)WDXRF Monochromatic Wave Length Dispersive X-Ray (WDXRF) Fluorescence – The (M)WDXRF Sulphur analysers are more sensitive in comparison to other X-ray analysers measuring lower concentrations down to 2 ppm weight according to ISO20884, ASTM 2622 and ASTM D7039. The use of crystals and slits to filter out unwanted wavelengths improves the sensitivity. To have a reasonable signal after the filters, a more powerful X-ray source is inevitable making the instrument more expensive.



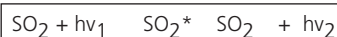
X-Ray Sulphur Analysers are non-destructive analysers, simple to use and are reliable in a certain Sulphur concentration range, but they lose sensitivity when water or oxygen are present in the sample, although there are correlation factors that can be applied to correct for the matrix oxygen. More over volatile samples cannot be measured with high precision. The use of disposable cells makes them expensive in use and not using disposable cells increases the risk of carry over.

c) Total Sulphur by Ultraviolet Fluorescence

The use of combustion ultraviolet fluorescence (UVF) provides a lower detection limit of 30 ppb and a measurement range of 30 ppb to 1 wt% total Sulphur. Different analyser manufacturers claim different detection limits and different dynamic ranges.

The detection limit is dependent on the sample matrix and on the furnace position, whereas vertically positioned furnaces have a lower detection limit than horizontal positioned furnaces (up to three times). The Combustion of hydrocarbons and the organic Sulphur species into CO, CO₂, H₂O and SO₂ where the purity of oxygen as the combustion gas and helium or argon as the carrier gas have tremendous influence on the detection limit. The detection of Sulphur is accomplished using Ultraviolet light to convert SO₂ in an electron-excited molecule (SO₂*).

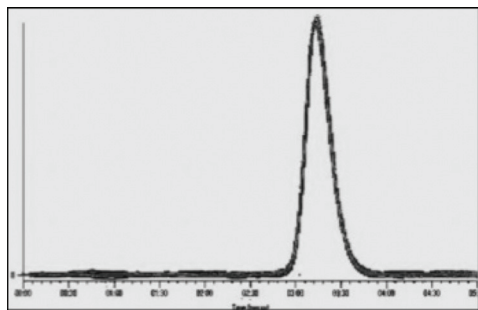
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* = excited state

hv_1 = Exposure Light @ Excitation Wavelength

hv_2 = Exposure Light @ Excitation Wavelength



Total Sulphur Signal with UVF

The unstable SO_2^* immediately falls back to a more stable and lower energy level, emitting photons with a specific wavelength that are detected by a Photo Multiplier Tube (PMT) to give a signal.

There are many methods depending on the sample combustion ultraviolet fluorescence to decide for the preferred method: ASTM D5453, ISO20846, ASTM D6667, ASTM D7183, ASTM D7359, ASTM D7551, ASTM D7011 and ASTM D6920.

Sulphur measurements by combustion ultraviolet fluorescence (UVF) provides an accurate and sensitive method to measure total Sulphur in different matrixes using different injection techniques (Boat, ALS, Gas Sampling Valves, etc...) with low detection limits that can reach down to 10

ppb, however combining Sulphur analysis with Nitrogen and/or halides analysis decreases the sensitivity of this method. As there are advantages using this method, the disadvantages are more related to sample matrixes, where heavy samples cause residual soot contaminating the system and acting as a trap for Sulphur, decreasing the sensitivity and life time of the combustion tubes. This method can only determine total Sulphur and not individual Sulphur components. The life time of the UV lamp is considered as a weak point of this method.

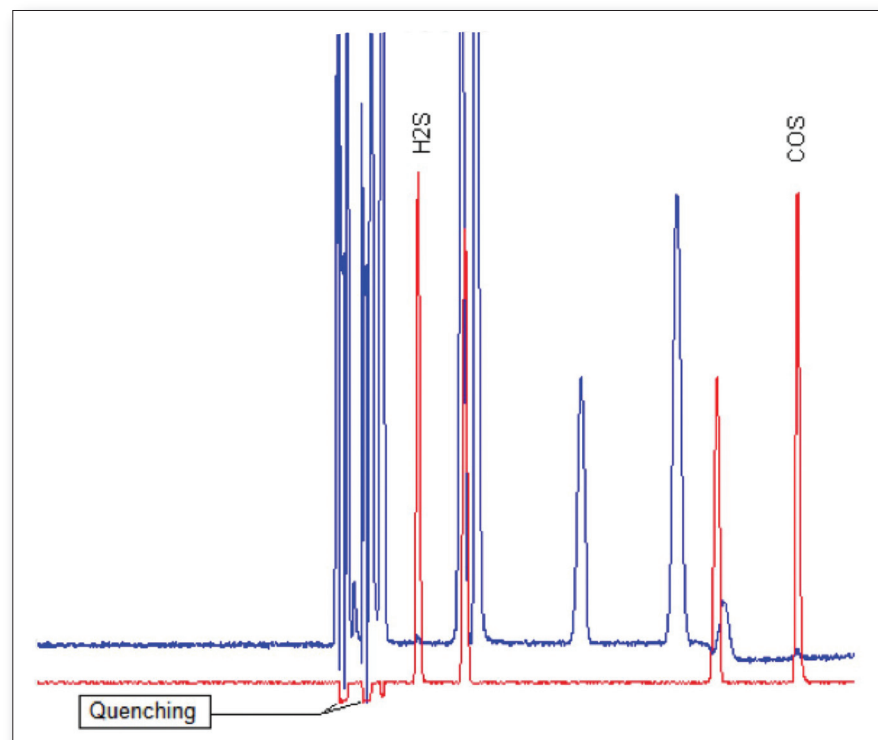
d) Sulphur Analysis by Gas Chromatography

Sulphur analysis by Gas Chromatography using different Sulphur selective detectors is widely used. There are several methods available depending on the sample matrix for the measurement of Sulphur species and total Sulphur. Available detectors are FPD (Flame Photometric Detector), PFPD (Pulsed Photometric Detector) and SCD (Sulphur Chemiluminescence Detector).

Sulphur in gases using FPD, PFPD detectors are described in ASTM D6228, while using SCD detectors is described in ASTM D5504. Thiophene in benzene using SCD is described in ASTM D7011, while Sulphur in more complex matrixes as gasoline is described in ASTM D5623.

The Gas Chromatograph is responsible for the separation of the Sulphur species from the hydrocarbon matrix and from each other. This separation is very important in combination with FPD or PFPD detectors as these hydrocarbons quench the Sulphur signal to reach the Photo Multiplier Tube (PMT). FPD has the lowest dynamic range and is not linear in response, where PFPD is a better detector with less quenching than the FPD and has a bigger linear range (3 decades). Gas samples with high propane or propylene concentrations must have a good separation from COS (carbonyl sulphide) to prevent signal quenching:

An optimal separation between the Sulphur species and the hydrocarbons when using FPD and PFPD is necessary, making the column choice very important. Most used columns are Gaspro columns and methyl siloxane columns. Gas pro columns separates the COS from propane and propylene, however the column packing is a perfect trap for H_2S (hydrogen sulphide).



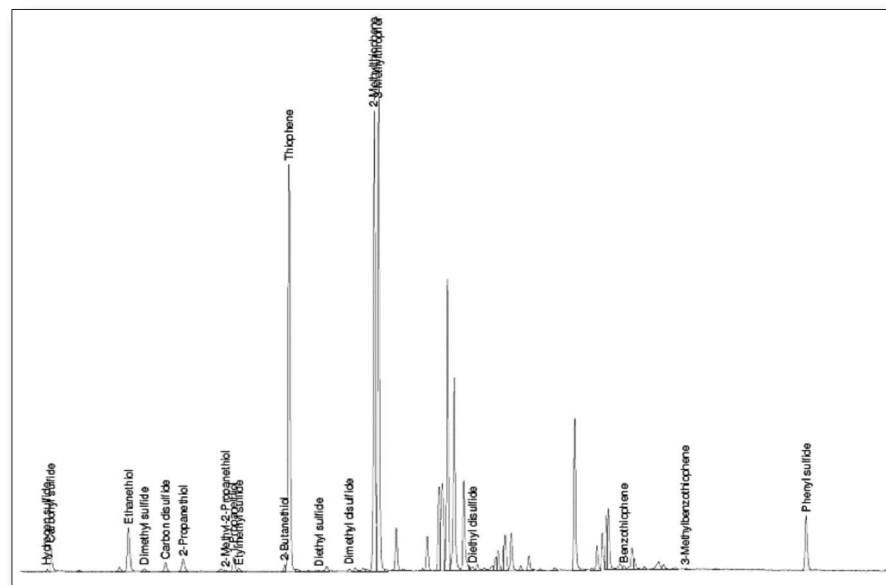
Same gas sample analyses with FID and PFPD detector

Methyl siloxane columns are not active to reactive Sulphur compounds like H_2S (hydrogen sulphide), however COS and propane/propylene are not separated, unless cryogenic cooling is used.

FPD and PFPD are very stable detectors that do not need much maintenance and do not need to be calibrated often, compared to the SCD detector, which does not suffer from hydrocarbon quenching. This advantage is used to analyse Sulphur species in more complex matrixes like gasoline, gasoline blends, diesel, jet fuel and even crudes and residual samples.

The SCD detector is more sensitive (down to 20 ppb in a gas sample) comparable to FPD and PFPD with detection limits of around 100 ppb, of course depending on the carrier and combustion gas purities. The Sievers SCD detector uses air and the Antek SCD detector uses oxygen as combustion gas. Using oxygen results in better combustion and more sensitivity, however oxygen requires safety measures to be taken in comparison to the use of zero air. The SCD detector requires more maintenance than the (P) PFPD detectors. The SCD detector is less stable and requires regular calibration.

It is obvious that Sulphur analysis with gas chromatography requires advanced knowledge about chromatography and Sulphur analysis. However there are more factors to be taken into consideration



Gasoline sample analysed with a Sulphur Chemiluminescence Detector

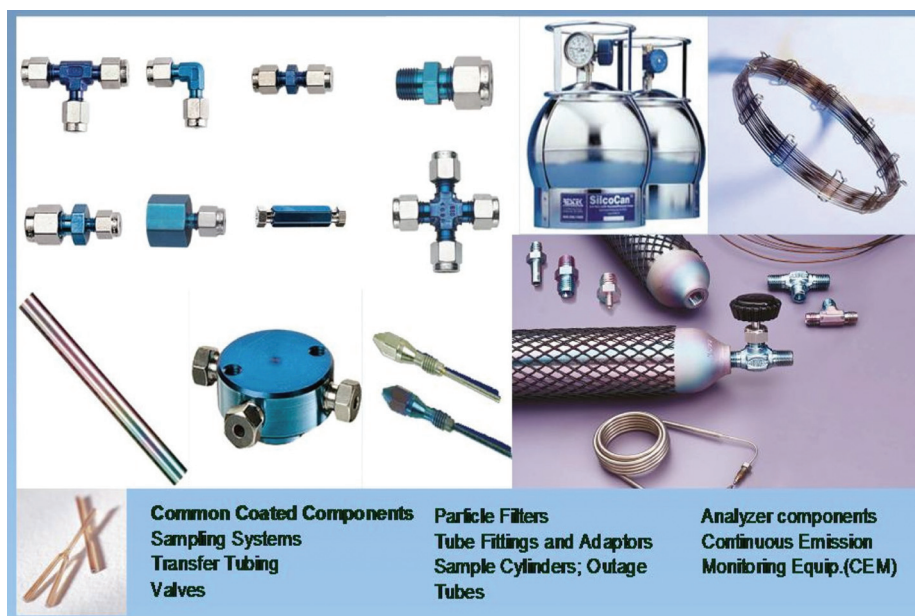
when analysing Sulphur, especially low level Sulphur concentrations. Detecting 10 ppb Sulphur is one challenge; getting 10 ppb Sulphur into the analyser without losing it before introduction is the other challenge. Sulphur species are reactive compounds that require special attention for sampling, transport and the materials that are in contact or will be in contact with the sample.

All of the above requires the use of deactivated metal surfaces. All the components that are in contact with the sample are required to be coated or special treated to ensure they do not react with the Sulphur species. This includes the sampling gas bottles, connections, tubing, valves, columns, liners, injection ports and detectors.

The Silcosteel®, Sulfinert®, and Siltek® deactivations are especially known for their performance in accurate Sulphur analysis at ppb levels. Volatile Sulphur compounds, like hydrogen sulphide, Sulphur dioxide, and mercaptans are extremely reactive and usually are present in low concentrations. Correct quantification is a big challenge. The Siltek® deactivation contributed a lot here as all parts that are in contact with the sample can be passivated using Siltek® deactivation. That means sample canisters, transfer lines, injection port liner, connectors, fittings, and every part of the GC system should be passivated. Siltek® treatment is very recognisable, as the refraction shows the silicon layer reflecting from light blue to purple.

The relevance of using this deactivation is here the response of H_2S and methyl mercaptan was tested using an untreated metal liner and a Siltek® deactivated liner. The differences are very clear. Hydrogen sulphide completely disappears in the untreated stainless steel liner. This happens very quickly in just a short time the analytes are exposed to active metal in the injection stage of the separation.

It is critical that samples are stored in an inert environment. ASTM has methods in place that require samples to be stored for 3 months in case of a dispute. Therefore, it is imperative that sample integrity be protected during storage. This is only possible using gas storage devices (bombs) that are Siltek® deactivated shows how the Sulphur levels change after storage in deactivated and normal stainless steel canisters. Due to the Siltek® deactivation, the Sulphur compound levels do not change, even after 15 days.



Conclusion

The Above mentioned methods do not compete with each other, but are used next to each other, depending on the required and preferred method.

All the different mentioned analysers and detection methods show disadvantages and advantages that are known or must be known when using the analysers.

Sulphur analysis in general is a complicated analysis that requires a lot of attention to be paid to every stage in the analysis, starting from the sampling point in the plant to the results interpretation.

Requirements for lower and lower detection limits push the analyser's manufacturers to enhance their existing analysers or develop new technology to perform better. The developments in this field are a continuous process. The pressure that lies on the petroleum industry is to produce cleaner fuels with lower Sulphur concentration, requiring more sensitive and less maintenance sensitive analysers. The challenge is there for the analyser's manufacturers to respond to this downward spiral of detection limits.