

Evaluation of Sulphur Measurement Analytical Techniques for Sulphur in Gases and Fuel

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Over the last decade, the importance of detecting sulphur in petroleum-related products has increased dramatically. This is likely related to the necessity of complying with increasingly stringent government regulations, protecting expensive catalysts, and ensuring product quality. Reasons for detection and control of sulphur in different process streams have existed for the last fifteen years, but detection limits have been reduced dramatically in recent times. For example, in order to protect expensive, sulphur-intolerant catalysts, the production feed for polypropylene or polyethylene must be monitored for sulphur content. The sulphur analyser used in this application must now have the ability to detect sulphur from 1 parts per billion to 10 parts per million.

C.I. Analytics provides the best solution for each client's sulfur analysis requirements. We are able to do so since, we offer any of the three best-known technologies in the field:

Country	Sulphur Levels in Gasoline by 2002	Sulphur Levels in Gasoline by 2005	Sulphur Levels in Diesel by 2006
Canada	< 200 ppm (At present the levels range from 300-600 ppm)	< 30 ppm	< 15 PPM
USA		< 30 PPM	< 15 PPM
Europe		< 30 PPM	< 15 PPM

This paper describes and evaluates all the latest techniques available to perform these analyses with high levels of accuracy and speed.

The most Popular Technologies available to meet Ever-Tightening Regulations and low level detection for catalyst protection:

Sulphur measurement may prove to be difficult, particularly at low levels, but choosing the best technological fit for the application often minimises such difficulty. This article examines the strengths and weaknesses inherent with each sulphur measurement technology currently available for detection of low levels of sulphur in hydrocarbon fuel samples and analysers used for blending operations.

Best known and used Technologies offered world-wide for low-level detection of sulphur in inert gases, hydrocarbon gases, and hydrocarbon liquids include the following:

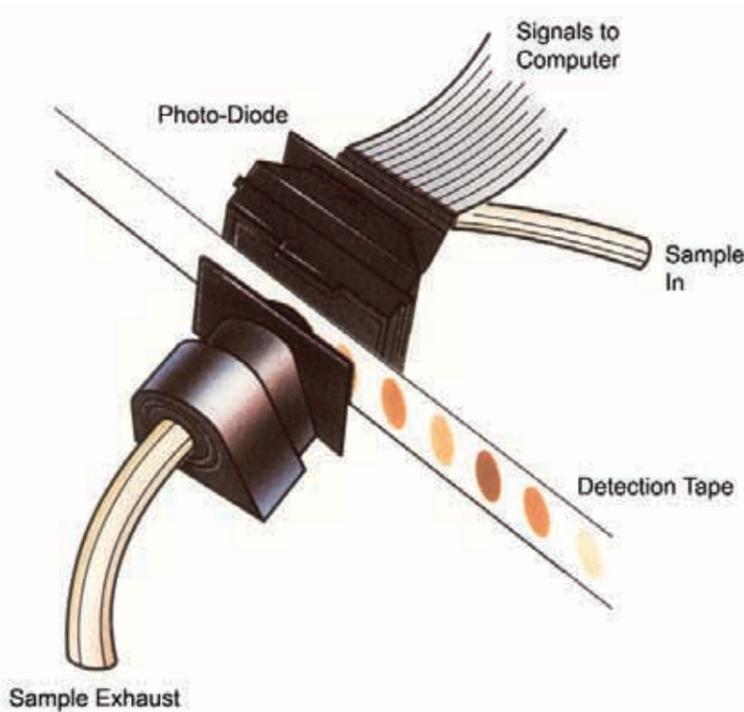
1. GC-Flame Photometric Detector (FPD and PFPD)
2. Dry Colorimetric Method (Tape-based)
3. Sulphur Chemiluminescence Method (SCD)
4. UV Fluorescence (UVF)
5. X-Ray Fluorescence (XRF)

1. Flame Photometric Detector (FPD) and Pulsed FPD:

These sulphur analysers, with gas chromatograph and Flame Photometric Detector, are based on technology that has not changed over the last 40 years. The FPD, with its high selectivity for sulphur compounds, was generally the detector of choice for on-line applications in the sixties and seventies. Unfortunately, however, it suffers from a squared response, which limits its ability. The FPD is also subject to quenching of the signal by hydrocarbons and carbon dioxide. This limitation requires that the sulphur compounds be separated from the interfering matrix before detection by FPD.

To reduce the hydrocarbon quenching, and to get a linear response from this detector, the following technique has been used. Using a high temperature pyrolyzer, a small amount of hydrocarbon sample is burned in air to form SO_2 , CO_2 , and H_2O . These three gases are then separated on a packed column. The SO_2 peak is sent to the FPD for detection while the CO_2 and H_2O peaks are sent to vent. At times the GC separation of H_2O and SO_2 is a problem.

The pulsed FPD was designed to improve upon the 'old' traditional FPD design but has failed to perform well especially for on-line analysers. Even in the lab the PFPD offers many challenges and requires special training.



2. Tape Based Detectors: Dry Colorimetric Detector (DCD)

Dry Colorimetric Detector Technique to detect sulphur in petroleum samples is still the most widely used and reliable technique.

Theory of Operation

Classical colorimetry utilises an impinger to collect gas in a liquid medium.

Chemical reagents are then added to the medium to cause it to change colour in proportion to the concentration of gas present. The resulting colour change is measured by a laboratory spectrophotometer and compared to standards.

Sensi-Tape Detectors are also colorimetric based, but are dry reaction substrates which serve as gas collecting and analysing media. Individually formulated for a specific gas or family of gases, each Sensi-Tape is a nontoxic, proprietary chemical reagent system. When exposed to a target gas, the tape will change colour in proportion to the amount of gas: the higher the concentration, the darker the stain will appear.

The change in colour, or stain, on the Sensi-Tape is read by a photo-optical system, then compared to a standard response curve preprogrammed into the system.

Chemical formulations deposited on the tape provide a detection medium that is fast, sensitive, and specific.

Each of the proprietary detector tapes reacts instantly to the target gas, providing a visible colour reaction. As a result, tape detectors provide a method of detecting and analysing toxic gases that must be identified in process streams at PPB levels and removed.

While the Tape Detection System is extremely sensitive to its target gas, it is also very specific to that gas. It will not react to other substances (solvents, hydrocarbons, etc.) often found in process streams. Thus, expensive downtime due to false alarms is virtually eliminated.

Sulphur Analysis

The Tape detector is the most 'loved' or 'hated' technique depending upon the application. The organically bound sulphur is first converted to H₂S. The H₂S formed reacts with the moist paper tape impregnated with chemicals. An electronic eye detects the change in colour of the tape as H₂S passes by the tape and forms a stain.

The tape detection method is the only detection system that can determine H₂S without any interference. This fact is clearly stipulated in ASTM method. This is an important feature in a detector when one is detecting very low levels of sulphur in a complex hydrocarbon matrix.

There are two ways to convert organically bound sulphur to H₂S. The first technique is to use reductive pyrolysis. The organically bound sulphur is mixed with excess of hydrogen and passed through a high temperature ceramic tube held at 1200°C. The sulphur combines with hydrogen to form H₂S while the hydrocarbons are reduced to methane gas. The tape detects the H₂S.

The second technique for this conversion requires, first, oxidative pyrolysis, and then, reductive pyrolysis.(based on ASTM 6313). This technique is used to solve the coking problem. A sample containing sulphur compounds and hydrocarbons is blended with air at 1200°C. The sulphur compounds are oxidised to SO₂ and SO₃ and the hydrocarbons to CO₂ and H₂O. In the second zone, a flow stream of hydrogen then reduces the oxides of sulphur to H₂S. The water and carbon dioxide formed as by-products interfere with the tape detector and must be removed.

Dry Colorimetric technique's strength is that it is based on simple chemistry, and there are no known interferences. Both chemiluminescence and UV fluorescence suffer interference from hydrocarbons, requiring GC separations and/or an extremely efficient high temperature reactor to make clean combustion.

Recent advances in the detector (Optics Block) have contributed to this low PPT level detection in a big way. The sample is now passed through the tape as opposed to the sample just passing-by the tape. This allows the "tape" to act as a H₂S trap (collector). As sample size is increased, so is the amount of the converted H₂S. When sample amount of 300 CC of propylene is passed through the tape, one can get full scale response for 1 PPB level of COS in the sample. In comparison, all other techniques struggle to give 20-50 PPB level result as their signal at that level of detection is lost in the noise, The ability of the tape to trap H₂S and allow use of very large sample amounts is unique in the industry.

Another advance is the amplification of the signal is done using a tiny PCB planted in the optics block. The state of the art, Solid Optics Block is shown. In the diagram.

Key Features and Limitations of Dry Colorimetric Detector (Tape)

1. Low Level Detection with ease and accuracy:
Passing large sample volumes through the chemically impregnated tape, lets one detect analytes (H₂S) at ppb or even ppt levels, while avoiding time-consuming need for GC separations.
2. The tape is specific to H₂S. This is extremely useful when measuring small concentrations of H₂S in streams containing sulphur compounds. Other technologies usually have interfering compounds.
3. These systems are relatively simple and easy to work on because simple visual inspection of the tape is a good indication of what is happening with the analyser.
4. This technology is a proven technology has a number of ASTM Standards (American Standard for Testing Materials) written around the use of Tape analysers.
5. The tape technology as used in the nineties suffered from poor quality control standards of one company. This company became victim of aggressive corporation take over while owners were changing like one changes shirts, the technical support group was lost one at a time. The point is simply, the Tape is still one of the best analytical techniques for sulphur analysis.

3. Sulphur Detector based upon chemiluminescence:

Two very desirable features of detectors are high sensitivity and high selectivity toward a particular class of compounds. A detector having these two desirable features for detection of sulphur compounds is the sulphur chemiluminescence detector (SCD) based on the chemiluminescent reaction of ozone with SO, H₂S, or other unknown species produced by the oxidative and reductive reactions inside the electrical furnace. Chemiluminescence is defined as the emission of ultraviolet, visible, or near-infrared radiation through the chemical excitation of a reacting species. In most cases of chemiluminescence, a chemical reaction results in an excited product that emits radiation upon relaxation to its ground electronic state. In general form, chemiluminescence reactions can be expressed as follows:

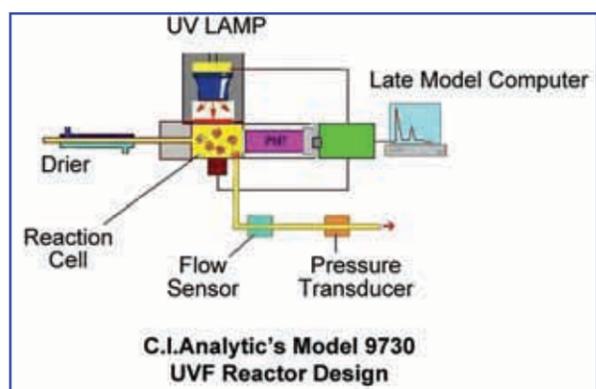


Gas phase chemiluminescent reactions have been observed for over a century since Salet first observed the blue emission from sulphur compounds burned in a hydrogen flame. In the past twenty-five years, chemiluminescence has been extensively used in analytical instrumentation. For example, the best-known technique to measure small amounts of oxides of nitrogen is the reaction of NO with ozone.

This method, like others, requires the use of a high temperature reactor to convert organically bound sulphur to detectable species.

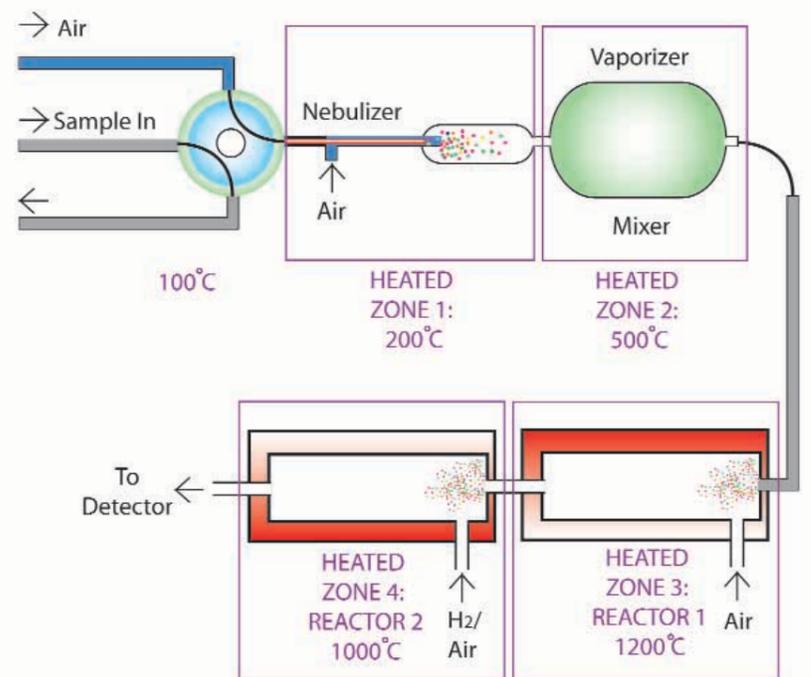
Key Features and Limitations of Sulphur Chemiluminescence Detector

1. Ideal for sulphur species analysis. Is easier to work with when compared with pulsed flame photometric detectors for sulphur species application.



2. Olefins in the hydrocarbon streams will interfere with sulphur signal. Use of GC separations or conversion of olefins to non interfering compounds is required.

3. The detector has failed in the field for on-line sulphur detection applications due to high maintenance required. The 'SulfTane' developed by Fluid Data is a perfect example of it. It is not manufactured anymore.



C.I.'S DYNAMIC COMBUSTION TECHNIQUE:
SULFUR IN DIESEL

4. Pulsed UVF detectors require sample mixing chamber. This mixing chamber makes cycle time needed to change from one stream to another stream very long. In blending operations short cycle times are required.

4. UV Fluorescence (UVF)

This detection technique has been used in detection of SO₂ in stacks and air monitoring for many years. The adoption of this detector for detection of total sulphur measurements in Diesel is new and is getting very popular.

This is a new and recent technique that achieved ASTM and EPA approvals. It is very popular and the most desired method for diesel blending operations.

These analysers are based on the classical fluorescence spectroscopy principles. The measurement principle relies on the excitation of SO₂ molecule which occurs in the presence of a specific wavelength (214 nanometers) of UV light and subsequent relaxation which produces a photon of light. A photo multiplier tube allows the light emissions to be measured as the SO₂ molecule returns to a ground state

How UVF detector works for the detection of sulphur in diesel:

Sulphur-containing molecules in the sample stream are oxidised to SO₂ using the Dynamic Combustion technique. The water formed in this process is removed by the drier.

The SO₂ formed, as it enters the reaction cell, is excited with a specific wavelength of UV light.

Excited SO₂ decays, emitting a second, specific wavelength of light.

This light is detected by a photomultiplier tube, amplified and the software converts it to a peak that can be measured.

Key Features and Limitations of UV Fluorescence (UVF)

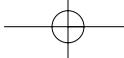
1. New and recent ASTM and EPA approvals have made a method of choice for all sulphur detection needs for blending applications.
2. The lower detectable limit of UVF is 500 PPB, although some vendors will claim, lower detection limit of 250 PPB. This is not an issue for blending operations where this is most popular.
3. The U.V. lamp intensity will deteriorate over time. This used be a problem. A built in reference detector continuously monitors the intensity of the U.V. lamp and allows use of a ratiometric measurement technique which compensates for lamp degradation
4. In blending operations, the desired features include, fast analysis time, multi stream capability, data validation, automatic, and remote calibrations. One example is C.I.Analytics Model 9705 offering all these features as standard item. The analysis time is less than a minute, the analyser has six stream capability and automatic calibrations are based on time interval selected by user or remote calibration on demand.
5. The combustion of hydrocarbons is extremely important. To ensure complete combustion, C.I.Analytics Model 9730 uses Dynamic Combustion Technique explained later in this article.

5. X-Ray Fluorescence (XRF)

In the early nineties, on-line analysers for sulphur blending operations using X-ray detectors gained popularity. However the need for high service and maintenance costs is forcing lot of companies to revert back to other options. The sulphur spec used to around 500 ppm and these detectors could perform. However, with specifications for sulphur at levels below 10 ppm will be a major challenge for the XRF detectors.

Conventional XRF using energy dispersive spectrometry is not good for low level sulphur detection in fuels like diesel. The problem with any XRF/EDS systems is that the strong scattering of the primary beam from the sample can enter and swamp the energy dispersive detector. This limits the intensity of the primary beam due to the counting limitation of the energy detector.

XRF with polychromatic excitation using wavelength dispersive spectrometry (WDS) provides better S/B, but a high power x-ray tube is necessary due to the low efficiency of WDS system.



Key Features and Limitations of analysers using X-Ray technique

1. Does not require conversions. That is, there is no need for a pyrolyzer.
2. Most of the models need license from Radio Active Government bodies.
3. Not ideal for sulphur detection below 20 ppm.
4. Not ideal for on line applications because of expensive maintenance due to complicated optics system.
5. Ideal for laboratory analysis for samples over 50 ppm sulphur content
6. Replacement of X -Ray tube is required every one to two years and this is expensive.

The challenges facing the most popular Sulphur Detection Methods using conversions prior to detection:

The three, most popular sulphur analysers, UVF, Tape and FPD analysers in the world have one item in common: **High Temperature Furnace.**

The high temperature furnace has been referred to as pyrolyzer or reactor. It is the area where most of the problems in the detection of sulphur may be encountered, if the pyrolyzer design is not adequate. For example, incomplete combustion will cause erroneous results due to hydrocarbon interference or non-equimolar response due to poor conversions to SO₂ or H₂S.

The Pyrolyser used by the tape detectors or some of the new reactors used for UVF models are poorly designed. Most of these models have single tube pyrolyzer with one heat zone. In this single tube, the sample conversion from liquid to gas state must occur, then mixing of the vaporized sample with reactor gas (for conversions) must occur. The change of sample state from liquid to gas involves change of volume by 200-300 times. This exerts back pressure on reactor gas (required for conversion) and in doing so, there is lack of conversion gas for a few seconds. That is all it takes for the partial coke formation to happen. The challenge to redesign and improve combustion efficiency was undertaken by C.I.Analytics and the solution is described below.

Solution to the Analytical Challenge:

The single tube pyrolyzer with one heat zone (always set at 1200C) was modified to have four, independently controlled, heat zones. In the first zone, as the liquid sample is introduced, it is

nebulised, that is broken into hundreds of tiny liquid molecules. The second zone, allows for the expansion and mixing of reactor gas at controlled low temperature of 450 C. No pyrolysis reactions occur as the temperature is set at 450C.

The next two heat zones are set at high temperature and in the presence of excess reactor gas (H₂ or O₂) organically bound sulphur is converted to H₂S or SO₂ for detection by the detector

Conclusion

Any single sulphur detection technology, described above, is not applicable to all sulphur detection applications. Choosing the best technological fit for the application is the first consideration when it comes to selecting the analyser for a particular application. The table below matches application needs with the detection technique.

Sulphur Analyser Selection Guide		
Application	Main requirement	Recommended analytical technique
1 Catalyst Protection	Low 1 PPB level Detection Lab or On-line	Dry Colorimetric detector (Tape)
2 Diesel Blending operations	Fast , equimolar response Multistream Capability Auto Calibrations Low Cost	Oxidative Combustion followed by UVF detection
3 H ₂ S in Natural Gas	Fast and accurate response Low Cost On line	Dry Colorimetric detector (Tape)
4 Species Sulphur in Natural gas	Lab or on-line	GC-with Sulphur Chemiluminescence Detector
5 Sulphur in LPG	Low 1 PPB level Detection Lab or on line	Dry Colorimetric detector (Tape)