

Analytical Techniques for Sulphur Determination

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Stringent environmental regulations require sulphur reduction in petroleum products and flue gas to low levels. Furthermore, sulphur is toxic and corrosive to delicate catalysts and industrial units. Sulphur detection at low levels plays an important role in monitoring sulphur reduction in industries.

There are a number of analytical techniques available in the market; each is associated with different pros and cons. Here, we focus on seven methods including gas chromatography, chemiluminescence, ultraviolet fluorescence, diode array spectroscopy, X-ray fluorescence, dry colorimetry, and tunable diode laser absorption spectroscopy.

The growing concern about air pollution has been generating a far higher need than ever for accurate analytical technology, to prevent further pollution of the atmosphere. People's new understanding of the need for environmental protection, the severe regulations on sulphur content in petroleum products, and the poisonous and corrosive effects of sulphur to industrial catalysts and units call for an innovative analytical technique providing an extremely high degree of sensitivity and precision.

In industrial and monitoring applications the key factors on gas detectors are: high accuracy, excellent linearity, high sensitivity (low detection limit), good selectivity (free from interferences), versatility (multi compounds measurement), real-time and continuous measurement capabilities, easy to integrate and to operate (no sampling, user friendly, free of maintenance, no skilled operator). Moreover, operation in industrial units often means that the equipment has to be compact, flexible, and so-called rugged (insensitive to harsh conditions such as shocks, noise, contaminants, and high temperatures).

Emission levels

It is impossible to clean the air, or in particular to reduce air pollution from industrial and transportation sectors, without getting sulphur out of fuels. Table 1 shows the regulated sulphur levels in diesel and gasoline in Canada, USA, and Europe.

Table 1. Regulations on sulphur levels in diesel and gasoline in Canada, USA, and Europe

Region	Current sulphur level in diesel	Current sulphur level in gasoline	Sulphur level in gasoline by 2017
Canada	< 15 ppm	< 30 ppm	< 10 ppm ^a
USA	< 15 ppm	< 30 ppm	< 10 ppm ^b
Europe	< 15 ppm	< 30 ppm	< 10 ppm ^c

^a: <http://gazette.gc.ca/rp-pr/p1/2013/2013-06-08/html/notice-avis-eng.html>; ^b: <http://yosemite.epa.gov/opa/admpress.nsf/d0c6618525a9efb85257359003fb69d/ce8984957ffefa6a85257c90004fe802!OpenDocument>; ^c: http://www.greencarreports.com/news/1090661_sulphur-in-gasoline-to-fall-by-two-thirds-in-2017-to-cut-emissions

Analytical techniques

Various analytical techniques have been developed for the determination of sulphur in different industrial environments. In this article we focus on gas chromatography (GC), chemiluminescence detector (CLD), ultraviolet fluorescence (UVF), diode array spectroscopy (DAS), X-ray fluorescence (XRF), dry colorimetric detector (DCD) or Sensi-Tape technology, and tunable diode laser absorption spectroscopy (TDLAS).

The applicable ranges of these analytical techniques are summarised in Table 2.

Table 2. Applicable ranges of the common analytical techniques

Application	GC-FPD/PFPD ^a	CLD ^c	UVF ^e	DAS ^f	XRF ^g	DCD ^h	TDLAS ⁱ
Total sulphur	0.04-500 ppm LDL ^b : 40 ppb	NA ^d	NA	0-10 ppm	1 ppm-%	0.002-250 ppm LDL: 1 ppb	0-20 ppm LDL: 500 ppb
H ₂ S in natural gas	0.01-100 ppm LDL: 10 ppb	NA	0-5 ppm LDL: 100 ppb	0-10 ppm	NA	0.002-250 ppm LDL: 1 ppb	0-20 ppm LDL: 500 ppb
H ₂ S in fuel gas	0.01-100 ppm LDL: 10 ppb	NA	0-5 ppm LDL: 100 ppb	0-10 ppm	NA	0.002-250 ppm LDL: 1 ppb	0-20 ppm LDL: 500 ppb
H ₂ S in flue gas	0.01-100 ppm LDL: 10 ppb	5 ppb-1% LDL: 5ppb	0-5 ppm LDL: 100 ppb	0-10 ppm	NA	0.002-250 ppm LDL: 1 ppb	~20 ppm LDL: 500 ppb
SO ₂ in flue gas	0.01-100 ppm LDL: 10 ppb	5 ppb-1% LDL: 5ppb	0-250 ppm LDL: 100 ppb	0-500 ppm	NA	0.002-250 ppm LDL: 1 ppb	NA

^a: gas chromatography-(pulsed) flame photometric detector; ^b: lowest detection limit; ^c: chemiluminescence detector; ^d: not available; ^e: ultraviolet fluorescence; ^f: diode array spectroscopy; ^g: X-ray fluorescence; ^h: dry colorimetric detector; ⁱ: tunable diode laser absorption spectroscopy.

Gas chromatography

GC measures the species of interest in a compositional background. It first separates the desired components from the bulk chemicals in a packed or capillary column and then directs the components to a detector. The commonly used detectors for sulphur analysis are (pulsed) flame photometric detector (FPD/ PFPD) and CLD. Packed columns are often chosen over capillary columns, since they allow greater injection volume.

Total sulphur in the gas and liquid phases may be determined measuring a number of individual sulphur species and adding up the total or first converting all present sulphur species to SO₂ (or H₂S) and reporting the total sulphur as SO₂ (or H₂S) concentration.

However, the GC technique is expensive, complex, and slow (i.e., total sulphur analysis takes 720 sec). It requires highly skilled analytical chemists to interpret the data.

Chemiluminescence detector

Chemiluminescence is a chemical process in which light is emitted as a by-product of a chemical reaction. This process can be used to measure total sulphur.

By mixing the fuel gas with oxygen and passing it through a pyrolyser furnace the sulphur species will react to produce SO₂ and sulphur monoxide (SO). Further, the effluent of the pyrolyser is mixed with ozone (O₃) which has the effect of oxidising the SO portion of the effluent into SO₂ at an excited electrical state. As this excited SO relaxes to its ground state it emits its extra energy in the form of photons. The intensity of the luminesced light, which is proportional to the SO concentration, can then be detected with a photomultiplier tube and related with the total sulphur concentration.

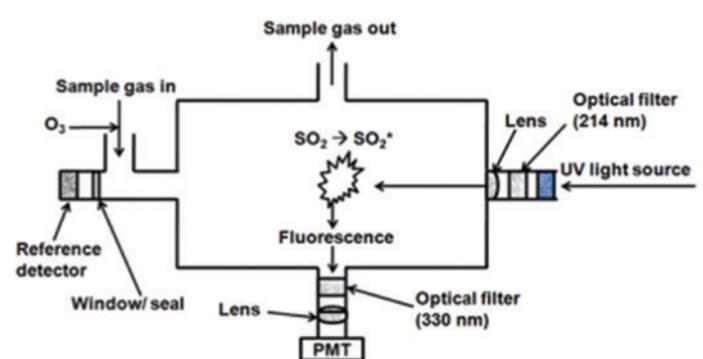
Ultraviolet fluorescence

The UVF method is an analytical technique utilising fluorescence in the ultraviolet region. UVF spectrometry is a method for detecting low levels of H₂S in hydrocarbons and flue gas. H₂S highly absorbs UV light in the UV range and is detected at a wavelength of preferably 228 nm to minimise interferences from other species such as hydrocarbons.

The light near 214 nm is also absorbed by SO₂ in the flow cell and then re-emitted from SO₂ as fluoresced light near 330 nm. A photomultiplier tube can be used to measure the intensity of the fluoresced light which may then be correlated with the total sulphur concentration (see the image above).

However, the UVF technique suffers from interferences such as Nitric oxide (NO). To prevent such interference from NO, an ozone (O₃) injection technique has been adopted in the UVF sulphur analyser. NO is easily oxidised into NO₂ by ozone whose radiation wavelength is longer than that of the excited SO₂.

Its sample cell set-up facilitates the technique to operate at high temperature (500 °C) and pressure (350 kPa – 15 MPa) and can be used to run at high levels of SO₂ (0 – 10%) and H₂S (0 – 100%).



Diode array spectroscopy

DAS uses a tungsten, xenon flash, or deuterium light source as the optical source, and uses the continuous spectrum over a wavelength of 190 – 800 nm or 400 – 1100 nm. The analyser uses fibre optics to transmit the light through the sample in the flow cell. The adsorption spectrum is generated by a holographic grating and a diode array with 1024 detectors. It is a continuous spectrometer without moving parts.

The fibre optics allows the sample cell to be installed away from the source, electronics and detector or the use of a direct sample probe. Due to the use of a holographic grating in combination with 1024 diode array detector the instrument is capable of analysing multi component species without the use of moving parts. However, it suffers from the same interferences as described with the UV technique and possesses less linearity compared to spectrometers which employs discrete spectral line light sources.

X-ray fluorescence

XRF is used to detect the total sulphur content of fuels. Instead of oxidising or reducing the fuel to SO₂ or H₂S respectively, X-rays can be applied to measure individual sulphur atoms regardless of the compounds. The ASTM D2622 method (American Standard Test Methods) describes sulphur absorption at 0.5373 nm and a reference at 0.5190 nm or 0.5437 nm. The method suggests a wavelength dispersive X-Ray fluorescence spectrometer (WDXRF), equipped with X-ray detection in the wavelength range of 0.52 – 0.55 nm.

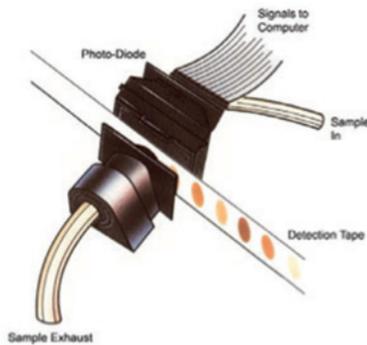
Because X-rays are high energy waves, they have very short wavelengths. The wavelengths are short enough that they can be utilised to ionise individual sulphur atoms by exciting their low energy electrons to higher energy orbitals. Then, the ionised sulphur atoms relax back to their ground state and fluoresce the extra energy as photons with a wavelength equal to the energy difference between the two orbitals. The fluoresced light can be measured with an X-ray detector and correlated with the total sulphur concentration.

XRF is not ideal for sulphur detection below 20 ppm, yet ideal for laboratory analysis for samples over 50 ppm sulphur content. It is not ideal for on-line applications because of expensive maintenance due to complicated optics system. Replacement of X-ray tube is required every one to two years and this is expensive.

Dry colorimetric detector

Like classical wet colorimetric techniques, the Sensi-Tape detectors are 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 photodiode (see the left image), and then compared to a standard response curve pre-programmed into the system.

The organically bound sulphur is first converted to H₂S in a high temperature reactor tube. The H₂S formed reacts with the moist paper tape impregnated with chemicals. A photodiode detects the change in colour of the tape as H₂S passes through the tape and forms a stain. The tape detection



method is the only detection system that can determine H₂S literally without any interference.

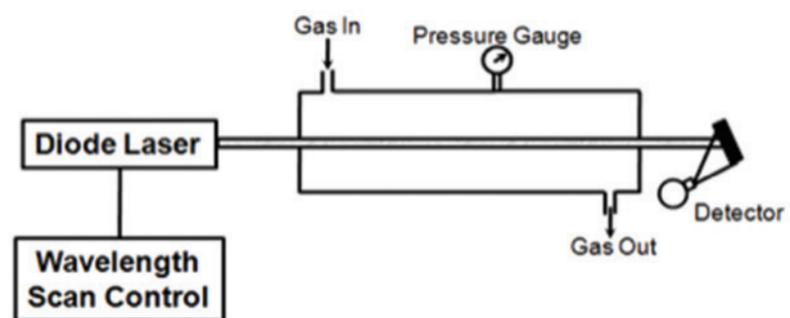
Chemical formulations deposited on the tape provide a detection medium that is fast, sensitive, and specific (free of any interference) that can detect impurities down to ppb levels. The cycle time to perform one analysis is 10-60 sec (in ppm levels). The system has a number of ASTM approvals which makes the measurement reproducible, comparable and traceable such as D2420, D4045, D4084, and D4468.

Tunable diode laser absorption spectroscopy

TDLAS uses a tunable near infrared laser. A tunable diode laser is a kind of semiconductor based laser that can be tuned to optically choose a particular wavelength (or colour) of light (see the image below). The laser emits near-infrared radiation (1.2 – 2.5 μm) with a line width less than 0.003 cm⁻¹, which is narrower than molecular absorption line widths (typically 0.1 cm⁻¹ at atmospheric pressure). Tuning to a specific wavelength is done by varying the diode temperature and the diode current going through it.

As the light passes through the gas sample, energy is absorbed, reducing the amount of light arriving at the detector. The length of the laser beam influences sensitivity of the sensor; therefore, in most applications a dual-pass optical path is necessary.

The range for H₂S analysis is 20 ppm with the lowest detectable limit of 500 ppb and it needs a multi path cell. The analyser can be installed in a stack, pipeline or flare and is, therefore, capable of measuring over a long distance.

**Conclusion**

On one hand, stringent environmental regulations require reducing the sulphur content of the petroleum products and flue gas to low levels. On the other hand, sulphur is toxic and corrosive to the expensive catalysts and industrial units. Therefore, the low level sulphur detection plays an important role in monitoring sulphur reduction in industries.

Among other analytical techniques mentioned above, the Sensi-Tape technology is a proven analytical technique with a number of ASTM standards and one analyser is capable of detecting multiple impurities, if the need should ever arise, simply by changing the sensi-tape (lab version). Not only is it easy and simple to operate, but it also is capable of detecting extremely low levels of sulphur in any applications such as water, beverage, and hydrocarbon media with virtually no interference and considered more robust than the other technologies mentioned.

Finally, there are a number of emerging analytical techniques such as TDLAS that can analyse sulphur in low levels and seemingly free of any interference. It does not require a complex set up compared to GC.

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