Gas Chromatography: an Accurate, Fundamental Tool in Sulphur Analysis

Khalid Tafrasti, Era Analytics FZCO
Dubai Airport Free Zone Building 5EA, Office G01,PO BOX 293619 Dubai, United Arab Emirates
Email: Khalid.tafrasti@era-analytics.com • Web: www.era-analytics.com

Khalid Tafrasti

Sulphur Analysis is an essential analysis for refineries, petrochemical, food and environmental industries. Gas Chromatography is widely used nowadays in all petroleum, petrochemical and refinery laboratory for the analysis of various components, group of components, impurities and of course sulphur. A Gas Chromatograph is in general a very accurate tool for qualification and quantification for sulphur species and total sulphur.

Several ASTM methods are available for the identification and quantitation of sulphur species in petrochemical and refinery products by means of Gas Chromatography. Depending on the sample matrix, ASTM methods are available using different detectors. The ASTM methods describing analysis with GC recommend sulphur specific detectors including PFPD, FPD, SCD and AED. Another suitable detector is the Mass Spectrometer.

Many Gas Chromatograph's manufacturers (PE, Shimadzu, Thermo, Agilent Technologies, Bruker, etc) and Value Added Resellers such as Era Analytics (VARs) offer applications to determine sulphur in various matrices. To meet the customer's requirements many factors have to be taken in to consideration to be able to deliver a gas chromatograph specific for the customer's application: sensitivity, selectivity, linearity, repeatability, equimolarity and robustness are just a few of the requirements.

There are also many limitations that need to be taken into consideration where other improvements can be applied to enhance the GC and detector performance.

Calibration and sample handling systems are an integral part of the sulphur measurement system. Due consideration must be given to the reactive nature of sulphur compounds when designing sulphur measurement systems and when verifying and troubleshooting these systems.

Many factors must be considered when deciding on the best sulphur selective detector to employ for a given application. Attributes such as selectivity, response factor behaviour, quenching, column compatibility, and sensitivity should be considered and matched to the application.

The first consideration: Sample Matrix

The sample, sample matrix and component of interest that have to be detected and quantified are very important for the choice of detector.

Gas samples show less quenching because of the low boiling point and less hydrocarbon present in the matrix. A column separation is enough to use a FPD or a PFPD detector. For liquid samples with higher boiling points a detector like SCD is more desirable.

Equimolar detectors with a big linear range like SCD and PFPD have the advantages over FPD and AED. Equimolarity is a big advantage when calibrating a system. Equimolarity is more important when the sulphur compound elutes together with the hydrocarbon matrix. That is the reason why SCD is a more desirable detector for more complex samples like gasoline and middle distillates. Calibrating an equimolar detector requires not more than one component; for identification individual components are required.

The second consideration: Passivation

Sulphur compounds are very active compounds that will react with every active site, resulting in the loss of these compounds before reaching the detector. Deactivation of every part that comes in contact with the sample is inevitable. That means sample canisters, transfer lines, injection port liner, connectors, valves, fittings, and every part of the GC system should be passivated. Besides the deactivation of the active sites, the prevention of active chemical compounds entering the system is as equally important, including moisture, air and other contaminants. Gas filters are highly recommended in combination with high carrier gas purity.

Any active site in the Gas Chromatograph can cause a headache that can only be solved by replacing that part. However there are users who do attempt to deactivate the active site in their gas chromatograph by purging the sample and flow paths with high concentrations of Hydrogen Sulphide. An active liner as shown below cannot be deactivated by purging high concentration of sulphur through the liner.

The Siltek® deactivation contributed a lot here as all parts that are in contact with the sample can be passivated using Siltek® deactivation.

Hydrocarbons are non-reactive but sulphur compounds, especially hydrogen sulphide and methyl mercaptan, are easily adsorbed by undeactivated surfaces. Therefore, there are two areas of concern with micropacked or packed column sulphur analysis: one is the inertness and selectivity of the solid support, and the other is the inertness of the tubing walls. Packed and micropacked

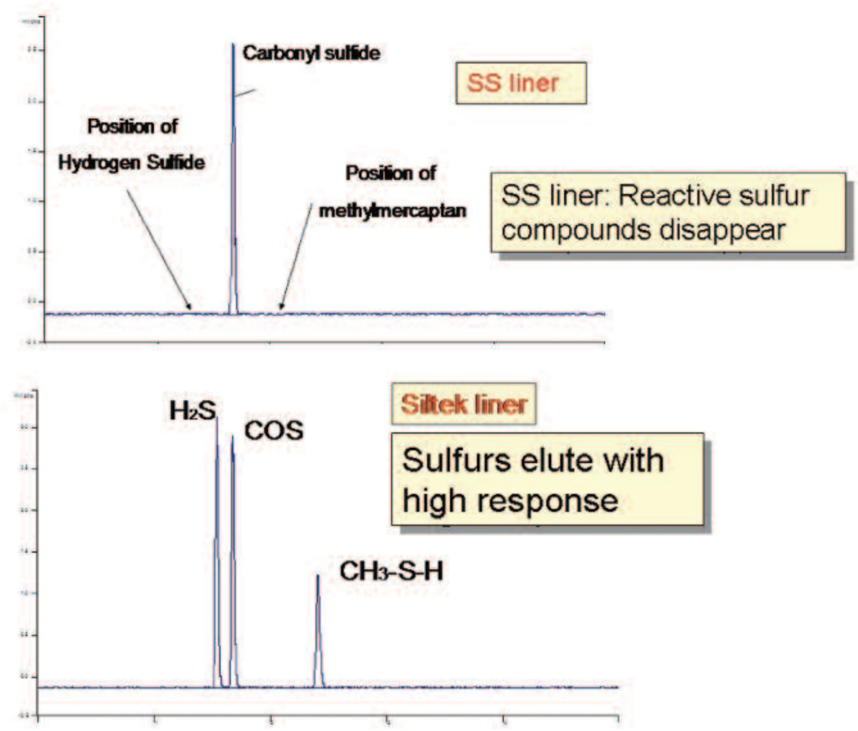

Figure 1: effect of an active liner on sulphur adsorption

columns typically use metal tubing for ruggedness but the surface is very adsorptive for sulphur compounds. PTFE tubing is also an option, but it has a limited temperature range, is permeable, and will expand and contract during temperature changes. These characteristics will negatively affect column efficiency and stability.

Apart from totally losing the sulphur species in the system, the sulphur species can be partly absorbed and will show a tailing (Figure 2) indicating the presence of adsorption in the system.

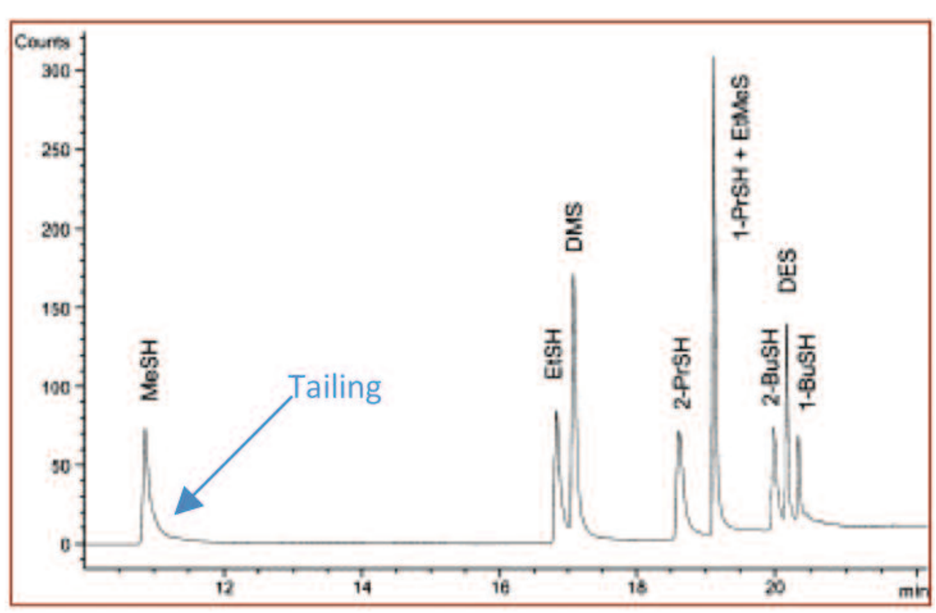

Figure 2: tailing peaks as result of partly adsorption

The third consideration: Hydrocarbon quenching

As requirements for sulphur detection become more stringent, the importance of good chromatographic separation of the hydrocarbons from the sulphur compounds and the inertness of the analytical column increases. Detectors used for sulphur determination generally are specific (e.g., sulphur chemiluminescence detection, FPD, PFPD) and help eliminate positive response from chromatographic interferences. Unfortunately, when high levels of hydrocarbons elute through the detector simultaneously with sulphur compounds, the signal for sulphur is quenched and area counts are nonlinear. For a successful analysis, the analytical column must resolve the hydrocarbons from the sulphur compounds.

Quenching of the sulphur responses by the hydrocarbon combusted products, such as CO, CO_2, H_2O, S_2O and not fully combusted hydrocarbons appears in sample matrixes with high hydrocarbon concentration and where the column separation is not optimal. The quenching is mostly seen using a FPD and PFPD detectors.

All detectors mentioned in this article have at least three orders of magnitude dynamic range, making them suitable for a relatively wide concentration band. A summary of

the detector characteristics used in this work is given in the table below. The values for sensitivity, selectivity, and dynamic range are those claimed by the respective suppliers.

Detector characteristics

Detector	FPD	PFPD	SCD	AED
MDL sulfur	20 pg/s	5 pg/s	1 pg/s	4 pg/s
Selectivity	10^5	10^5	10^5	105
Dynamic Range	10^5	10^5	10^5 linear	104, linear
Quenching	Yes	Yes	No	No
Equimolar response	No	Yes	Yes	Yes
Packed column compatible	Yes	No	Yes	Yes
Other elements	P,Sn	P	N	Total 26
Approximate relative cost	$	$$	$	$$$$

Figure 3: PE TOF MS

New Technologies: Analysis of sulphur species with conventional Gas Chromatography can extend to gasoline. Even then not all the sulphur species are identified. However sulphur speciation in more complex matrices like diesel, jet fuel and heavier is not possible due to limitation of the separation performance of the conventional one column configuration.

In combination with Simulated Distillation, sulphur fraction can be determined with boiling points cuts. However to separate sulphur species in complex matrices, powerful separation performance is necessary.

GCxGC is such a tool that increases peak capacity allows separation of relevant constituents that cannot be differentiated by one dimensional GC alone. This technology can be useful to be used with conventional detectors if the data speed of these detectors can handle the speed of the peaks coming from the GCXGC modulation. This new technology is best used with a TOF MS. As the data speed of the TOF MS is high enough to detect and identify the species. However there are no known

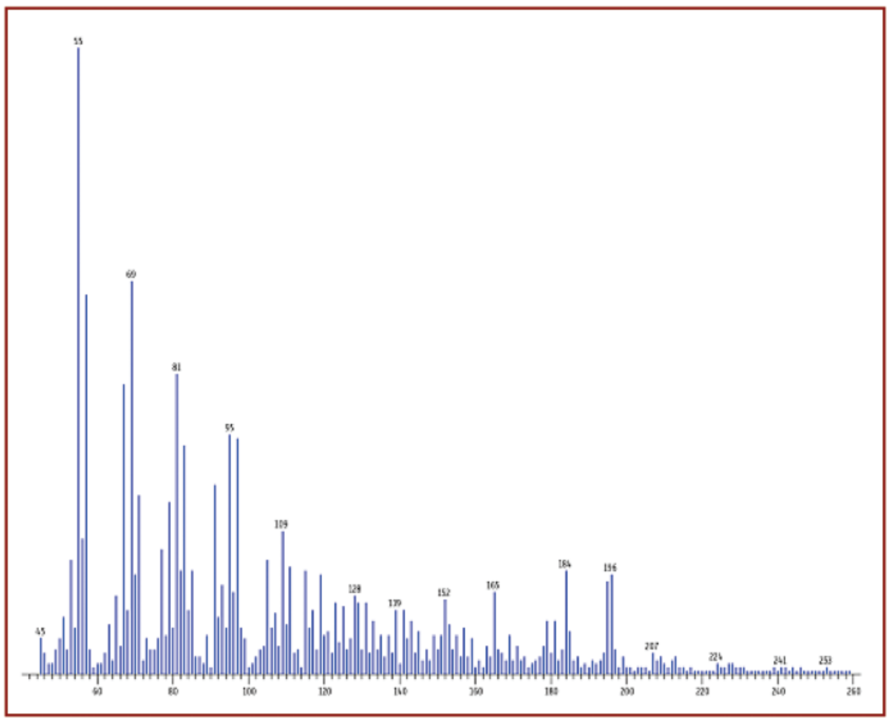

Figure 3: GCxGC separation of a diesel sample (part of a diesel spectrum)

libraries available specific for sulphur species, however there is a lot of work done to identify these species.

A standard GC-MS or tandem MS is not sufficient to identify the sulphur species that elute at the same time as many other isomers. With GCxGC combined with TOF MS and application knowledge makes these complex identification and quantification more feasible.

Remarks and conclusion

Gas Chromatography is a significant tool in sulphur analysis. The available detectors are sufficient to quantify sulphur species in low boiling range samples. For the heavy and more complex samples the separation is a limitation. If the matrix is reasonably simple and sulphur levels are in the low ppm to 50 ppb range then the FPD will usually be a good choice.

The PFPD also is capable of excellent sensitivity to low ppb levels. Because of quenching, it is best suited for light sulphur and hydrocarbon streams where good separation is achievable. Dynamic range must be considered as well. The AED and SCD can handle the widest concentration range from low ppb to high ppm levels. SCD is suitable for low boiling point ranges and for complex samples. However sulphur speciation is not possible in complex samples due to the difficulty of separation.

Many manufacturers try to improve their supplied applications for the sulphur analyses by taking into account all of the above considerations.

The use of dedicated detectors, sample handling, result interpretation is an art that only few master.

The development for the sulphur speciation in more complex samples are slow, even though attempts are made using conventional detectors to achieve this. As technology is improving and new technology takes a part in the petroleum laboratories including GC-MS, GC-MS-MS and GC-TOFMS. These technologies are more used in research and development and are complicated and not user friendly for routine analysis.

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