THE BLACK BOX OF TRICKS: Part one

STEPHEN HARRISON, LINDE, GERMANY,

DISCUSSES TRENDS IN GAS CHROMATOGRAPHY AND TROUBLESHOOTING IN PETROCHEMICAL ANALYSIS.

Gas chromatography (GC) is at the fore in the petrochemical sector as an analytical method that can be applied across a broad range of applications. Analysis of chemical components for plant process control has been elevated to unprecedented levels of accuracy to ensure optimal performance. The focus is not only on the main process stream components, but also on trace impurities which have a definite influence on the process and the final product. Against this background, GC technology has advanced towards higher sensitivity, or lower detection limits, and detecting more chemical components within a sample, even if they occur in extremely small quantities.

In tandem with this trend, GC is also advancing out of the laboratory setting and into the realm of miniaturisation, with instruments small enough to be located in the refinery itself. These miniature GC systems are placed at the location where the sample is generated, making it possible to conduct an analysis without having to move the sample to the laboratory. Micro gas chromatographs also have a positive impact on refinery running costs because they require very low flow rates of carrier gas.

In the world of complex analysis, there is also a move towards combining multiple detectors, with resultant instruments having multifaceted and highly involved configurations designed for special tasks. A specialist GC like this could analyse 30 components or more, from a single sample injection. The high sensitivity and low detection levels presently required demand ever higher purity carrier gases, often as high as a quality of 6.0, that is, 99.9999% purity, or not having more than 1 part per million (ppm) total reported impurity level. The purity of the carrier gas is crucial for performance, maintenance and longevity of refinery GC instrumentation.

Yet another trend is the evolution of the gas chromatograph instrument itself becoming a versatile, comprehensive, 'do everything' piece of equipment. Today, a typical gas chromatograph is a

Figure 1. The SCD has emerged as a powerful tool in refinery GC applications.

'black box' with everything needed to conduct a specific type of analysis built into it. In addition to the fundamental column and detector, additional examples are flow controllers, purifiers and gas pressure regulators which are all built into the gas chromatograph, so that it can be used on a 'plug and play' basis with maximum convenience and reliability.

Specialty gases are integral

Specialty gases are essential for efficient operation of a gas chromatograph. Separation takes place in the gaseous phase by introducing a sample which is transported by a carrier gas that separates the sample over the static medium in the column. Typical carrier gases for a range of applications include helium, usually supplied in cylinders, nitrogen supplied in cylinders, from liquid sources or via a gas generator, argon for niche GC applications, also supplied in cylinders, or hydrogen in cylinders or via gas generators. The choice of carrier gas depends on the type of detector, column, application and safety requirements and will also be dependent on separation efficiency or speed requirements.

Hydrogen is finding increased popularity as an effective substitute for helium, which is becoming scarce. Hydrogen also has certain benefits over helium, making its use preferable on some occasions. It has the lowest viscosity of all gases, thereby providing the highest mobile phase velocity and the shortest analysis time. Helium, on the other hand, gives the best overall performance and peak resolutions for many applications, making it an optimum choice of carrier gas where that is the primary concern.

A GC's detector will often harness specialty gases such as a combination of air and hydrogen which are used in a flame ionisation detector (FID), or helium which is used in a helium ionisation detector (HID). Other specialty gases used in association with GC are gas mixtures to calibrate the detector in order to ensure accurate measurement, or zero gases to set a zero reading on the detector.

The information received by laboratory technicians is essentially a graph called a chromatogram, with peaks representing the different chemicals in the sample (analytes) and the volume and proximity of peaks indicating the amount of these analytes present in the sample. Each chromatogram illustrates the fingerprint of the mixture of chemicals introduced into the chromatograph from the sample, the specialty gases used and any contaminant gases unintentionally introduced from the surrounding atmosphere. With the complexity of modern GC operations, the possibility exists for things to go wrong. When errors occur they are likely to show up in the chromatogram and cause problems in the interpretation of the analytical results.

Troubleshooting

As in other industries, laboratory operators in the petrochemical sector sometimes encounter problems of the type which occasionally beset all GC users. But, in this sector, with such a broad range of analytes, so many potential impurities and such wide concentration ranges encountered during analysis, problems which invariably arise in the hydrocarbon processing sector can sometimes be difficult to resolve.

As a leading industrial gas company, Linde is committed to helping petrochemical industry GC users troubleshoot problems. This can be somewhat challenging, particularly in cases where the analysis technology is contained in one box, as in order to identify a problem, you need to examine what is going on at each stage of the process. Although the merging of a number of pieces of equipment into one GC unit simplifies the process when everything runs smoothly, it is when problems are encountered that the identification of the cause can be more complicated than in simpler systems used 20 years ago. This is due to the greater number of potential failure points contained inside the instrumentation setup.

The sulfur chemiluminescence detector (SCD) has emerged as a powerful tool in refinery GC applications. GC-SCD is used for the quantitative determination of various sulfur organic species, such as hydrogen sulfide, mercaptans, thiophenes, benzothiophenes and sulfides in hydrocarbon samples. Because sulfur speciation is essential during oil catalytic processing in a refinery, this technology is a highly sensitive and useful technique to characterise crude oils of different origin.

When it comes to troubleshooting issues associated GC-SCD technology, a key consideration for laboratory personnel is the physical properties of the sample delivery lines. It is essential that these delivery lines be constructed from an inert material, such as Hastelloy®, since the incorrect material could result in the component reacting on the walls of the line and displaying a zero result on the chromatogram. Although 316 stainless steel is the most common choice in general industry for this application, it is not appropriate for refinery analysis because certain sulfur compounds in the sample line could adhere to the walls and would therefore not reach the analyser at the same time as the bulk of the sample. Therefore even though these compounds are present in the process stream, they would not be detected in real time, leading to a false reading.

This can prove to be a challenging problem to troubleshoot, as laboratory personnel would have no way of knowing that these compounds are present, but are being removed by the sample delivery line. Only when the line eventually becomes saturated, resulting in a sudden concentration of the substance being released and then detected, would the operator become aware of an anomaly. What is actually happening is a time delay in the measurement response associated with the length of the sample delivery line. For example, with a substance present in small concentrations of low ppb, it could take hours before the walls of the delivery line become sufficiently saturated for the component to stop adsorbing to the sample line walls and move into the analyser.

So if a lab technician were to suddenly see sulfur compound peaks in an analysis result but several hours after they might have been expected, the reason could be that the sulfur concentration is actually several hours old. Conducting some test injections of known concentration calibration gas mixtures into the sample delivery pipework upstream of the analyser could validate or rule out this problem. If this problem is identified during trouble shooting, the solution could be to change the pipework in the sample delivery system to a material such as Hastelloy.

When considering the use of hydrogen, an emerging application among the fuels of the future, sulfur is an impurity that can render this clean new fuel harmful to the 'engine' where it is being used, notably where hydrogen is being produced for fuel cell applications in motor vehicles. In this case, it is essential to measure sulfur content to ensure it is low enough to comply with the standard specification for this application, which is less than 10 ppb of hydrogen sulfide content. These low levels of sulfur in a background matrix of hydrogen are very difficult to identify using conventional analytical equipment, and GC-SCD is generally the most suitable technology to measure these low levels of hydrogen sulfide within a hydrogen matrix.

The petrochemical industry also uses hydrocarbons and solvents with low vapour pressures. Owing to their low vapour pressure these chemicals evaporate very rapidly into the environment and, with increasing environmental awareness, emissions control focused on these volatile organic compounds (VLCs) is high on the global agenda. To reduce volatile organic compound (VOC) emissions both for environmental reasons and to recover valuable solvents for economic benefits, the emission levels of VOCs must be continuously monitored and measured. However VOCs can be some of the most difficult environmental pollutants to identify and measure, requiring dedicated analytical instruments such as GC-MS (gas chromatography mass spectrometry) to ensure that a refinery's measurement capabilities are sufficiently accurate, with legally compliant traceable gas mixtures.

A common cause of GC problems in this area is a lack of precision in the calibration of the instrument and detector. Therefore the most fundamental troubleshooting step in this instance is checking the quality of the calibration gas mixture. Calibration should be precise and must often be proved to be so. The certificate supplied with the calibration gas mixture must be read and clearly understood to ensure that the component concentrations are similar to the concentrations that will be measured. Also, the accuracy of the reported values in the calibration mixture should be appropriate for the measurement being undertaken and all required components must be present in the calibration gas mixture. Furthermore, the operator should check the certificate to ensure that the gas mixture is still within its shelf life or expiry date. Beyond these fundamentals, use of appropriate cylinder connection techniques is vital and this may involve purging the system with an inert gas to remove atmospheric air after calibration cylinder connection, but prior to calibration sample introduction.


Figure 3. Gas chromatographs are becoming versatile, comprehensive, 'do everything' instruments.


Figure 2. Analysis of chemical components has been elevated to unprecedented levels of accuracy.

Linde's state of the art capabilities allow for production of very traceable, stable, low level, multi component VOC mixtures, and they routinely supply calibration standards containing more than 60 components at 100 ppb and below. To date, the most components supplied in a single cylinder are 110, earning Linde a Guinness World Record. This ground breaking 110 component calibration standard, part of Linde's HiQ® specialty gases range, comprises the largest number of components, including more than a hundred VOCs of any known calibration gas in commercial use today and represents an extraordinary level of technological achievement.

In addition to ISO 9001 accreditation, Linde facilities worldwide are becoming ISO 17025:2005 accredited, which specifies the general requirements for the competence to carry out tests and calibration, including sampling. It covers testing and calibration performed using standard methods, non-standard methods and laboratory developed methods and is applicable to all organisations performing tests and calibration. In 2013, Linde was the first ever supplier to achieve ISO17025 accreditation for gaseous VOC mixtures.

While VOC monitoring today is all about emissions control to comply with legislation and prevent the loss of valuable VOCs, Linde indicates that in the not too distant future this arena could expand to include emissions trading. If or when this happens, it will have a direct financial impact on petrochemical companies. As soon as VOCs become molecules included in emissions trading programmes, the focus will shift dramatically beyond just keeping emissions within legal limits for the right to keep the refinery open, through minimising waste for financial benefit to VOC emissions as a source of revenue and profit through consent trading programmes.

Natural gas custody transfer

Natural gas custody transfer, which focuses on the point of a commercial transaction when a change in ownership takes place, is an extremely important concern for the hydrocarbon processing industry. The exact calorific value of the natural gas must be established for correct invoicing and, to add to the complexity, this is also often a taxable transaction when the transfer takes place across borders.

Troubleshooting issues in this area of the industry are associated with accuracy of measurement, since false measurements could inflate taxation payments or under recover revenue and impact invoicing dramatically. The solution is to purchase high quality calibration gases which are accurate within +/- 0.5 to 1% and are accredited to ISO Guide 34 or similar levels of accuracy accredited to ISO 17025, thereby ensuring the highest levels of accuracy and international traceability and the lowest levels of measurement certainty.

Perhaps the most common gas chromatography instrument used in refining and petrochemical applications is GC with a FID. In GC-FID, the FID detects analytes by measuring an electrical current generated by electrons from burning carbon particles in the sample. To do this, FID harnesses a combination of hydrogen and oxygen. The oxygen for the flame combustion is normally supplied by the use of high purity synthetic air to minimise the amount of impurities coming into the detector. Synthetic air is not simply compressed air from the atmosphere which would bring with it many impurities, but a blend of high purity oxygen and high purity nitrogen. In addition to avoiding impurities, it is equally important, when changing over from one cylinder of synthetic air to another, to ensure that the composition of the air in the new cylinder is consistent with that of the previous cylinders, in terms of blend tolerance. For example, the target oxygen concentration might be 20%, but that mixture might have a blend tolerance of +/- 1% absolute (5% relative) meaning that the actual oxygen concentration can be between 19% and 21%. While a small change in the consistency of the contents of the new cylinder might be acceptable, more pronounced differences will influence how the FID flame burns and could lead to a very different analytical result, even though the sample has not changed. So, if a very stable flame is required, the trouble shooting recommendation would be to purchase synthetic air mixtures with a very 'tight' blend tolerance of +/- 0.4% absolute (2% relative) and thereby limit the possible swing in oxygen concentration from 19.6% to 20.4%.

The same principle applies to ordering calibration gas mixtures, but the issue then is more about analytical accuracy than blend tolerance. Using a calibration gas mixture with an analytical accuracy of +/- 10% could create an apparent shift in process parameters when a process analyser is recalibrated and the instrument then begins to respond differently. Again, a calibration gas mixture with a +/- 2% analytical accuracy will avoid fluctuations and ensure optimal process control on the refinery, as well as the stability of other environmental monitoring and emission trading applications on the plant.

The GC story continues in *Hydrocarbon Engineering*'s June issue, when Linde looks further at troubleshooting issues encountered in gas chromatography.