Close up chemistry

Stephen Harrison, Linde, Germany, examines how gas chromatography-mass spectrometry can be utilised as a tool for forensic analysis.

Gas chromatography-mass spectrometry (GC-MS) is widely perceived as an essential analytical tool for forensic analysis in the petrochemical industry. In fact, its simplicity, sensitivity and effectiveness in separating and identifying components have made GC-MS one of the most important tools in analytical chemistry across a spectrum of contemporary industries.

GC-MS can be harnessed across the entire value chain in the oil and petrochemical arena. It can be used in the prospecting stage and in the refining process to monitor and improve quality, to final refined and formulated fuels and lubricants, as well as to ensure compliance with environmental standards. It can even be utilised as a forensic tool in criminal cases in which fuel has been used to perpetrate arson.

Other analytical techniques fundamentally determine the quantitative issues arising from analysis of a specific sample, answering the question of how much is present. GC-MS, by contrast, is one of a very few techniques that is able to qualitatively identify the actual nature of chemicals in the sample, answering the question of which molecules are present.

Regarding these two questions, in many analytical scenarios it is actually more important to determine what molecules are present, rather than their quantity. Conducting quantitative work alone on a sample with unknown content can be fruitless. The qualitative method is especially relevant to research applications and lays the correct foundation for the analysis. Only when it is known which chemicals are present can the quantitative analysis be performed.

The gas chromatography (GC) principle is that molecules in a sample separate in the chromatography column because of differences in their chemical properties. The mass spectrometry (MS) breaks the components as they exist from the column into ionised species and separates these based on their mass to charge ratio. This is the great advantage of the combination of GC as the first separation step and the MS as the qualitative detector.

With the massively burgeoning importance of petroleum products and their derivatives in all aspects of people's lives across the world today, GC-MS comes to the fore as a very important analytical technique. It is one of few techniques to determine exactly what is in a sample. Characterised by its quick screening abilities, GC-MS has been widely heralded as the 'gold standard' for forensic substance identification.

On the same standing with GC-MS, liquid chromatography-mass spectrometry (LC-MS) is also a qualitative analytical chemistry technique that combines the physical separation capabilities of high performance liquid chromatography with the qualitative analysis capabilities of mass spectrometry. Both techniques involve using a mass spectrometry detector, but GC-MS is used to screen a sample using a gaseous phase component separation process in the

Figure 1. High quality gas control equipment is essential to deliver high purity gases to the GC-MS instrument.

Figure 2. GC-MS separates components and analyses in the gaseous phase, in addition to some samples that normally exist in the liquid phase.

GC column. By comparison, LC-MS is able to detect and identify chemicals using a liquid phase component separation process in the liquid chromatography column.

The medium in which the sample exists and is most effectively separated in the chromatography column (gaseous or liquid) determines which technique is more appropriate. While many samples can be vaporised for GC-MS, other samples are better dissolved in a suitable solvent and examined using LC-MS. However, GC-MS is preferred when quick screening is required because the column separation is generally faster in the gaseous phase.

Sample preparation

In the petrochemical sector, GC-MS can be dynamically applied across a broad range of applications. However, critical to the success of the analytical process is the correct handling and preparation of the sample. Samples requiring GC-MS analysis could include heavy liquids, such as tars (which behave like solids), or solids such as coal. In cases like this, analysts are able to use pyrolysis MS to convert the sample into the gaseous phase required for characterisation by GC-MS.

Pyrolysis MS is an important technique in the overall analysis armoury and has been noted for its ability to analyse small amounts of material with minimum sample preparation to obtain, within minutes, fingerprint data that can be used for identification and typing. Pyrolysis MS samples are heated up rapidly to very high temperatures so that they convert from solid to gaseous phase instantaneously and can then be passed through the GC-MS process.

Another sample preparation technique is called thermal desorption mass spectrometry (TDMS). This technique involves collecting desorbed molecules from a surface when the surface temperature is increased and then introducing these individual components into the GC-MS process. This method is generally used to analyse volatile organic compounds, commonly the source of odours in the ambient air, either inside a building or outside in the open air. Samples are collected using thermal desorption tubes.

A third technique for preparing samples is called headspace GC-MS and involves heating a liquid sample to boiling point, collecting the vapours emitted from the liquid as it is heated up to approximately 100 - 200 ˚C and passing them through a GC-MS.

GC-MS applications

GC-MS has an important role to play in prospecting for crude oil or natural gas. As drilling proceeds, exploration personnel need to determine the value of the resources they come across.

GC-MS will be able to tell the prospecting company exactly what they have uncovered. It is a useful tool for determining the quality of the stream of crude oil or natural gas emanating from the well. A significant part of the financial valuation of petrochemical companies is based on the reserves that companies believe they hold: much more than the value of their processing assets, ships or oil rigs. It is all about the potential value of the oilfield to which the company has rights. Therefore, an accurate assessment of the quality of these reserves is absolutely critical for a fundamental evaluation of the reserves being declared. A technique such as GC-MS can play an essential role in quantifying the value of such oilfield reserves.

The most typical use of GC-MS in the petrochemical industry is process troubleshooting. The composition of crude oil is never consistent, creating the opportunity for operational problems to arise as raw material feedstock changes between incoming crude oil batches. Production pressures require the source of the problem to be identified as quickly as possible. The best way to achieve this is often to use GC-MS as a forensic tool to identify the presence and type of chemical responsible and at what point it entered the process. It is important to note whether the chemical was introduced with the feedstock, or if it was created by a reaction during the process. Chemicals that enter the process can poison catalysts, or they may be non-condensable and create a negative effect on the heat exchange or distillation processes. Once the root cause of the problem is known, remedial measures can be quickly applied to balance out the impact of the chemical causing the reaction.

Beyond the production process, but still related to the petrochemical industry, GC-MS is an effective way to identify the source of oil spills. The technique can be successfully applied if a port authority or a nature reserve reports an oil release arising from anything between a major oil spill from a tanker, to a minor spill caused by a ship rinsing out its tanks and discharging the contents into the ocean, or an accidental oil spill in the harbour.

Coastal and environmental authorities are always on the lookout for insidious oil pollution and, to bring the perpetrators to book, GC-MS can be harnessed as a forensic tool to trace the origins of the pollution, matching the oil fingerprint to its source. This very precise fingerprinting technique is able match the sample from the oil spill to the vessel that carried the oil.

Knowing that GC-MS can deliver such certain identification makes this analytical method a powerful deterrent to those considering polluting the ocean in this manner. Sloppy practices by the companies who transport oil by sea will increasingly be brought to light allowing for more prosecutions and stimulating better operating practices.

Deeper into the criminal practices, this time on land, arson is often perpetrated using automotive fuels. GC-MS can be utilised to determine how the fire started and even who was responsible. This is possible by following the links in the chain of events leading up to the incident: identifying the type of fuel involved, then determining

Figure 3. Linde HiQ specialty gases come in highly portable cylinders for calibration of remotely located lower explosive limit and lower flammable limit sensors.

where it was sourced. CCTV footage at a local fuel station could reveal someone purchasing fuel in a portable container. GC-MS therefore has a role to play in criminal investigations of this nature. As with the perpetrators of pollution, the knowledge that it is possible to solve arson cases by fingerprinting residual fuel to trace it back to source certainly serves as a deterrent.

Origins

Roland Gohlke and Fred McLafferty developed the use of an MS as the detector in GC in the USA in the 1950s. These sensitive devices were bulky, fragile and originally limited to laboratory settings. The development of affordable and miniaturised computers and other parts of the instrument have helped in the simplification of the use of this instrument, and facilitated great improvements in reducing the amount of time it takes to analyse a sample.

In 1996, the top of the line high speed GC-MS units completed analysis of fire accelerants in less than 90 secs, whereas a first generation GC-MS would have required at least 16 mins. This has led to their widespread adoption in a number of fields in the past two decades.

The first GC-MSs, which were bigger than a dining room table and could fill a large room, were extremely costly and not commonplace. Today, the contrast is significant. A GC-MS can be put into a small suitcase and carried to any location in a plant or factory, or even a crime scene. Over the past 20 - 30 years, this technology has moved from being hallowed and rare, to becoming very commonplace and portable (while still remaining highly important).

As a result of its rapid evolution as an increasingly accessible technique, applications for GC-MS are expanding rapidly. With such increased portability, analysing samples at the source has become a reality, which generally leads to an optimum result.

As a supplier of gases for this equipment, it is important that Linde keeps up with the changing modes of supply. Previously, when spectrometers were huge machines residing in laboratories, Linde could supply the different essential gases required to operate these instruments in standard 40 or 50 ltr water capacity cylinders or liquid gas supply such as CRYOSPEED® to the laboratory site.

When GCs were miniaturised and 'micro GCs' invented, Linde was obliged to come up with an appropriate solution. Design engineers solved the portability issue with a product called the HiQ® MICROCAN. The size of a beer bottle, it contains enough gas to keep a micro GC running for several months.

HiQ MICROCAN is a high pressure cylinder with a maximum of 200 bar filling pressure. It is therefore a miniature version of approximately 1/250th in scale in comparison to the 50 ltr high pressure cylinders that are more common in the market. Due to its high filling pressure, the HiQ MICROCAN has more gas content than conventional small compressed gas cylinders which might typically be filled to 12 bar or 34 bar, while also being much smaller. The HiQ MICROCAN is part of Linde's 'gases in small cylinders' range, which was developed in response to universal gas application needs, wherever it is critical that light containers are used in a mobile way.

High purity

GC-MS requires high quality specialty gases for instrument operation and for calibration. Specialty gases are used as carrier gases (helium is most common), collision gases (nitrogen or helium) and can also include reagent gases. The carrier gas plays an important role by transporting the sample through the chromatography column into the mass spectrometer. The carrier gas must be inert or at least must not react with the stationary phase in the column. The choice depends on the sample, column, application and safety requirements.

The choice of carrier gas is also dependent on requirements relating to separation efficiency and speed. Hydrogen has the lowest viscosity of all gases, thereby provides the highest mobile phase velocity and therefore 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 in those cases.

The purity of the carrier gas is a critical factor for the performance, maintenance and lifetime of the column. Impurities in the carrier gas, especially hydrocarbons, cause base line noise and reduced sensitivity, and might increase detection limits. Traces of water and oxygen may also decompose the stationary phase, which leads to premature destruction of the column. Linde's HiQ specialty gases range in purity up to 7.0, which is the highest commercially available grade, being 99.99999% pure with 100 ppb of total impurities. The gas company also provides certificates of analysis on these types of gases to reassure users of these quality attributes.

While the reliability of analysis is only as good as the quality of gas being used, distribution systems and equipment for high purity gases and specialty gas mixtures must also be able to meet increasing demands for high standards of performance and new analysis methods. Impurities occurring in concentrations as low as parts per billion can have serious consequences, particularly if the analyst is not sure which molecules are present in the sample.

Demands made on regulators and valves in petrochemical environments are extremely high. Components must be capable of dealing with high and low pressures, large and small flows. They must also be suitable for high purity inert gases as well as reactive, flammable, corrosive or toxic gases.

REDLINE® from Linde is a hi tech range of regulators, modularly designed to slot into central gas supply systems, containing gas panels, points of use and cylinder regulators generally suitable for purities up to 6.0 (99.9999%). In addition to common models, REDLINE regulators also have models for vacuum dosage and low pressure precision adjustments. The most recent introduction to REDLINE is a range of regulators and gas supply panels with face seal fittings to reduce the possibility of contaminant ingress. With this new range, launched in 2010, gases of 7.0 grade purity can be handled and supplied without purity deterioration.

The Linde BASELINE® range provides alternative entry level laboratory equipment with a high tech range of specialty gases cylinder regulators for basic applications up to 5.0 grade purity. Linde also has HiQ laboratory gas generators providing high purity hydrogen and nitrogen, both suitable for GC-MS applications.