HOW TO TURN YOUR OFF-THE-SHELF GC-MS INTO A PROBLEM-SOLVING POWERHOUSE!

Over the years I have visited many refinery and petrochemical laboratories and they all look pretty similar with facilities for elemental analysis, molecular spectroscopy, physical testing and separation science.

In general, for the petroleum based industries, gas chromatography (GC) dominates the separation science space and it is not uncommon to see rows of GC instruments on the benches in such labs. These GC instruments are often predominantly single application based and are running ASTM/DIN standard methods such as SIMDIS, PIONA or Refinery Gas Analysis. In addition to running standard and specification tests, most laboratories are required to provide a forensic type role when operational problems occur where the standard tests have limited applicability. As a result, many laboratories will have acquired a bench-top GC-MS system for just such events and the identification of unknowns. These operational problems are generally urgent, high profile and often have high potential cost implications and therefore having access to technology specifically configured for problem solving is an important consideration.

In many cases GC-MS systems have been bought in the standard "off the shelf" configuration with split/splitless injectors and perhaps an FID detector installed in addition to the mass spectrometric detector. This type of configuration generally restricts these instruments to the analysis of volatile liquids or solutions and therefore limits their direct applicability to a range of problems commonly encountered in the industry.

In this article we explore how a range of options and accessories can be employed to convert both old and new instruments into multi-purpose problem solving tools capable of tackling a wide range of sample types and chemistries.

These options can be broadly characterised into 3 synergistic areas:

1. Install a Multimode Injector capable of programmable heating to at least 600°C

2. Exploit the benefits of Micro-Fluidic flow control and switching devices

3. Exploit Plug and Play detector technology

Each of these can be installed and used, either as an option in new GC-MS systems, or can be retrofitted in the majority of mainstream GC manufacturers instruments. They all have individual benefits, but it is when they are all employed together with the GC-MS that the full flexibility of the instrument can be achieved. So, let's look at each of these in a bit more detail.

Install a Multimode Injector capable of programmable heating to at least 600ºC

This option offers the biggest bang for your buck of any of the upgrades options discussed here and would be my first choice to dramatically increase the capability of a conventional GC-MS instrument. There are a number of Multimode or Programmable Temperature Vaporiser (PTV) injectors on the market provided either by the GC instrument manufacturers themselves or by specialist companies such as the OPTIC 4 (GL Sciences), the CIS (Gerstel) and the UNIS (JAS) and all have slightly different performance features and accessories depending on their targeted application areas. The basic principle of these injectors is that they allow the temperature in the injector to be programmed over a wide range and are capable of fast, repeatable, multi-step programmable temperature profiles which when combined with electronic flow control allow great flexibility.

My experience has mainly been with the OPTIC series of instruments and the latest variant OPTIC4 (GL Sciences) has a wide field of applicability for petrochemical problem solving analysis. It can be easily installed and integrated into all the major GC

manufacturers instruments and the picture in Figure 1 shows an OPTIC 4 installed on a Shimadzu instrument. The OPTIC 4 can be used for hot injections, cold injections, large volume injections, on-column injections, in liner derivatisation, thermal desorption, thermolysis, pyrolysis and more due to a combination of its operating temperature specification and the suite of specialised liners and sample introduction accessories available. This means that a wide range of sample types from volatile solvents through viscous liquids, sludges and solids can be examined directly using an OPTIC 4 equipped GC-MS instrument. Kaal and Janssen (1) produced an excellent review article giving details and benefits of many of the specialist techniques listed above.

Figure 1: OPTIC 4 Installed on a Shimadzu GC-MS. Reproduced courtesy of GL Sciences

Take as an example a typical industry problem such as looking for high boiling contaminants often at ultra-trace levels in a volatile feedstock. With a conventional split/splitless injector you may be able to inject 1-2ul, and you can also still do this using the OPTIC if desired, but you can also use the Large Volume Injection (LVI) capability where sample volumes of circa 100ul can be injected on a controlled manner thus giving a 100x increase in sensitivity. By utilising the precise temperature control the volatile feedstock matrix can be evaporated and vented to waste leaving the contaminants concentrated in the injector. The total injected volume, and therefore sensitivity, can be further increased by using multiple injections. The injector temperature is then programmed to volatilise the higher boiling contaminants and transfer them to the GC column for subsequent separation and unknown identification. Furthermore, after the first GC run then any residual organic material, for example dissolved polymer, which has not been volatilised, can then be pyrolyzed by ballistically heating the injector to 600°C and the pyrolysis products determined. Therefore, a huge amount of information on the semi and non-volatile organic species contaminants can be obtained from a single sample injection.

Derivatisation of polar and low-volatility analytes is a common technique in GC analysis (1) which can also be carried out directly in the Optic injector. Lynch (3) described a fast and effective technique for quantifying levulinic and succinic acid in petrochemical process streams using in-liner derivatisation to silyl ethers in a GC equipped with an OPTIC. The PTV in-liner derivatisation technique gave efficient conversion to silyl ether derivatives with good precision, minimal sample preparation, low sample volume/reagent consumption and resulted in a circa 5-fold decrease in the analysis time.

A particularly useful feature of the OPTIC 4 for problem solving (where samples are often sludges or wet solids) is the Difficult Matrix Introduction (DMI) capability which is based on the patented Direct Sample Introduction (DSI) technique (2). It enables sample introduction into the GC column to be performed from a disposable microvial placed inside the inlet liner (Figure 2). This has a great advantage over traditional injection because large volumes (up to 30 or 60 µl) of dirty sample extracts or even raw samples can be introduced directly into the GC/MS. Using the principle of selective exclusion, the volatiles and semi-volatiles are transferred onto the column, while non-volatile residues are retained in the microvial. The microvial can be discarded after the analysis or submitted to pyrolysis to gain further information on non-volatile organics. This is also a very useful technique for the examination of solids samples from equipment fouling, the analysis of polymers and the direct analysis of process catalysts for contaminants.

The DMI technique can even be automated using GL Sciences Linex automated GC liner exchange accessory.

Exploiting the benefits of Micro-Fluidic Flow Control and Switching devices

The PTV injector has already dramatically increased the capabilities of our lab GC-MS instrument but we now find that the capability is limited to using our standard single column set up which often does not provide sufficient resolution or capacity to cope with the wider range of samples we can now analyse using the system. Flow switching techniques such as Deans Switching (first published 1965), backflush and detector splitting have been employed in GC for many years, but early systems suffered from high dead volumes and were not well suited for use with modern capillary columns. Early micro-fluidic flow control devices such as "live switching" developed by Freidhelm Mueller at Siemens in the 1980s were very effective but difficult to set up due to the use of manual pressure controllers. However, the advent of accurate and precise electronic pressure and flow control facilitated the development of new
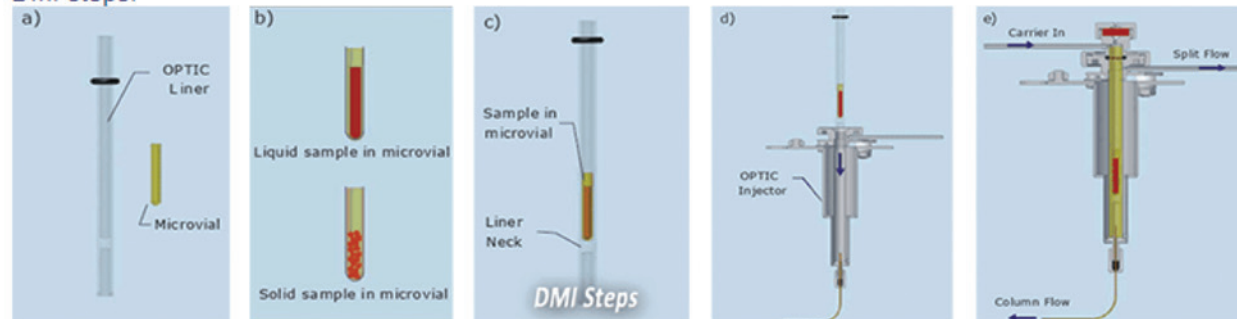

Figure 2: Schematic of the steps involved in the application of Difficult Matrix Introduction techniques using the OPTIC 4 injector. Reproduced courtesy of GL Sciences

approaches leading to technologies such as the Agilent Capillary Flow Technology (CFT) devices, Perkin Elmer's Swafer, the SGE SilFlow, Shimadzu's Advanced Flow Technology and Thermo Fisher Microfluidic kits. When used in conjunction with the flexibility of the PTV these technologies further expand the application areas for GC Instruments and now virtually all major GC manufacturers and accessory suppliers offer devices for a range of applications.

A good example of how the combination of PTV and microfluidic flow switching can work together is in the characterisation of polymers and deposits by in-liner pyrolysis. Polymers are widely employed in the industry within components and seals and as additives in process streams and final products. They are also often found in deposits and sludges and the analyst is often charged with identifying the polymer species. Deposits and polymers can be studied directly in an Optic liner using thermal desorption for the volatile species followed by pyrolysis to study the polymer structure. Differentiating between similar chemistry polymers (propylene/ethylene/isobutylene/isoprene etc.) can be difficult using single column systems as the high concentrations of C1 to C6 species generated are not well resolved on the typical 30m boiling point column employed for GC-MS. However, by employing microfluidic devices for Deans switching and detector splitting (as shown in Figure 3) excellent results can be obtained for both the low and high boiling point components from polymer pyrolysis. The sample can be examined firstly by thermal desorption in the injector with the 30m BPX50 column effluent flowing to the MS and FID detectors via the splitter device. The sample remaining in the injector can then be pyrolysed, but this time the Deans switch device is employed to heartcut the C1 to C6 components from the BPX50 column onto a Carboplot column to achieve a high-resolution separation using FID for quantification. After the C6 components have been cut to the Carboplot the remainder of the C6+ components are fed directly to FID and MS detectors. This configuration has been employed to differentiate ethylene, propylene, isobutylene and isoprene based polymers both in their native state and in deposits and sludges (4).

This type of configuration allows a high degree of flexibility and can be employed for the analysis of a wide range of samples including deposits, solids and viscous liquids.

Exploiting Plug and Play detector technology

Many laboratory GC instruments can be equipped with at least 2 conventional detectors plus a mass spectrometer and some manufacturers now offer plug and play detectors which can be interchanged relatively easily. The ability to change detector configurations offers another option to extend the flexibility of a PTV equipped GC-MS system and it is worth considering purchasing a range of detectors to have ready to mix and match if they can provide unique selectivity for your problems. The FID employed in combination with the mass spectrometer is a powerful tool for most hydrocarbon-based problems but if you are interested in hetero atom species it can fall short and here detectors such as the Flame Photometric Detector (FPD), the Nitrogen Phosphorus Detector (NPD) and the Electron Capture Detector (ECD) can be employed to add selectivity and sensitivity for the species of interest.

As an example, let's consider our previous application for the analysis of polymer species. Many polymers and additives of interest in the industry are functionalised and the analysts wishes to get information about the polymer backbone and any end group functionality. Many of the additives of interest contain nitrogen-based functionality e.g. succinimides and amines but, many of the polar nitrogen containing components generated during pyrolysis of end group functionality are not resolved on a boiling point column. Using a polar wax column can give better resolution of the polar nitrogen species but the TIC is still dominated by the much higher levels of hydrocarbons from
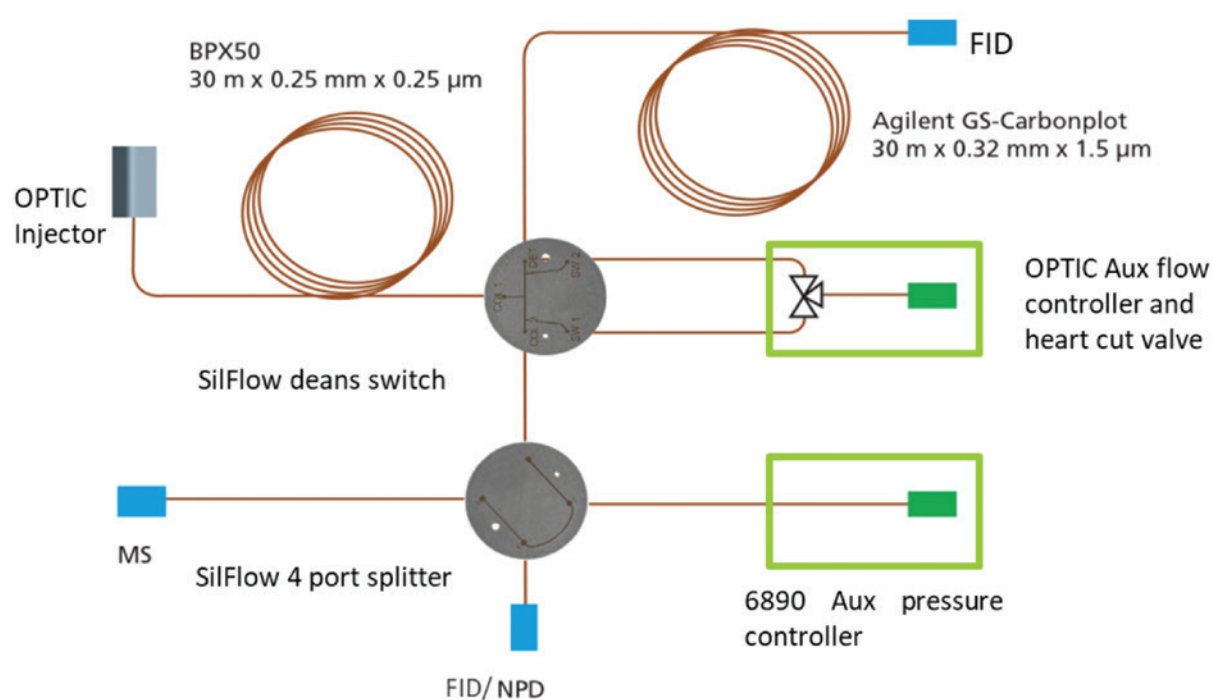

Figure 3: Schematic for a GC configuration for the identification of polymer backbone chemistry (4)

the polymer backbone as shown in top chromatogram in Figure 4. By employing a NPD coupled in parallel with the MS using a microfluidic splitter the nitrogen species can clearly be resolved as shown in the lower chromatogram in Figure 4. As long as any time offset between the parallel detectors is known the position of the peaks from the NPD can be used to identify peak maxima and background subtraction spectra in the TIC allowing identification of the end group functionality.

Conclusion

Multimode injectors, microfluidic flow devices and selective plug and play detectors all have a major role to play in adding flexibility to GC and GC-MS systems, especially for non-routine problem solving analysis. The multimode injector dramatically increases the type of samples which can be analysed directly by GC and GC-MS and the other two allow increased resolution and detection of the species of interest. However, the real power comes from the ability to combine these technologies in a flexible way to be able to target the species and chemistries of interest when tackling complex chemical mixtures presented in a range of physical forms.
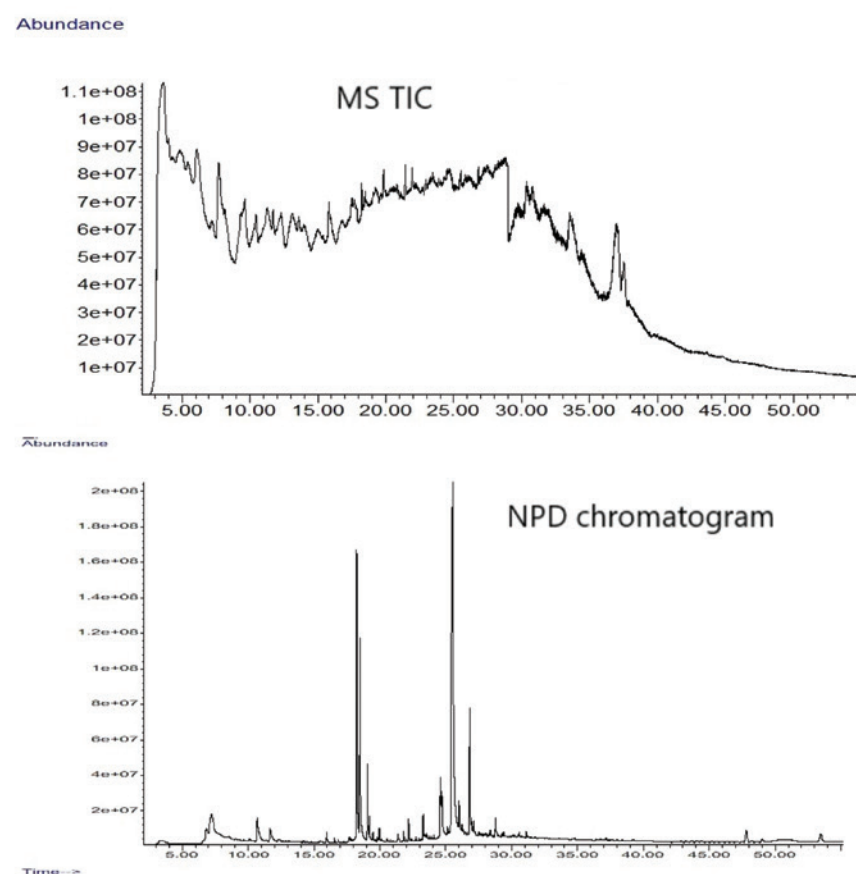

Figure 4: Chromatograms obtained from the pyrolysis of a sample with the GC effluent split to 2 detectors. The top trace shows the MS Total Ion Chromatogram (MS TIC) and the lower trace the response from the Nitrogen Phosphorus Detector (NPD)

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