Multiple Component Real Time Impurity & Process Composition Analysis Using Mid IR Process Analytical Tunable Laser Spectroscopy (PATLS)

Introduction

The development of Quantum Cascade Lasers (QCLs) in the early 1990s offered a range of compact, reliable devices operating in the mid infra-red\(^{(1)}\), a spectral region containing the fundamental absorption bands of a number of molecules. This region was previously limited to devices such as lead salt lasers, which require cryogenic cooling, thus limiting the adoption of the technology in field-based applications. The QC laser is a semiconductor laser which relies not on the bandgap of the semiconductor material, but on the spacing of a series of quantum wells. An applied electric potential offsets the quantum wells from each other and aligns them in a staircase pattern. A single electron travelling down the staircase emits a photon at each step. A typical QCL might contain anywhere between 20 and 100 steps. As a result the efficiency of QC lasers can be considerably higher than that of other devices. The wavelength of most QCLs is governed by a distributed feedback method (DFB). In this method a grating is etched into the laser waveguide to force the cavity standing wave to a specific wavelength. As the laser is switched on, joule heating causes the grating to expand, changing the wavelength imposed on the laser. This wavelength sweep is known as a frequency chirp. The intrapulse technique patented and used by the analyser vendor\(^{(2)}\), and as described in this paper, utilises the frequency chirp to rapidly sweep across the spectral region of interest. Each sweep typically lasts a few hundred nanoseconds and covers a 2 to 4 cm\(^{-1}\) (wavenumber) region. The range of wavelength chirp and the high resolution achieved by a QCL makes it particularly suited to the spectroscopic analysis of narrow rotational structures\(^{(3)}\). This makes it ideal for measuring small molecules in the gas phase. For example, it has found a great deal of utility in the monitoring of combustion byproducts such as NO, NO\(_2\), CO and CO\(_2\) wherein the speed of measurement makes it ideal for process monitoring and control.

Careful laser wavelength selection allows the user to sweep across spectral absorption lines of a molecule of interest\(^{(4)}\). Implementation of the Beer-Lambert law and a heuristic fitting algorithm allows for the concentration of the molecule to be accurately determined.
Technology

In this section, an overview of the technology and measurement techniques is provided as well as examples of how these techniques have been incorporated into robust analyser designs.

Key Analyser Technology Concepts

The PATLS core sensor engine is an array of QCLs pulsed rapidly in sequence to achieve continuous monitoring of multiple target species simultaneously. Each QCL is housed in a field swappable, factory aligned and collimated module, allowing for a high degree of user customization. The PATLS process analyser is capable of supporting multiple unique mid-IR QCL lasers (typically 4–6). The individual beams are co-aligned using an optical manifold and their profile reduced using an optical beam reducer before being directed into the sample cell. The sample cell consists of a low volume measurement cell with both short and long path lengths. To achieve actual pathlengths up to ~100 m in a small volume, the optical pathlengths are folded within the measurement cell. Each pathlength is adjustable to meet the requirements of the application. The advantage of having two optical pathlengths is that it allows for a wide dynamic measurement range of the gases of interest, as the measured signal scales with pathlength through the sample. Use of a beamsplitter allows the lasers to be directed to both paths in the sample cell simultaneously. The optical schematic of the dual path system is shown in Figure 1.

In addition to this, an illustration of how these dual paths enable high sensitivity LOD measurements as well as high concentration upper range measurements is provided for an example of carbon monoxide (CO). On exiting the cell, the laser radiation is directed onto a Mercury Cadmium Telluride (MCT) detector on each path, and the detected signal is fed into a custom developed dual channel digitiser for continuous real-time measurements over a wide dynamic operating range.
Four lasers are combined and simultaneously directed through the process gas sample on “long” and “short” paths.

The long path
- Enables high sensitivity (LOD) measurements
- For CO, as low as 0.05 ppm can be measured

The short path
- Enables high concentration measurement
- For CO, as high as 800 ppm can be measured

Figure 1. Optical schematic of the dual path system (upper) as well as illustration of the large dynamic range achievable utilising the dual path (lower) for CO.

The analyser controller is typically an integrated compact PC configured to run custom developed software and utilises a fitting algorithm to calculate the concentration of up to four gas species per laser. For an analyser with 4 lasers, measurements of up to ~12 gases is typically required for customer applications.

Gas concentrations can be communicated to the user using a wide range of digital and analogue outputs and can be configured to meet specific application and user requirements.
Hazardous Area Analysers

Utilising the key concepts described above, PATLS analysers suitable for working in hazardous areas can be further application engineered to meet the required measurement and operation criteria of these environments. Typical measurement criteria include a measurement capability of sub parts-per-million (ppm) limit of detection (LOD), and measurements up to maximum concentrations of 10–1000 ppm of common impurities in process gases, such as CO, CO₂, and C₂H₂. This detection capability is also maintained in a background of up to 100 % process gas, which normally consists of complex and varied hydrocarbons such as ethylene (C₂H₄) and propylene (C₃H₆).

For the prototype hazardous area analyser utilising the PATLS technique, the design was based on the requirements for operation in hazardous areas, and to maintain compliance with regional regulations and guidelines. Therefore the enclosure is designed to segregate the analyser into an interlock controlled safe zone, housing the analyser power supply, control electronics and I/Os which is rated for hazardous environments. The measurement cell and its associated intrinsically safe peripherals are mounted on the outside on the top of the housing. This design is outlined in Figure 2.

![Prototype process gas analyser for hazardous area operation utilising PATLS technique. Left hand side shows internal structure and right hand side shows complete enclosed system for use in hazardous areas.](image)
The main objective of process analysers in these environments is that the information they provide can be utilised in plant management and operation, and therefore communication of measurement results and analyser status can be tailored for a variety of plant types, with all standard interfaces supported. This includes Modbus and analogue outputs (4–20 mA) for measurement data as well as the option of digital healthlines to report on analyser status.

The analysers also include an integrated and intuitive human-machine interface (HMI) for on-site monitoring of the analyser measurements, analyser status, fault diagnosis, and for performing measurement validation or calibration if desired. Connection to a remote PC facilitates more extensive troubleshooting and data files are easily downloaded for a transmission to the vendor for full remote support if required.

The use of PATLS in hazardous environments has been demonstrated as a viable technique through testing of the prototype design in a recent field trial, the results of which are described in the following section. From this prototype design and the learnings of the field trial, the technology has been further developed as a new product line. These developments of the measurement technology include the addition of near infrared (NIR) capability, as well as MIR capability. Whilst the MIR is ideal for measuring a large number of gaseous species due to the strongly absorbing fundamental bands, there are a minority of gases of interest that are more suited for measurement in the NIR, such as oxygen (O₂). Therefore, the dual capability of the MIR and NIR allows for an even greater range of compounds of interest to be simultaneously monitored. In Figure 3, the key components of the analyser design are illustrated.

Compared to the prototype, the platform has a reduced volume, with its primary purpose intended to be use in the Petrochemical and Natural Gas monitoring markets. The modular measurement concept is extended to 6 individual lasers per analyser, allowing for the addition of NIR tunable diode laser technology.

The measurement technique has also been further enhanced with increased sensitivity through the implementation of wavelength modulation spectroscopy (WMS). The developed system is controlled by a core system based on an embedded architecture using an ARM processor. As with the prototype hazardous area analyser, standard industrial interfaces are supported including Modbus TCP/IP & RTC, configurable 4–20mA analogue output and digital health lines. The certification offered includes, for Europe, ATEX II 2 G, groups IIC and for North America, Class I Division II, groups A, B, C, D.
Intelligent system functionality allows the condition of the analyser to be constantly monitored and autonomous corrective action to be taken where possible and pre-emptive service warnings to be issued when appropriate.

This analyser therefore has a decreased footprint and increased measurement capability whilst maintaining the key advantages of the PATLS technique, and with these technical developments, the technology aims to meet the growing market need for process monitoring in hazardous environments, where current technologies are rapidly reaching obsolescence.

**Field Trial of Hazardous Environment Prototype Analyser**

A field trial of a hazardous environment prototype analyser was recently and successfully completed. The analyser was installed at a major petrochemical company ethylene plant to measure typical impurities in the ethylene product stream, namely, ammonia (NH₃), water (H₂O) and methanol (MeOH). The measurement goals for the analyser were to demonstrate the performance as outlined in Table I, and to operate successfully in a petrochemical plant environment. The measurement sensitivities were specified to be able to confirm that the ethylene product specification has been met. In addition to this, the achievable measurement range allows for dynamic behaviour of the impurities due to plant activity to be monitored in real-time.

**Table 1 - Summary of Measurement Criteria for Ethylene Plant Field Trial**

<table>
<thead>
<tr>
<th>Gas</th>
<th>LOD/PPM</th>
<th>Range/PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.2</td>
<td>0–5</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.1</td>
<td>0–5</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.0</td>
<td>0–10</td>
</tr>
</tbody>
</table>

An example of the detection capability of the analyser is shown in Figure 4, which illustrates the successful detection of 0.1 ppm concentration changes of moisture in ethylene. This measurement shows step decreases in the ethylene moisture concentration as samples of lower water content are progressively analysed.

![Figure 4. Example of 0.1 PPM H₂O concentration changes in ethylene.](image-url)
The analyser was installed for several months onsite to assess its operation and measurement stability. From the trial the following key achievements resulted.

- The simplicity of integration of the analyser onsite and into typical petrochemical sample handling systems was demonstrated
- The analyser measurement performance successfully met the outlined criteria for the three trial gases of interest, and in fact exceeded expectations. A summary of the achieved measurement stability, measured as a $3 \sigma$ of the data, during the pre-shipment factory acceptance testing (FAT) and during the trial are outlined below in Table II

**Table 2 - Summary of Measurement Stability During Fat and Trial Testing of the Hazardous Environment Analyser**

<table>
<thead>
<tr>
<th>Gas</th>
<th>LOD Specification/PPM</th>
<th>Fat $3 \sigma$</th>
<th>Trial $3 \sigma$</th>
<th>Pass/Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.1</td>
<td>&lt; 0.01</td>
<td>0.02</td>
<td>Pass</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.0</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>Pass</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.2</td>
<td>0.05</td>
<td>0.06</td>
<td>Pass</td>
</tr>
</tbody>
</table>

- The PATLS analyser functioned successfully within the hazardous environment. Thus the design concept was successfully proved for hydrocarbon processing industry environments, and certification by an independent authority has been undertaken for this product
- The functionality of the analyser was demonstrated, including use of the user interface to monitor analyser activity and health, as well as perform routine calibrations and measurement verification
- The serviceability of the analyser was tested and successfully demonstrated through replacement of one of the laser modules. Whilst the laser was operating normally and did not require removal, this replacement was performed as a test of the analyser’s on site serviceability, and its successful completion shows the ease of installing new components into the analyser in the field. This therefore negates the need to return analysers to base for maintenance
- Overall the analyser design and measurement technique was demonstrated as reliable, and requiring low maintenance

With the successful completion of the trial, a second long term field trial monitoring additional gases of interest will commence in 2014. In this application, gaseous impurities, CO, CO₂, and C₂H₂, which are also typically present in product ethylene, will be monitored at sub ppm levels. The following section of the paper describes how the technology can be application engineered for the appropriate gases of interest, such as CO, CO₂ and C₂H₂ measurements in ethylene, and illustrates the typical capability that can be achieved using PATLS.

**Application Development**

When operating in a hydrocarbon rich environment the broad optical absorption bands of the process stream make choosing a suitable absorption line for the target species challenging. Factors that must be taken into consideration are line strength, wavelength, the presence of cross interfering molecules and spectral resolution.

In many cases the absorption spectra of the target species or the carrier gas are not well documented or exist at a resolution too low for accurate concentration measurements. For this reason in house capability has been developed to generate spectral databases using a high resolution Fourier transform spectrometer (FTS) capable of achieving a spectral resolution of 0.002 cm⁻¹. This enables selection of suitable spectral regions to measure the gases of interest. To demonstrate this process, a typical example of the work performed to determine suitable regions for monitoring NH₃ in propylene is outlined in Figure 5.
Figure 5. Outline of the process utilising high resolution FTS data to select suitable measurement regions for an example of NH$_3$ impurities in propylene.

Once a region has been selected, a laser suitable for measurement of the desired spectral region is sourced, and work can begin on developing spectral databases that allow for accurate modeling, and hence accurate measurement, of the gases present in the process stream.

To do this, a series of measurements are made to allow accurate modeling of the absorptions of all relevant gases. Since the infrared absorption characteristics of a gaseous species are influenced by the physical condition of the particular gas (pressure, temperature, etc.) as well as the presence of other absorbing and non-absorbing species, it is necessary to collect a suitable range of measurements. This allows the proper calculations to be made that determine accurate values for the various parameters used to accurately model the spectral absorption profiles of gases.

Typically, low pressure spectra are obtained to isolate individual absorption line positions and relative strengths. This is then refined with a series of measurements obtained with varying pressure, temperature and concentration. The recorded spectra and the environmental parameters are provided to proprietary software developed by the analyser vendor specifically for this task. The database development software (DDS) uses a series of minimization algorithms to refine a spectral database that fits the recorded spectra to a level comparable to the noise floor of the initial measurements.

An example of the typical output from the DDS, when provided with a single spectrum, is shown below in Figure 6. In this spectrum, the broadband absorption due to the convolution of ~60 ethylene absorption lines has been accurately modeled in a region of interest from measuring MeOH in ethylene. In Figure 7, the residual of the fit to the real data is shown to highlight the quality of the modeling of the data, represented by low peak-to-peak amplitude that is of the order of the typical noise floor of the analyser system, and which is ~1/1000 of the measured absorbance level.
Figure 6. An example of the fit of a spectral model to an ethylene spectrum recorded by a QCL. The upper graph shows the laser data (black) and modelled data (red) in absorbance. The point of low absorption in the centre of the graph shows the area where a methanol impurity measurement is made.

Figure 7. The resultant residuals of the fit to the real data.

Once a process specific spectral database has been generated, the PATLS mid IR QCL based process gas analyser uses this spectral database to calculate a concentration through implementation of the Beer-Lambert law and a heuristic fitting algorithm. The pressure and temperature of the gas are continuously monitored and fed to the fitting algorithm to provide accurate, process specific measurements in real time.

Because of the unique absorption spectra displayed by molecules present in typical process gases, the analyser is capable of generating a theoretical fit that simultaneously incorporates the spectral absorption of up to four molecules per laser over the spectral region of interest, as demonstrated in Figure 8. In these data, the capability of the software to accurately monitor the dynamic behaviour of individual gaseous components, for example NH$_3$ and C$_2$H$_4$, in a complex gas mixture is shown.
Figure 8. Demonstration of PATLS multi-gas measurement capability on complex mixtures of NH₃ and C₂H₄.

A case study example of utilising the DDS to model background ethylene for an analyser developed for measuring CO is provided in Figure 9. In this case study, the databases developed with the DDS have been installed on a hazardous environment analyser and tested against samples of differing concentrations of CO in ethylene. The modeling of the two main components, namely the changing CO absorption and the ethylene background, is demonstrated, and data indicating the typical measurement capability that is achievable when measuring CO in this manner is also presented.

Figure 9. Demonstration of analyser measurement of varying CO in ethylene. Left hand graphs show the modeling of varying CO in C₂H₄ levels. Right hand graphs show the achievable LOD and linearity of response of the analyser.
As can be seen from the presented data, the hazardous environment analysers and associated software allow for the sensitive and selective detection of impurities in petrochemical product streams, such as CO in ethylene. The measurement capability covers sub ppm LOD sensitivity, as well as linearity of response exceeding R2 of 0.999 over the expected measurement range. For this analyser, the multi component capability of the design is being used to simultaneously measure CO2 and C2H2 in ethylene, and similar examples of the measurement of these gases are shown in Figures 10 and 11.

![Sub ppm CO2 measured in 100 % ethylene gas](image)

This capability, especially when duplicated for multiple gas measurement on a single analyser, makes the technology ideal for petrochemical and industrial process applications.

**Conclusion**

The use of MIR QCL based technology to develop gas analysers suitable for hazardous environments is ideal for petrochemical and industrial applications. Unlike alternative technologies used in these environments, these analyser systems offer the following key advantages:

- Large dynamic range due to the utilisation of multiple optical pathlengths
- Increased detection sensitivity, selectivity and specificity due to the exploitation of the MIR fingerprint region
- Low cost of ownership, requiring minimal consumables and maintenance
- Immunity to cross interference due to high spectral resolution
- Fast response time
- Multi-component capability due to several measurements per laser and multi-laser capability
- Plug and play modular design for ease of service.

Overall, this results in a highly adaptive technology that can provide vital information to aid efficient monitoring and management of industrial processes.
The performance of such systems has already been demonstrated in a successful field trial at a major petrochemical plant, and this success is to be followed with a second longer term installation of a production unit in 2014.

In parallel to this, and in response to market needs, the technology is continually being developed to reduce cost, and to improve measurement capability. These improvements include the addition of new target gases and target applications to the analyser portfolio, including monitoring NIR gases such as O₂, HF and HCl, sulfur based compounds such as H₂S and OCS, and key industrial applications such as monitoring water in natural gas.

References