Advances in Tunable Diode Laser Systems for Gas Analysis in Natural Gas

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1. Abstract

Advances in laser technology have made a ground-breaking technique for gas analysis that is cost effective for natural gas applications. The quality of on-line gas analysis for water vapour, carbon dioxide and hydrogen sulphide measurements can be improved. These systems represent the commercialisation of a $16M development programme by **NASA** for deep space, and Earth upper atmosphere missions. A Tunable Diode Laser (TDL) system is now able to provide high accuracy measurements of gases active in the infra-red spectrum.

This non-contact technique has good long-term stability, high specificity and is not affected by contamination from glycol, amine or methanol. Its simplicity and low maintenance makes it a very good candidate for use the natural gas industry. It is a fundamental measurement, monitoring the gas *itself* rather than measuring an effect on the surface of a sensor.

2. A Short History of Development

The development of this instrument came primarily from the requirements of **NASA** to improve water vapour measurements in the upper atmosphere.

Water vapour levels drop from around 13,000 PPM_V at ground level to about 5 PPM_V at high altitudes. Understanding the transportation and the effect of water vapour on upper atmosphere reactions is extremely important for long- and short-term climatic studies. In the upper atmosphere, water vapour effects ozone levels and cloud cover, which controls radiation and cooling rates in the atmosphere. It is *the* most important greenhouse gas and there is a long history of water vapour measurements using various techniques: chilled mirror, polymer capacitance, Lyman α and others. There are many Earth-, and satellite-based research programmes for water vapour activity the National Oceanographic and Atmospheric Administration (**NOAA**), and **NASA** operate DC-8, and ER-2 research aircraft and balloon platforms which provide gas analysis in the upper troposphere and stratosphere[2]. Satellites using infra-red and microwave techniques also provide extensive information on the distribution and transportation of water vapour. However, there is often disagreement among measurements of water vapour made by different techniques, even from the same platform. With up to 15% disagreement between techniques uncertainty was impacting on the ability to draw definitive conclusions about the detailed behaviour of water vapour.

Figure 1 Instrument pod on the side of a DC-8 bound for Hurricane

Improved techniques were needed and the Jet Propulsion Laboratory (JPL) in California initiated development of laser based systems in an effort to provide such a capability. Years of development have seen laser operating temperatures rise from liquid helium and nitrogen temperatures, with systems weighing over 1000Kg, to today's diode lasers operating at ambient temperatures, eliminating the bulk and power consumption of cooling systems. Since diode lasers are monolithic semiconductor devices, they are inherently robust with an expected lifetime of around 15 years. In 1995 compact and lightweight instruments were built for mounting on the DC-8 (*Figure 1*) and ER-2 (*Figure 2*) research aircraft and, after a series of engineering and calibration flights, were declared science-flight ready. From April to September 1997 instruments provided stratospheric water vapour measurements as part of the **NASA** POLARIS (Photochemistry of Ozone Loss in the Arctic Region In Summer) ER-2 mission[2]. Extensive measurements have been made during these and other research flights investigating convection of moisture and ozone loss validation.

Figure 2 ER-2 Research Aircraft

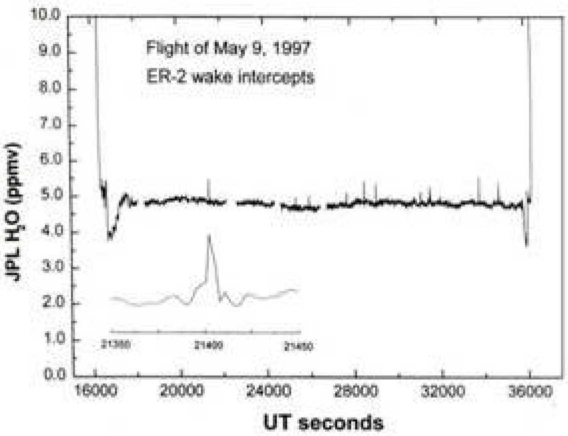


Figure 3 Wake Intercept

Figure 3 shows a circular flight path Where the ER-2 repeatedly crossed it's own exhaust wake. Sharp upward spikes in the data correspond to a wake-crossing event, with an expanded view of one wake-crossing is also shown. Analysis of this and other gases monitored on the ER-2 provide emission indices for the aircraft engine and are useful for characterising the potential impact of aircraft emissions on climate[2].

ure 4 TDL System mounted the Mars Polar Lander

The small size, weight and power requirements made this technology an excellent candidate for interplanetary missions. The potential for this technique to make high precision, multi-parameter measurements attracted much interest within JPL and **NASA**[2]. Further development led to the system being space-qualified and is used by **NASA** to determine the presence of water on deep-space interplanetary missions.

The experience gained in the research project is now being used to develop commercial instruments that offer significant advantages over present techniques

The SS2000 has given us an extra tool, leading us to question our assumptions of how water vapour behaves.

Systems for natural gas, monitoring both water vapour and carbon dioxide concentrations in natural gas, have been available in the USA for about two years now. Many trials have proven the advantages of this technique and the response from the industry has been very encouraging.

3. Basic Principle of Measurement

The basis of all spectroscopy is a fundamental molecular property. When a molecule is hit with an energy source at a certain wavelength, it will cause it to vibrate and thereby absorb energy. The wavelengths at which these absorptions occur are fixed, unique, and are a function of that particular molecule and the type of molecular bonds it possesses. Apart from the fundamental wavelengths, there are many overtones and combination bands that also absorb energy at shorter wavelengths where ambient temperature lasers operate.

For water vapour and many other gases this is in the near infra-red (NIR) region and Figure 5 shows the absorption lines for 100 PPM_V of water vapour. Note that there are many lines here that could be selected.

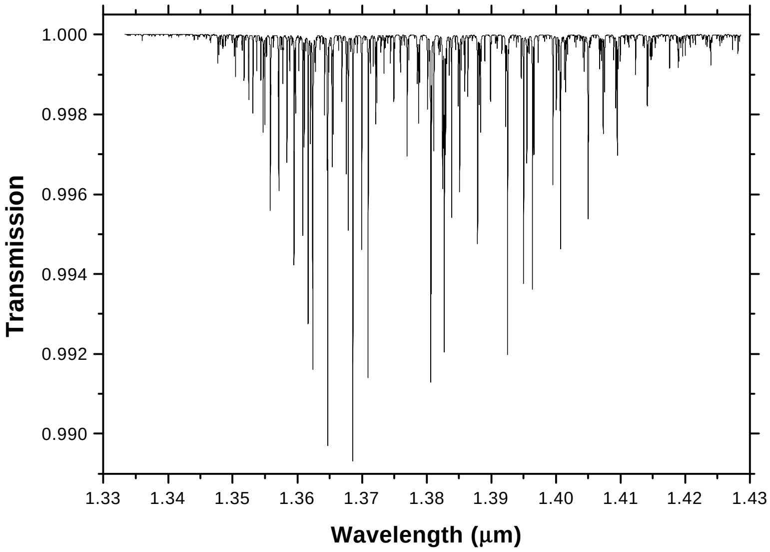


Figure 5 Water Vapour Absorption in the 1.38 micron area at 100 PPMv

The SS2000 uses an advanced version of a low power semiconductor laser. The actual laser structure is fabricated on a piece of semiconductor material typically only 0.5 mm square and 0.1 mm thick. When mounted (*Figures 6 ,7 and 8*), these devices produce laser light at a very specific wavelength that can be smoothly and continuously tuned over small wavelength intervals. Different lasers are produced depending upon the parameter to be monitored.

Figure 6 A diode laser

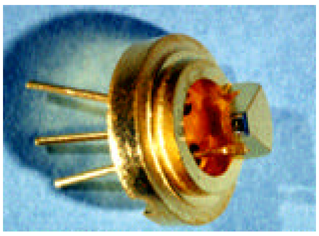


Figure 8 A TDL

Figure 7 A TDL Close up

Adjustment of the material composition of the laser, and application of several complex laser growth processes, has resulted in a laser suitable for gas sensing. It is possible to fabricate TDL's that operate within the 0.5 to 30 micron wavelength region.

The exact wavelength the laser emits depends on the specific material of composition. Further tuning of the wavelength output is accomplished by adjustment of the device temperature, and even finer tuning can be obtained by adjustment of the laser operating current.

With temperature fixed, it is the adjustment of current to this single light source that "tunes" the wavelength of the emitted light to sweep it through an absorption peak at a particular wavelength. The resolution of the laser is also fine enough to determine the shape of the peak. The processed signal from the detector analyses the amplitude of the absorption peak and therefore the density of the target gas.

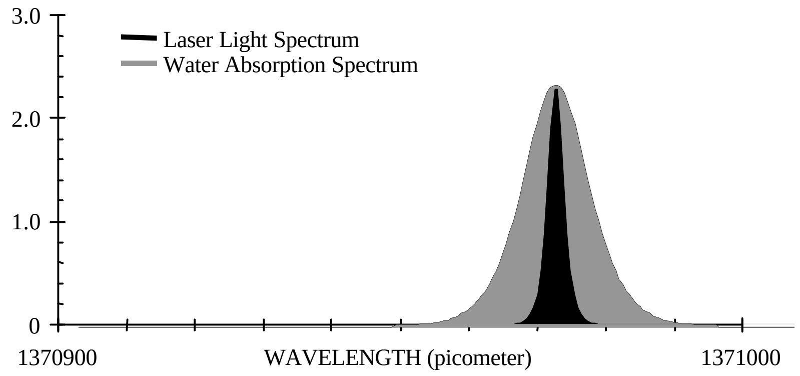


Figure 9 Absorption determination

As a light source, TDL's provide the highest available power density in a spectrally narrow window as can be seen in *Figure 9.* offering a significant improvement over analysers using other infrared sources. This is important when considering the effect of other gases also active around the spectral line for the particular target gas. By tuning this bright source across the spectral range of interest, highly sensitive measurements can be obtained for specific gases with good long term stability.

The precise wavelength emitted by the laser is swept across the absorption peak of interest by ramping the current in a saw tooth pattern.

A small amplitude sine wave is superimposed on top of the main saw-tooth ramp signal. The sine wave is modulated at a certain frequency and the detected signal is de-modulated at double that frequency giving a response that is proportional to the rate of change of the signal and therefore improving signal to noise ratios[1].

By monitoring the absorption peak at specific wavelengths, the concentration of the target gas within the sampling volume can be accurately determined. The electronics and software control the laser wavelength, process the detected signal, analyse the acquired spectra and calculate a quantifiable gas concentration in real time[1].

A number of spectral parameters are monitored to apply optical laws which provides the SS2000 system with remarkable linearity over it's operating range of 0 to 20 Lbs/MMSCF (to 422 PPM_V). The absorption coefficient is affected by temperature and pressure, which are monitored and inserted into the data processing algorithms[2].

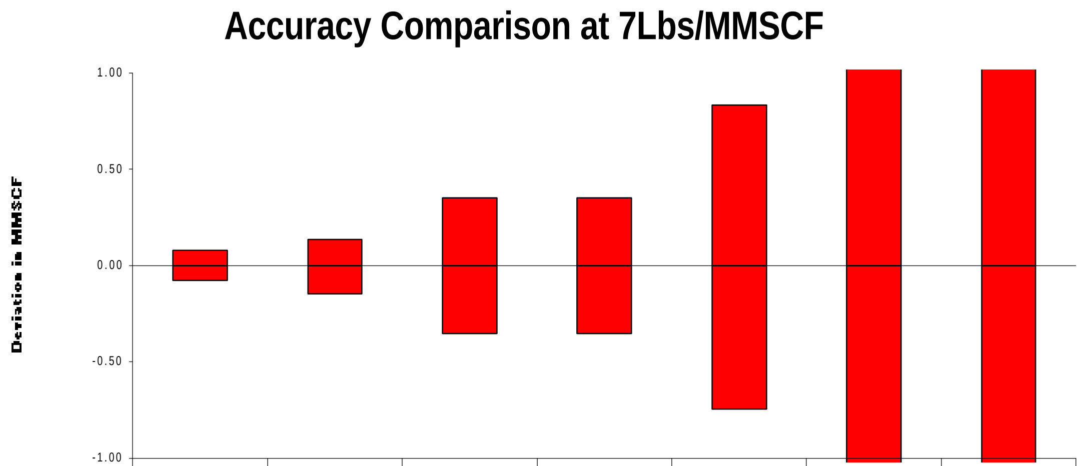
With currently available configurations, the lowest limit of detection for water vapour available with the standard configuration is 4 PPM_V in a natural gas background. Development work continues to improve coefficients to maintain accuracy at lower and lower moisture levels.

The combination of sensitivity, specificity, and speed of response offered by TDL based systems has now attracted interest from the process industries for measurement of many critical gases and a number of long term trials have been undertaken.

4. Moisture Comparisons

Absorption at particular wavelengths is a fundamental property and the level of absorption at these wavelengths is proportional to the density of target gas at a particular temperature and pressure[1&2]. The relationship between these three parameters is fundamental molecular properties. The accuracy of the laser system is 2% of reading or 2 PPM_V whichever the greater and this compares favourably with other techniques on the market. *Figure 10* shows a comparison of other techniques. and their published accuracy statements.

It can be noted that the only technique with a higher accuracy statement is the chilled mirror device. To achieve this level of accuracy requires an automated chilled mirror. Using chilled mirror devices as on-line instruments for natural gas is not usual because of the likelihood of other contamination and high maintenance. However, portable cross checking devices have been successfully used down to around -50 °C (40 PPM_V) providing the operator is aware of the symptoms of contamination on the mirror and the level of possible contaminants (glycol, amine, methanol and heavy hydrocarbons).



	C. Mirror +/- 0.1°C	Laser +/-2% Reading	P2O5 +/- 5% Reading	Q Crystal +/- 5% Reading	AlO2 +/- 1°C	AlO2 +/- 2°C	AlO2 +/- 3°C
positive data	-0.08	-0.14	-0.35	-0.35	-0.75	-1.43	-2.05
negative data	0.08	0.14	0.35	0.35	0.83	1.76	2.79

Figure 10 A comparison of published accuracy statements

Methane interference was a major factor when selecting an absorption line for water vapour and the SS2000 uses a wavelength with a small methane peak lying underneath the water vapour peak. At lower concentrations this is the major influence of accuracy. Accurate subtraction of the methane line allows good lower limits of detection and accuracies can be maintained and, as work continues on uncertainty budgets, both the lower limit of detect and the accuracy will improve.

5. Speed of Response

The laser absorption technique is not flow dependent. Work of both IMA and the National Physical Laboratory to establish the lowest flow possible has encountered an influence of ambient moisture back-flow with a flow rates below 3 litres a minute. Using an NPL traceable calibration rig, IMA have been working with various manufacturers and various techniques for over 10 years. Low level work always takes time. Normal settling time for systems drying from ambient conditions down to 1 PPM_V is 6 to 8 hours and 24 to 48 hours before full equilibrium if the data is to be used for calibration purposes. The Tunable Diode Laser systems have shown us that short term moisture events can now be successfully detected. *Figure 11*illustrates an SS2000 in an air background settled at 3 PPM_V, ambient air was then pulled through the system for two minutes and the system then returned to the 3 PPM_V dry air. The instrument settled back at the original 3 PPM_V figure within 11 minutes from the start of the test with a speed of response of 98% in less than 6 seconds.

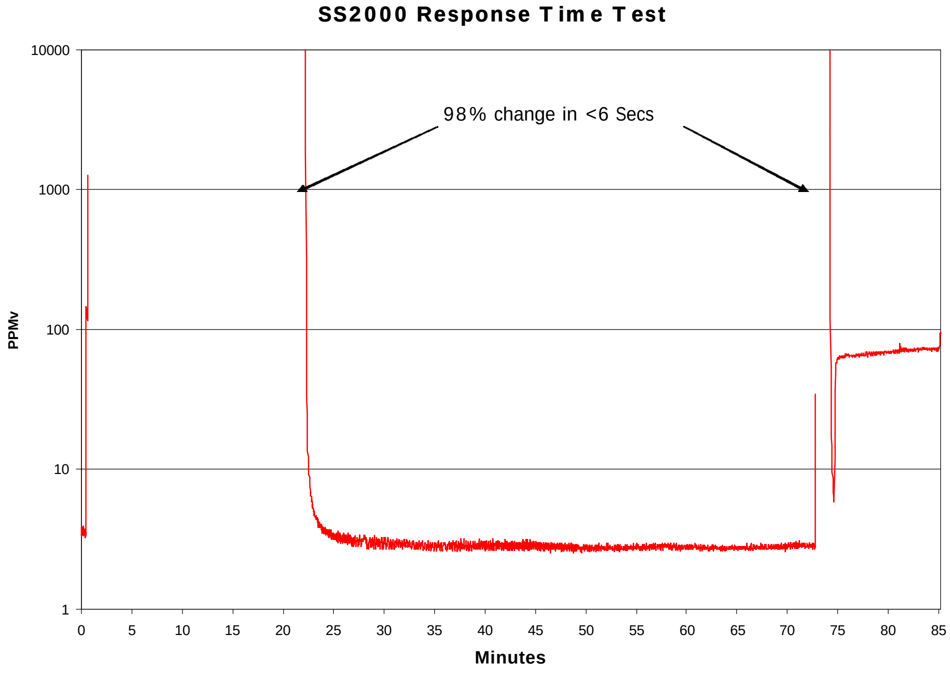


Figure 11 Speed of response tests in an air background

This dramatic speed of response has allowed greater visibility of processes. Without exception, we have learned more about every process where we have installed a system. A short sample system with minimal volume provides almost real time data and diagnostics of plant problems becomes easier. When applied to natural gas and the cases where shut-ins occur because of out of specification gas, every minute that an operator is off line is costing money.

6. Natural gas comparisons and field trials

A number of trials in natural gas have taken place. *Figures 12 and 13* show a section of data in a field comparison between the SS2000, P_2O_5 and Aluminium Oxide systems. All three systems were installed at the same sample point. The temperature trace shows the temperature inside the analyser house. This was heated during the night and a cyclic pattern can be seen where the thermostat is controlling the temperature, indicating some dependence on temperature. This seems to be reflected in the data from both the P_2O_5 and Aluminium oxide systems. Figure 13 is a closer look at the same data and the moisture event that took place. It can be seen that laser responded quicker than either of the other two systems and recovered to the alarm point 1.7 hours ahead of the P_2O_5 system and 3.5 hours ahead of the aluminium oxide system. Operators also like the lower maintenance requirements of the laser system. Once installed there is no inherent drift or routine cleaning required. The normal mode of operation is that the system is cross checked with a chilled mirror system only when a moisture event occurs to make sure data is correct before shutting a valve to the offending gas well. Operators tell us that while they used to accept a reading of +/- 3Lbs/MMSCF, now they have the laser they have narrowed the acceptable limit to +/- 0.5 Lbs/MMSCF.

It has been known for some time that methanol is a particular problem for many moisture analysers causing them to read incorrectly. A field trial was instigated to compare the effect of methanol on a variety of techniques.

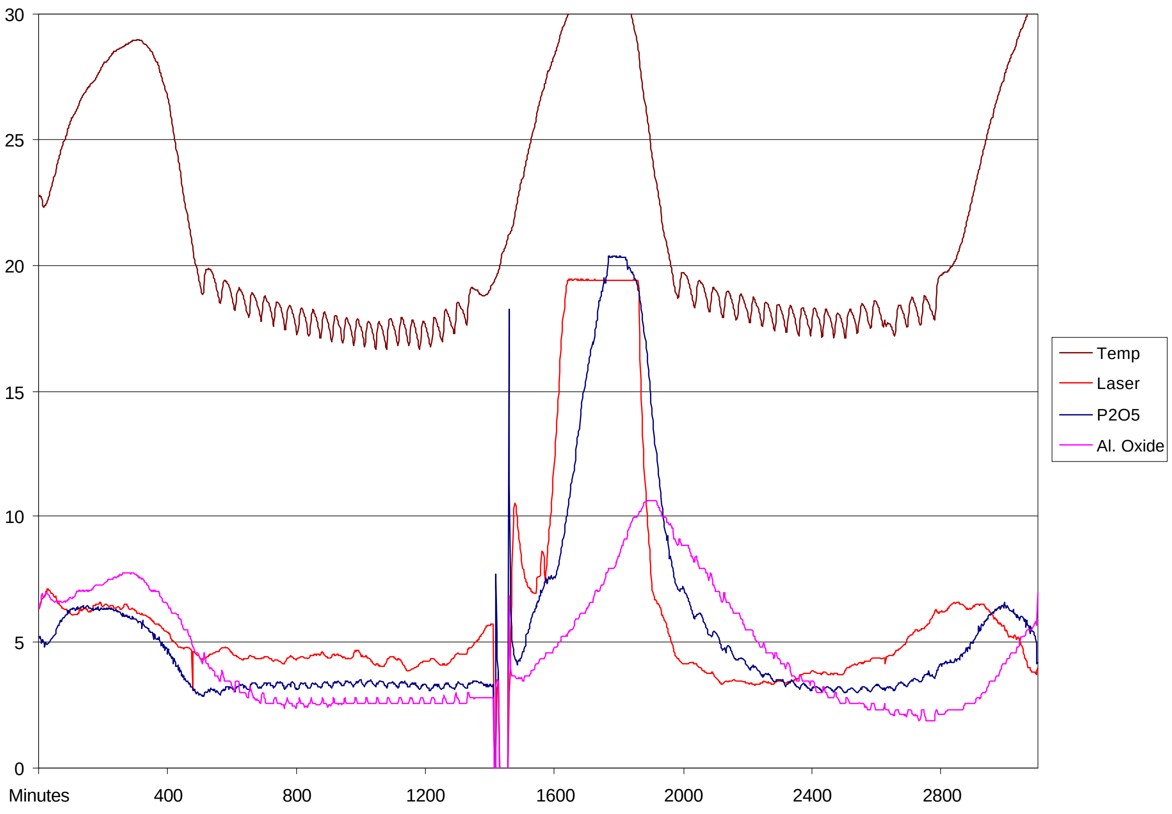


Figure 13 Natural Gas Trial

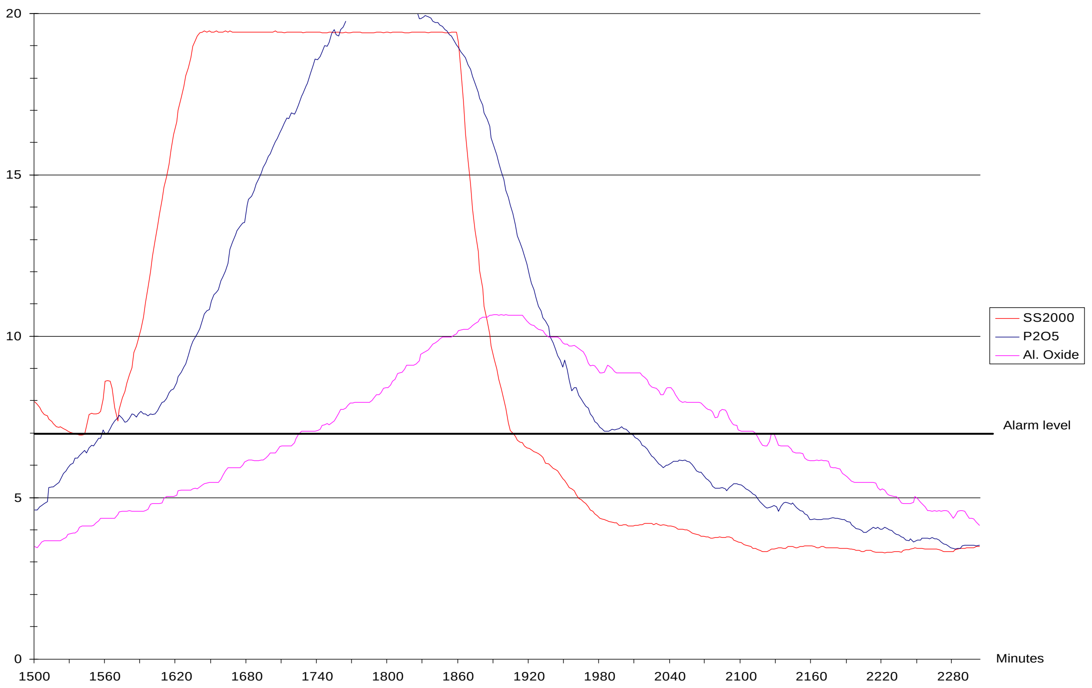


Figure 12 Natural Gas

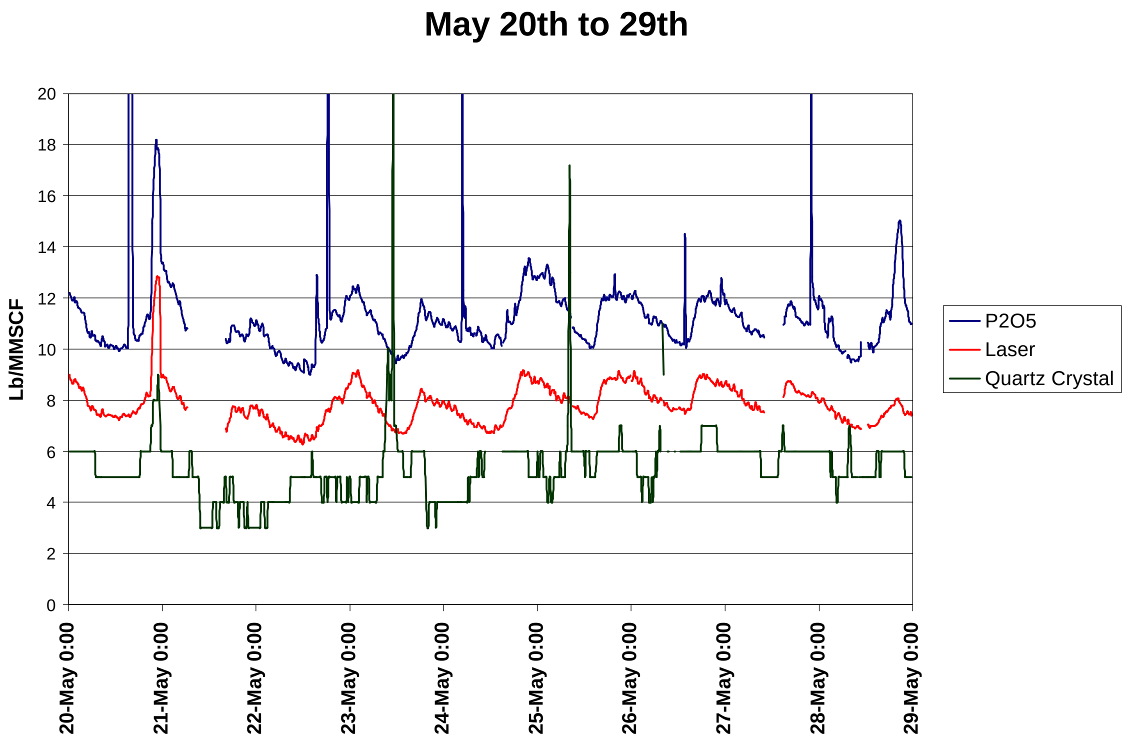


Figure 14 The Effect of Methanol Injection on moisture analysers

Methanol is injected when the combination of pressure and moisture content give a high risk of methane hydrate formation, a solid ice-like structure that blocks gas lines reducing or even stopping the gas flow.

The trial site, in the USA, was a large pipeline running between 500 to 600 MMCFD and of the 475 wells

feeding the line many of them inject methanol continuously and some pulse methanol only when they have a problem. After laboratory tests with an SS2000 and methanol it was demonstrated that methanol is not active in the infra-red region that the SS2000 operates and therefore no interference with the spectral lines for water vapour when methanol is present. An SS2000 was installed alongside a P_2O_5 system, and a quartz crystal system was also monitoring the same gas at a slightly different point on the pipeline. *Figure 14* shows an 8 day section.

The trace from the laser highlights the diurnal changes caused by the efficiency of glycol contactors changing with ambient temperature. It can be seen that the P_2O_5 system also exhibits the same diurnal effect. However, although the P_2O_5 systems were calibrated on the same calibration gas cylinder the P_2O_5 system has both an offset and occasional spikes or excursions that could be explained by methanol pulses. It was attempted to tie these up with actual methanol injection events but because of the great number of gas wells feeding the pipeline and their distance from the measuring point it was difficult to confirm the identify specific methanol injection times. However, the pulsed response would strongly suggest methanol influences. During the trial there were occasional data logger problems and some data was lost indicated by gaps in the traces.

The quartz crystal also had data loss and was only able to log integers giving a less responsive trace. Although some diurnal effect can be seen, it does not seem to follow the other two analysers and there are also excursions that do not appear to be due to water vapour changes. It is not known if the excursions are due to methanol or some other contaminant. The system re-calibrates against an internal standard and was not included in the calibration check on the gas standard.

7. Resistance to Contamination

The laser and detector assembly are installed behind a fused silica window making the SS2000 a non-contact system. Another factor allowing the SS2000 a high resistance to contamination is the very narrow wavelength on which it operates. As the laser is swept through the peak of absorption, the peak is established by comparing the absorption line directly before and after the absorption peak. It is therefore comparing detection levels on and off peak; automatically compensating for a general loss of signal strength returned to the detector that could be caused by either a power loss of the laser or contamination on the mirrors. In fact, 80% of mirror reflectivity can be lost before it impacts on precision. There is a caveat to this: it is essentially a gas system and liquid within the flow cell will cause problems! It is important to use membrane or coalescing filters if a risk of liquid carry-over exists.

8. Maintenance

Tunable diode lasers are used extensively in the telecommunications industry. They are solid state devices and MTBF figures have established an expected life of 15 to 20 years. Figures for the Peltier thermo-electric coolers are similar or longer when used to maintain a fixed temperature.

Should an incident occur where gross contamination causes a problem and the self-diagnostics indicate that cleaning is required, the system is designed so that the mirror may be easily removed for cleaning, and the optical head may also be removed, cleaned and reassembled in about 1 hour without the need to return to the manufacturer or re-calibrate.

9. Conclusion

A Tunable Diode Laser system takes a dramatically shorter time to come to equilibrium and remains very responsive. The advantages for the gas industry are many: the speed of response means that production can be maintained. Man-hours can be saved or systems that would require several measurement points can now be handled with one TDL and a rapid switching flow cell, only possible because of the very short response time. Being a non-contact method enables aggressive and toxic chemicals to be monitored accurately on-line.

The features of laser absorption make a very strong case. The advantages it gives in terms of accuracy, ease of maintenance, and speed of response offer the natural gas industry access to high quality, real time data. This extra information is proving invaluable for diagnosing plant problems. We believe hygrometry has moved a significant step forward with this technology.

Two channel system monitoring both water vapour and CO_2 are available now and development continues on a system that will monitor H_2S: this is currently at a $10PPM_V$ lower limit of detection. Improvements in subtracting spectra and other signal to noise upgrades lead us to believe that a system to monitor all three components at pipeline concentrations will be available soon.

References:

[1] R. D. May and C.R. Webster — *Data processing and calibration for tunable diode laser harmonic absorption spectrometers. Journal of Quantitative Spectroscopy and Radiative Transfer Vol. 49, No 4 1993*

[2] R. D. May — *Open-path, near infrared tunable diode laser spectrometer for atmospheric measurements of H_2O, Journal of Geophysical Research Vol. 103. No. D15 1998 No: 98JS01678*