

Tunable Diode Laser Systems Break New Ground in Water Vapour Analysis.

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1. Abstract

Recent advances in laser technology have made a ground-breaking technique for gas analysis systems that is cost effective for the process control industry. The quality of on-line water vapour measurements can be dramatically improved. These systems represent the commercialisation of a \$16M development program 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 infrared spectrum: water vapour (H₂O), carbon dioxide (CO₂), carbon monoxide (CO), acetylene (C₂H₂), ammonia (NH₃), hydrogen fluoride (HF), methane (CH₄), oxygen (O₂), hydrogen chloride (HCl), nitrous oxide (NO) and others.

This non-contact technique has good long-term stability, high specificity and is resistant to contamination. Its simplicity and ease of maintenance makes it a very good candidate for use in process applications. 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 at ground level to about 5 PPM 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 stratosphere and upper troposphere, water vapour effects ozone levels and in the troposphere, water vapour effects 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 active Earth-, and satellite-based research programmes for water vapour activity. The National Oceanic and Atmospheric Administration (NOAA), and NASA operate DC-8, and ER-2 research aircraft and balloon platforms which provide measurements of water vapour in the upper troposphere and stratosphere². Satellites using infrared 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. Improved techniques were needed. The Jet Propulsion Laboratory (JPL) in California therefore initiated development of a tunable diode laser based system in an effort to provide such a capability. In 1995 compact and lightweight instruments were built for mounting on the DC-8 (*Plate 1.*) and ER-2 (*Plate 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 mission². Extensive measurements have been made during these and other research flights investigating convection of moisture and ozone loss validation.

A laser absorption technique enables the instrument to be mounted on the outside of the airframe with air passing between two mirrors. This “open path” configuration means that a sampling system is not needed, simplifying requirements and improving speed of response.

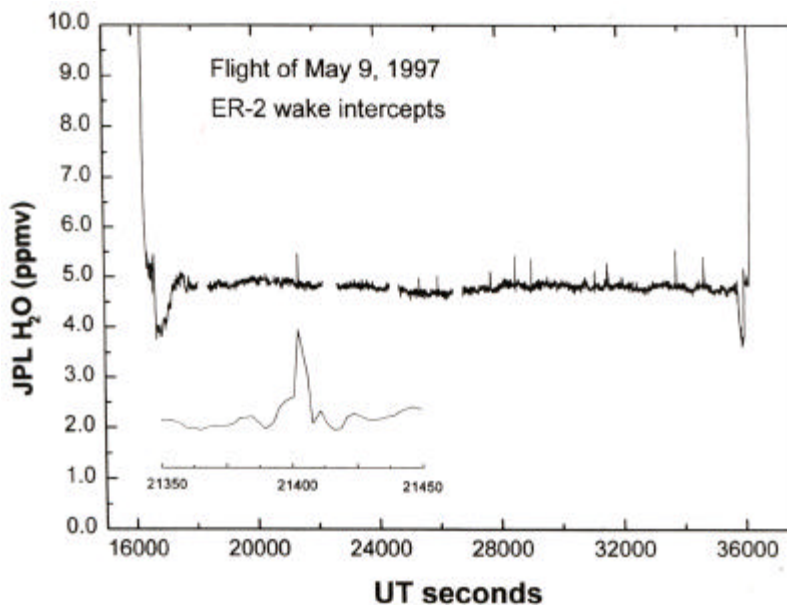


Figure 1. Wake intercepts on an ER-2 flight²

Figure 1. 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, 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 climate².

The small size, weight and power requirements made it an excellent candidate for interplanetary missions. The potential for this technique to make high precision, multi-parameter, measurements attracted much interest within JPL and NASA². 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.

Plate 3. shows a TDL system installed on the Mars Polar Lander.

The experience gained in the research project is now being used to develop commercial instruments that offer significant advantages over present techniques. In 1999 the Director of the Centre for Space Microelectronics Technology at JPL, Dr Carl Kukkonen, and the key scientists, Dr Randy May and Dr Siamak Forouhar, acquired the patents and created a spin-off company (SpectraSensors Inc.) to commercialise the technology. The technical team at SpectraSensors have long experience with laser design and fabrication as well as optical systems, software and data analysis.

TDLs offer the first practical laser technology for many commercial and research applications. Years of development have seen laser operating temperatures rise from liquid helium and nitrogen temperatures, with systems weighing over 1,000 Kg, to today's lasers that, in most cases, can be operated at room temperature, 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.

The LH2000 has given us an extra tool, leading us to question our assumptions of how water vapour behaves, particularly at low levels. These assumptions may have been based more on the sensing techniques available than on the properties of water vapour itself.

System for natural gas, monitoring both water vapour and carbon dioxide, has been available in the USA for several months. Users are already aware of the advantages of this technique and many orders have been placed despite the instrument still awaiting hazardous area certification.

3. Basic Principle of Measurement

The basis of all spectroscopy is the fundamental property of a molecule. 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.

The LH2000 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 (*Plate 4.*), these devices produce laser light at a very specific wavelength that can be smoothly and continuously tuned over small wavelength intervals. Different TDL's are produced depending upon the parameter to be monitored, and for multi-parameter systems more than one TDL can share one flow cell.

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 fine 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.

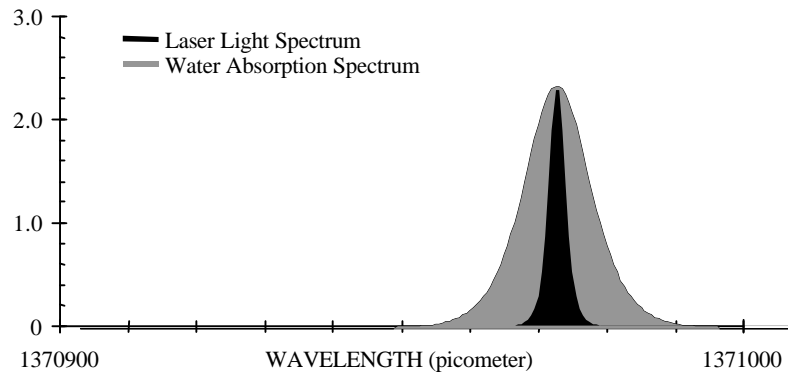


Figure 2. TDL wavelength compared to a gas absorption band

As a light source, TDL's provide the highest available power density in a spectrally narrow window as can be seen in *Figure 2.* 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. The development of tunable diode laser sources has brought about a revolution in scientific spectroscopy over the last two decades; path-lengths can be much longer giving PPB and PPT sensitivity.

The electronics pack stabilises the temperature of the laser (usually 10 to 50°C depending upon the exact laser requirements) by the use of a small Peltier device, which provides both heating and cooling. 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 frequency f and the detected signal is de-modulated at $2f$ improving signal to noise ratios¹.

By monitoring the absorption peak at specific wavelengths, the concentration of the target gas within the sampling volume can be accurately determined. The detector, electronics, and software subsystem controls the laser wavelength, processes the detected signal, and analyses the acquired spectra to derive a quantifiable gas concentration in real time¹.

Various optical configurations are incorporated into the systems depending on the requirements for optical pathlength. Greater optical pathlength offers higher sensitivity, and folded optical paths, using a set of customised mirrors, allow this to be accomplished in a compact system.

A number of spectral parameters are monitored to apply the Beer-Lambert law that relates the observed absorption to the density of the target gas:

$$\rho = \frac{-\ln [\tau(\nu)]}{k(\nu) L}$$

Where:

ρ = Density of the target gas

$\tau(\nu)$ = The observed transmission at wavenumber ν

$k(\nu)$ = absorption coefficient at wavenumber ν (dependent upon line strength and shape)

L = Optical pathlength

This provides the system with remarkable linearity over its operating range. The absorption coefficient is effected by temperature and pressure, which are monitored and inserted into the data processing algorithms².

The range of instruments available includes several optical path configurations: a direct path to the detector, reflectors for cross-stack or long-path perimeter monitoring, as well as multipass absorption cells. Short pathlengths of just a few millimetres can be used with, high concentration applications. Extended pathlengths, improve the analysers lower limit of detection, the ability to miniaturise the optics in a Herriott cell provides a stable and reliable method of trace gas analysis.

The following standard ranges for water vapour are currently available:

0.01 to 10 PPM	0.01 to 1000 PPM	1 to 1,000 PPM	1 to 10,000 PPM
100 to 10,000 PPM	100 to 100,000 PPM	1000 to 100,000 PPM	

With currently available configurations, the lowest limit of detection for water vapour available to special order is 10PPB with the upper limit being saturation at 100°C.

As this is a non-contact system operating temperatures can be quite wide and special systems for hot or cryogenic gases are being considered.

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.

4. Accuracy

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 fixed. Uncertainties are currently being reviewed, with recent independent testing indicating uncertainty to be somewhere between 1% to 2% of reading. Various factors that could effect uncertainty may be improved as further research is completed.

The raw data is a density measurement and all accuracy and uncertainty statements are therefore proportional to PPM and converted, where necessary to dewpoint. *Figure 3.* Shows $\pm 1\%$ and $\pm 2\%$ as deviations in terms of dewpoint. High accuracy chilled mirror devices have uncertainties of between 0.5 and 0.1°C dewpoint. These instruments are excellent transfer standards, or calibration masters, with good long-term stability but, it is generally thought that maintenance requirements are too high to maintain accuracy when used directly on line. Presentation of a wet mirror to the process gas means that they can be susceptible to contamination, affecting accuracy. For trace moisture applications, they are generally used as a master instrument to calibrate a secondary technique like aluminium oxide or capacitance polymer relative humidity sensors.

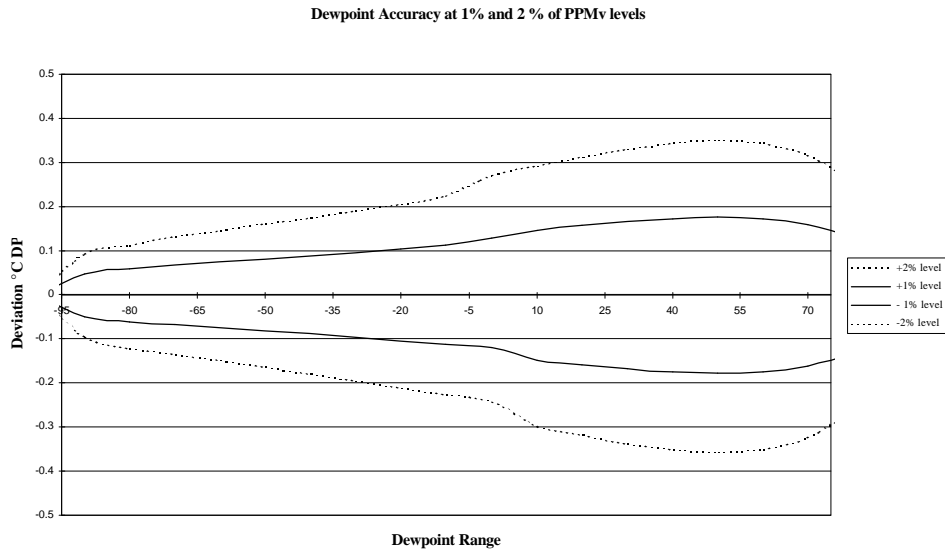


Figure 3. $\pm 1\%$ and $\pm 2\%$ accuracy expressed as dewpoint

5. Speed of Response

The laser absorption technique is not flow dependent and can, in fact, be extremely high which may be useful for some applications. Work of both IMA and the National Physics 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. It is not yet confirmed whether this is due to cell configuration or if it is a general rule for instruments working at low moisture levels. The first test IMA performed with a prototype system proved one of the most dramatic aspects of this technique. Using an NPL traceable calibration rig, IMA have been working with various manufacturers and various techniques for over 10 years. We know that low level work always takes time. Normal settling time for systems drying from ambient conditions down to 1 PPM is 6 to 8 hours and 24 to 48 hours before full equilibrium if the data is to be used for calibration purposes. The prototype system settled in less than 10 min. It then was able to highlight a fault on our dry compressed air supply caused by a short-term pressure drop every two minutes on dryer changeover. All the other moisture analysers installed on the rig could not see the small, short term spikes of moisture simply because they happened so quickly.

Figure 4. shows an LH2000 settled at 3PPM, ambient air was then pulled through the system for two minutes and the system then returned to the 3 PPM dry gas. The instrument settled back at the original 3 PPM figure within 11 Minutes from the start of the test.

The LH2000 has allowed greater visibility of processes. Without exception, we have learned more about every process where we have installed a system. Sometimes the very simple tests have made us think again about how water vapour is transported in a system. Figure 5. shows dry down time for 6 metre lengths of electro-polished stainless steel pipe compared to the same length standard 316 stainless steel. Vinyl tubing is also shown for comparison. The pipes were purged for 1 hour with ambient air prior to the test to ensure that the pipe walls were in full equilibrium before initiating the dry gas at -87°C Dewpoint.

From 3 PPM to ambient 2 minute hold return to 3 PPM

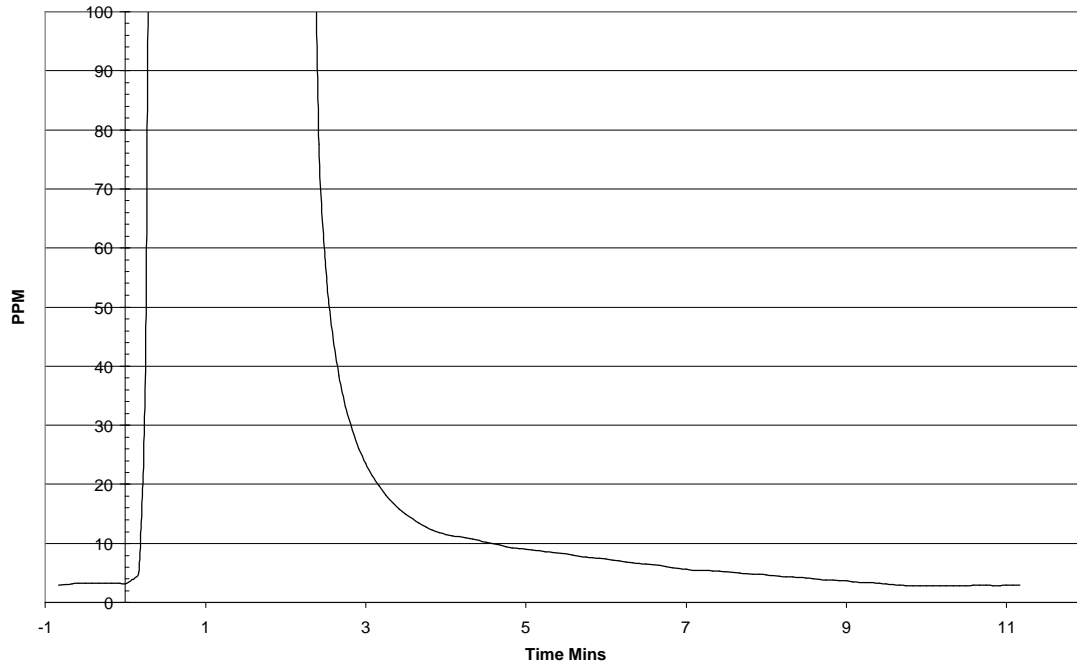


Figure 4. A wet-up and dry-down test

Dry Down Test to -87°C DP

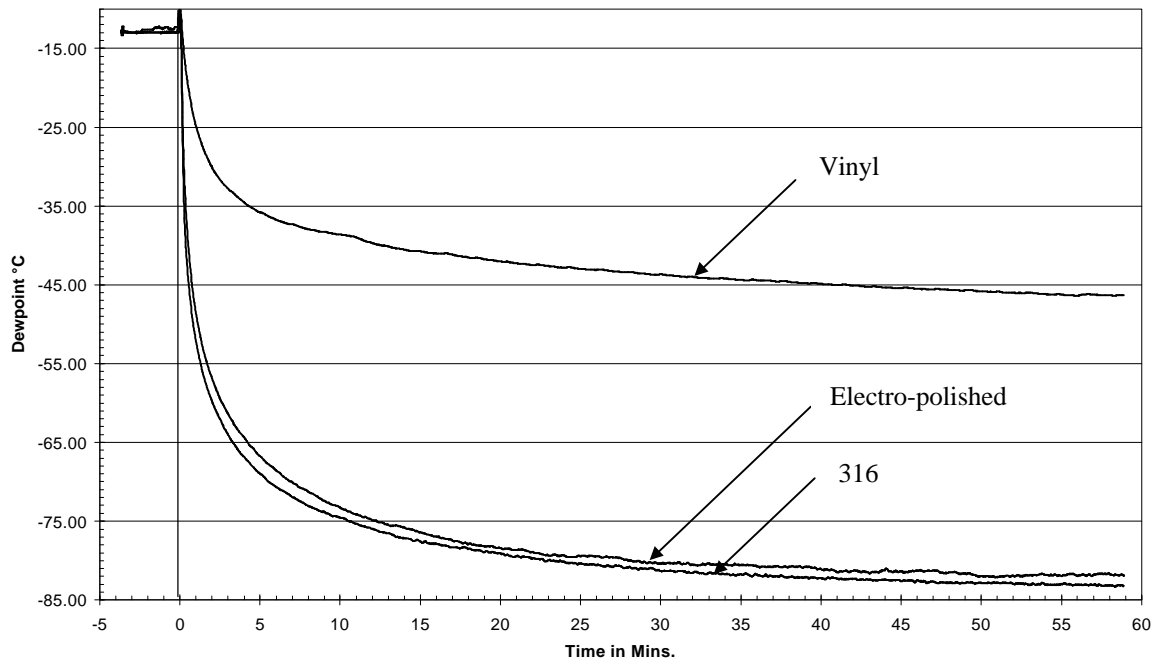


Figure 5. Dry down comparison

6. Contamination

The laser itself is normally installed behind a fused silica window making it a non-invasive technique. Many of the more aggressive gases like chlorine or ammonia where moisture is a critical factor can now be established at low moisture levels.

Another factor allowing the LH2000 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. Field tests are continuing to establish the minimum level of filtration required for long term use.

The flow cell used consists of two concave (*Plate 5.*) hemi-spherical mirrors. The laser is introduced at one end and is then reflected between the mirrors in a circular pattern until the exit point. This “Herriott cell” configuration allows the mirrors to twist and flex without altering the entry and exit points. making it very stable in high vibration conditions. Indeed the DC-8 aircraft regularly flies sorties into hurricanes with an instrument mounted on the outside of the airframe.

There is a small caveat to this. It is essentially a gas system. High liquid levels within the Herriott cell will cause problems!

Another factor that could effect the result is small temperature changes due to instability of the temperature control for the laser. Firstly, tests have proven this system to stabilise the temperature to 0.01°C across the normal operating range of -20°C to +40°C and secondly, “tracking” software automatically compensates if the peak of absorption should appear to drift.

7. Maintenance

Tunable diode lasers are used (at different wavelengths) extensively in the telecommunications industry. They are solid state devices and MTBF figures have established an expected life of 15 to 20 years. Should an incident occur where gross contamination causes a problem and the self-diagnostics indicate that cleaning is required, the flow cell may be flushed with solvent. If this should prove to be insufficient the flow cell may be removed and the mirrors cleaned with normal lens cleaner.

8. Conclusion

TDL's work well across the entire spectrum of gas concentrations and an area where TDL's particularly excel is accurate measurements of trace gases, particularly water vapour. Currently many hours are spent waiting for existing sensors to dry down. A TDL takes a dramatically shorter time to come to equilibrium and remains very responsive. The advantages for industry are many: the speed of response means that production on many processes can be more efficient. Man-hours can be saved or systems that would have taken two or three sensors can now be handled with one TDL and a rapid switching flow cell. 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, dry end performance, and speed of response offer industrial processes access to high quality, real time data. This extra information is proving invaluable for diagnosing plant problems and improving productivity. We believe hygrometry has moved a significant step forward. Data is now available without the inherent time lag and hysteresis that occurs on systems when water vapour absorbs or disorbs from the surface of a sensor. The LH2000 offers a measurement better or on a par with the best transfer standard instruments yet robust enough for use even on the most contaminated of gases.

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 H₂O, Journal of Geophysical Research Vol. 103. No. D15 1998 No: 98JS01678*

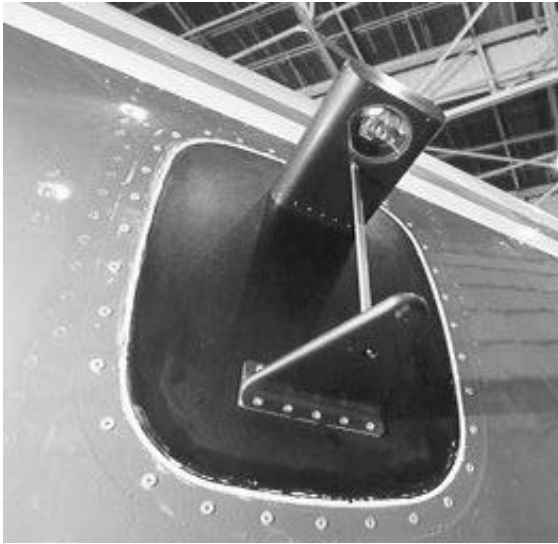


Plate 1. Laser hygrometer mounted on a NASA DC-8 bound for Hurricane Bonnie.

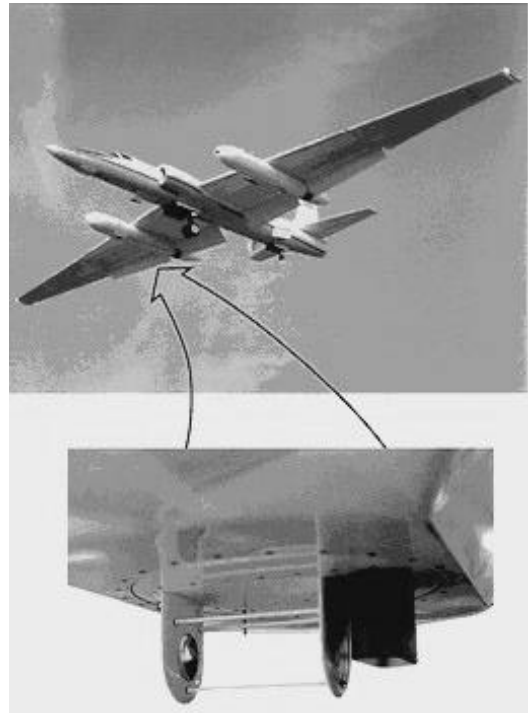


Plate 2. Laser hygrometer for the NASA ER-2 research aircraft.

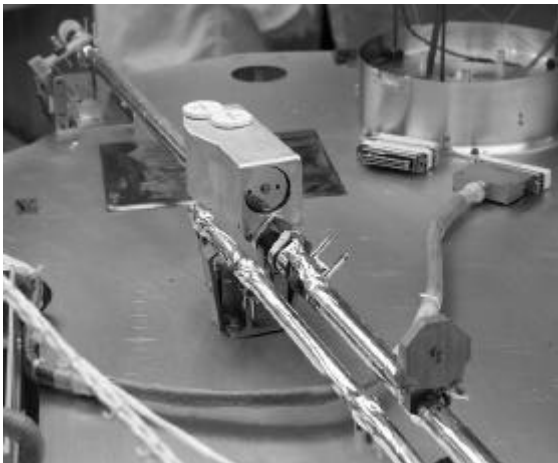


Plate 3 A TDL system on board the Mars Polar Lander

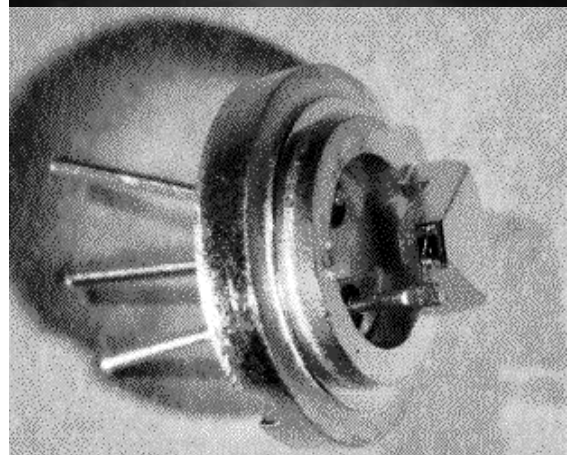


Plate 4. A Tunable Diode Laser

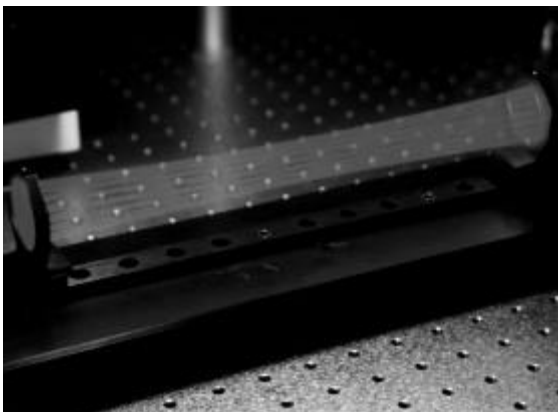


Plate 5. A Herriott Cell with visible light