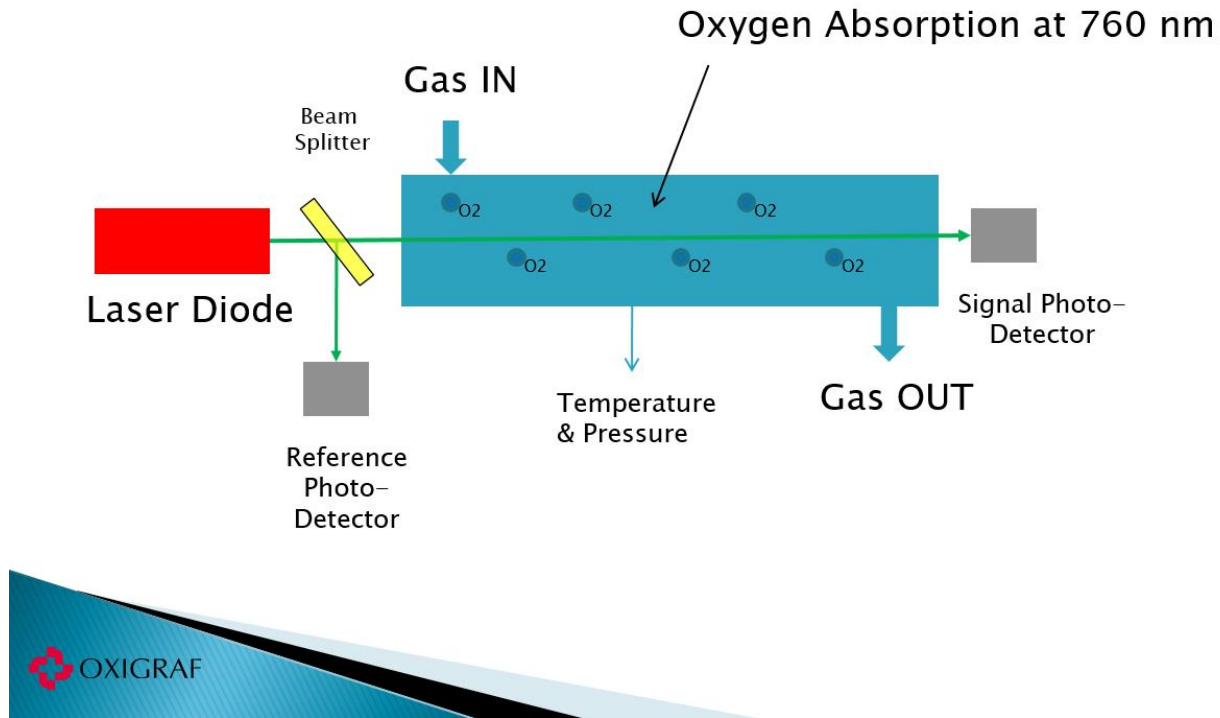


Laser Absorption Spectroscopy



Basics of the Oxigraf Analyzer.

The Oxigraf oxygen sensor uses absorption spectroscopy similar to the absorption spectroscopy method used to measure CO₂. Absorption spectroscopy for oxygen occurs in a region of the visible spectrum near 760 nm where no interferences by other gases are known. The emission line width of the laser diode source used by Oxigraf and the absorption width of the individual electronic-rotational lines of O₂ are very narrow, both less than 0.01nm, compared to about 100 nm for the CO₂ absorption band. This makes the specificity of laser diode spectroscopy for oxygen much greater than the black-body and filter technique of infrared spectroscopy used today to measure CO₂. To measure oxygen the spectrally pure laser is tuned thermally and electronically to an oxygen absorption line. As the oxygen concentration increases in the sample chamber, the light intensity, measured with a photodiode detector, is attenuated by the energy absorbed by oxygen molecules. The oxygen analyzer response varies *linearly* with oxygen concentration.

Laser Spectroscopy of the Oxygen A Band.

History:

The oxygen A band near 760 nm was first analyzed by Mulliken in 1928 and by Van Vleck in 1934; also high resolution measurements were reported using an argon-ion pumped dye laser by Ritter and Wilkerson¹. Absorption by oxygen has been of interest for measurement of atmospheric variables using lidar². Philippe and Hanson have used these lines and diode laser spectroscopy to measure several gas dynamic parameters, including mass flux in shock tubes³, and have noted several earlier references to this possibility. Smith and Casey report on a differential absorption ranging technique (DART) used to range helicopters by comparing on and off-resonance transmission of laser diode radiation tuned to the oxygen A lines.⁴



Physics:

Molecular oxygen has four rotational energy bands corresponding to an electronic transition in the visible spectrum. The ground electronic state has a total electron spin of unity, while the upper electronic level has zero spin. "Magnetic dipole" transitions require a spin flip, so the line strengths are very weak. The line widths of 54 lines studied between 760 and 770 nm are typically 0.05 cm^{-1} at atmospheric pressure. The line strengths are $5 \times 10^{24} \text{ cm}^{-1}/\text{mole}/\text{cm}^2$ or more at room temperature and the line pairs are separated by only about 2 cm^{-1} (see Fig. 1).

- ❖ The P-branch extends from $13,120 \text{ cm}^{-1}$ downward in frequency
- ❖ The R-branch extends upward from $13,125 \text{ cm}^{-1}$.

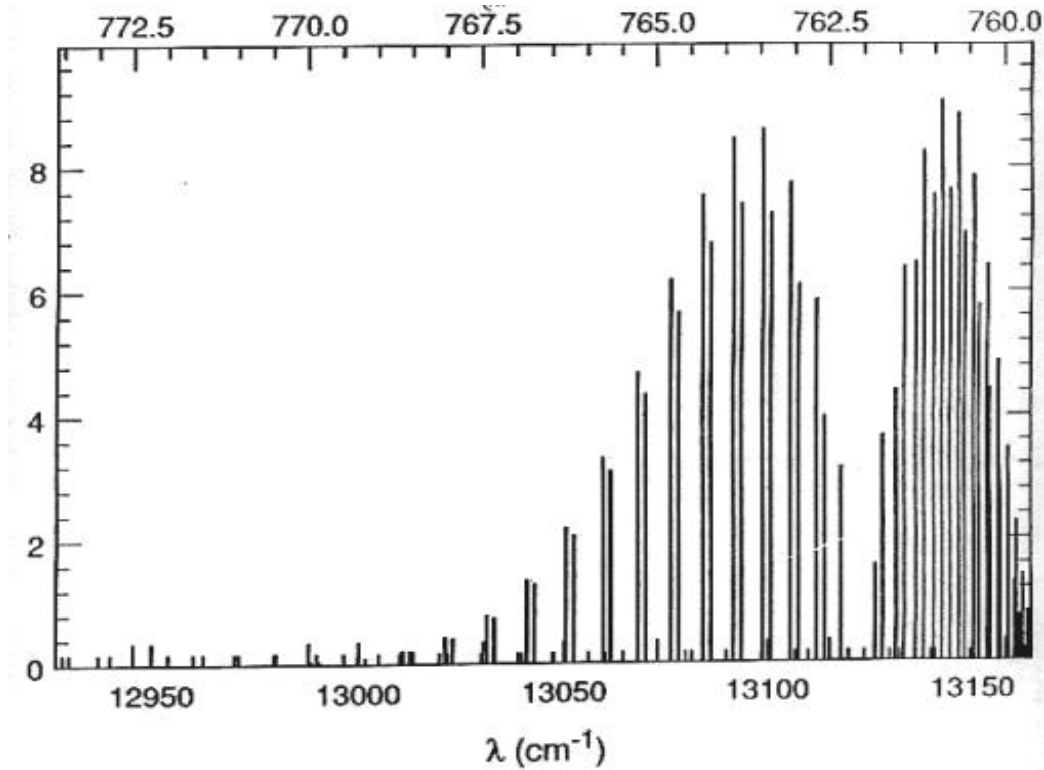


Figure 1. O₂ A-Band Line Strengths at Room Temperature

Oxigraf Innovation in Laser Diode Spectroscopy.

Although there are many suitable absorption lines, only one is used by the Oxigraf method for the measurement of oxygen. The spectral width of the laser output is near 0.1 GHz, while the oxygen linewidth is near 1GHz. By controlling the laser's temperature and current, precise tuning of the excitation wavelength is possible. The particular line to be used is chosen for its absorption strength and for its spectral match to the laser's output wavelength.

1. Temperature control

Two means are used to control laser wavelength. A thermoelectric device precisely regulates the temperature of the laser diode. The thermal mass of the laser mount results in a long thermal time constant and slow response time for this control loop.

2. Current Control

Fast control of laser wavelength is done by modifying laser current. The laser current and output wavelength are varied stepwise to provide multiple absorption samples. A baseline selected away from the absorption peak, the absorption peak itself, and the half-height or shoulders of the line are measured. These values are measured during each sample cycle.

The baseline or zero sample gives a measure of the optical attenuation with no oxygen absorption. The shoulder samples are forced to be equal in amplitude by adjusting the laser current thus centering or “locking” the laser emission wavelength to the oxygen absorption wavelength. This also provides a measurement of the line width allowing corrections to be made for pressure or collision broadening. Finally the product of the absorption peak and line width less the average baseline is used as a measure of oxygen absorption. Because of the baseline correction, the oxygen concentration measurement is not affected by attenuation due to dirt on the cell windows or laser aging.

The Oxigraf stepped-laser-drive waveform, has numerous advantages.

- ❖ Every period contains a zero oxygen correction and a line-centering function.
- ❖ Every period also contains a measure not only of absorption but also of line width.
- ❖ All the functions can be accomplished on a single, low cost module with board-mounted sample cell for a unit cost in quantity of about \$1000.

Oxigraf technology is protected by several patents see references 6,7,8

Laser Mode Structure.

Low cost laser diodes, using temperature scanning, typically have narrow regions of linear wavelength interrupted by abrupt wavelength change caused by mode hopping every 0.1 nm or so. Oxigraf has adopted a Vertical Cavity Surface Emitting Laser (VCSEL) diode, which is single mode over at least 1 nm. The mean lifetime of these laser diodes is estimated to be 500,000 hours. The slope of single mode operation is 0.07 nm/C; over a 20° C thermoelectric tuning range, there are usually 4 to 10 oxygen lines available in the range from 760 to 765 nm. The oxygen line width and the laser emission bandwidths in these units are roughly 0.003 and 0.0003 nm, respectively. To find a usable oxygen line, Oxigraf software performs an automated search process. The lines are automatically evaluated and only the best one is selected. Also, during calibration the software corrects for any temperature drift. Drift can occur as the laser diode and other components age.

Calibration.

Two-point, straight line calibration routine is provided in software. Normally the instrument is calibrated at 100% and 20.9%. To maintain $\pm 0.5\%$ accuracy, calibration is recommended every 1000 hours of operation. To maintain $\pm 0.1\%$ accuracy, calibration is recommended more often.

Temperature Control and Compensation.

Regulation of the temperature of the gas sample minimizes the need for corrections to be made to the oxygen measurement. At room temperature the error may be positive or negative and as large as 1% per °C. To minimize errors the sample gas is

heated to about 45° C, this also prevents condensation of water onto the optics when water is in the sample. Additional corrections are made to the measurement during warmup and other times when the sample is not at 45°. The temperature compensation factor is only good for the absorption line selected, but will be constant for the life of the instrument. The reference cell is also heated and maintained at a constant temperature.

Pressure Correction.

Pressure is monitored inside the sample chamber with a pressure transducer. Changes in pressure due to barometric changes or pneumatic variations in the sample circuit are corrected in real time. The pressure of the sample at time of measurement is also needed to convert from partial pressure to per cent oxygen. In addition, during low pressure applications, as would occur at high altitude, the pressure measurement is used together with an empirical look-up table to compensate for collision and Doppler broadening over the pressure range of 10 to 120 kPascal.

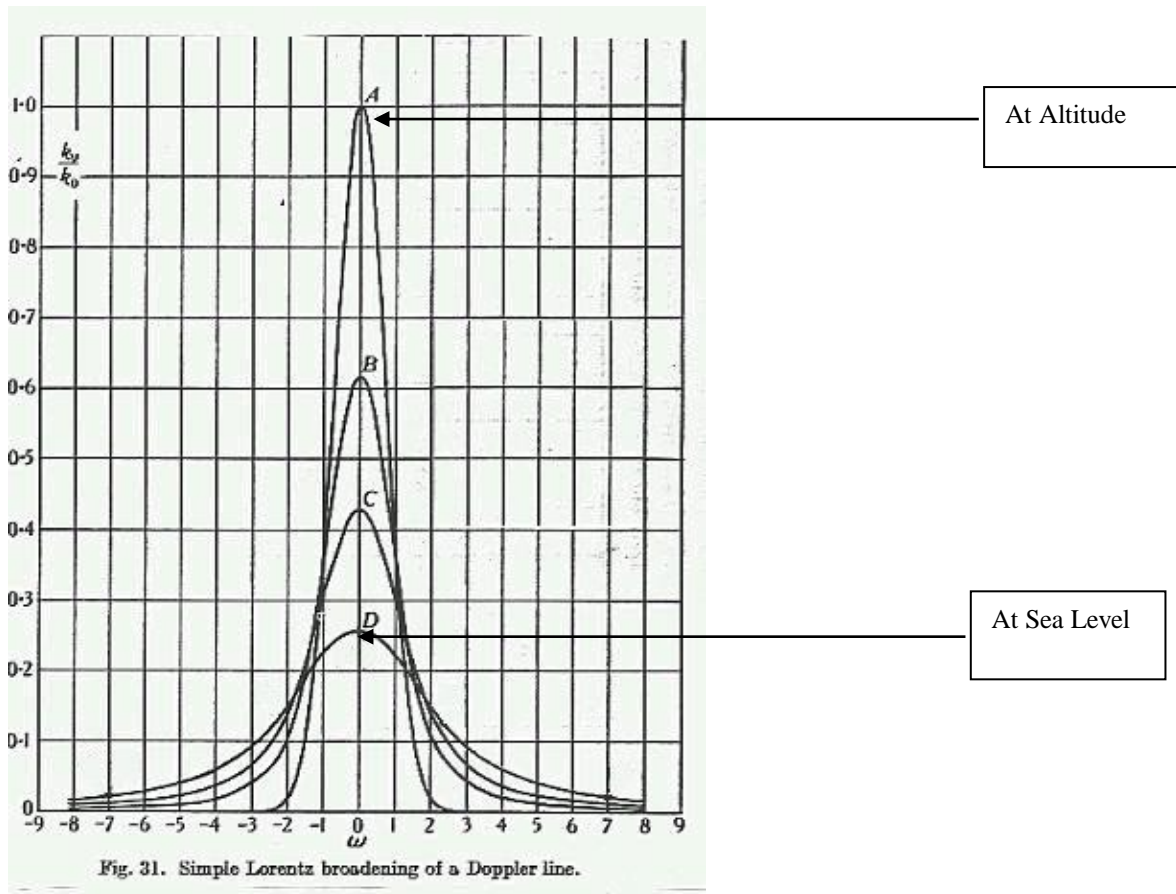


Figure 2 Pressure broadening of a Doppler line

Cross Sensitivity.

Cross sensitivity refers to errors caused by a pressure broadening of the oxygen line from foreign gas molecules in the sample mixture.

Cross sensitivity is caused by the pressure or Lorentz broadening of the oxygen absorption line due to their collision with other gas molecules. These collisions subtract or add a little energy to the natural or the Doppler-shifted energy of transition. The absorption amplitude is reduced at the center frequency and is increased at adjacent frequencies, broadening the spectral absorption line (see fig. 2). This effect is increased as the collision frequency or pressure is increased. The peak absorption amplitude is also affected by the type of molecule colliding with the oxygen molecule absorbing the light. Large CO₂ or N₂O molecules interact more strongly with oxygen than argon atoms, for example, and couple translational energy to the quantum state of oxygen more efficiently. For example, the oxygen absorption line is about 3% wider in air, due to pressure broadening with nitrogen, than in pure oxygen. Without correction for cross-sensitivity, certified mixtures of 50%O₂ / 50%CO₂ or 50%O₂ / 50%N₂O read oxygen as being only 45%. Argon/oxygen mixtures without correction would read higher oxygen concentration.

Cross sensitivity customarily is corrected by measuring the foreign gas concentrations independently and computing a correction factor. By measuring the pressure and the line-broadening independently Oxigraf is able to correct to within 0.1% for cross-sensitivity without reference to foreign gas types or concentrations.

Oxigraf Sensors Today:

Performance of the Oxigraf Fast Oxygen Sensor, as developed to date, incorporating the design philosophies above are as follows: The range of operation is 0 to 100% at full accuracy. The sensor measures oxygen every 20 ms with all corrections. The noise performance is 0.02% at an 80 ms averaging time. The long-term accuracy is +/- 0.5%. At a sampling rate flow of 200 ml/min., the response time, limited by pneumatic effects, is about 100 ms. Typical power use is about 7 W. The sensor footprint is about 6.5" x 2.5" x 1.75" and weighs 10 oz. The complete analyzer (Model O₂) with pump, display, and instrument case is 7.5 x 3 x 11" and weighs 5 lbs. The initialization time is 30 seconds from turn-on; full accuracy is achieved after 5 minutes warm-up.

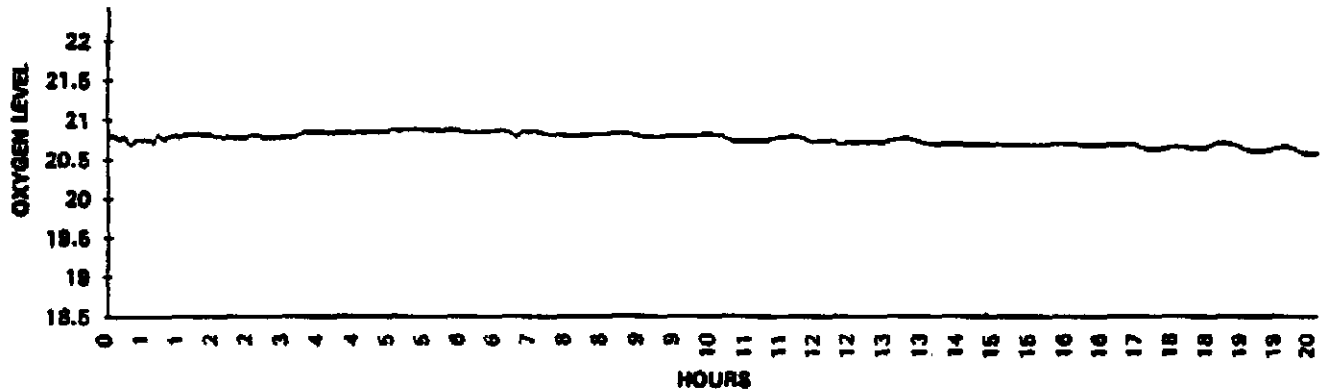
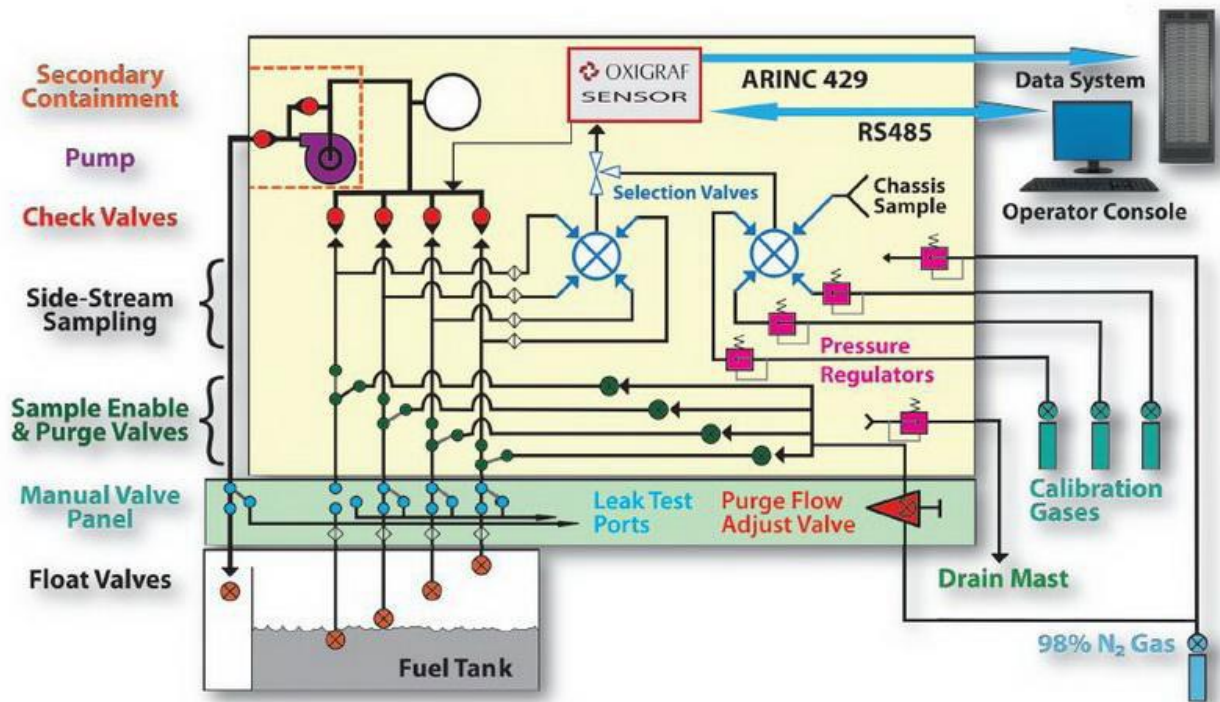


Figure 3: This plot of the 1-second averaged oxygen measurements of room air calibrated at 20.8% shows a variation over 20 hours from 20.7 to 20.9% (less than 0.2%)



The above system process schematic shows the O₂N₂ analyzer in relation to the float valves in the fuel tanks, the purge and calibration gasses and flows, and the control and data system. Communications to the control and data system are through RS-232/485 links and an ARINC-429 interface is provided to communicate with customer furnished data monitoring and recording systems.

References and Patents

- 1 Ritter, K.J., and T.D. Wilkerson. "High Resolution spectroscopy of the oxygen A band". Journal of Molecular Spectroscopy 121: 1-19,1987.
 - 2 Kroll, M., J.A. McClintock, and O. Ollinger. Applied Physics Letters. 51: 1465,1987. Kanamori, H., M. Momona, and K. Sakurai. Can J. Phys. 68: 313,1990. Bruce, D.M., and D.T. Cassidy. Appl Opt. 29:1327,1990.
 - 3 Philippe, L.C., and R.K. Hanson. "Laser absorption mass flux sensor for high speed airflows". Optics Letters 16 (24): 1991. Philippe, L.C., and R.K. Hanson. "Laser diode wavelength-modulation spectroscopy for simultaneous measurement of temperature, pressure, and velocity in shock-heated oxygen flows." Applied Optics 32: 6090-6103, 1993.
 - 4 Smith, R.J., and William L. Casey. Dart: "A novel sensor for helicopter flight safety." Photonics Spectra 110-116, July 1992.
 - 5 Silver, Joel A., "Frequency-modulation spectroscopy for trace series detection: theory and comparison among experimental methods." Applied Optics 31(6): 707-717,1992. Bomse, David S., Alan C. Stanton, and Joel A. Silver. "Frequency modulation and wavelength modulation spectroscopies: comparison of experimental methods using a lead-salt diode laser." Applied Optics 31(6): 718-730,1992.
 - 6 Wong, Jacob. United States Patent Number 5,047,639, Concentration Detector. September 10, 1991.
 - 7 McCaul, Bruce W., Doggett, and Thorson. United States Patent Numbers 5,448,071, 5,491,341, 5,625,189, and 6,150,661 Gas Spectroscopy, Sept. 5, 1995, Feb 13, 1996, Apr. 29, 1997 and Nov 21,2000. European patent pending.
 8. Doggett, David F., and McCaul. United States Patent Numbers 5,500,768 and 5,615,052, Laser Diode/Lens Assembly, Mar 19, 1996 and Mar 25, 1997.
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