High Sensitivity, High Reliability Trace Gas Sensors USING OPTICAL DETECTION

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Pranalytica, Inc. located in Santa Monica, CA specializes in technology and products for ultra low level, high reliability detection of trace gases. Pranalytica uses tunable laser based photoacoustic spectroscopy (O-Nose™ Technology) for the detection of many molecular gases at ppb and sub-ppb levels without interference from other gases that may be present in the sampled gas. Pranalytica's instruments are field proven, rugged and reliable; they are able to operate autonomously without operator intervention or assistance; they provide data on a continuous basis with a fresh measurement every 12 seconds and they can be interfaced with central data collection systems in using a broad variety of communication protocols.

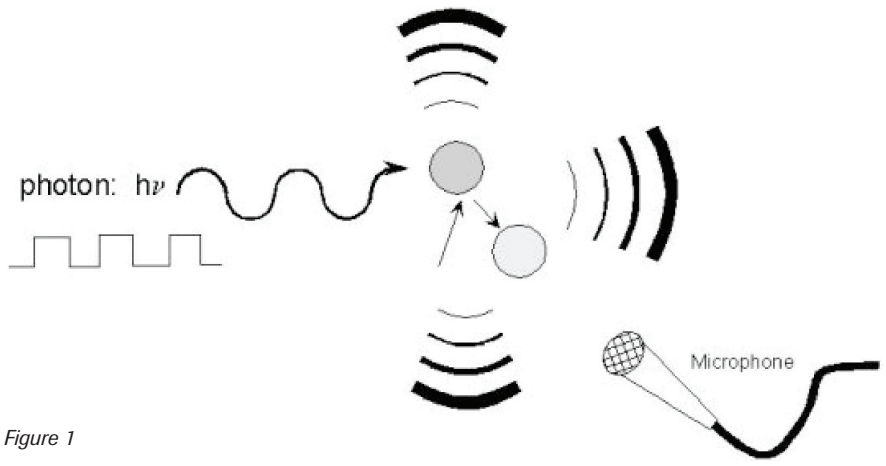

Figure 1

Principle of photoacoustic spectroscopy can be understood through figure 1. The sample gas is illuminated by a radiation at frequency ν. When the frequency ν coincides with the absorption frequency of the target molecule, the photon can be absorbed by the molecule and the molecule is now excited to a higher state from which the molecule can relax back to the initial state by radiative or nonradiative mechanisms. Nonradiative relaxation converts the internal excitation energy of the molecule into translational energy and the molecular gas is now heated. If the incoming radiation is periodically interrupted, as shown in the figure, the gas is periodically heated. Such periodic heating is equivalent to periodic variation in the gas pressure. If the amplitude modulation occurs at an audio frequency, the resultant pressure fluctuations, sound, can be detected using a sensitive microphone as shown and the electrical signal corresponds to the rate at which the excited molecules decay back to their initial state. It is instructive to point out that

1. The sensitivity is derived from the amount of incoming radiation absorbed by the target molecule and
2. The selectivity is derived from choosing a frequency ν (or frequencies) that are absorbed by the target molecule but not by other constituents of the sample to be analyzed.

It should be clear from the observation in 2 above that in case the incident radiation frequency is not tunable, i.e., is fixed, there can be no assurance that the photoacoustic signal from the target molecule is not corrupted by absorptions arising from other interfering molecules present in the sample.

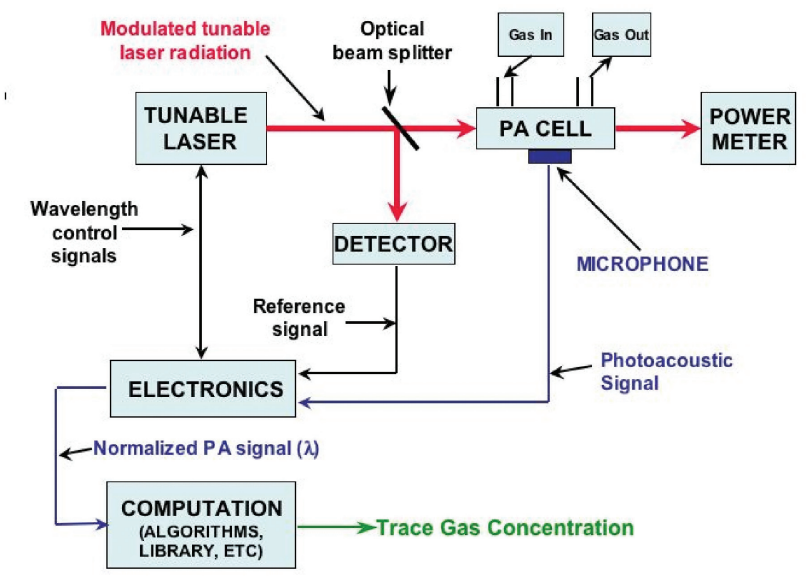

Figure 2

Figure 3

Incidentally, photoacoustic detection principle was first described through a series of elegant experiments by Alexander Graham Bell in 1884.

The functional details of Pranalytica's gas sensing instrumentation are shown in Figure 2. A tunable laser, whose output wavelength is computer controlled, provides the radiation for interrogating the sample gas in the photoacoustic (PA) cell. A small part of the radiation entering into the cell is tapped off to provide a laser power level reference as the laser wavelength is tuned. A sensitive microphone converts the acoustic signals corresponding to the absorbed optical radiation into electrical signals and is normalized to the input laser power laser to account for power level fluctuations. The electronics module compares the normalized PA signal as a function of the laser wavelength with the sample spectra stored in the on-board computer memory and using appropriate optimization algorithms, provides the trace gas concentration in parts-per-billion. The modular nature of the system permits use of a variety of tunable laser sources including CO2 laser (covering 9-11 μm region), near IR semiconductor laser (covering the 1.5 μm region), quantum cascade lasers (covering 4-12 μm region) and a broad variety of other tunable laser sources. This permits matching the radiation source wavelength with the absorption wavelength of any target molecule.

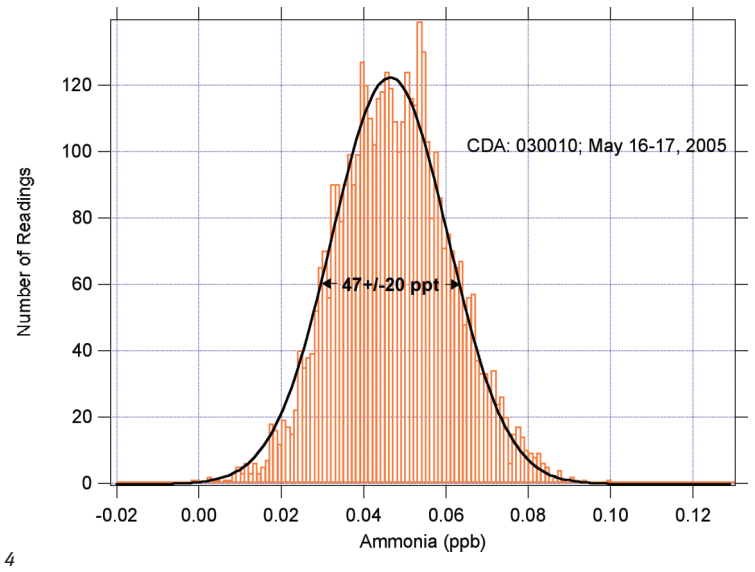

Figure 4

Figure 3 shows a photograph of a Nitrolux-100 sensor that has the minimum field-proven, long-term reproducible sensitivity of 100 parts-per-trillion (PPT) for ammonia detection. The sensor is completely self-contained and uses a CO_2 laser as the source of tunable radiation. All of the electronics and the

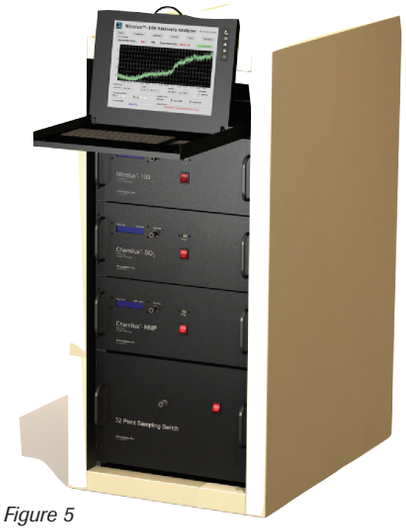

Figure 5

control computer are contained inside the enclosure and the sensor works on a Linux operating system based software for ultrahigh reliability. The vacuum pump, for drawing the sample into the PA cell is also located inside the sensor. The Nitrolux operates completely autonomously, providing measurements of the gas sample every 10±2 seconds, without operator intervention and consumes less than 250 watts of AC power. Ammonia concentration data as a function of time are stored in the internal solid-state memory and can be accessed through a front panel USB port or through a LAN connection. Optional wireless connectivity permits data access over mobile telephone network.

An example of the long-term reproducibility of the performance is shown in figure 4 where we see a histogram of apparent ammonia readings obtained when the sensor is exposed to clean dry air (CDA) for over two days of continuous data collection. Such histograms are the best way of demonstrating the performance of a sensor. The data show excellent fit to a Gaussian distribution demonstrating a noise limited sensitivity of 47±20 ppt for ammonia detection. A distinguishing feature of Pranalytica's gas sensors is that they are immune from false readings that may result from other inferring components in the gas sample. For example, the Nitrolux series of ammonia sensors are unaffected by the presence of many of the commonly used solvents as well as moisture. There are very few, if any, trace gas sensors that detect ammonia at a sensitivity of <100 ppt and do not exhibit severe interference problems that are encountered when using these sensors in semiconductor fab lines and for environmental monitoring. The capability of Nitrolux results from a proprietary laser tuning technology and the use of proprietary data reduction algorithms.

Pranalytica also supplies complete systems for measuring multiple gases and sequentially sampling as many as 32 gas streams, shown in figure 5. This system, designed for molecular contaminant monitoring in semiconductor fab lines, consists of an ammonia sensor (Nitrolux), a SO_2 sensor (Chemilux-SO_2), a NMP sensor (Chemilux-NMP) and a 32-point sequential sampling switch.

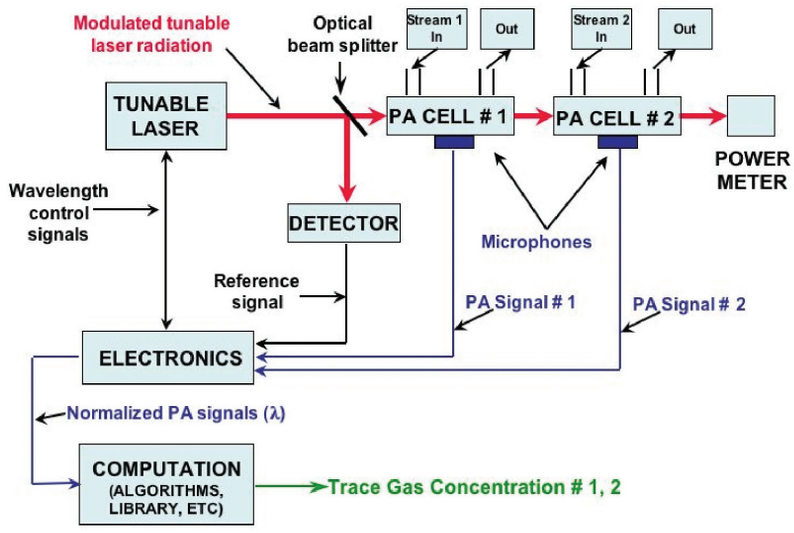

Figure 6

Finally, the O-Nose™ technology for trace gas detection lends itself readily to optical multiplexing for monitoring multiple gas streams simultaneously rather than sequentially. The principle of optical multiplexing is shown in Figure 6, which involves letting the tunable laser radiation traverse multiple PA cells to provide PA signals corresponding to multiple gas streams. This is possible because for trace gas level detection, the amount of optical radiation absorbed in each of the PA cells is less than $1{:}10^6$. Figure 7 shows a photograph of a four cell Nitrolux-200 (capable of minimum sensitivity of 200 ppt) that was recently supplied to an environmental monitoring laboratory. Pranalytica is the only supplier of multiplexed cells for simultaneous measurement of multiple streams of gas samples.

Figure 7

Table I

GAS	SENSITIVITY (ppb)	LASER
Ammonia	0.02	$^{12}CO_2$
1,3-Butadiene	0.5	$^{13}CO_2$
Benzene	3	$^{12}CO_2$
DMF	0.4	$^{12}CO_2$
Ethylene	0.2	$^{12}CO_2$
Formaldehyde	15	$^{12}CO_2$
HCl	1	Near IR diode
HF	1	Near IR diode
Methylamine	5	$^{12}CO_2$
Nitric Acid	0.4	$^{13}CO_2$
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Nitrogen Dioxide	1	
O-Xylene	5	$^{12}CO_2$
Silane	0.2	$^{13}CO_2$
Sulfur Dioxide	1	
Sulfur Hexafluoride	0.001	$^{12}CO_2$
Toluene	10	$^{12}CO_2$

As mentioned earlier, the use of an appropriate tunable laser source in the O-Nose™ platform permits trace level measurements of virtually any gas. The Table 1 below lists the availability of trace gas sensors for a broad spectrum of gases and the sensitivity levels for detection.

In conclusion, the interference free trace gas level detection capability of the O-Nose™ technology makes it possible to detect many chemical warfare agents (CWA) at sensitivities at or below 6 μg/m³ (1 ppb) with false alarm rates below $1{:}10^8$. Pranalytica is working on DARPA contracts to produce CWA sensors using CO_2 lasers for stationary applications (such as subways, airports, large buildings, etc) and using quantum cascade lasers for a portable version. These sensors, called the FREEDOM™ (Fast Response Environmental and Explosive Detection using Optical Methods) will have a substantial impact in protection general population against terrorist attacks involving CWA and other toxic gases.