

Trace Gas (and Isotope) Analysis: A Portable, Turnkey Instrument

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Environmental Problem

Acrolein or acrylaldehyde is a volatile, flammable material that is relatively chemically unstable and has a chemical formula of CH_2CHCHO . It is commonly produced as a byproduct in the combustion of most organic materials and can be found in automobile exhaust, wood smoke, smoke from grass fires, and even in cigarette smoke. Acrolein also is used in the chemical industry in the production of polyesters, acrylics, and glycerol. It is extremely toxic to humans via inhalation and dermal exposure. Short-term inhalation exposure may result in upper respiratory tract irritation and congestion. Consequently, parties as diverse as forest firefighters and chemical plant operators could benefit from monitoring the level of acrolein vapor in high-risk areas. This need could be met by a trace-gas analyzer that combines both sensitivity and selectivity—the ability to quantitatively measure trace acrolein in the presence of numerous other gas species.

SBIR Technology Solution

With support from the EPA's SBIR Program, Picarro, Inc., worked to develop an analyzer based on

wavelength-scanned cavity ring down spectroscopy (WS-CRDS) technology. The principles of the approach are simple: to use high resolution infrared absorption to uniquely identify and quantify acrolein vapor, and to utilize WS-CRDS in particular to avoid all of the major inherent limitations of conventional infrared spectrometers and non-dispersive infrared (NDIR) gas analyzers. These limitations include a lack of sensitivity due to the small amount of vapor and low signal/noise, and a lack of spectral resolution necessary to uniquely identify acrolein in the presence of other trace gases (i.e., crosstalk).

The heart of the WS-CRDS analyzer is a thermally controlled optical measurement cavity with an effective path length of ca. 20 kilometers, which thereby eliminates the “small sample size” sensitivity issue. In addition, an onboard wavelength monitor controls the narrow line tunable laser diode source, ensuring that absorption lines unique to acrolein can be scanned repeatedly, precisely, and rapidly, providing both fast (seconds) detection and a high degree of species selectivity. Signal/noise is further enhanced by the fact that this analyzer measures the decay within the optical cavity each time the laser is repeatedly and rapidly switched off. Thus, random variations in laser intensity do not affect the time-based data, unlike conventional intensity-based absorption measurements. Using this approach, a WS-CRDS-based acrolein analyzer that provides parts per billion sensitivity and precision as well as a high degree of selectivity (no crosstalk from other gases) was developed successfully. In addition, the analyzer supports sampling

rates as fast as 1 Hz in a portable, rugged instrument that does not require frequent calibration or any other type of maintenance, thus allowing remote unattended operation.

Commercialization Information

Picarro engineers recognized that this revolutionary instrument was more than ideal to meet the fast-growing needs of many gas sensing applications across the environmental science field, particularly for carbon/water cycle studies and greenhouse gas measurements. This includes at sources (e.g., power plants), sinks (e.g., sequestration sites), and directly/remotely in the ambient atmosphere. Specifically, the combination of high sensitivity and massive dynamic range of this WS-CRDS analyzer means that it can measure high ambient concentrations of CO_2 and water vapor in a plant canopy or trace



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amounts of CH₄ from a landfill. Moreover, the dynamic range also means that the concentration of trace isotopes can be measured directly, for example, by comparing spectral features unique to H₂O and HDO as well as ¹²CO₂ and ¹³CO₂. This provides the ability to directly measure isotope ratios in real-time, with no sample preparation, in a portable instrument. This is a tremendous advantage, because the isotope ratio in detected greenhouse gases allows their source to be identified and classified (e.g., anthropogenic [fossil fuel] or biogenic). Even CO₂ from grass and forest fires has different and characteristic isotope signatures.

In addition, the company recognized the potential for WS-CRDS to monitor several other gases such as hydrogen sulfide, ammonia, and hydrofluoric acid for which monitoring at trace levels is required, either for safety (toxicity) reasons or for process control (e.g., in semiconductor fabrication). A family of WS-CRDS-based portable trace-gas and isotope analyzers was launched in 2007 to meet the needs of several of these applications.

Company History and Awards

Headquartered in Sunnyvale, California, Picarro, Inc., was founded in 1998 to develop trace-gas sensing applications based on WS-CRDS technology licensed from Stanford University, and then further strengthened by nine additional Picarro patents. The company continues to experience strong compound growth for its family of analyzers targeting the environmental and semiconductor markets.

In 2008, Picarro's carbon dioxide isotopic analyzer was recognized with the prestigious R&D 100 Award. Dubbed the "Oscars of Invention" by the Chicago Tribune, the R&D Awards are presented annually by the editors of R&D, a unique broad-

spectrum publication targeted at technical innovations in industry, universities, and government/national laboratories for applications as diverse as environmental, life sciences, pharma, metrology, semiconductor, and nanotechnology.

SBIR Impact

- Acrolein is a noxious byproduct of combustion and chemical manufacturing for which a simple yet precise trace sensor is needed.
- Picarro developed an ultra-sensitive and portable trace gas analyzer based on wavelength-scanned cavity ring down spectroscopy technology.
- This instrument meets the needs for established and emerging sensing applications in the environmental and semiconductor markets, including providing the first remote isotope sensing capability.
- This instrument has the ability to monitor several other gases including CO₂ and other important greenhouse gases.
- Picarro continues to experience strong commercial sales for its analyzers, which also have been recognized with a prestigious R&D 100 Award.

