Gas Analysis Using OA-ICOS Technology

LORI HOWE, PH.D.

Supplying a new analysis technology to meet the demanding real-time needs of the industry

Abstract:

This paper describes a new gas analytical instrument, based on a novel laser diagnostic technique, off-axis integrated-cavity-output spectroscopy (OA-ICOS), which provides facile, real-time in-situ trace gas analyses of many commercially and environmentally important gases in ambient air. This article addresses the technology behind these measurements and its advantage over traditional techniques such as NDIR. The technique may be applied for measurements of several environmentally and commercially relevant gases for process control, compliance monitoring, and trace gas sensing. In this paper we present examples of measurements of CH_4 in ambient air and in commercial gas cylinders to test and verify the concentration in commercial gas cylinders, CO_2 in ambient air, and HF for safety and compliance monitoring. The measurements of gas mixing ratios from the commercial cylinders yielded surprising results. In some cases, the fractional error as as high as 18%.

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Significance of Real-time Trace Gas Analysis

There is an ever increasing demand for the measurement of trace gases in ambient air at lower and lower thresholds. Whether one is interested in studying changes in the natural environment and global climate variation, or monitoring gases in production and manufacturing sites, measuring of trace gas concentrations in air is a major challenge. There is significant interest on the industrial front for measuring gases in production and manufacturing situations, for example, measuring combustion and emission by-products is important for the automotive industry to test engine design and manufacturing protocol. Other industrial gas measuring demands included the monitoring of HF production in aluminum smelting plants and measurements of ambient gas concentrations in semiconductor manufacturing. Yet, despite these commercial demands, and the fact that many gases can now be detected at low concentrations, the greatest challenge remaining is the ability to obtain precise and accurate measurements of gas concentrations in real-time at ambient conditions. Since these measurements are demanding and sensitive, new techniques are being developed to meet these needs. Recent results indicate that laser based diagnostics are the most promising for providing more sensitive reliable measurements in real time without external calibration.

Off-axis Integrated-cavity-output Spectroscopy (OA-ICOS)

Absorption spectroscopy is a simple technique often used to measure concentrations of component mixtures. In this technique, a laser is directed through a sample and a detector located after the sample cell measures the change in light, or absorption, due to the presence of known chemical components. The mixing ratio of the absorbing gas is determined from the measured absorption using the Beer-Lambert Law which depends, among other things, on the concentration of the absorbing species and the pathlength through the sample. Since different molecules absorb light at different wavelengths, mixing ratios of multiple gases can be determined by tuning the laser over a predetermined wavelength range. This technique is generally highly specific since spectrally narrow lasers are used. Conventional laser absorption methods for measurements of CO_2, CH_4 and other gases often employ liquid-N_2 cooled lasers and detectors operating at mid-infrared wavelengths, and multi-pass Herriott cells (100 meters, 3 liter volume) to yield reasonable sensitivi-

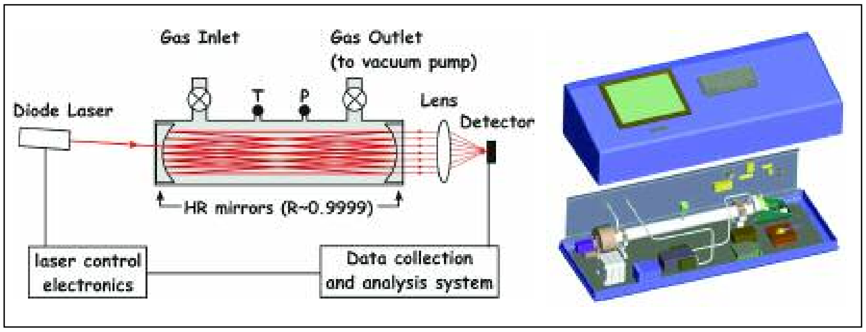

Figure 1. (left) Schematic diagram of the OA-ICOS-based instrument. (right) Engineering drawing of the autonomous instrument containing all control, data collection and data analysis subsystems.

Specification	OA-ICOS	NDIR analyzer
Accuracy	(+) Intrinsic (absolute measurement requires no calibration)	(-) Requires routine calibration (span and zero level drifts)
	(+) Permits direct comparison of measurements at different geographical sites at the limit of instrument precision	(-) Very difficult to compare measurements at different sites at the limit of instrument precision
Precision	(+) Very High (better than 1 part in 1000)	(+) High (better than 1 part in 100)
	(+) Based on weak absorption at 1.6 μm. CO2 absorption strengths are 50x greater at 2 μm and 10,000x greater at 4 μm, so future instruments have potential for improvement as reliable lasers become available at these wavelengths.	(–) Highest performance instruments already based on absorption at 4.3 μm. This is a mature technology with only marginal opportunity for incremental improvements
Linearity	(+) Excellent	(–) Poor
Speed	(+) Fast	(+) Fast
Service	(+) Not required under normal operation	(-) Routine calibration required to insure measure ment integrity
	(+) Limited to filter change, minimal expertise required	(+) Minimal expertise required
Cost	(+) Low	(+) Low
Track record	(–) New	(+) Mature

Table 1

ty and time response. These systems are expensive and often need regular calibration.

OA-ICOS provides extremely long paths (2-20 km, typical) in a rugged, compact package due to a unique cavity design. Instead of passing the beam through a hole in the mirror of a multi-pass cell, the beam enters the gas cell by passing through the input mirror and is later collected as it passes through the output mirror as shown in Figure 1a. Since the mirrors are partially transmissive and do not have holes, unlike conventional Herriott cells, the optical alignment is simple and robust. Light entering the optical cavity bounces between the mirrors and propagates an effective pathlength that is given by the mirror reflectivity. For example, by using highly reflective mirrors (R=99.99%, typical), the light makes thousands of passes through the cell, providing a significant improvement over standard multi-pass cells. This technique was developed by Los Gatos Research (Mountain View, CA). This OA-ICOS technique allows measurement of small changes in transmitted laser light propagating extraordinarily long pathlengths to yield both high precision and high sensitivity. Since the pathlength only depends on optical losses in the cavity, and not on a unique beam trajectory, the system is insensitive to the laser cavity alignment. Off-Axis ICOS is inherently self-calibrating, and typically uses off-the-shelf room-temperature semiconductor diode lasers operating in the 1.5 to 2.0 micron spectral region. The system may be configured for a standard 19-inch instrument rack or as a stand-alone instrument (Figure 1b). All these design features make the system robust enough for unattended field use in environmental studies or easily integrated into on-line production and monitoring systems.

Comparison of OA-ICOS to Conventional Gas Measurement Methods

OA-ICOS offers several advantages over traditional gas concentration measurement techniques such as gas chromatography (GC), or non-dispersive infrared spectroscopy (NDIR), or Fourier transform infrared spectroscopy (FTIR). OA-ICOS offers simple, real-time analysis of gases in ambient conditions with ultra high precision and accuracy. Table 1 below summarizes the side-by-side comparison of OA-ICOS and NDIR, and shows OA-ICOS to be superior in several key areas: 1) OA-ICOS requires yields absolute measurements 2) OA-ICOS yields higher precision 3) Ease of use. OA-ICOS does not require maintenance, re-alignment or external calibration.

High Accuracy CO_2 Analyzer

Studies of global warming require quantitative monitoring the global

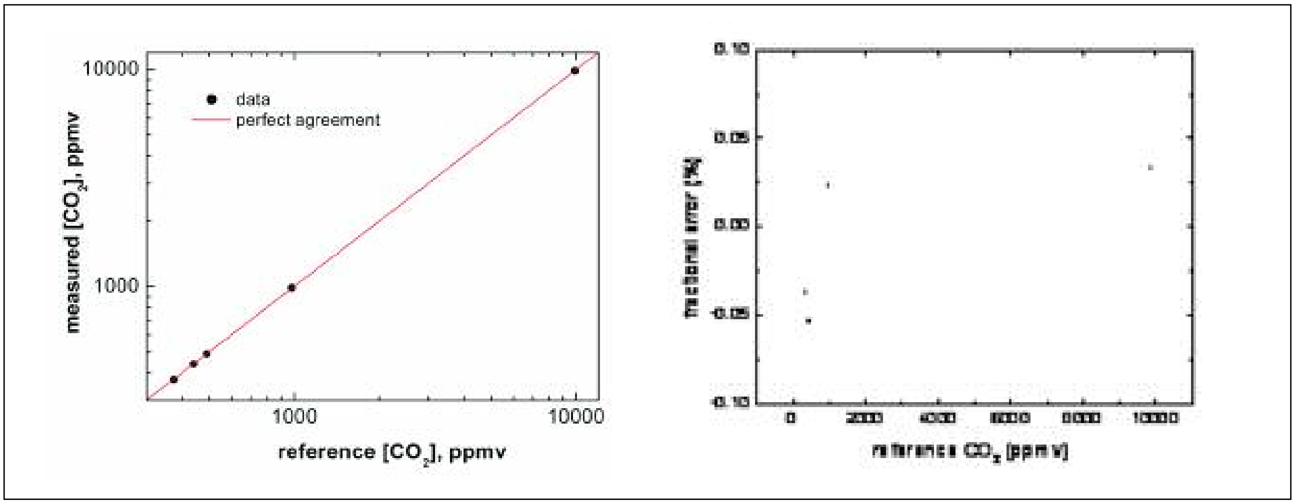

Figure 2 (left) shows measurements of CO_2 in ambient air compared with NIST gas standards over a range 350-10000 ppmv in air. The slope of the fit suggests that the instrument performs linearly over the measurement range. Figure 2 (right) plots the variation or fractional error with concentration. These results show that the instrument is capable of reporting measurements of CO_2 with a total uncertainty of less than 1 part in 2000 over the entire range, without external calibration gases.

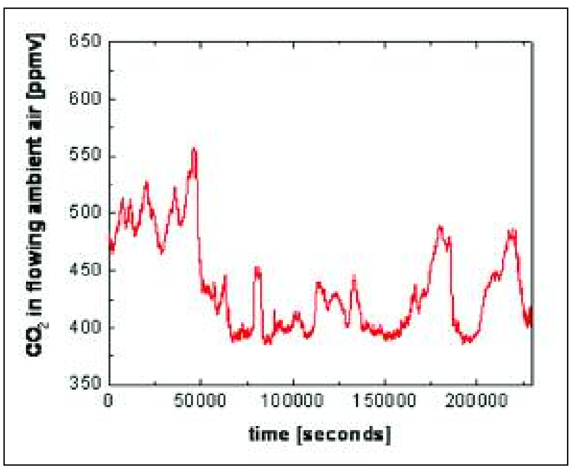

Figure 3 reports continuous measurements of CO_2 in flowing samples of outside air (in Mountain View, CA) over to illustrate the ability to record measurements unattended for extended periods. Variations in CO_2 are due to automobile traffic patterns outside our facilities.

carbon cycle on large spatial scales so that scientists can generate reliable models of climate change. Since variations in CO_2 often do not exceed several ppmv, studies attempting to draw connections between local human and biological activity and carbon fluxes require sub-ppmv precision. In order to perform studies across a long time base or across geographically distant locations, high absolute accuracy at the measurement location is preferred. Accuracy refers to the closeness of a measured value to its true value and is thus a higher standard than precision. CO_2 analysis based on OA-ICOS is intrinsically accurate and does not require calibration gases.

Figure 2. shows measurements of various CO_2 mixing ratios from calibrated gas standards supplied by NIST CMDL. The measurements for 350 ppmv-1% mixtures agreed with the reference values to within the uncertainty of those gas mixtures (0.1%). The slope of the linear fit suggests that the instrument performs linearly over the measurement range. The instrument precision was determined from replicate measurements of gas mixtures. Figure 3 shows continuous measurements of CO_2 in flowing samples of air outside Los Gatos Research to illustrate the systems ability to record measurements unattended for extended periods. Variations in CO_2 correlate well to automobile traffic patterns outside our facilities.

Measuring HF in Production Plants

Hydrogen fluoride (HF) is a highly corrosive and extremely dangerous gas and monitoring its release is essential in manufacturing and production, for example in aluminum smelting and semiconductor manufacturing. Because of the extreme nature of this gas, detection at even low levels is essential since even a low level leak could prove devastating. In order to test the threshold and precision of HF measurement, Los Gatos Research employed a calibrated permeation oven to generate known concentrations of HF. The values generated were recorded with an OA-ICOS instrument designed for HF detection. Results are shown in the Figure 4 below, and show the measured HF concentration matches the standard reference to within 2% over the entire measurement range.

Measuring Environmentally Relevant Gases

OA-ICOS based instruments have been shown to be useful for measurements of many other interesting gases, including NH_3 (ammonia), C_2H_2 (acetylene), CO (carbon

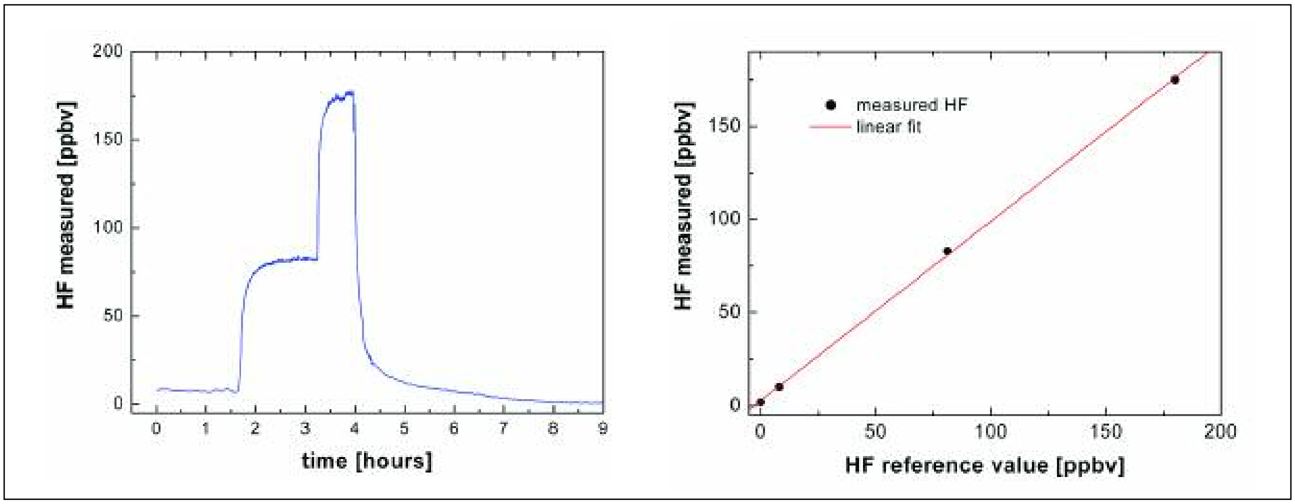

Figure 4. Measurements of HF from the output of a calibrated permeation oven over a range of mixing ratios from 11-180 ppbv. Time response is limited by the oven thermal equilibration time (30 minutes).

monoxide), NO_2, HONO (nitrous acid) and CH_4 (methane). For brevity, we will not discuss these other gases, but will focus on CH_4.

CH_4 in the Environment

CH_4, at the earth's surface, has increased significantly and correlates with human population growth and industrialization. This is of interest because methane is considered a prime component of the greenhouse gases. Pre-1750 ice core data indicates that pre-industrialization levels were ~700 ppbv, while current levels are ~1745 ppbv. The global CH_4 mixing ratio is increasing, with an average growth rate of approximately 0.6% per year. In current budget estimates of atmospheric CH_4, major contributors include both natural (wetlands) and anthropogenic sources (energy, landfills, ruminants, biomass burning, rice agriculture). The strengths of these sources vary spatially and temporally. Estimates of emissions from wetlands are also uncertain due to the extreme variability of these ecosystems. Because methane lifetime is long (8.4 years), atmospheric variations in concentration are small and accuracy in measurement is important for understanding spatial and temporal variability.

It is with these environmental interests in mind that OA-ICOS was tested in the lab to measure standard CH_4 concentrations, with an unexpected result. Commercial gas suppliers of air and nitrogen were found to have CH_4 concentrations well beyond their specified levels. Experimental details and results are discussed in the section following.

Since the pathlength only depends on optical losses in the cavity, and not on a unique beam trajectory, the system is insensitive to the laser cavity alignment.

Fast CH_4 Analyzer

An OA-ICOS instrument developed for methane monitoring was applied for measurements in calibrated mixtures obtained from NOAA Climate Monitoring Diagnostics Laboratory (Boulder, CO) to determine instrument accuracy and linearity. The results for measurements over the range 0.1-20 ppmv are presented in Figure 5.

The measurement accuracy of the OA-ICOS system was better than 1.0% with better than 0.1% replicate precision. The CH_4 detection limit (S/N = 3) is about 2 ppbv in a 1-Hz bandwidth. Since CH_4 is determined every 3 milliseconds, measurements may be reported very quickly if desired for process control or other applications requiring fast response time. The instrument was then used to measure CH_4 in calibrated gas samples from major gas suppliers in the United States, the results were found to deviate significantly from supplier specifications (1%). The results are shown in Figure 6, below and summarized in Table 2.

As shown in Table 2, five calibrated mixtures of methane in nitrogen or air from various US gas suppliers were tested for the presence of CH_4. Error from specification varied from 0.1% to 18.1%. These measurements are significant because production facilities often rely on gases purchased from these suppliers, and it seems that for specific applications where gas concentration must be known precisely, one must be

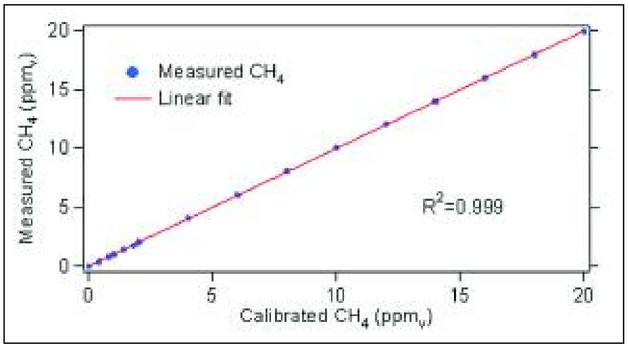

Figure 5. Measurements of CH_4 in calibrated mixtures obtained from NOAA CMDL over a range of mixing ratios over the range 0.1-20 ppmv.

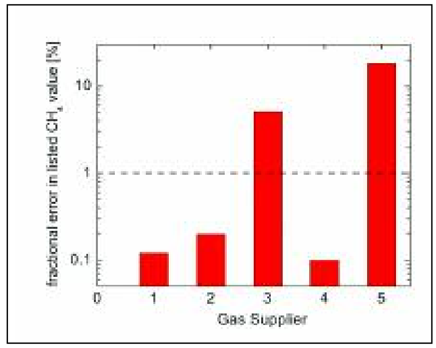

Figure 6. Measurements of methane obtained from commercial gas suppliers determined using the OA-ICOS instrument used to record data presented in Figure 5. The accuracy specification (1%) is given by the horizontal dashed line.

Vendor	Listed CH_4 (ppmv)	uncertainty listed, ppmv	Balance Gas	Measured CH_4	uncertainty measurement, ppmv	fractional error [(listed/ measurement -1)x100%]
1	1.71	0.00	Air	1.71	0.002	0.12
2	2.535	0.03	N_2	2.53	0.002	0.20
3	25.44	0.25	Air	24.2	0.01	5.12
4	2	0.02	Air	1.998	0.002	0.10
5	17	0.34	N_2	14.4	0.005	18.1

Table 2:

careful when relying on manufacturer's specifications.

Conclusion

OA-ICOS is a new technology for providing real-time measurements of gas concentrations with high accuracy and precision. Applications such as environmental monitoring, and on-line manufacturing/production monitoring may benefit from the availability of this new technique and the robust gas analysis system developed by Los Gatos Research. Whether testing in the field or in production line, real-time, accurate, calibration-free gas analyses will make gas monitoring easier and cost effective.

Lori Howe, Ph.D. is Photonics Marketing Consultant and Freelance Science Writer with L. Howe Consulting. 1164 N. Abbott Ave., Milpitas, CA 95035. She can be reached at 408-221-1662 or lori@lhoweconsulting.com.