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Petrolchimico

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J. Berthold, N. Bonavita, ABB Measurement & Analytics - mcT Petrolchimico, 25.11.2015

Advances in Laser Spectroscopy

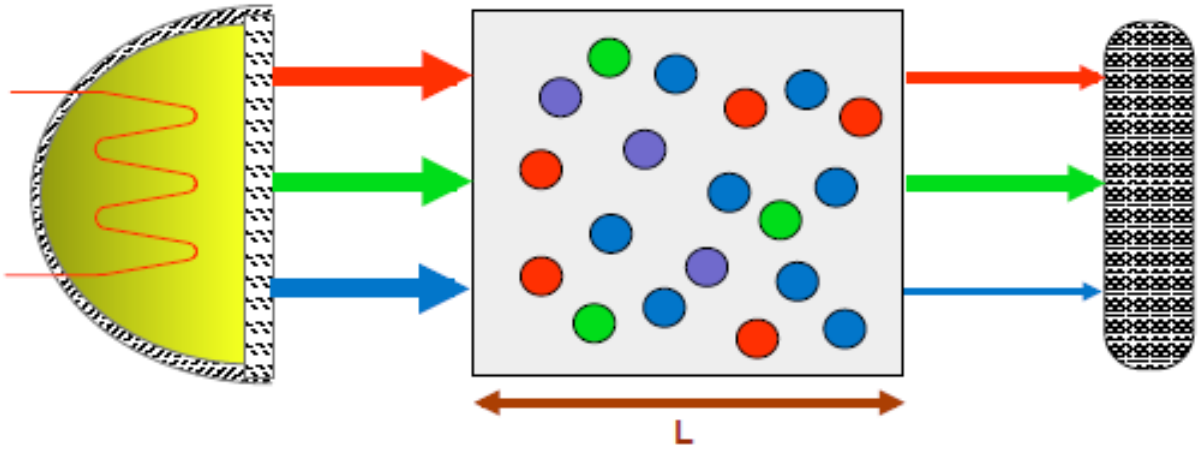
High resolution and ultra-precise multi-gas applications by OA-ICOS technology for both environmental monitoring and process control

Advances in Laser Spectroscopy: OA-ICOS
Outline

- **Laser Analyzers Benefits and Limitations**
- **OA-ICOS Technology**
- **OA-ICOS Implementation**
- **OA-ICOS Applications and Results**
- **Further Developments and Applications**

Laser Analyzer Generalities
Basics

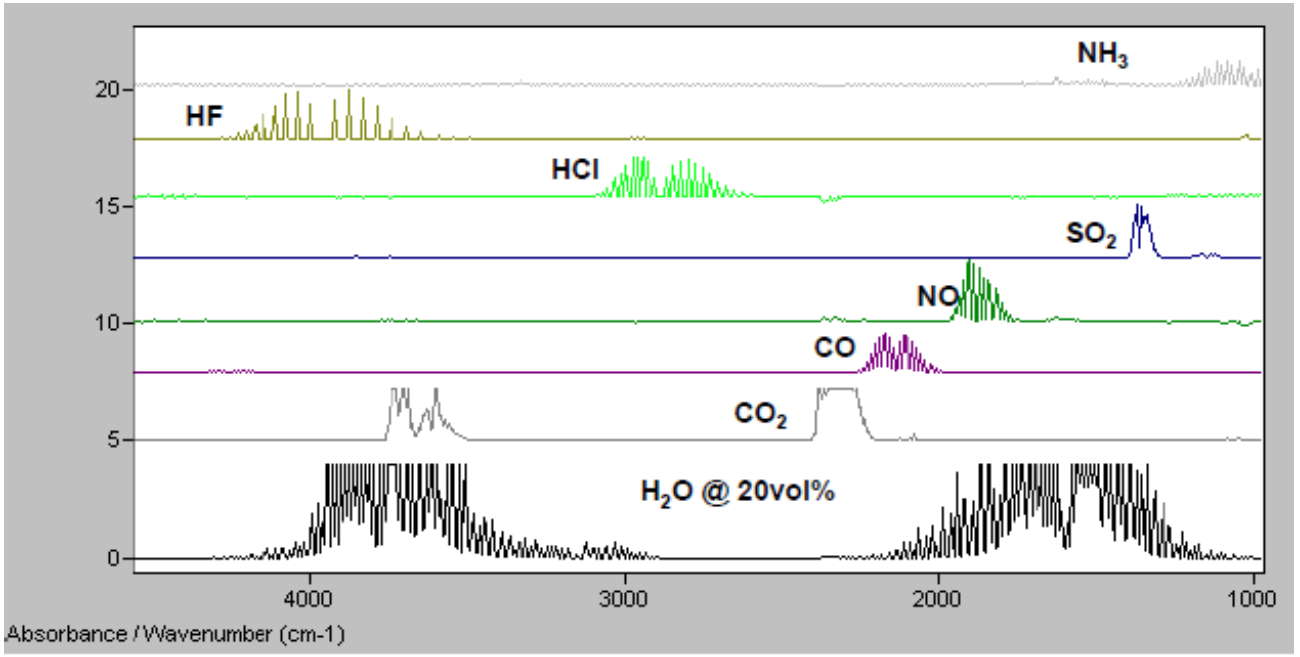
- Radiation (e.g. light) is energy
- Selective absorption of radiation at specific wavelengths
- Absorption proportional to the concentration of gas molecules



Length of optical path (L) affects measurement sensitivity

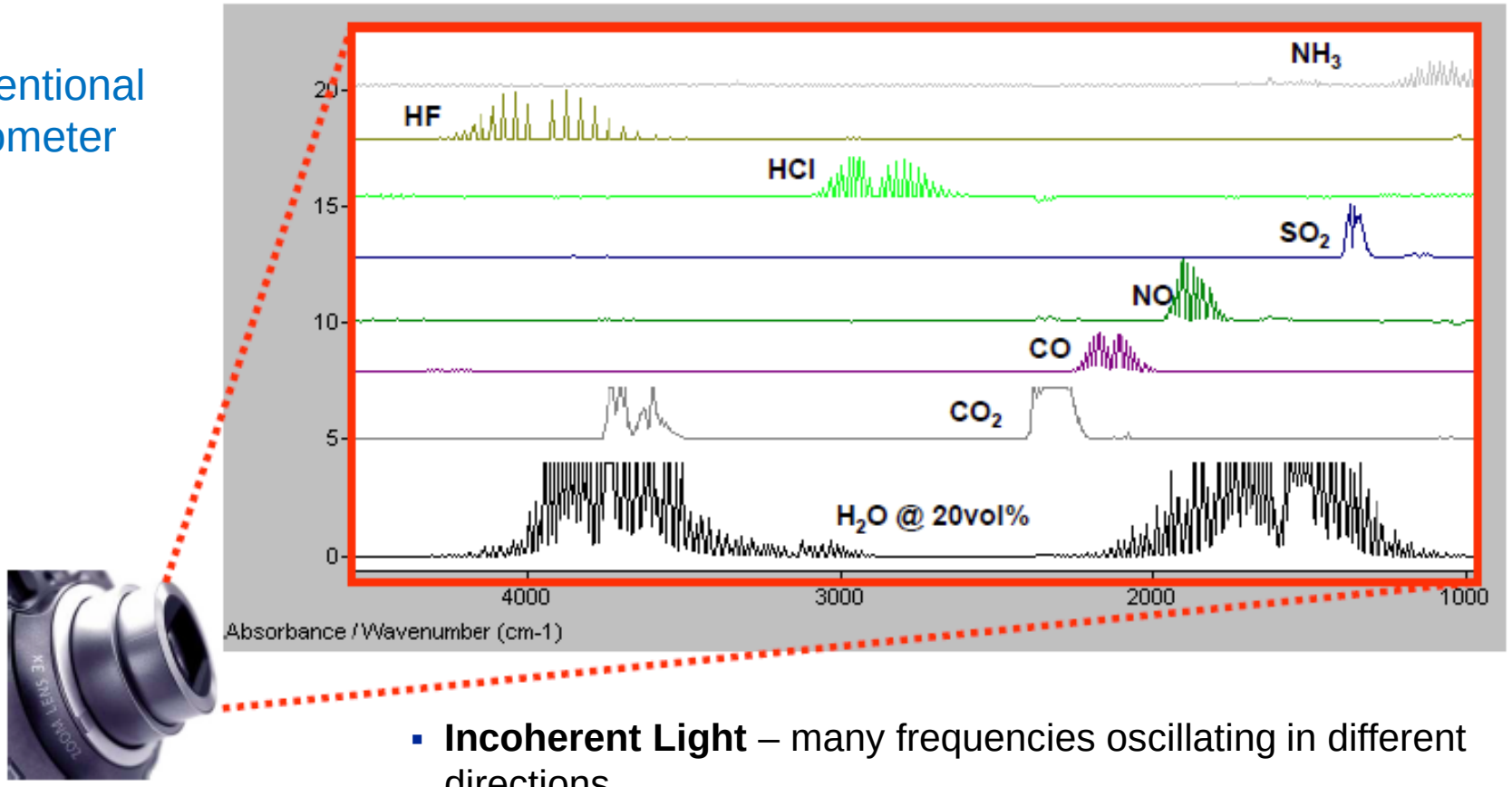
Laser Analyzer Generalities
Basics

Studying the absorbed spectra provides the gas molecule Fingerprints



Laser Analyzers Generalities
Basics

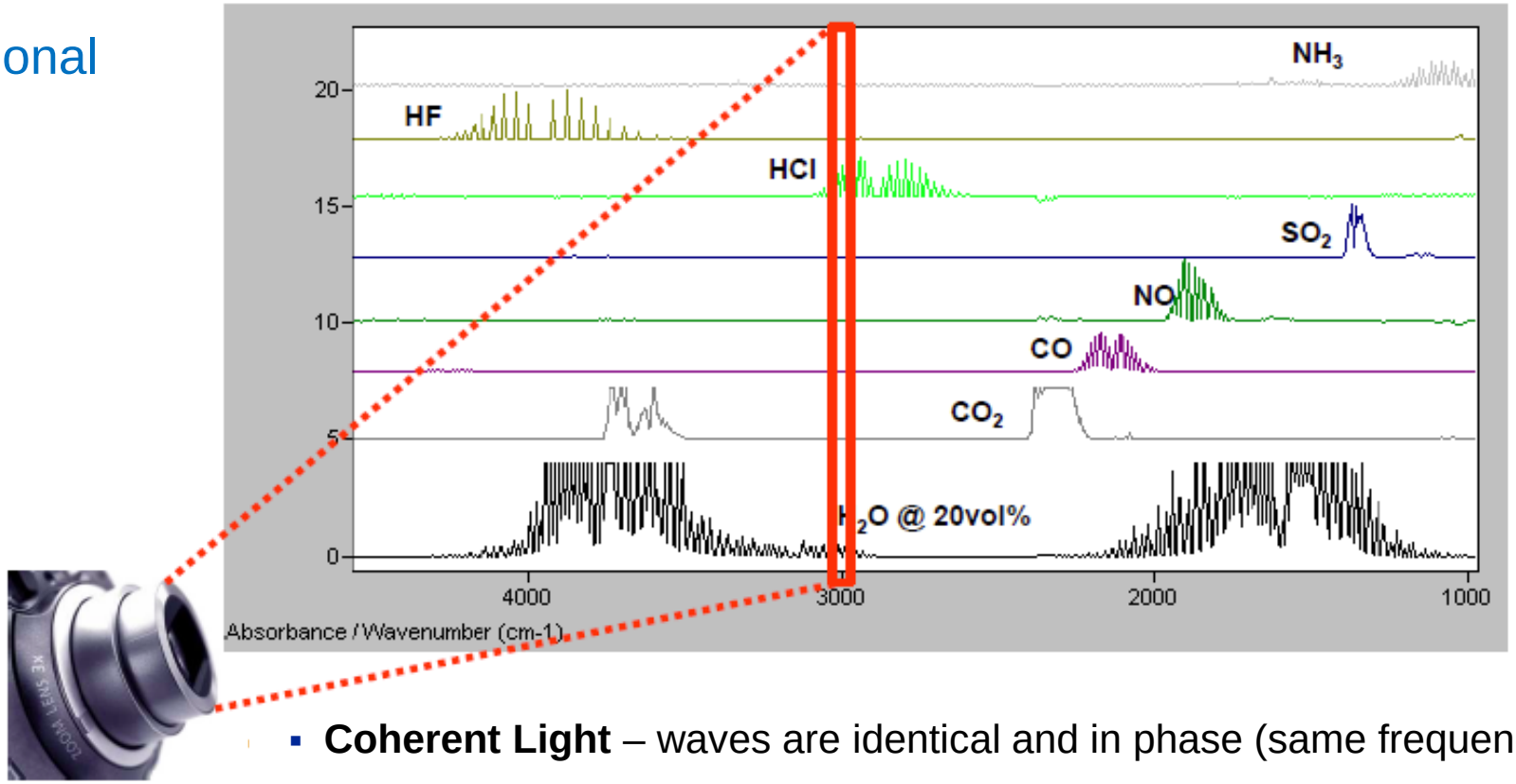
Conventional Photometer



- **Incoherent Light** – many frequencies oscillating in different directions
  - Optical filters can be used to cancel out unnecessary frequencies
  - Or advanced software used to interpret the data (i.e. Chemometrics)

Laser Analyzers Generalities
Basics

Traditional Laser

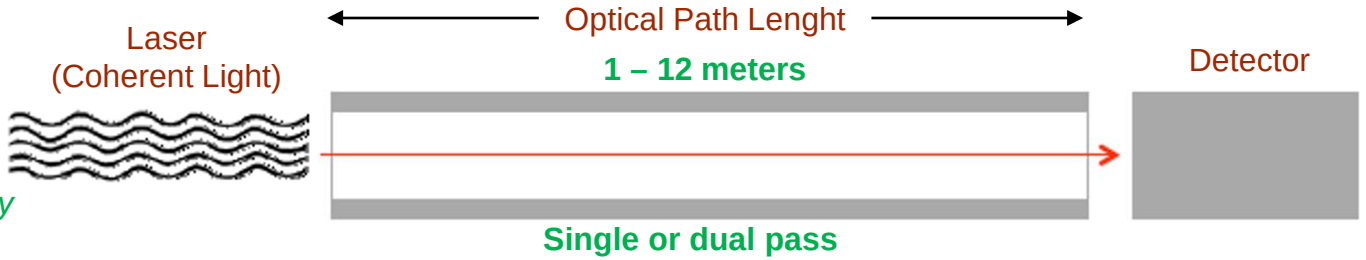


- **Coherent Light** – waves are identical and in phase (same frequency)
  - Laser selected to focus on specific frequencies with known absorption lines
  - Interferences are reduced, but scope to measure multiple components also limited (to 1 or 2 components)

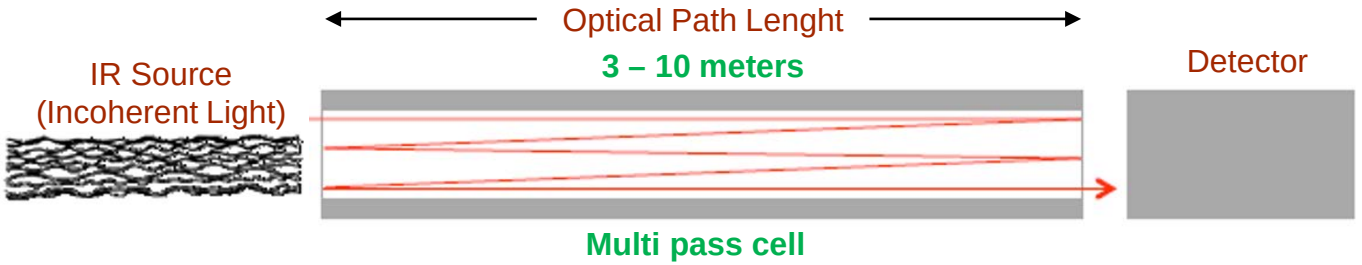
Laser Analyzers Generalities
Basics

Three Main Technologies

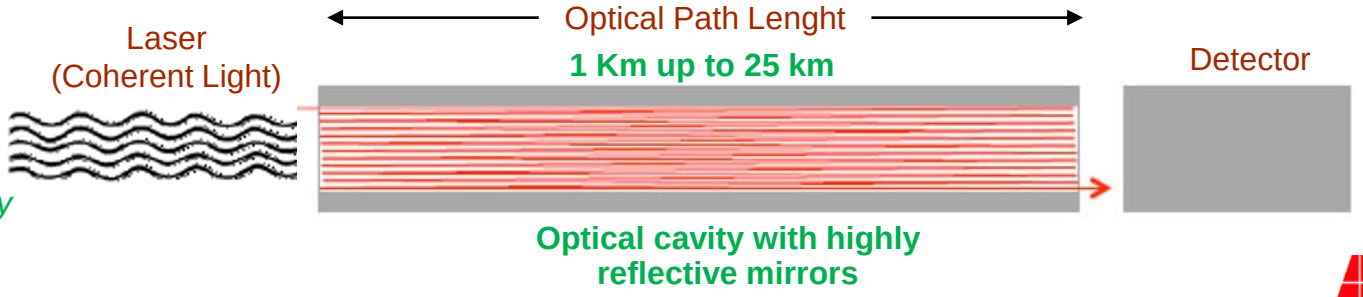
TDLAS
Tunable Diode Laser Absorption Spectroscopy



FTIR
Fourier Transform InfraRed



ICOS
Integrated Cavity Optical Spectroscopy



Limitation of Conventional TDLAS
Limited to little or no background absorption

- Limited sensitivity
  - Significant signal/noise issues
  - Light source/Laser noise (RIN)
  - Short path lengths

- Nonlinear at high concentrations
- Cross interferences and false positives
- Limited dynamic range
- Optical bench alignment issues
- Sensitive to vibration and obscuration

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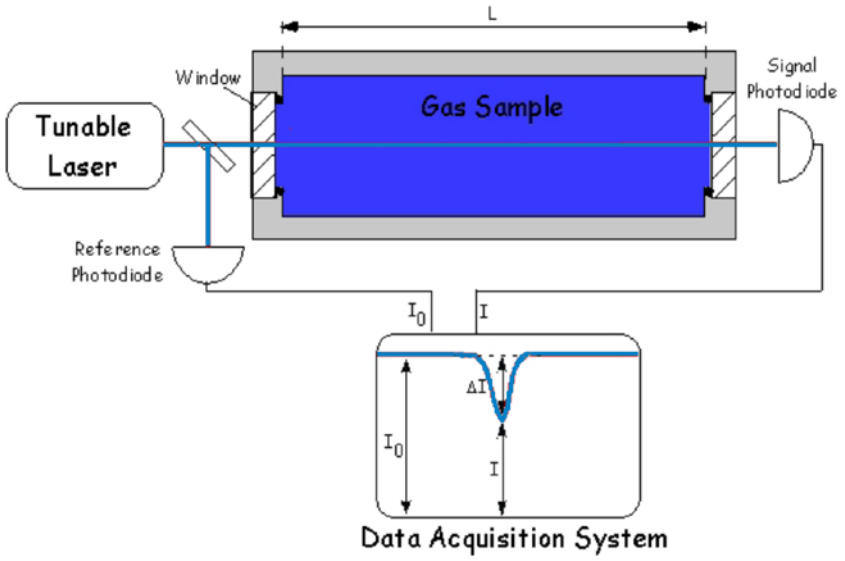
Laser Analyzers Generalities
Conventional TDLAS: Overview



Beer-Lambert Law:

$$\frac{\Delta I}{I_0} = 1 - e^{-\alpha L_{eff}}$$

$\frac{\Delta I}{I_0}$ = change in laser intensity

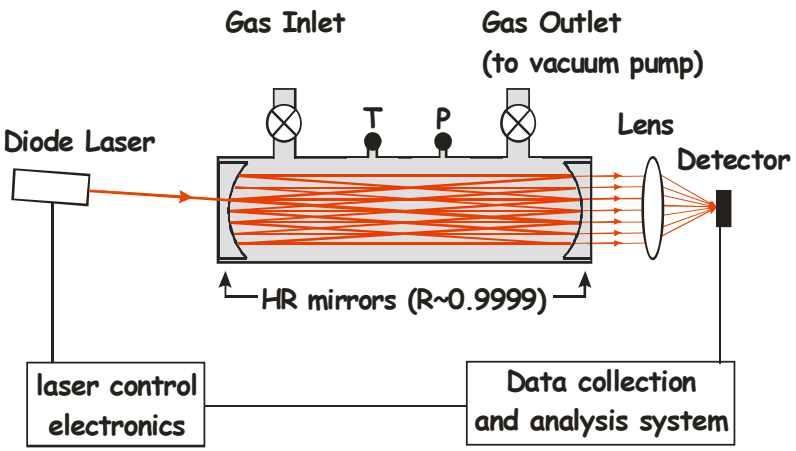
$\alpha(\lambda)$ = absorption coefficient

L_{eff} = effective optical path length

- TDLAS: direct measurement of gas concentration → minimal calibration
- Provides fast, gas-specific measurements with no consumables
- Non-intrusive: Ideal for monitoring in hostile conditions
- LGR uses TDLAS for cross-stack measurements of O_2, NH_3, HCl, etc
- 'Single pass' TDLAS may not provide sufficient sensitivity for some apps
- Limit of Detection in the "ppm" (1 part in 10^6) range, typically

OA-ICOS: Off-Axis Integrated Cavity Optical Spectrosc.

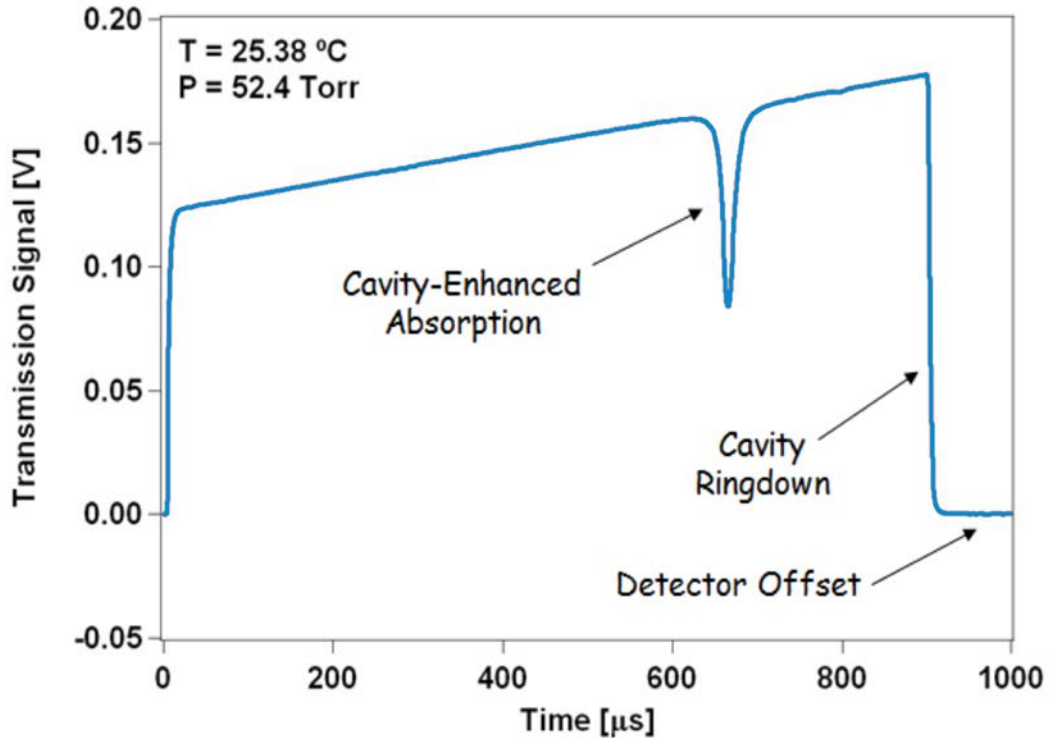
Combines high resolution with long path lengths



- Optical cavity provides longest effective path length of any laser analyzer available (up to 25 *kilometers* or longer)
- Very robust – exact optical bench alignments are not critical
- **Mirrors cleaned in the field in <20 minutes**!
- OA-ICOS can be employed at any wavelength from UV to mid-IR
- LDL's generally @ 1-50 ppb in complex matrices and as low as 200ppt range for some gases in ambient air
- Single and Dual lasers in single cavity for multi-species detection

Cavity Enhanced Absorption Spectroscopy (CEAS)

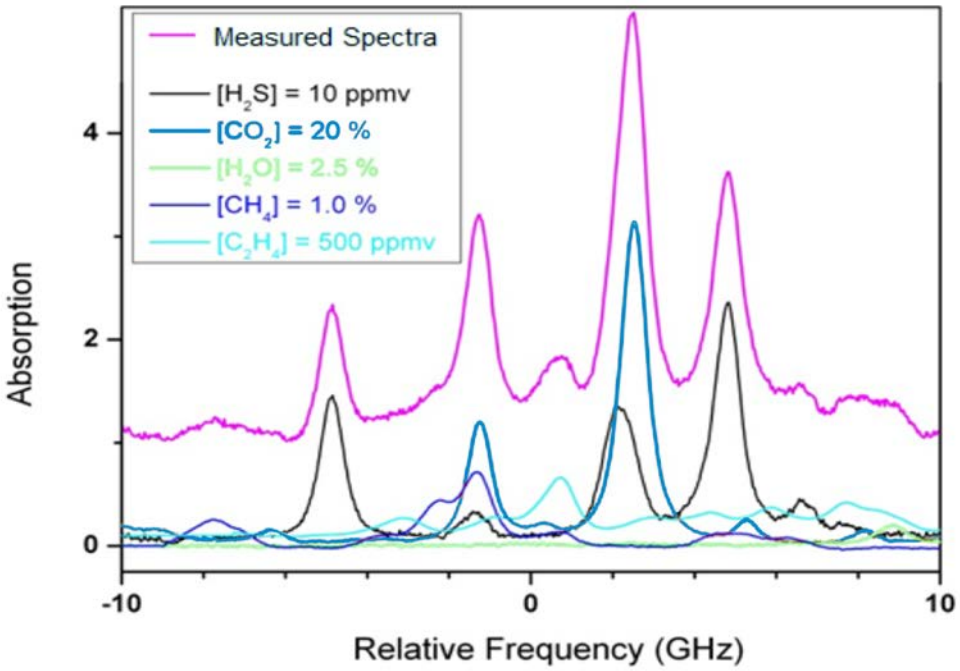
Measured *high-resolution* spectra yields *accurate* data



- Measures baseline, absorption, detector offset and Ring down time in every sweep to confirm path length at every data point!
- Operating at lower than ambient pressure to narrow spectral peaks and improve Voigt Profile for “fit”
- Scan laser at 100-1000 Hz, measurements every 1-10 ms
- Averaging ~ 1 sec of data (typical)

CEAS: Cavity-Enhanced Absorption Spectroscopy

Measurements based on high-resolution absorption spectra



- Chemometrics enables quantification of multiple gases in complex mixtures
- Enables single-laser instrument to accurately report multiple gas species for best value proposition

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OA-ICOS Implementation
LGR Experimental Setup – simple, robust, serviceable

Simple to service anywhere by anyone – mirrors may be cleaned in minutes

OA-ICOS Implementation
The Company

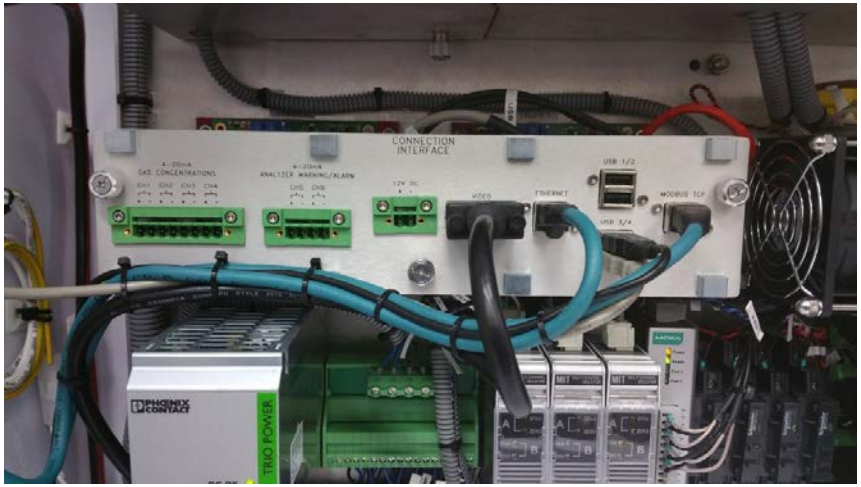
Los Gatos Research
A MEMBER OF THE ABB GROUP

- Founded in 1994, **acquired by ABB** in October 2013
- Located in Silicon Valley (Mountain View, California)
- 47 employees
  - 12 Ph.D. scientists
- Pioneer and world leader in laser-based gas sensing
- Invented all cavity enhanced absorption spectroscopy methods including cavity ringdown spectroscopy (CRDS), ICOS, Off-axis ICOS
- Many patents (>12) granted for analytical methods
- Hundreds of scientific papers/articles published in peer-review journals
- Serves environmental, research, industrial, and medical markets
- Sold >1500 instruments on all 7 continents

OA-ICOS Implementation
ABB-LGR ICOS Laser Process Analyzer

- IP 54, NEMA 4 and ATEX, ZONE 2
- MODBUS RTU, 4-20 mAmp & Relays, w/ unique certified USP file port for diagnostics and file download access
- Options for heated flow path and Hastelloy components

OA-ICOS Implementation
Reliable ABB Electrical/Mechanical Components



- Easy access for install & serviceability
- Industry Standard Analogue 4-20 mAmp, Digital MODBUS, and Relay Contact
- Smart Leak Compensation X purge system
- System integrity sensors & warnings for fast diagnostics via MODBUS or discreet 4-20 mAmp outputs

OA-ICOS Implementation
ABB-LGR ICOS: Application Table

Analyzer Type	Precision (1σ) @ 1 second of averaging	Minimum Detectability @ 100 seconds of averaging	Linearity	Time Response	Measurement Range
CH_4, CO, CO_2	CH_4: 4 ppb CO: 130 ppb CO_2: 190 ppb	CH_4: 2 ppb CO: 65 ppb CO_2: 95 ppb	R^2 = 0.99969	<10 seconds	CH_4: 0 – 200 ppm CO: 0 – 5000 ppm CO_2: 0 – 5000 ppm
H_2S, CO_2	H_2S: 13 ppb CO_2: 100 ppb	H_2S: 7 ppb CO_2: 50 ppb	R^2 = 0.99995	<10 seconds	H_2S: 0 – 500 ppm CO_2: 0 – 4000 ppm
O_2	O_2: 200 ppm	O_2: 100 ppm	R^2 = 0.99993	<10 seconds	O_2: 0 – 100%

OA-ICOS Implementation

ABB-LGR ICOS: Reliable, Accurate, Easy and Economical CoO

- Demonstrable and swift ROI on both CAPEX and CoO over traditional techniques
- No consumables, columns, carrier gases or liquids, or pre-scrubbers are required
- Simplified sample conditioning reduces system complexity and maintenance cost
- Minimal annual PM requirement estimated at 4 hours
- Significantly higher sensitivity compared with conventional laser analyzers
- Higher accuracy and precision enables improved process and quality control
- Fast response time allows rapid adjustment to process changes and upset conditions
- Lack of consumables reduces cost of ownership and increases ROI

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List of Industrial Applications

Industrial Process Control

- Acetylene/Ammonia in Ethylene
- Methane Carbon Isotope Analyzer for Energy Exploration
- Syngas Analyzer (CO, CO_2, H_2O, C_2H_2, HCN, …)
- Combustion Analyzer (CO, CO_2, H_2O, C_2H_2, HCN, O_2, …)
- Isotopic Carbon Dioxide Analyzer for Mining Applications

Environmental Monitoring

- Ammonia Analyzer (NH_3, H_2O)
- Greenhouse Gas Analyzer (CH_4, CO_2, H_2O)
- HCl Analyzer
- HCl/HF Analyzer
- H_2S/NH_3 Analyzer (in air or natural gas)
- Natural Gas Leak Detector (CH_4, C_2H_4)

OA-ICOS Applications and Results
Success Story # 1: Semiconductor & Electronics

- **Safety Leak Detection & Contamination Process Monitoring**
  - Ambient Air & Clean Room Monitoring for acid & neutralizing process solutions. >150 analyzers installed over the past 15 months
  - Process Contamination Monitoring for Acid Etching, Vapor Deposition, etc.
    - Customer needs improved sensitivity & speed of response @ best COO
    - LGR offers best performance against legacy technologies; 0.2 to 0.5 Parts per Billion HCl + HF and NH3
  - Ultra-trace leak detection measurements for minimizing long term exposure for personnel
    - Fast response for safety alarm systems: 1 second, 10 seconds
    - Two gases in one analyzer; such as HF+HCL, HCl + NH3 for value purchase
    - 24-hour Global Service Support

OA-ICOS Applications and Results

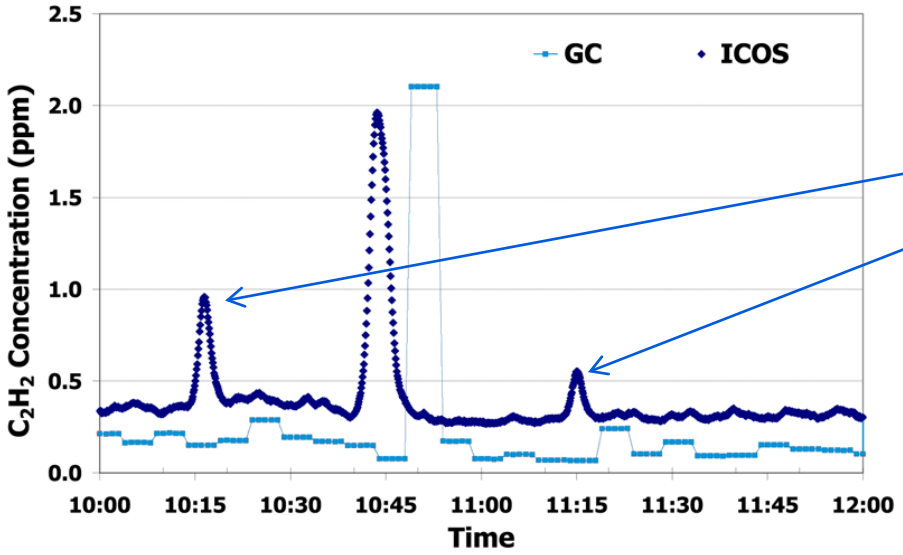
Success Story # 2: Industrial Gas & Specialty Chemicals

Quality Assurance in Trace H2S, HCl, NH3 and others

- Trace Gas analysis for Contaminants in Industrial Reagent & Blanket Gases such as Nitrogen and Hydrogen
- Ultra-trace measurements of H2S in high purity Nitrogen for Gas Chromatography calibration cylinders.
- LGR providing parts per billion level analyses with accuracy & precision
- GP analyzer for Quality Assurance, and matching Process Analyzer for Production volumes
- Air Products, Air Liquide, Praxair and others moving to Laser Spectroscopy for best product quality.

OA-ICOS Applications and Results
Success Story # 3: O&G, Chemicals & Petrochemicals

Ethylene Purity



High levels of C2H6 undetected by GC, but reported by OA-ICOS

- OA-ICOS is up to 10X faster than GC; enables active control of processes
- No mirror fouling or misalignment issues; no columns or carrier gases
- LGR's OA-ICOS can be an order of magnitude more sensitive than GC
  - Speed of response improves process efficiency
  - Field Serviceability of OA-ICOS reduces downtime
  - Economic Cost-of-Ownership shows swift Return after Investment

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Further Developments and Applications
Natural Gas, BioGas, Food & Beverage, Refining …

- Natural Gas/BioGas Production & Distribution
  - H_2S + CO_2 + Oxygen and Moisture measurements
  - Purity & Custody Transfer Applications
- Natural Gas Leak Detection
  - Methane and Ethane differentiation for Source confirmation
  - Aging public utilities' pipeline leak monitoring, with GPS location
- Food & Beverage Quality
  - Wine Verifications by Isotope Ratio
  - CO_2 purity in carbonated beverages & Carbon Sequestration
- Refinery & Petrochemical Combustion Efficiency
  - Trace Oxygen in Combustion Recovery
  - Hydrogen Purity in Catalyst Regeneration

The ABB-LGR Advantages
Summary

LGR
Los Gatos Research

LGR ADVANTAGES

Unique Technology

All LGR analyzers utilize a unique laser absorption technology called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). This technique, which was patented by LGR, offers superior performance, value and reliability as compared to any other technology.

Cavity enhanced absorption was first developed as an ultra-sensitive detection method by LGR founder Anthony O'Keefe in 1988 (Review of Scientific Instruments (ISSN 0034-6748), vol. 59, Dec. 1988, p. 2544-2551) in the form of cavity ringdown spectroscopy (CRDS). While innovative, unfortunately this first-generation technique requires sub-nanometer alignment of its internal optics, which translates directly into limitations in terms of high cost, and vulnerability to vibrations and temperature/pressure changes. To overcome these drawbacks, scientists at LGR developed a fourth-generation cavity enhanced laser absorption technology called OA-ICOS. This approach delivers superior performance, yet is orders of magnitude less sensitive to internal alignment of components. As a result, OA-ICOS is ideal for use in commercial instruments for even the most demanding applications in remote locations.

The inherent advantages of OA-ICOS technology make LGR trace gas and stable isotope analyzers the best choice, whatever the application.

Superior Performance

All LGR analyzers deliver superior performance (in terms of accuracy, precision, sensitivity, linearity and dynamic range) and ease of use compared to any competitive technology.

That's because all LGR trace gas and isotope analyzers are based on our unique and patented OA-ICOS technology. This fourth-generation cavity-enhanced laser absorption method offers several inherent advantages over older, multipass and cavity based (e.g., conventional CRDS) methods. For instance, OA-ICOS provides the same optical path lengths (20 km or longer) as conventional CRDS but without the expense and vulnerability of a sub-nanometer opto-mechanical setup. This enables it to easily deliver parts per billion precision (or better) quickly and in an easy to use package. And, because OA-ICOS directly measures absorption rather than only a cavity decay time, it offers a linear response over a significantly wider dynamic range than conventional CRDS, e.g., up to 100% mole fraction for some gases.

LGR trace gas and stable isotope analyzers deliver the world's best performance for applications such as climate research, water cycle studies, petrochemical exploration, and emissions compliance monitoring.

Unmatched Reliability

All LGR analyzers combine state-of-the-art performance with robust operation and unmatched reliability, enabling continuous operation in challenging environments, as well as in mobile (truck, ship, aircraft) and remote applications.

LGR achieves this exceptional reliability because all our trace gas and isotope analyzers are based on our patented OA-ICOS technology. This fourth-generation, cavity-enhanced laser absorption method offers several inherent advantages

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1. LGR invented all major cavity enhanced absorption spectroscopy techniques

2. LGR patented OA-ICOS, 4th-gen CEAS

3. Easiest and least expensive to build and have highest reliability

4. *Only* LGR records absorption spectra by continuously tuning laser wavelengths. This yields highest accuracy, superior linearity and largest dynamic range.

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Thank You!

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