Picarro Product Portfolio Update: The new frontier in Cavity Ring-Down Spectroscopy

Kate Dennis, PhD
Product Manager

ASITA Conference, University of California-Davis
June 17th, 2014
Picarro Areas of Expertise

- Spectroscopy Instruments
- Applications & Peripherals
- Software & Services
- Network & Industrial Solutions
Innovation to Enable Scientists

**Atmospheric Science**

Diverse, precise, and accurate measurements of both small or large range of time scales, from seconds to decades.

Picarro analyzers can be deployed in remote locations—without restriction—making them ideal for atmospheric applications.

- Global networks
- Regional and local studies
- Aircraft measurements

**Research Applications**

Global network of monitoring greenhouse gases

Picarro’s greenhouse gas analyzers not only meet the World (WMO) uncertainty requirements for measuring greenhouse gases, but also to the network of stations worldwide.

**Ecology**

By taking high-precision, lab-quality isotope and concentration measurements, Picarro enables scientists to answer relevant questions at all scales.

From an organism’s metabolism, to a soil’s interactions with its environment, Picarro measurements cover it all. With the ability to monitor on the fly to address the most interesting questions.

**Research Applications**

Assess metabolism

This forge primarily during daylight, leading daylight field vegetation monitoring stations at the National Institute for Zoo and Wildlife Research.

**Ocean Science**

Stable isotopes are a powerful tool for understanding aquatic sources and sinks in marine food webs. They also enable scientists to the ocean’s influence on the fluxes and molecular transformations of carbon, water and nitrogen cycles.

**Research Applications**

Stable isotopes can be used to track the movement of water and carbon through plants.

Rugged and mobile Picarro analyzers enable plant scientists to apply precise stable isotope techniques in the field, gaining unprecedented understanding across a range of spatial and temporal scales.

**Plant Science**

Bring new insights to a variety of studies—from global climate modeling to agricultural efficiency optimization—by tracking the movement of water and carbon through plants.

Rugged and mobile Picarro analyzers enable plant scientists to apply precise stable isotope techniques in the field, gaining unprecedented understanding across a range of spatial and temporal scales.

**Research Applications**

Evapotranspiration

Evaporation and transpiration of water from a plant’s leaves transports water from the soil to the atmosphere. In a seminal study, researchers used the oxygen and hydrogen isotope ratio of water vapor collected at different heights above the ground to determine the relative rates of evaporation of water from the ground and transpiration of water from the plants. In addition, the relative transpiration ratios of leaves were distinguished from those of the underlying grasses.

Picarro isotope analyzers have been used to make measurements such as these.
Game-changing measurement technology

Isotope Ratio Mass Spectrometry

Laser Spectroscopy

Field deployable
Application Examples
Crowdsourcing sampling of isotopic weather events

Superstorm Sandy, Gabe Bowen, University of Utah – constructing spatiotemporal water transport patterns from high-density stable isotope monitoring

Photo courtesy of Gabe Bowen
Paleoclimatology

- Water isotopes from ice cores are used to infer past climatic conditions, including temperature reconstructions during the ice ages

- Methane concentration (gas bubble)
- Water isotopes (δD of ice)
- CO₂ concentration (gas bubble)
Water isotopes in real-time

**Continuous analysis of δ¹⁸O and δD values of water by diffusion sampling cavity ring-down spectrometry: a novel sampling device for unattended field monitoring of precipitation, ground and surface waters**

Niels C. Munksgaard*, Chris M. Wurster and Michael I. Bird
James Cook University, Earth and Environmental Sciences, MacGregor Road Building A2, Smithfield, 4878, Australia

**First continuous shipboard δ¹⁸O and δD measurements in sea water by diffusion sampling—cavity ring-down spectrometry**

N. C. Munksgaard · C. M. Wurster · A. Bass · L. Zagorski · M. I. Bird

Photos courtesy of Niels Munksgaard

Air pump and auxiliary power for diffusion sampler

Drierite canisters for dry air supply

L2130-i on a tidal estuary

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Dissolved gases: going beyond water isotopes

Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction

Robert B. Jackson\textsuperscript{a,b,c}, Avner Vengosh\textsuperscript{a}, Thomas H. Darrah\textsuperscript{a}, Nathaniel R. Warner\textsuperscript{a}, Adrian Down\textsuperscript{a,b}, Robert J. Poreda\textsuperscript{c}, Stephen G. Osborn\textsuperscript{d}, Kaiguang Zhao\textsuperscript{a,b}, and Jonathan D. Karr\textsuperscript{a,b}

\textsuperscript{a}Division of Earth and Ocean Sciences, Nicholas School of the Environment and \textsuperscript{b}Center on Global Change, Duke University, Durham, NC 27708; \textsuperscript{c}Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627; and \textsuperscript{d}Geological Sciences Department, California State Polytechnic University, Pomona, CA 91768

Edited by Susan E. Trumbore, Max Planck Institute for Biogeochemistry, Jena, Germany, and approved June 3, 2013 (received for review December 17, 2012)

- G2121-\textit{i} for methane concentrations and $\delta^{13}$C
- Analyzed discrete samples via headspace equilibration
- Study found homeowners living < 1 km of drilling site likely had groundwater contaminated with stray gas
- Similar study by Duke and USGS showed no contamination in Fayetteville shale, AR (Kresse et al., 2012)
Mobile measurements for quantifying emissions
Isotopic Analysis of Dissolved Organic Carbon in Produced Water Brines by Wet Chemical Oxidation and Cavity Ring-Down Spectroscopy

– Randal Thomas¹, Christopher Conaway¹, Nabil Saad², and Yousif Kharaka¹

¹ USGS Menlo Park, CA
² Picarro, Inc., Santa Clara, CA

Picarro G2101-i coupled to OI Aurora at Menlo Park:

• $\delta^{13}C$ of DOC measurements via persulfate oxidation
• $\delta^{13}C$ of DIC measurements by acidification
Honey Adulteration using $\delta^{13}C$

- Honey adulteration with corn syrup using an established AOAC Method
- A single isotope can detect, even potentially quantify, adulteration

![Graph showing $\delta^{13}C$ values for different corn syrup adulteration levels.](image)

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Picarro Surveyor™ for Natural Gas Leaks

Mobile Form Factor:
System hardware designed to be easily vehicle-mounted and mobile, including mobile wireless connectivity, vehicle electrical power.

CRDS Technology:
World’s most sensitive and stable technique for measuring methane and carbon isotopes in methane for gas source identification.

P-Cubed™ (Picarro Processing Platform):
Web-based repository and algorithmic engine for collecting, cataloguing, processing and displaying visually-rich geospatial survey data from multiple Picarro Surveyors.

Field of View
Peak Bubbles
Leak Indication Search Area (LISA) (Wind Markers)
Isotopic Analysis Results

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CRDS: Cavity ring-down spectroscopy
CRDS: time, not absorbance

- CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration and isotopic composition of H₂O (and other molecules, e.g., CO₂, CH₄, N₂O, H₂S, etc.)
- Measure decay rate, rather than absolute absorbance

- Small 3-mirrored cavity ~ 35 cc
- Long effective path-length (> 10 km)
- Time-based measurement
- Laser is switched on and off, and scanned across wavelengths
Turning ring-down times into concentrations

1. Select wavelength using $\lambda$-monitor

2. Measure decay time using CRDS

$$I_{\text{circ}}(t) = I_{\text{circ}}(t_0) \exp\left(-\frac{t}{\tau}\right)$$

3. Calculate loss ($\alpha$)

$$\alpha = \frac{1}{c\tau}$$

Gas concentration is proportional to the area under the curve, given constant $T$ and $P$.
Picarro CRDS Technology

• Concentration analyzers:
  – CO₂, H₂O and CH₄
  – CO₂, H₂O, CH₄ and CO
  – CO₂, H₂O, CH₄, N₂O, NH₃
  – HF
  – CH₂O
  – H₂O₂
  – NH₃

• Isotope analyzers:
  – Δ¹³C in CO₂
  – Δ¹³C in CH₄
  – Δ¹³C in CO₂ and CH₄
  – Δ¹⁸O, Δ¹⁷O, δD and ¹⁷O-excess in H₂O
  – Δ¹⁵N, Δ¹⁵Nα, Δ¹⁵Nβ in N₂O
Isotopic water product line

**L2130-i**: Our most popular three-phase water isotope analyzer for $\delta^{18}O$ and $\delta D$, in the lab or in the field.

**L2140-i**: High-precision triple oxygen isotope research and $\delta D$ in waters.

With associated peripheries:
- High Precision Vaporizer
- Autosampler for liquid injection
- Standards Delivery Module
- Micro-Combustion Module
- Induction Module
- ChemCorrect™
- Dual Mode Kit
# Configuration examples

<table>
<thead>
<tr>
<th>Liquid Water &amp; Vapor</th>
<th>Water Vapor</th>
<th>Matrix-bound water</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>Isotope laboratory</strong>&lt;br&gt;Hydrology&lt;br&gt;Oceanography&lt;br&gt;Ice cores</td>
<td><strong>Evapotranspiration</strong>&lt;br&gt;Climatology&lt;br&gt;Atmospheric research</td>
<td><strong>Plant physiology</strong>&lt;br&gt;Ecology&lt;br&gt;Food authenticity and adulteration</td>
</tr>
<tr>
<td>L2130-(i) or L2140-(i) with A0211 and A0325</td>
<td>L2130-(i) with SDM or L2140-(i) with A0211 and A0325</td>
<td>L2130-(i) with IM or A0211 and A0214 (MCM)</td>
</tr>
</tbody>
</table>
L2140-i: Why triple oxygen isotopes and $^{17}\text{O}$-excess?

- Measure all three isotopes of oxygen in water: $^{18}\text{O}$, $^{16}\text{O}$ and $^{17}\text{O}$

- In itself, $\delta^{17}\text{O}$ is not very useful:
  - Most natural processes that prefer $^{18}\text{O}$, do so twice as much as for $^{17}\text{O}$
  - The result: $\delta^{17}\text{O} \sim 0.5 \delta^{18}\text{O}$

- If both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are determined to a high enough precision, small anomalies in $^{17}\text{O}$ become apparent:

$$^{17}\text{O} - excess = \delta^{17}\text{O} - 0.528 \delta^{18}\text{O} \quad \text{where } \delta' = \ln(\delta + 1)$$

- The current technology for measuring $^{17}\text{O}$-excess is complex, expensive and time-consuming:
  $$< 10 \text{ labs globally measure } ^{17}\text{O}\text{-excess using conventional IRMS techniques}$$
$^{17}$O-excess: a unique tracer for hydrological cycle

Luz and Barkan (2010), GCA, 74, 6276-6286.
$^{17}$O-excess: a unique tracer for hydrological cycle

$^{17}$O-excess can be used to:
- Reconstruct air mass trajectories
- Determine source water regions
- Reconstruct past humidity
- Identify stratospheric injections of water vapor in the atmosphere
- Constrain evapotranspiration budgets at the leaf scale
- Understand cloud convection in the tropics
- And more…

Luz and Barkan (2010), GCA, 74, 6276-6286.
## L2140-i specifications

<table>
<thead>
<tr>
<th></th>
<th>Precision</th>
<th>$\delta^{17}O$</th>
<th>$\delta^{18}O$</th>
<th>$\delta D$</th>
<th>$^{17}O$-excess</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquids</strong></td>
<td>0.025 ‰</td>
<td>0.025 ‰</td>
<td>0.1 ‰</td>
<td>0.015 ‰</td>
<td></td>
</tr>
<tr>
<td>(L2140-i plus High Precision Vaporizer)</td>
<td>Drift (24-hour, for liquids and vapor)</td>
<td>0.2 ‰</td>
<td>0.2 ‰</td>
<td>0.8 ‰</td>
<td>0.2 ‰</td>
</tr>
<tr>
<td>Throughput</td>
<td>up to 160 injections per day [1]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Memory (within X % of final value after 4 injections)</td>
<td>99</td>
<td>99</td>
<td>98</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

| **Vapor** [2]   | Guaranteed precision (1σ) at 12,500 ppm (‘normal mode’) | 0.12 / 0.04 ‰ at 10/100 sec | 0.3 / 0.1 ‰ at 10/100 sec |          |                |
|                 | Guaranteed precision (1σ) at 12,500 ppm (‘$^{17}O$-excess mode’) | 0.04 ‰ at 300 sec | 0.04 ‰ at 300 sec | 0.1 ‰ at 300 sec | 0.015 ‰ at 3,600 sec |
| Measurement range | 1,000 to 50,000 ppm |          |                |          |                |
| Measurement rate | > 1 Hz |          |                |          |                |

[1] Dependent on the number of replicates, this allows for up to 26 samples per day (or 13 if running replicates for $^{17}O$-excess). For ‘normal mode’, high throughput mode of vaporizer gives up to 360 injections per day.

[2] Specifications are given for both the ‘normal mode’, i.e., operating as a standard L2130-i, and in the ‘$^{17}O$ mode’.
Isotopic Carbon Product Line

**G2101-i / G2121-i**: For ambient or high concentration measurements of $\delta^{13}C$ in CO$_2$

**G2131-i**: For ambient concentration measurements of $\delta^{13}C$ in CO$_2$ and [CH$_4$]

**G2132-i**: For ambient concentration measurements of $\delta^{13}C$ in CH$_4$

**G2201-i**: For dual isotopic carbon measurements on CO$_2$ and CH$_4$

With associated peripheries:
- OI Aurora for DIC/DOC
- Autosampler for liquid injection
- Costech Elemental Analyzer
- Small Sample Isotope Module
- Automate FX for carbonate d13C and DIC
- Closed System Recirculation

Enabling a broad range of carbon cycle studies.
One Analyzer…Many Applications

- **OI 1030W** for δ¹³C in DIC & DOC
- **Costech EA** for δ¹³C in bulk materials
- **Combustion module** for δ¹³C in bulk materials
- **AutoMate** for δ¹³C in DIC in water and solid carbonates
- **SSIM2** for small or high concentration samples
- **G2201-i** for δ¹³C in CO₂ and CH₄
- **Closed System kit** for recirculation

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G2201-i: Two analyzers in one

- Measure critical GHGs with one analyzer simultaneously, and continuously, in the lab or in the field:
  - $\delta^{13}C$ on CH$_4$
  - $\delta^{13}C$ on CO$_2$
  - [CO$_2$] and [CH$_4$]

- Two modes for iCH$_4$:
  - High precision for best results at near-ambient concentrations
  - High range for variable concentrations, up to 1,000 ppm

<table>
<thead>
<tr>
<th>Specifications</th>
<th>G2201-i iCO$_2$ mode</th>
<th>G2201-i High Precision - iCH$_4$</th>
<th>G2201-i Simultaneous mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}C$ CO$_2$ Precision (1σ, 5-min average)</td>
<td>&lt;0.12‰ at 380 – 2000 ppm</td>
<td></td>
<td>&lt;0.16‰ at 380 – 2000 ppm</td>
</tr>
<tr>
<td>$\delta^{13}C$ CO$_2$ Drift (peak-to-peak of 1 hr average over 24 hrs)</td>
<td>&lt;0.6‰ at 380 – 2000 ppm</td>
<td></td>
<td>&lt;0.6‰ at 380 – 2000 ppm</td>
</tr>
<tr>
<td>$\delta^{13}C$ CH$_4$ Precision (1σ, 5-min average)</td>
<td></td>
<td>&lt;0.8‰ at 1.8 – 12 ppm</td>
<td>&lt;1.15‰ at 1.8 – 12 ppm</td>
</tr>
<tr>
<td>$\delta^{13}C$ CH$_4$ Drift (peak-to-peak of 1 hr average over 24 hrs)</td>
<td></td>
<td>&lt;1.5‰ at 10ppm</td>
<td>&lt;1.5‰ at 10ppm</td>
</tr>
</tbody>
</table>
Greenhouse Gas and Atmospheric Applications

Concentration Measurements

- G2301 → CO₂ CH₄ H₂O
- G2401 → CO₂ CO CH₄ H₂O
- G2401-m → CO₂ CO CH₄ H₂O for flight

Isotope Measurements

- L2130-i → δD and δ¹⁸O in H₂O
- G2131-i → δ¹³C in CO₂
- G2132-i → δ¹³C in CH₄
- G2201-i → δ¹³C in CH₄ and δ¹³C in CO₂
Nitrogen Cycle and Soil Applications

- **G5101-i**: Concentration and isotope measurements on N\textsubscript{2}O in the mid-IR ($\delta^{15}\text{N}$, $\delta^{15}\text{N}_\alpha$, $\delta^{15}\text{N}_\beta$)

- **G2508**: Simultaneous measurement of five critical greenhouse gases (CO\textsubscript{2}, N\textsubscript{2}O, NH\textsubscript{3}, CH\textsubscript{4}, H\textsubscript{2}O) for soil flux measurements

- With associated peripherals:
  - Closed system recirculation (G2508 and G2201-i)
  - SSIM2
**G5101-i for δ^{15}N, δ^{15}N^\alpha and δ^{15}N^\beta**

### Guaranteed Performance Specifications

<table>
<thead>
<tr>
<th>Target Species</th>
<th>Precision 1-σ</th>
<th>Concentration Range (ppm N₂O in Air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O (Concentration)</td>
<td>&lt; 0.05 ppb</td>
<td>0.3 - 2</td>
</tr>
<tr>
<td>δ^{15}N, δ^{15}N^\alpha, δ^{15}N^\beta</td>
<td>&lt; 0.5 %</td>
<td>0.3 - 2</td>
</tr>
</tbody>
</table>

### Graph

- **HITRAN model at 990 ppb**
- Wavenumber [cm⁻¹]
- Loss [ppm/cm]
- Peaks at 2187.0, 2187.1, 2187.2, 2187.3, 2187.4, 2187.5, 2187.6, 2187.7 cm⁻¹
- Peaks for N₂O, N₂O, H₂O
- δ^{15}N^\beta and δ^{15}N^\alpha

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G2508 for soil flux measurements

- Each molecule is measured every 7 seconds
- Dry mol fraction is calculated and reported
- Continuous gas flow at ~ 240 sccm

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Specified Precision (1σ of 5 min averages)</th>
<th>Guaranteed Specification Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>&lt; 5 ppb</td>
<td>0.3 to 200 ppm</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>&lt; 200 ppb</td>
<td>380 to 5,000 ppm</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>&lt; 5 ppb</td>
<td>1.5 to 12 ppm</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>&lt; 1 ppb + 0.05% of reading</td>
<td>0 to 300 ppb</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>&lt; 100 ppm</td>
<td>0 to 3 %</td>
</tr>
</tbody>
</table>

For comparison with GC, see Nabil Saad’s poster.
Easy Integration with Chamber Systems

- Picarro G2508 & G2201-i are capable of measuring dynamic soil flux when used with closed & open system chambers.

**Closed Loop**
G2508 / G2201-i
Closed System
Recirculation system includes a leak free vacuum pump.

**Open system**
G2508 / G2201-i
Standard vacuum pump.
# Picarro Performance and Certification

**APPLICATION:** Isotopic Water Liquid  
**MODEL:** L2130-i  
**INSTRUMENT SN:** xxxx

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SPECIFICATION</th>
<th>VALUE</th>
<th>UNITS</th>
<th>Pass/Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LIQUID WATER SPECIFICATIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D/H PRECISION PER SAMPLE</td>
<td>≤ 0.100</td>
<td>0.066</td>
<td>permil</td>
<td>Pass</td>
</tr>
<tr>
<td>D/H DRIFT PER SAMPLE</td>
<td>≤ 0.800</td>
<td>0.261</td>
<td>permil</td>
<td>Pass</td>
</tr>
<tr>
<td>18O/16O PRECISION PER SAMPLE</td>
<td>≤ 0.030</td>
<td>0.017</td>
<td>permil</td>
<td>Pass</td>
</tr>
<tr>
<td>18O/16O DRIFT PER SAMPLE</td>
<td>≤ 0.200</td>
<td>0.059</td>
<td>permil</td>
<td>Pass</td>
</tr>
<tr>
<td>D/H MEMORY</td>
<td>≤ 98</td>
<td>98.1</td>
<td>percent of final value</td>
<td>Pass</td>
</tr>
<tr>
<td>18O/16O MEMORY</td>
<td>≤ 99</td>
<td>99.0</td>
<td>percent of final value</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Proof point # 1: minimal drift

Picarro L2130-i has minimal drift

- Fewer calibration standards are required

Continuous liquid injection of the same sample over 64 hours (almost 3 days!)

\[ \delta D = -100.67 \pm 0.12 \% \]

\[ \delta^{18}O = -13.54 \pm 0.05 \% \]
Proof point #2: L2140-\textit{i} performance over 48 hours

Two samples run back-to-back on an L2140-\textit{i} with High Precision Vaporizer (no calibration)

- OH16: $0.034 \pm 0.008$ \textperthousand
- Kona Deep: $-0.001 \pm 0.005$ \textperthousand
Proof point # 3: insensitive to ambient fluctuations

A 30°C change in ambient temperature has no significant effect on $\delta D$

- Data was acquired over ~ 8 hours
- Any change related to temperature is within analyzer noise

- 0.002 ‰ per ºC
Proof point # 4: destruction of alcohols

See Rhian Rees-Owen’s poster (with Paul Brooks/Todd Dawson.)
Proof point # 5: G2401 Stability and Precision

- **Guaranteed stability** over 30 days ($\text{CH}_4$): < 3 ppb ($0.16\%$ @1.9 ppmv)

- **Guaranteed stability** over 30 days ($\text{CO}_2$): < 50 ppb ($0.012\%$ @390 ppmv)

Picarro analyzer stability measured over 30 days:

- $\text{CH}_4$ 0.5 ppbv (1-$\sigma$)
- $\text{CO}_2$ 11.2 ppbv (1-$\sigma$)
- $\text{H}_2\text{O}$ < 2.5 ppm (1-$\sigma$)
Proof point # 6: G2508 drift over 2 days

- **CO₂**: 2.5 ppm
- **CH₄**: 3.5 ppb
- **N₂O**: 50 ppb
Challenges and tips for users

Measuring water isotopes by CRDS, or any other laser technique, has its challenges:

1. Water is sticky…memory

2. Not all water is created equal…spectral interferences

3. Salty samples leave residues…vaporizer performance

4. All systems drift with time…calibration

5. Water can evaporate…storing standards

6. Moving parts can fail…syringe lifetime

Useful references include:
- Picarro community: http://www.picarro.com/community/community_info
- van Geldern and Barth (2012), L&O: Methods, 10, 1024–1036
- LIMS for Lasers
- Wasenaar, Coplen and Agaarwal (2014), Environmental Science and Technology, 48, 1123-1131
Questions?

• Feel free to contact me offline:
  – kdennis@picarro.com
  – +1 (408) 962 3965

Picarro isotopic water analyzers: used and recommended by the world’s leading scientists, in industry and academia, and by governmental bodies.

*selected Picarro customers
High Precision Vaporizer and Autosampler (A0211 and A0325)

Simultaneous and automated measurements of $\delta^{18}O$ and $\delta D$

- Standard injection volume < 2 $\mu$L (< 20 $\mu$L per sample)
- Recommend 6 injections per sample
- TDS < 200 g/L (seawater is ~ 35 g/L)
- Two modes of operation:
  - High precision: 9 min/injection
  - High throughput: 4 min/injection
- Requires either dry N$_2$ tank or zero air
- Autosampler is controlled by on-board computer for improved remote access
Eliminate organic interferences in-line by combusting alcohols to CO₂ and H₂O

- Proprietary MCM connects directly to high precision vaporizer
- Optimized for efficient removal of organics typically found in plant extracts
  - Alcohols, terpenes and green-leaf volatiles
- Requires zero air carrier gas for oxidative removal of organics
- Must be purchased with High Precision Vaporizer (A0211)
Induction Module (A0213)

Quick and easy analysis of matrix-bound water from solid samples

- Prepare and analyze water extracted from solid samples and liquids with high total dissolved solids
  - Plant leaves
  - Stems
  - Juices
- Easily integrated with the L2130-i
- Substitutes for traditional cryogenic distillation systems which require skilled operators
- Micro Combustion Cartridge is in-line to remove interfering organics (zero air required)
- Guaranteed precision for calibration waters:
  - $\delta^{18}O = 0.35 \%$
  - $\delta D = 1.5 \%$
- Customer must be willing to doing methods development for their sample type

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ChemCorrect™

Clear and easy identification of contaminated sample

- On-board software identifies and flag samples based on comparison to standard, clean waters
  - Spectra are analyzed for changes in baseline features, fit residual, and the presence of alcohols or methane
- Tested with methanol and ethanol solutions up to:
  - 5% EtOH, 0.1% MeOH and mixtures
- Standard on all L2130-i

Standard waters used for calibration

Unknown, clean samples

Sample suspected of contamination

Contaminated samples that require pre-treatment or cannot be using laser techniques

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Small Sample Isotope Module

- Measure very low concentration of CO₂, CH₄ and other small samples
  - 20ml of soil flux from a chamber, CO₂ and CH₄ at ambient concentrations
  - 5ml of headspace from a water sample, 500ppm CH₄
  - 2ml of underground soil gas, 3% CO₂
  - 100μl of pure CO₂
- Inject samples by syringe, bags or any other sample container
- Introduce single samples manually, or automatically process up to eight samples using Picarro’s 16-Port Distribution Manifold

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High Precision DIC/DOC/TIC/TOC/NPOC and δ13C of acidified or oxidized samples

OI Aurora 1030W TOC Analyzer
- Direct TC/TIC/TOC/NPOC analysis using NDIR detector
- TIC as CO2 via acidification
- TOC of aqueous samples as CO2 via wet oxidation
- TC = TIC + TOC (LDL 2 ppb)

PICARRO G2121i, G2201i, G2131-i δ13C in CO2
- δ13C guaranteed precision 0.3 ‰ (5 min, 1-σ)
- δ13C typical precision of 0.2 ‰ (5 min, 1-σ)
- δ13C guaranteed ambient air precision of 0.1 ‰ (5 min, 1-σ) when used independently of TOC
- CO2 guaranteed concentration 200 ppb (30 sec, 1-σ)
- Equipped with pulse integration software for direct handling of TOC analyzer byproducts
Picarro Caddy for interfacing front-ends

**A0201 Combustion Module**
- Combustion of bulk samples
- Fully automated
- No chemical sample prep required
- Samples heated in O₂ to 980°C
- TOC/TC values available via calculation

**Aurora 1030W TOC Analyzer**
- DIC/TIC via acidification (10% phosphoric acid)
- TOC/NPOC via oxidation (sodium persulfate) after removal of DIC
- TC via TIC + TOC calculation
- Option for addition of Aurora 1088 Autosampler

**A2100 TOC/TC Integration Kit includes:**
- A0401 Caddy with manual valve for quick switching between two front-end devices and buffer volume to produce the optimal CO₂ concentration profile
- S0505 Pulse integration software to quantitate the concentration and isotopic ratios of CO₂

**Picarro δ¹³C in CO₂ Analyzer**
SOFTWARE/HARDWARE REQUIREMENTS:

- Costech 4010 (purchase from Costech)
- Picarro $\delta^{13}$C in CO$_2$ Analyzer
- A2100 TOC Integration Kit
  - Hardware connection kit with buffer volume
  - Pulse integration CRDS software upgrade
  - **Has two inputs with manual valve for simultaneous connection to Aurora 1030W TOC analyzer for complete liquid / solid analysis**
- A0504 Helium Fitter (Costech ECS 4010)
  - Accommodates the use of Helium as a carrier gas
- 30cm packed GC column (Standard column inside ECS 4010 is 3m)
  - Can be purchased directly from Costech
Liaison Universal Interface

In Parallel:

1. Admits gas sample from front-end
2. Collects current processed sample
3. Delivers previous sample to CRDS
4. Purges gas bag to collect next sample

Fully Automated
Automate FX for DIC and $\delta^{13}$C on carbonates
16-Port Valve Manifold

Automated sampling from multiple sources

• Features
  – Compatible with all instrument models except sticky/reactive gases like NH3
  – Fully controlled by analyzer
  – Valve state is recorded in user data file for easy data analysis

• Uses:
  – Switch easily between different tower heights
  – Switch between standards for calibration
Standards Delivery Module (A0101)

Automated delivery of isotopic water standards

- For use with L2130-\(i\) or L2140-\(i\)
- Requires High Precision Vaporizer (A0211)

- Features
  - Delivers **two standards at up three different concentrations** to calibrate ambient water vapor measurements in the field
  - Simple batch processing included with software
  - Guaranteed precision:
    - \(\delta^{18}O = 0.1 \, \%\)
    - \(\delta D = 0.5 \, \%\)
Isotopic Water: Dual Mode Kit (A0912)

Automatic switching between ambient water vapor and calibration using the Picarro Autosampler

- Alternative to SDM for dual analysis of liquid water and water vapor
- Sample ambient vapor from a tower and calibrate with liquid water injections
- Requires High Precision Vaporizer and Picarro Autosampler (A0211 and A0325)
Typical Atmospheric Monitoring Set-up

Tower
- 100m (L1)
- 70m (L2)
- 40m (L3)
- 10m (L4)

To Tower (L1, L2, L3, L4)

12 mm OD Dekabon/Synflex1300 tubing With Swagelok™ Tees (SS-400-3)

Secondary vacuum pumps (KNF or equivalent)

Exhaust

(16-port) Multiplexer

Analyzer

Calibration cylinders

Target/Reference cylinders

¼” OD Dekabon/Synflex1300 tubing to analyzers
## Picarro G2401 Specifications

<table>
<thead>
<tr>
<th>Performance Specifications, in dry air</th>
<th>CO₂</th>
<th>CO</th>
<th>CH₄</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision (5 sec / 5 min, 1-σ)</td>
<td>&lt;150 ppb / &lt;50 ppb</td>
<td>&lt;30 ppb / &lt;2 ppb</td>
<td>&lt; 1 ppb / &lt; 0.7 ppb</td>
<td>&lt; 200 ppm / &lt; 50 ppm</td>
</tr>
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<td>Guaranteed for below specified range &amp; conditions - reference gas not needed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max Drift at STP (over 24 hrs / 1 month) (peak-to-peak, 50-minute average)</td>
<td>150 ppb / 500 ppb</td>
<td>15 ppb / 50 ppb</td>
<td>1 ppb / 3 ppb</td>
<td>100 ppm ± 5% of reading</td>
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<td>Max Uncertainty Using Reference Gas* (1hr average, 2-sigma)</td>
<td>&lt; 50 ppb</td>
<td>&lt; 2 ppb</td>
<td>&lt; 1 ppb</td>
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<tr>
<td>Meets WMO Data Quality Objective for GAW Stations</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Automated Determination of Dry Mol Fraction</td>
<td>Included</td>
<td>Included</td>
<td>Included</td>
<td>n/a</td>
</tr>
<tr>
<td>Operating Range</td>
<td>0 – 1000 ppm</td>
<td>0 – 5 ppm</td>
<td>0 – 20 ppm</td>
<td>0 – 7 %v H₂O / 39 °C dew pt (non-condensing)</td>
</tr>
<tr>
<td>Guaranteed Specifications Range</td>
<td>300 – 500 ppm</td>
<td>0 – 1 ppm</td>
<td>1 – 3 ppm</td>
<td>0 – 3 %v H₂O / 25 °C dew pt (non-condensing)</td>
</tr>
<tr>
<td>Measurement Interval</td>
<td>&lt; 5 seconds</td>
<td>&lt; 5 seconds</td>
<td>&lt; 5 seconds</td>
<td>&lt; 5 seconds</td>
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<tr>
<td>Rise/Fall time (10 - 90 % / 90 - 10%)</td>
<td>&lt; 5 seconds</td>
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</tbody>
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# Picarro G2401 Specifications

Aligns with GAW Expert Group Recommendations:

- CO₂ ± 0.1 ppm (± 0.05 ppm in Southern Hemisphere)
- CH₄ ± 2 ppb
- CO ± 2 ppb
- 2σ inter-laboratory comparison for 1 hour averaging

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<td>Included</td>
<td>n/a</td>
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Isotopic flux measurement with Forerunner chambers
Dissolved Gas Methodologies

Gas extraction or equilibrium device

$\text{CH}_4, \delta^{13}\text{C}, \delta^{15}\text{N}, \text{etc.}$
Underway $f_{\text{CO}_2}$ and $\delta^{13}\text{C(CO}_2)$ measurements

- Commercial showerhead equilibration system coupled to first generation Picarro (EnviroSense 2050) for CO$_2$ and $\delta^{13}\text{C}_{\text{CO}_2}$

- Equilibrated gas was dried by thermoelectric cooler and Nafion pump prior to CRDS analysis

- Switching valve for sampling equilibrator, atmosphere and standard tank

- Results compared to LiCOR (concentrations) and discrete IRMS samples ($\delta^{13}\text{C}_{\text{DIC}}$)

- CO$_2$ ppm converted to $f_{\text{CO}_2}$ using Dickson et al. (2007)

Becker et al. (2012), L&O Methods, doi: 10.4319/lom.2012.10.752
Interfacing equilibrators with Picarro G2201-i

- 2 in-line showerhead equilibrators with drierite column
- *Used for:* estuarine survey and tidal time series

- Liqui-cel membrane contactor with drierite column in closed system water loop
- *Used for:* seagrass benthic chamber

**Maher et al. (2013), EST, doi: 10.1021/es4027776**
Innovative ways to measure DIC with a Picarro

Semi-continuous and autonomous methodologies:

**ISO-CADICA:** Bass et al. (2012), RCM, doi:10.1002/rcm.6143
- Membrane extraction with acidification
- \([\text{DIC}]\) and \(\delta^{13}\text{C}_{\text{DIC}}\)
- \(\delta^{13}\text{C}_{\text{DIC}} \pm 0.1 \, \text{‰ with DIC} > 0.3 \, \text{mM}\)

**Isotope dilution method:** Huang et al. (2013), L&O Methods, doi:10.4319/lom.2013/11.572
- \(^{13}\text{C}\) spiking method with acidification and membrane extraction
- \([\text{DIC}]\) only
- \([\text{DIC}] \pm 0.07\% (\pm 0.09\% \, \text{shipboard})\)
- Accuracy better than 0.1\%
Proof point #4: superior stability and precision

Blue data are Picarro
Red data are LGR
Crosses (+) are early generation analyzers
Circles (○) are current generation analyzers

Adapted from Figure 8 of Aemisegger et al. (2012), AMT
Proof point #8: Flight performance

- G2301-\textit{m} performance for simulated flight conditions using a barometric chamber during instrument testing.

With Picarro Pressure Correction

Without Picarro Pressure Correction
Proof point # 6: Allan variance and CO stability

- Comparison of long-term stability of CO measurements
- Picarro GHG analyzer (G2401) remains stable, and drift free, over hours
- Other techniques can start to drift after 5 to 15 minutes

# L2130-i specifications

<table>
<thead>
<tr>
<th></th>
<th>δ(^{18})O</th>
<th>δ(^{2}D)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L2130-i plus High Precision Vaporizer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precision</td>
<td><strong>0.025 ‰</strong></td>
<td><strong>0.1 ‰</strong></td>
</tr>
<tr>
<td>Drift (24-hour, for liquids and vapor)</td>
<td>0.2 ‰</td>
<td>0.8 ‰</td>
</tr>
<tr>
<td>Throughput</td>
<td>up to 360 injections per day [1]</td>
<td></td>
</tr>
<tr>
<td>Memory (within X % of final value after 4 injections)</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
<td><strong>Vapor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guaranteed precision (1σ) at <strong>12,500 ppm</strong></td>
<td>0.12 / 0.04 ‰ at 10/100 sec</td>
<td>0.3 / 0.1 ‰ at 10/100 sec</td>
</tr>
<tr>
<td>Guaranteed precision (1σ) at <strong>2,500 ppm</strong></td>
<td>0.25 / 0.08 ‰ at 10/100 sec</td>
<td>1.6 / 0.5 ‰ at 10/100 sec</td>
</tr>
<tr>
<td>Measurement range</td>
<td>1,000 to 50,000 ppm</td>
<td></td>
</tr>
<tr>
<td>Measurement rate</td>
<td>&gt; 1 Hz</td>
<td></td>
</tr>
<tr>
<td><strong>Solids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L2130-i plus Induction Module)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precision</td>
<td>0.35</td>
<td>1.5</td>
</tr>
</tbody>
</table>

[1] High precision vaporizer has two modes: high precision for up to 160 injections per day and high throughput for up to 360 injections per day.
Brainstorming... mule survey for fugitive emissions
Picarro Greenhouse Gas Analyzers

Built for flux chamber measurements

Iowa State University – Bio-char Experiments

CERN & CNEN – Haibei Alpine Station, Qinghai Province

CSIRO – Australian Reservoirs

Lab

Field

Floating

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