



# 28 Semana de la Salud Ocupacional

Lo humano y lo técnico  
en un mundo que se transforma

Organiza:

**CSOA**  
CORPORACIÓN DE SALUD  
OCUPACIONAL Y AMBIENTAL

42° Congreso de Ergonomía, Higiene,  
Medicina y Seguridad Ocupacional.

Hotel Intercontinental Medellín - Colombia  
2, 3 y 4 de noviembre de 2022

# PICARRO

Providing Solutions to the World's  
Most Challenging Environmental  
Questions



# AGENDA

1. Picarro Intro
  2. What makes CRDS so special?
  3. Analyzers for GHG & Trace Gases – Case Studies
  4. Solutions for Hazardous Air Pollutants – Case Studies
  5. Surrogate gas validation
  6. Q/A
- 





# WHO ARE WE?

- **Leading provider of solutions** to measure greenhouse gas concentrations, trace gases and stable isotopes in **industrial monitoring**, air quality, **energy and utilities** markets.
- Over 45 patents owned by Picarro or exclusively licensed from Stanford University
- ISO 9001:2015 Certified Corporate Headquarters, including R & D, Engineering and Manufacturing/Operations in Santa Clara, California
- 220+ employees including 35+ STEM PhDs
- Thousands of Picarro instruments in 95 countries world-wide



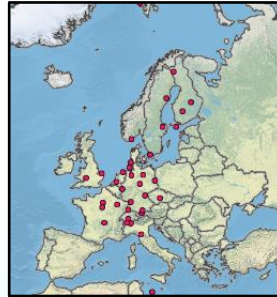
# 20+ YEAR HISTORY OF CONTINUOUS MONITORING

**28** Semana  
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National Ecological Observatory Network

**ICOS** Integrated  
Carbon  
Observation  
System

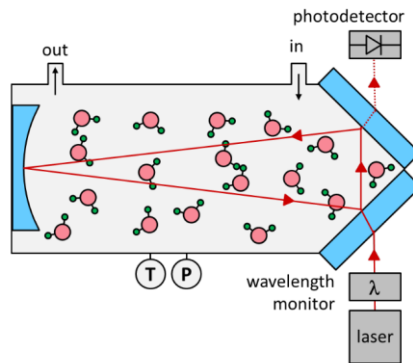


World Meteorological Organization

Global Atmospheric Watch



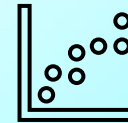
# WHAT MAKES PICARRO CRDS SO SPECIAL?



Real-Time, continuous measurements



No sample pretreatment, chromatographic separation, or complex peripherals



Specific & sensitive to a wide variety of compounds and applications



Turn-key, low operating costs, long-term stability

# ANALYZERS FOR GHG & TRACE GASES

Carbon Dioxide (CO<sub>2</sub>)



Carbon Monoxide (CO)



Methane (CH<sub>4</sub>)



Nitrous Oxide (N<sub>2</sub>O)



Water (H<sub>2</sub>O)



Acetylene (C<sub>2</sub>H<sub>2</sub>)



Ammonia (NH<sub>3</sub>)



Ethane (C<sub>2</sub>H<sub>6</sub>)



Ethylene (C<sub>2</sub>H<sub>4</sub>)





# CASE STUDY – GHG NETWORKS

**G2301:** CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O  
**G2401:** CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O



Eiffel Tower  
Paris, France  
~320m



Penn State Tower  
Centerville, IA  
~110m



KCRA Walnut  
Grove Tower  
(LBL/CALGEM)  
Walnut Grove, USA  
~470m



Shenzhen Meteorological Gradient  
Tower (SZMGT)  
Shenzhen, China  
~350m



Tokyo Skytree  
Tokyo, Japan  
~630m

## Stability

No need for constant  
adjustment for humidity  
or other atmospheric  
changes



*The Gold Standard for Atmospheric GHG Measurements*

# CASE STUDY – METROCLIMA MEGACITIES – Sao Paulo

**G2301-m:**  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$

**G2201-i :**  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and of  $\text{CH}_4$

**G2311-f:**  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$



- **PICARRO G2301-m - Pico do Jaragua:**  
<http://www.metroclima.iag.usp.br/stations/pico-do-jaragua/>
- **PICARRO G2401 - UNICID:**  
<http://www.metroclima.iag.usp.br/stations/unicid/>
- **PICARRO G2301 & G2201-I - IAG:**  
<http://www.metroclima.iag.usp.br/stations/iag/>
- **PICARRO G2311-f – ICESP:**  
<http://www.metroclima.iag.usp.br/stations/icesp/>



# CASE STUDY – FLIGHT MONITORING

**G2401-m** :  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  for flight @ 1 Hz



## Speed

Flight-optimized design elements minimize effects of aircraft vibration, pitch, roll, and rapidly changing ambient conditions.



# CASE STUDY – EDDY COVARIANCE

**G2311-f** :  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$



Picarro's Superflux at the Cabauw Superstation: InGOS Flux Instrument Trial | Picarro

## Speed

Flux mode precision of  
 $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  at  
10 Hz!





# CASE STUDY – MID-IR SOLUTIONS

**G5310:**  $\text{N}_2\text{O}$ , CO and  $\text{H}_2\text{O}$



Hai Luo Gou background station



ShenZhen CMA

## Sensitivity

Parts-per-trillion (ppt) sensitivity  
meets WMO & ICOS  
performance requirements for  
 $\text{N}_2\text{O}$  and CO monitoring



# CASE STUDY – SOIL FLUX

G2308:  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$

G2508:  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$



[Eri Saikawa Emory University](#)

## Simplicity

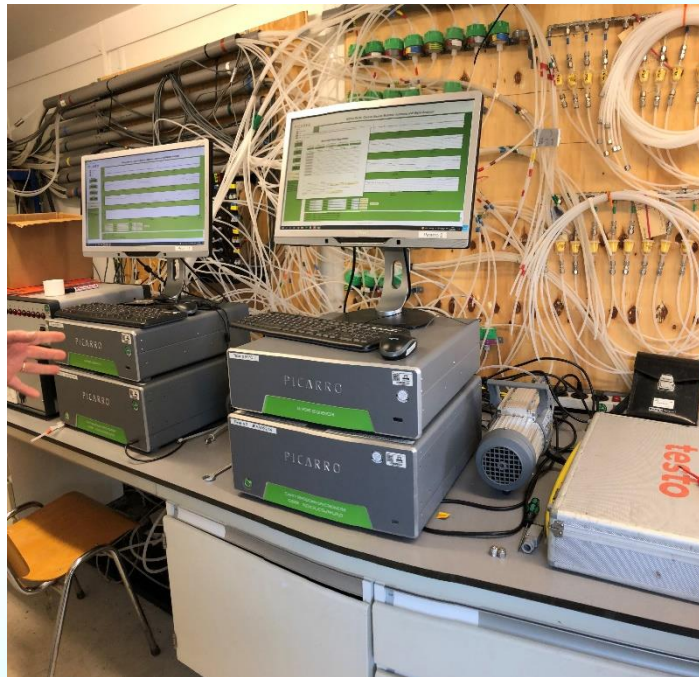
$\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  all in a single analyzer! Open or closed systems integrating easily with 3<sup>rd</sup> party/custom chamber systems





# CASE STUDY – LIVESTOCK FARMING

G2509: CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>O and H<sub>2</sub>O



## Speed

Optimized flow path for fast ammonia response!



[Dairy Campus](#) based in Leeuwarden, NL part of the [Wageningen University & Research \(WUR\)](#).

# CASE STUDY – PORTABLE SOLUTIONS

## G4301: CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O GasScouter



Methane emissions from trees: Resolving the drivers, fluxes and significance of this overlooked pathway...and how we got here | Picarro

### Scouter!

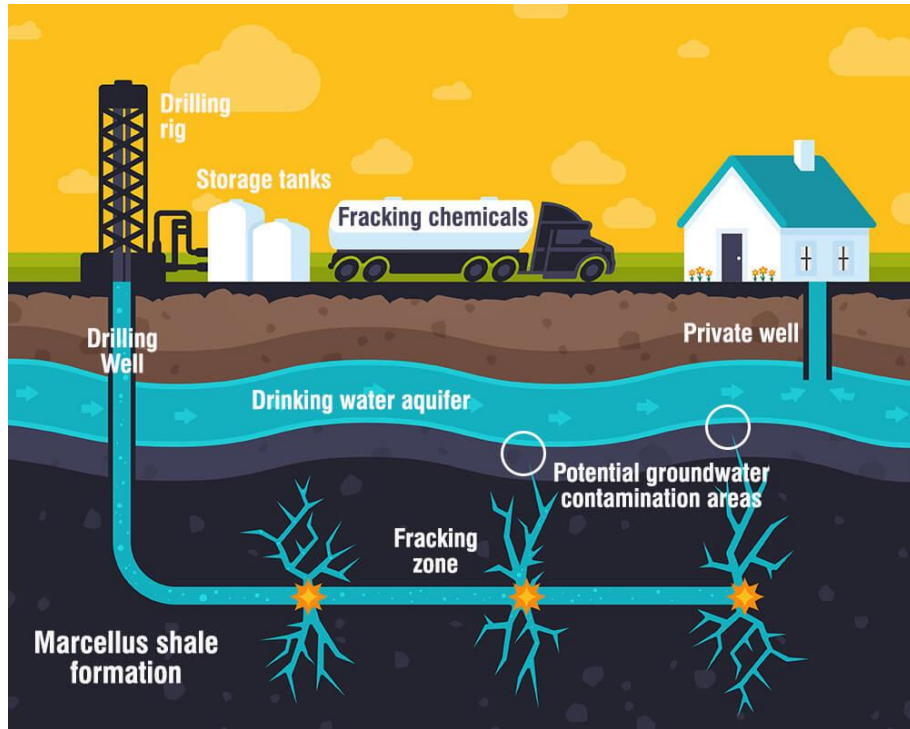
Lightweight, portable  
rugged solutions





# CASE STUDY – WATER TRACING

L2130-i:  $\delta^{18}\text{O}$  and  $\delta\text{D}$



# CASE STUDY – PALEOCLIMATE

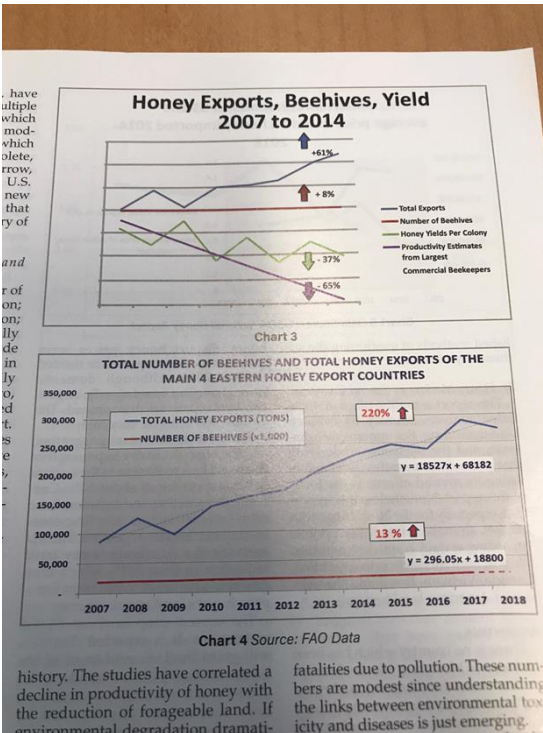
L2130-i:  $\delta^{18}\text{O}$  and  $\delta\text{D}$





# CASE STUDY – HONEY, LEMON JUICE ADULTERATION

## G2121-i : d13C of CO<sub>2</sub> A0201: Combustion Module



**A Comparison of IRMS and CRDS for the Detection of Economic Adulteration of Lemon Juice and Honey**

Madhavi Mantha, John R Urban and Kevin M. Kubachka  
US FDA, Forensic Chemistry Center, Cincinnati, OH  
ASITA June 2016, Philadelphia, PA

**Introduction**

In the last several years, economically motivated adulteration (EMA) of foods has received increased attention. Two popular targets are lemon juice and honey. For both of these types of adulteration analysis, the FDA is evaluating the use of Cavity Ring Down Spectroscopy (CRDS) to establish its suitability in comparison to the well established technique Isotope Ratio Mass Spectrometry (IRMS).

- Addition of Ca material will alter natural  $\delta^{13}C/^{12}C$  ratio, indicative of adulteration.
- Lemon juice adulterated with exogenous citric acid and/or low cost sweeteners → Ca plant source
- Honey adulterated with low cost sweeteners → Ca plant source.
- Lemon juice samples are imported, part of an FDA assignment.
- Honey samples bought from local markets.
- Basic Procedure: Citric acid precipitate from lemon juice or bulk honey and protein precipitate → combusted in IRMS and CRDS for determination of  $\delta^{13}C/^{12}C$  (converted to per mil basis ( $\delta^{13}C$ ‰)).
- $\delta^{13}C$  citric acid less negative than -20‰ is indicative of lemon juice adulteration.
- $\delta^{13}C_{\text{citric acid}} - \delta^{13}C_{\text{honey}}$  less negative than -1‰ is indicative of honey adulteration.

**Instrument and Operation EA-IRMS**

Cotech Elemental Combustion System (CECS 4103)

**Method Development and Validation for Lemon Juice**

- Doner L. "Carbon Isotope Ratio in Natural and Synthetic Citric Acid as Indicators of Lemon Juice Adulteration, J. Agric. Food Chem. 22(1985) 770-772
- Method development to optimize calcium citrate precipitation
- Varying amounts of Ca(OH)<sub>2</sub>
- Heating time
- Changing the pH with NaOH and NH<sub>4</sub>OH
- Measurable CO<sub>2</sub> background signal
- From carbonate contamination in Ca(OH)<sub>2</sub> reagent present in calcium citrate precipitate.
- On achieving satisfactory results, focus was shifted to Using Ca(NO<sub>3</sub>)<sub>2</sub> and CaCl<sub>2</sub>
- Varying the conditions as mentioned above
- Finally using 2 mL of 3M CaCl<sub>2</sub> solution at pH greater than 8.5 and heating at 60°C for 2 hours, produced calcium citrate precipitate, free of carbon contamination
- Validation
- Two commercially available citric acids
- Three locally purchased lemon juice from concentrates
- Freshly squeezed locally purchased lemons

**Methodology for Honey**

ADAC Method 908.12

**IRMS Vs CRDS for Lemon Juice**

Comparison of the  $\delta^{13}C$  (VPDB) (‰) values IRMS vs CRDS

$\delta^{13}C$  (VPDB) (‰) CRDS

$\delta^{13}C$  (VPDB) (‰) IRMS

$R^2 = 0.999$

- 69 samples were analyzed by CRDS and IRMS and the results were compared.
- From IRMS analysis, 9 were Adulterated, 7 were Inconclusive and 53 were Not Adulterated
- From CRDS analysis, 9 were Adulterated, 1 was Inconclusive and 59 were Not Adulterated
- The difference in  $\delta^{13}C$  (VPDB) (‰) values between IRMS and CRDS ranged from -0.13 ‰ to +0.58 ‰.

**Conclusion**

- For both IRMS and CRDS analysis for lemon juice and bulk honey and protein, the results were quite comparable.
- The average difference in  $\delta^{13}C$  (VPDB) (‰) values between IRMS and CRDS for lemon juice was 0.36‰.
- The average difference in  $\delta^{13}C$  (VPDB) (‰) values between IRMS and CRDS for bulk honey was 0.28‰.
- The above results indicate that the new CM-CRDS is quite suitable for adulteration analysis when applied to lemon juice and honey samples.

**Future Work**

- To explore the CM-CRDS instrument on more honey samples and extend to other matrices like maple syrup and other fruit juices.

**Acknowledgements**

PICCARO Support Group

**CM-CRDS Instrument and Operating Principle**

**CRDS Schematic and Operation**

**Reference Materials (RM) and Quality Control**

- NIST RM 8542 (Sucrose,  $\delta^{13}C_{\text{VPDB}} = -10.45 \pm 0.07$ ‰)
- NIST RM 8573 (L-glutamic Acid,  $\delta^{13}C_{\text{VPDB}} = -26.39 \pm 0.09$ ‰)
- Acetamide - used to condition reactors and verify measurement performance for  $\delta^{13}C$ .
- RMs are used to normalize instrument  $\delta^{13}C$  to sample based  $\delta^{13}C_{\text{VPDB}}$  using Excel for calculations

**Advantages and Disadvantages**

**EA-IRMS**

- Well established technique with good linearity and precision
- High maintenance
- High degree of technical knowledge needed for operation
- Very expensive
- Used for  $^{13}C/^{12}C$ ,  $^{14}C/^{12}C$ ,  $^{15}N/^{14}N$ ,  $^{18}O/^{16}O$ ,  $^{34}S/^{32}S$  and  $^{41}Ar/^{39}Ar$

**CM-CRDS**

- Relatively inexpensive
- Robust
- Simplified analysis technique
- Relatively new technique with no officially defined methods.
- Only works for  $^{13}C/^{12}C$  analysis



# SOLUTIONS FOR HAZARDOUS AIR POLLUTANTS

Acetylene ( $C_2H_2$ )



Ammonia ( $NH_3$ )



Ethylene Oxide ( $C_2H_4O$ )



Formaldehyde ( $H_2CO$ )



Hydrogen Chloride ( $HCl$ )



Hydrogen Fluoride ( $HF$ )



Hydrogen Sulfide ( $H_2S$ )





# HOW IS PICARRO CRDS BEING UTILISED?



Ambient Air Quality monitoring

Fenceline monitoring stations

Mobile monitoring surveys

Leak Detection & Repair (LDAR)

Continuous Emissions Monitoring (CEMS)

Multipoint Indoor Air Quality monitoring

Stack Testing

Real-Time Analyzers



Turnkey Systems



Mobile Solutions

# CASE STUDY – REFINERY COMMUNITY AMMONIA

**G2103:**  $\text{NH}_3$  and  $\text{H}_2\text{O}$



## Stability

Existing fenceline monitors in use required constant calibration and service





# CASE STUDY – INDOOR AIR HCl

## G2108: HCl and H<sub>2</sub>O



### Speed

Measurement rate at  
0.5 Hz major advance in  
observational capability  
compared to other  
established techniques

# CASE STUDY – MOBILE MEASUREMENTS

**G2204:**  $\text{H}_2\text{S}$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$



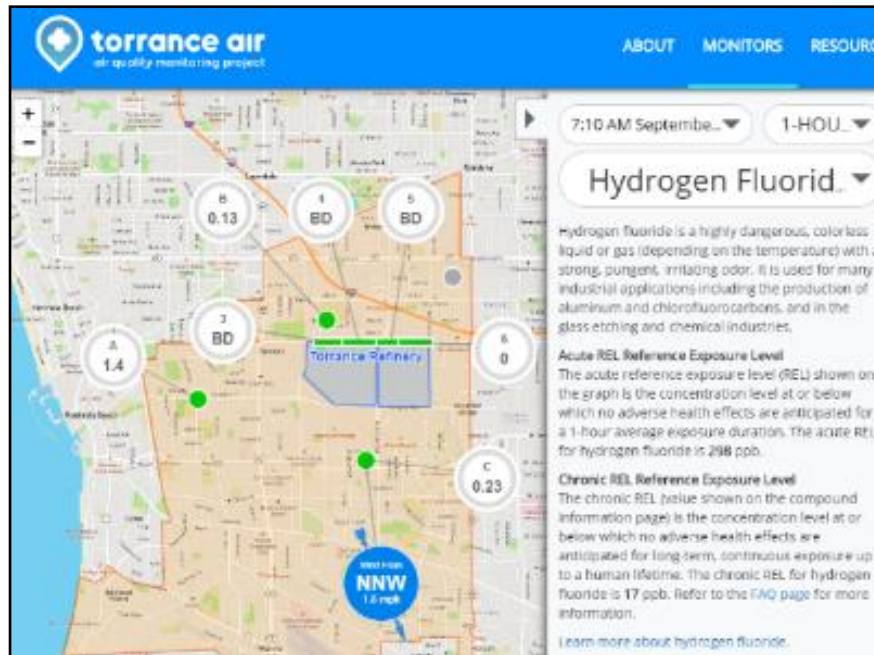
## Advanced Monitoring GMAP – Field Monitoring NEIC's Field Support Capabilities





# CASE STUDY – COMMUNITY MONITORING HYDROGEN FLUORIDE

**G2205:** HF and H<sub>2</sub>O



## Selectivity

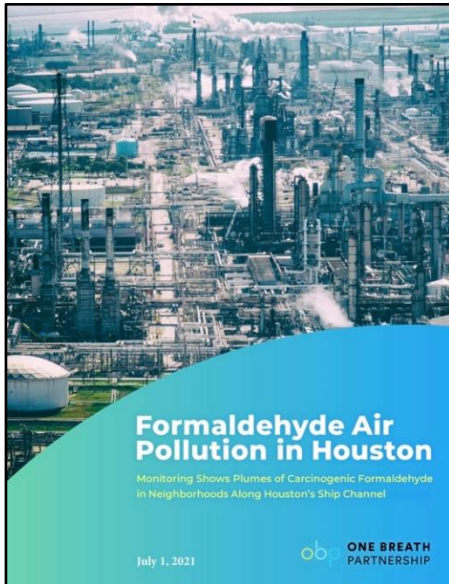
Presence of other compounds causes interference for legacy measurement systems



<https://www.torranceair.org/monitors.html>

# CASE STUDY – SHIPPING LANE FORMALDEHYDE

**G2307:**  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$



<https://environmentalintegrity.org/wp-content/uploads/2021/06/Houston-Formaldehyde-Report-Final-7.1.21.pdf>

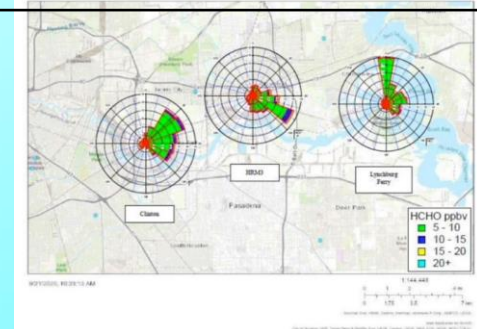
**Table 1: Demographic Information and Cancer Risk in Census Tracts Surrounding Monitors**

| Monitor Location                                   | 2014-2018 population | 2014-2018 % Below Poverty Level | 2014-2018 % Minority | EPA Modeling Estimate* of Formaldehyde Cancer Risk per 1 Million People | EPA Computer Modeling Estimate of Formaldehyde Concentration ( $\mu\text{g}/\text{m}^3$ ) |
|--|----------------------|---------------------------------|----------------------|---|---|
| Clinton Dr. census tract (Galena Park)             | 2,095                | 40%                             | 97%                  | 49  | 1.58 (1.29 ppb)   |
| HRM3 census tract (Cloverleaf)                     | 3,779                | 23%                             | 67%                  | 96  | 1.56 (1.27 ppb)   |
| Lynchburg Ferry census tract (east of Channelview) | 2,969                | 14%                             | 40%                  | 70  | 1.22 (0.99 ppb)   |

**Figure 3: Formaldehyde Point Sources Plotted Across Houston Ship Channel**



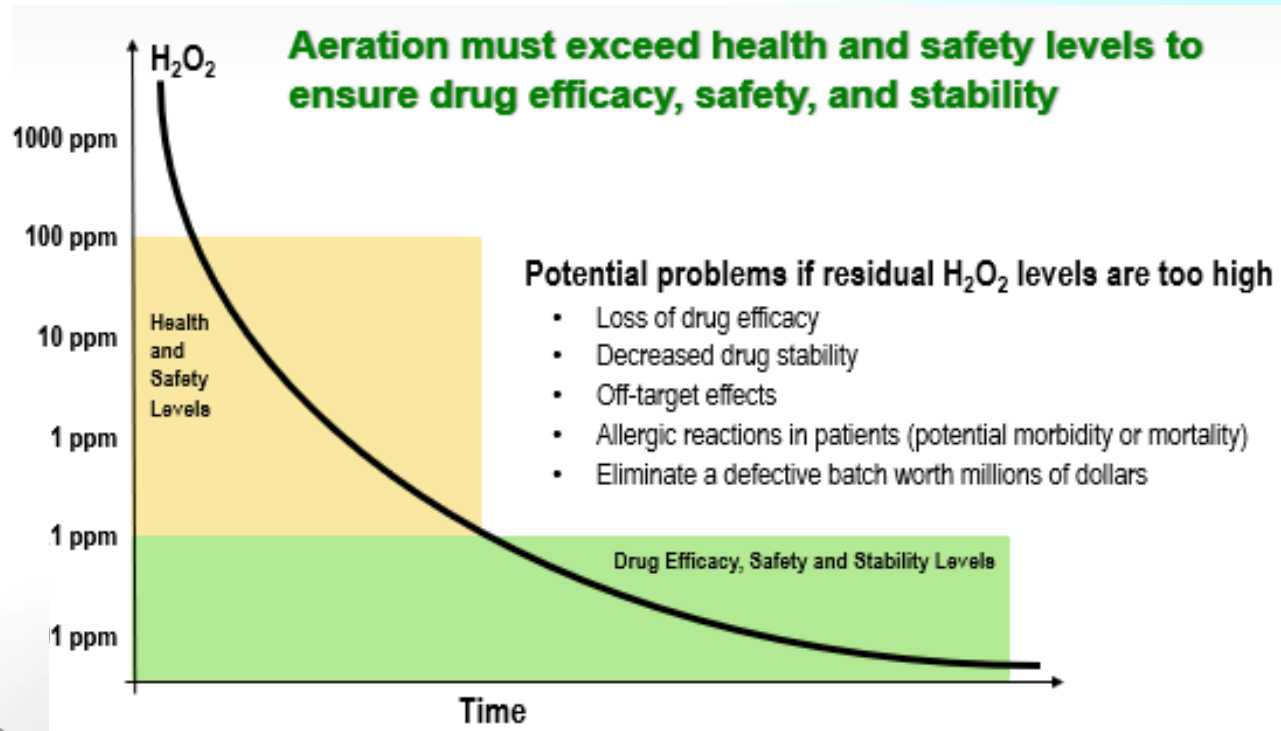
**Figure 2: Wind Direction Analysis of Formaldehyde Exceedances, 2019-2020**





# CASE STUDY – MANAGING PHARMACEUTICAL RISK – HYDROGEN PEROXIDE

PI2114:  $\text{H}_2\text{O}_2$

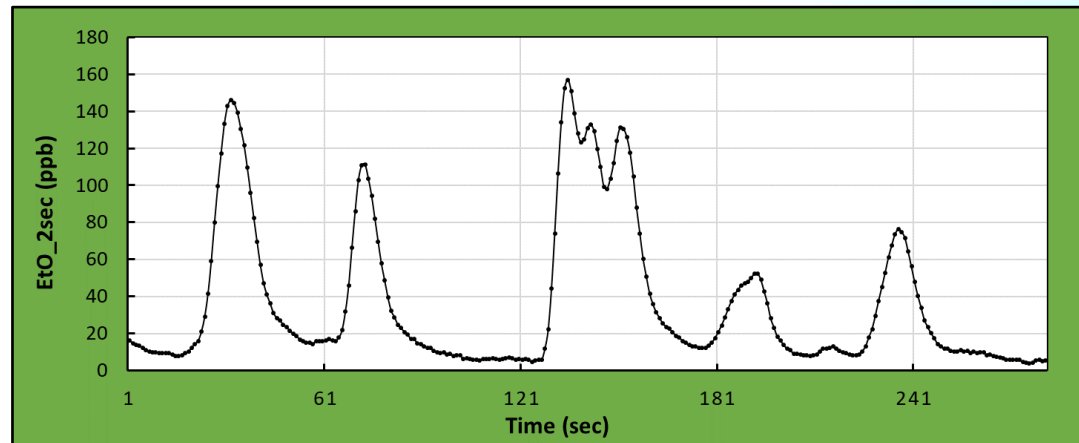


# CASE STUDY – PROCESS MONITOR ETHYLENE OXIDE

**G2910:**  $\text{C}_2\text{H}_4\text{O}$   $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$



EVENT DETECTION



- 2-sec measurement interval measurements of a process stream
- 2-sec MDL at 2-3 ppb
- **Events invisible to many incumbent technologies**

*Unprecedented Insight!*

## Sensitivity

Real-time quantification at parts-per-trillion (ppt) sensitivity designed to meet the most demanding regulatory requirements





# CASE STUDY – COMMUNITY MONITORING ETHYLENE OXIDE

**G2920:**  $C_2H_4O$   $CO_2$ ,  $CH_4$  and  $H_2O$   
**A0601:** Zero Reference Module



## Ambient Air Monitoring System (AAMS)



Zero Reference  
Module (ZRM) -  
peripheral

Picarro G2920  
Ambient EtO -  
analyzer

# VALIDATION WITH SURROGATE GASES

## PROBLEM:

- HAPS = hazardous gases
- Standards are challenging
- Hard to procure

## SOLUTION:

- SURROGATE gases = safer alternative
- Absorption spectra adjacent to original gas
- Commercially available gases



| Model | Primary Gas       | Surrogate Gas   | Recommended Gas Concentrations |
|-------|-------------------|-----------------|--------------------------------|
| G2103 | NH <sub>3</sub>   | CO <sub>2</sub> | 0, 200, 1000, 10000 ppm        |
| G2108 | HCl               | CH <sub>4</sub> | 0, 7, 50, 100 ppm              |
| G2205 | HF                | O <sub>2</sub>  | 0, 20.94% (ambient)            |
| G2307 | H <sub>2</sub> CO | CH <sub>4</sub> | 0, 7, 50, 100 ppm              |

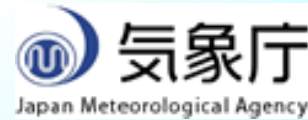


# USED BY LEADING ORGANISATIONS ACROSS THE GLOBE

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For more information, please visit [www.picarro.com](http://www.picarro.com)

or email [info@picarro.com](mailto:info@picarro.com)



\*selected Picarro customers



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42° Congreso de Ergonomía, Higiene,  
Medicina y Seguridad Ocupacional.

Hotel Intercontinental Medellín - Colombia  
2, 3 y 4 de noviembre de 2022

**MUCHAS GRACIAS**

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