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Experiences with Picarro G2307 HCHO Analyzers

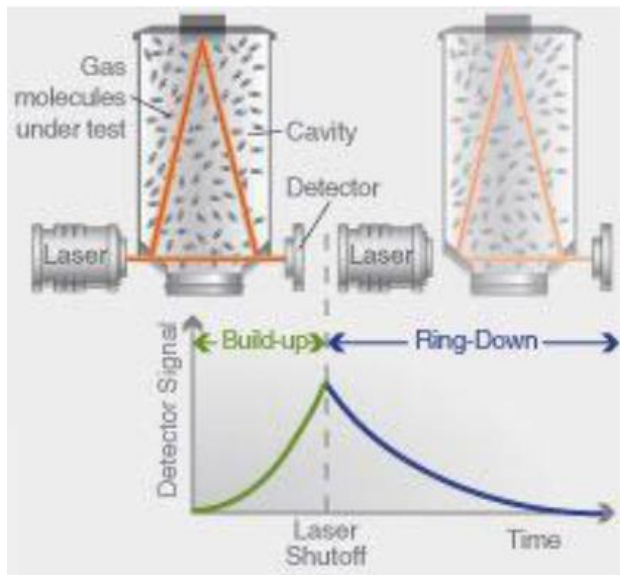
Peter Furdyna

New York State Department of Environmental Conservation
Division of Air Resources - Bureau of Air Quality Surveillance

NACAA Monitoring Committee
August 20, 2020
Bi-Monthly Call

Method – The Theory

Cavity Ring-Down Spectroscopy (CRDS)



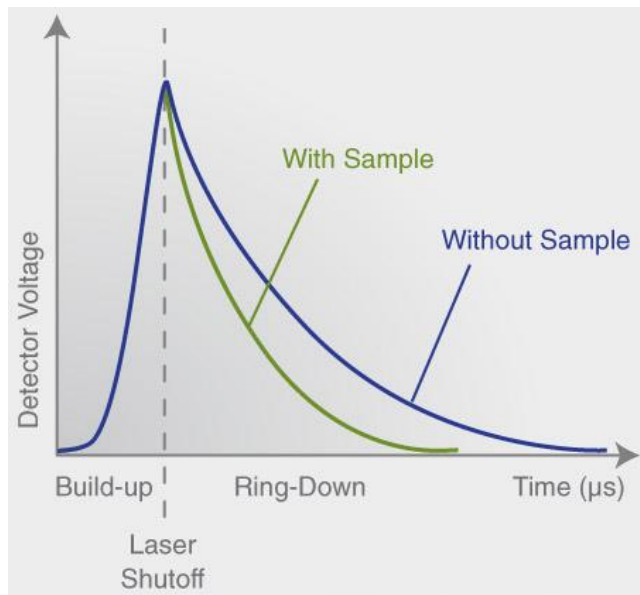
Light from a single frequency laser enters a cavity where three mirrors reflect the laser light (Left)

Then the laser is turned off (Right) and the intensity of the light reaching the detector decreases. The decay, or "ring-down," is measured in real time by the photodetector.

The light typically bounces between the mirrors 40,000 times in about 20msec, effective pathlength about 12 miles.

Method – The Theory

Ring down time difference
proportional to concentration



Key Concepts of CRDS

Under controlled temperature (45°C) and pressure (100 mTorr in cavity) near IR absorption bands are very narrow.

Tunable laser “lights” the cavity at a wavelength at which target molecules absorb. Ringdown time measured.

At a wavelength where the target molecule doesn’t absorb the cavity is relit. Ringdown time measured.

Because everything is known and the measurement is a differential, concentration can be directly determined.*

Method – The Reality: Formaldehyde

1. Zero Drift / Precision

Instr. Specifications: Zero Drift 1.5 ppb/day (Too much)
Drift was both positive and negative (not predictable)

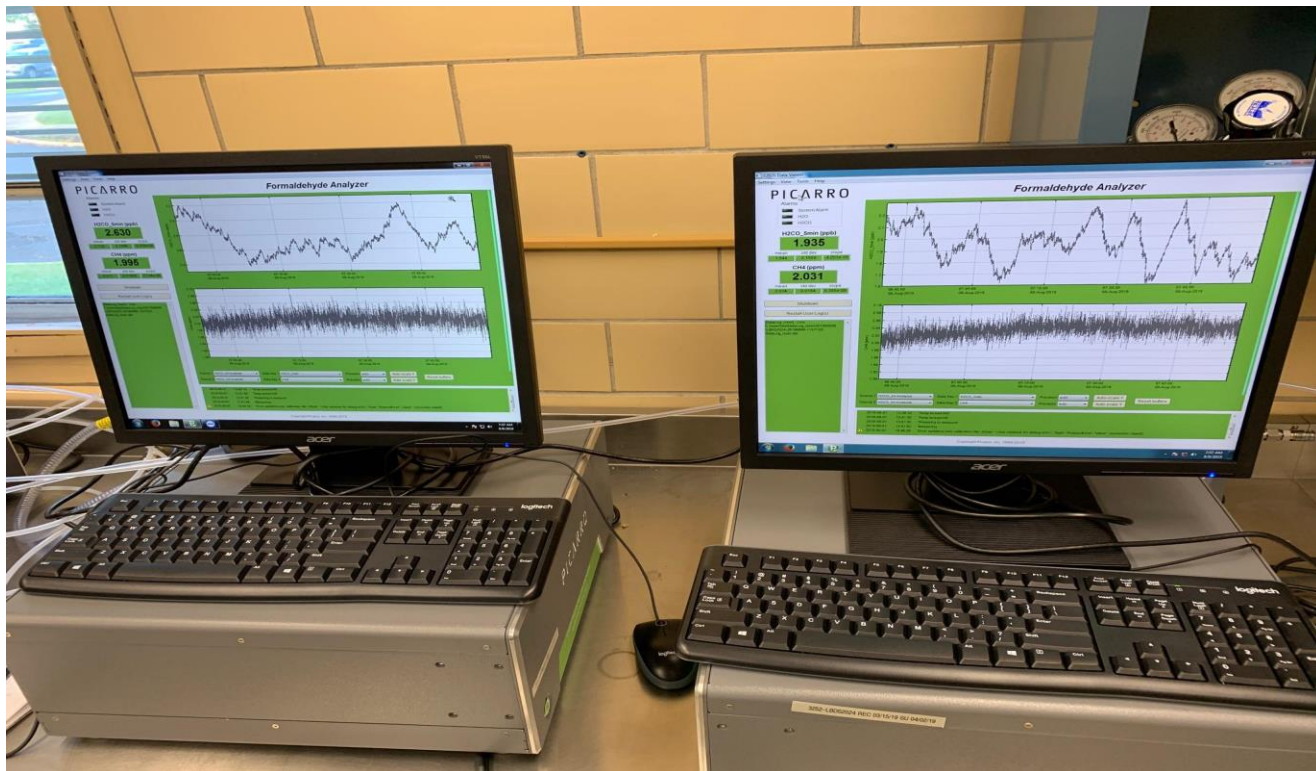
2. Determination of Accuracy

Calibrations using Methane/HCHO blended cylinders
gave low responses

3. Data Access and Usability

Downloaded analyzer data were in uneven Hz intervals
unique to specific instruments ringdown frequency
(Files were hourly, MBs to GBs and tedious to
download and difficult to parse)

Method Issues – Drift / Precision



2.5 vs 1.9 ppbV CH₂O Collocation – Lab Air

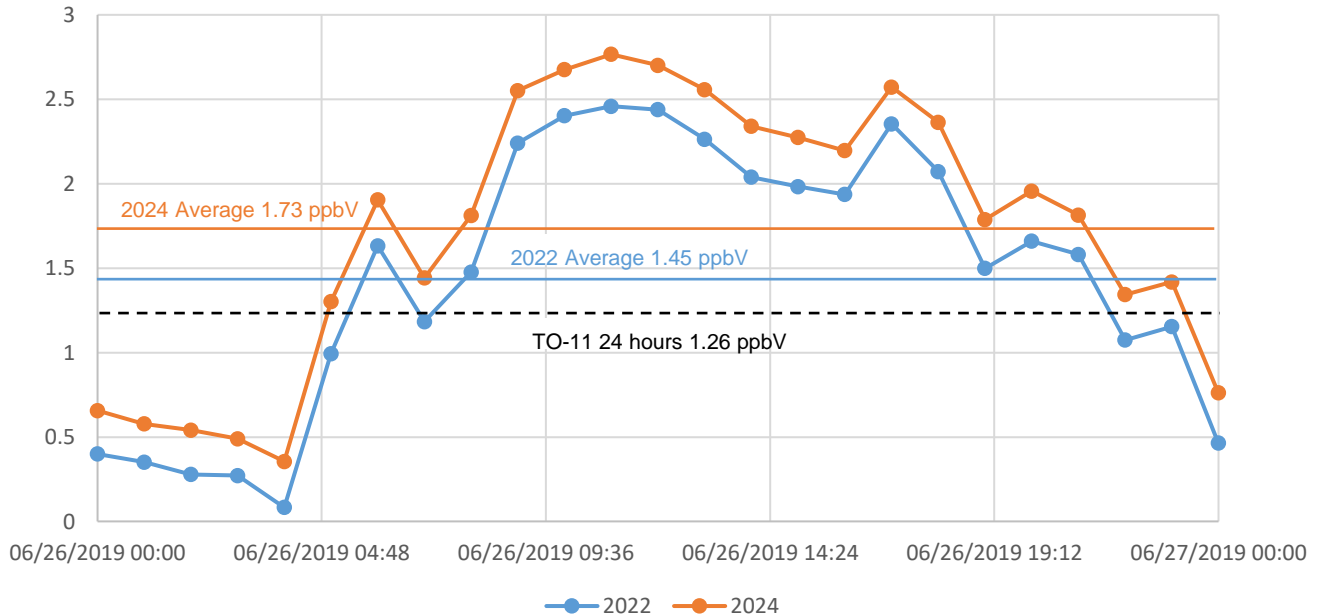


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Method Issues – Drift / Precision

Initial Evaluation – Continued to not look promising

24 Hour Data Comparison Formaldehyde - 2022 v 2024 v DNPH



Comparison to DNPH – 24 hour hourly data



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Drift / Precision - Resolution

Use 2-Min rolling average data output from Analyzer
Envidas Data Logger saves 1-Min data

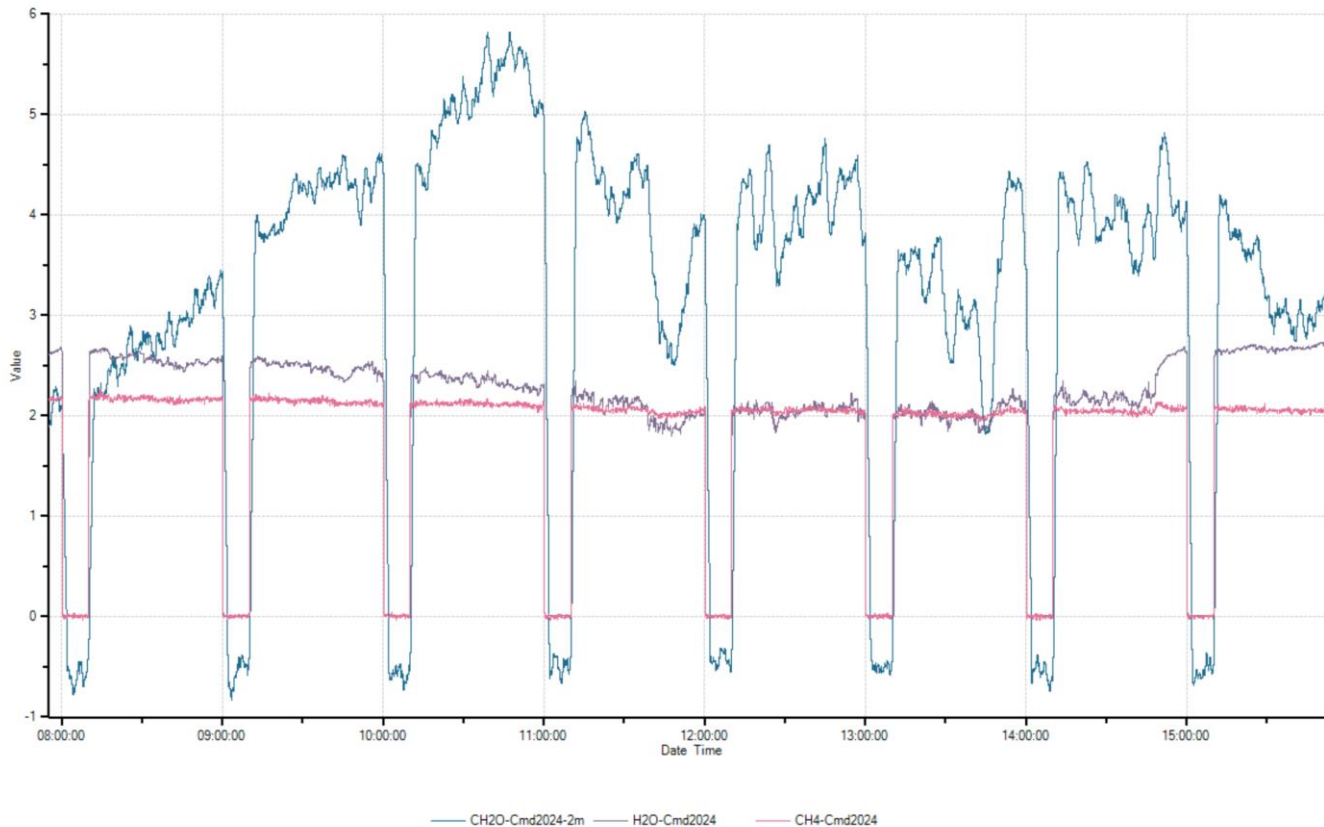
Auto-zero the analyzers for 10 min at the top of each hour
Envidas controlled solenoid, output from ZAG.
Solenoid – IPS 3 way, normally open, run closed to
keep hot – eliminates interferences

Subtract zero value (avg minutes 6-9) from the average of
the final 45 minutes of data in that hour.

Repeat every hour. Currently done off line with an Excel
macro. Goal is for Envidas to develop a calculated
channel to enable real time hourly data.

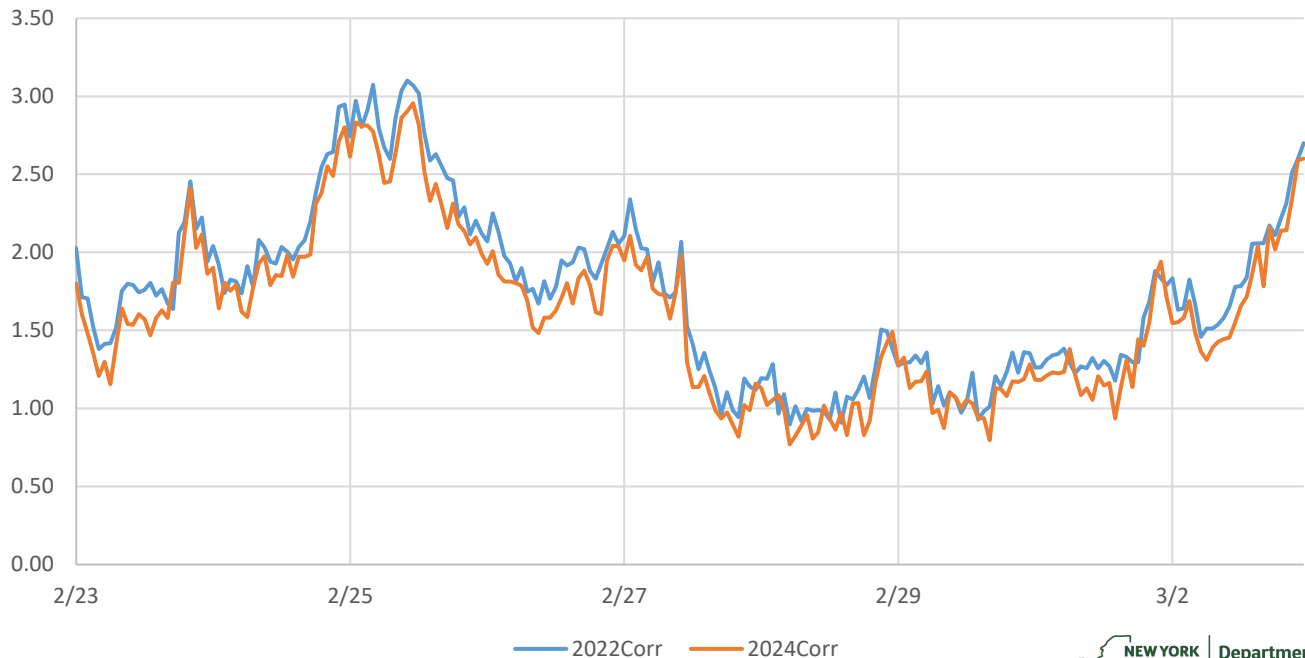


Drift / Precision - Resolution



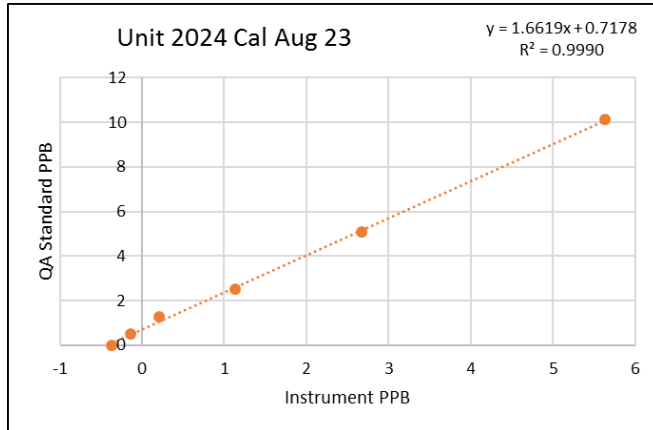
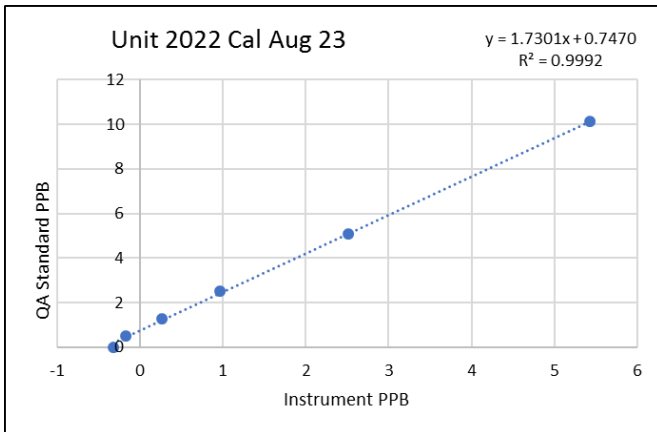
Drift / Precision - Resolution

Offset Corrected Hourly Ambient CH₂O - 02/23/20-03/02/20



Method Issues – Determination of Accuracy

The cal results using blended HCHO/Methane cylinders were abysmal. On the bright side, linearity was excellent



The experimentation began.....

Method Issues – Determination of Accuracy

At Picarro, the blended CH₄/CH₂O cylinder was 50% low for formaldehyde. Even though Picarro maintains that CH₄ up to 25 ppm is compensated for, this is not what we found.

With a formaldehyde only cylinder and Floropel coated flow controllers the results from April through June were better but still not acceptable:

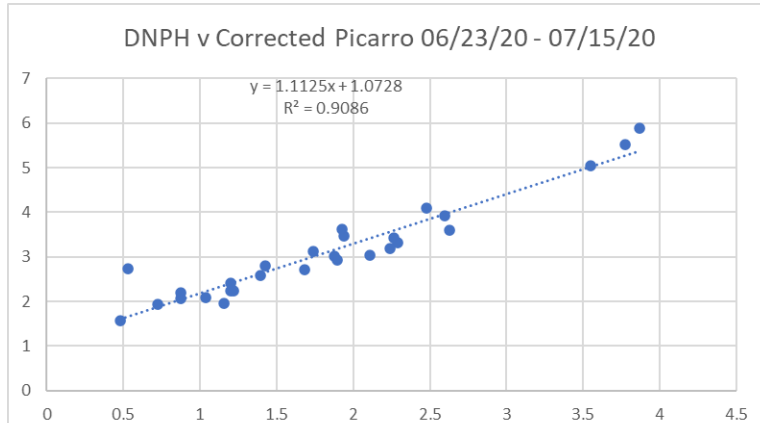
Slope: 0.76 – 0.88

Intercept: -0.83 to 0.16

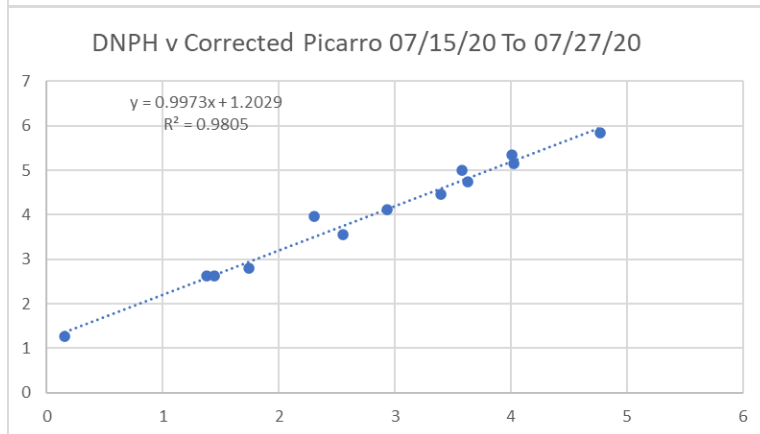
R Squared: 0.999



Picarro Compared to 8 and 24-Hr DNPH

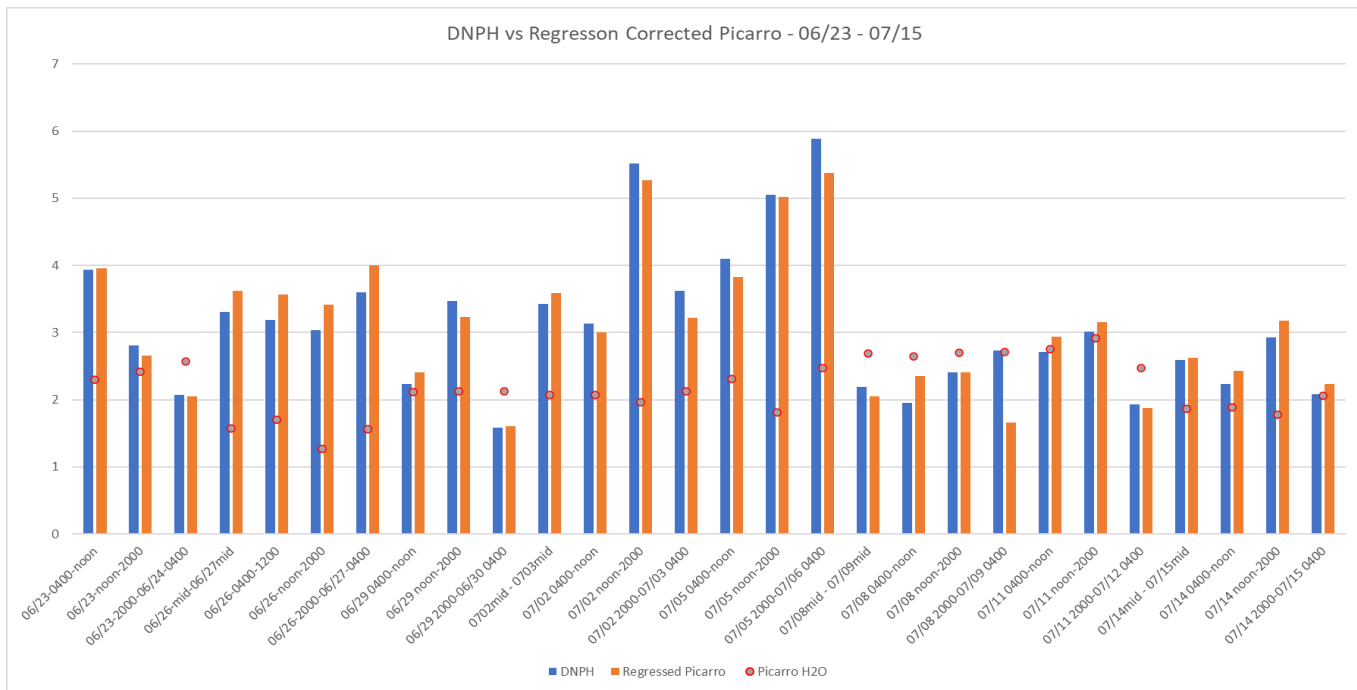


The Picarro data correlated well with DNPH but DNPH was higher and there was a 1 ppb offset



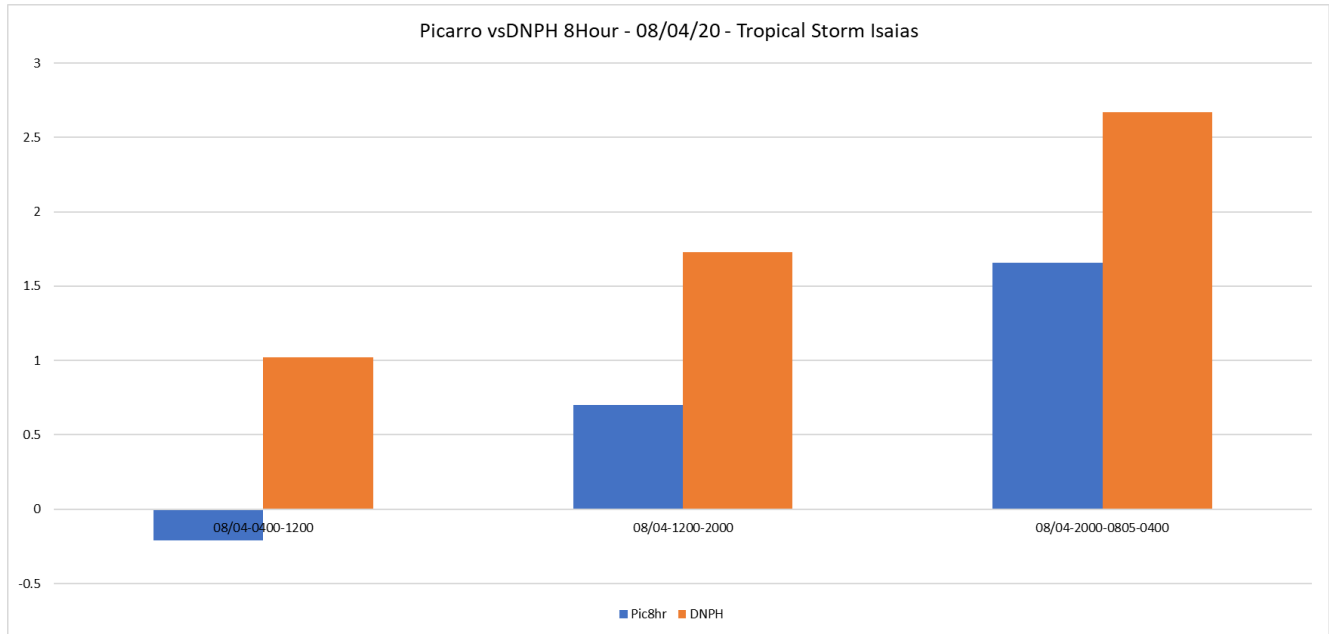
Method Issues – Determination of Accuracy

If DNPH data are considered true, Regressed Picarro data agree very well with integrated 8-Hr DNPH data



Tropical Storm Isaias Comparison

Ambient Formaldehyde should go to zero during a heavy rain event. The Picarro is close to zero, DNPH does not drop below 1 ppb.



Observations and Conclusions

- Instruments likely suitable for ambient monitoring after:
 - Intensive development work with Picarro to get units ready for ambient measurement of CH₂O
 - User unfriendly data interface made initial development work difficult.
- Third party instrument control/data management software(DrDas) had a large part in developing performance to a level that may well be acceptable for ambient monitoring.
- CH₂O Accuracy: 15 – 20% low in comparison to standard
- Analyzer performance for methane is superb

Thanks and Acknowledgements

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Andrew Montz – Dr. Das LTD

Helen Martin and Laura Miles – Markes International LTD

Jonathan Bent and Milos Markovic - Picarro



Thank You

- Peter Furdyna
- Chemist
- 11 University Place
Rensselaer, NY 12144
- peter.furdyna@dec.ny.gov
- 518-402-8508

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