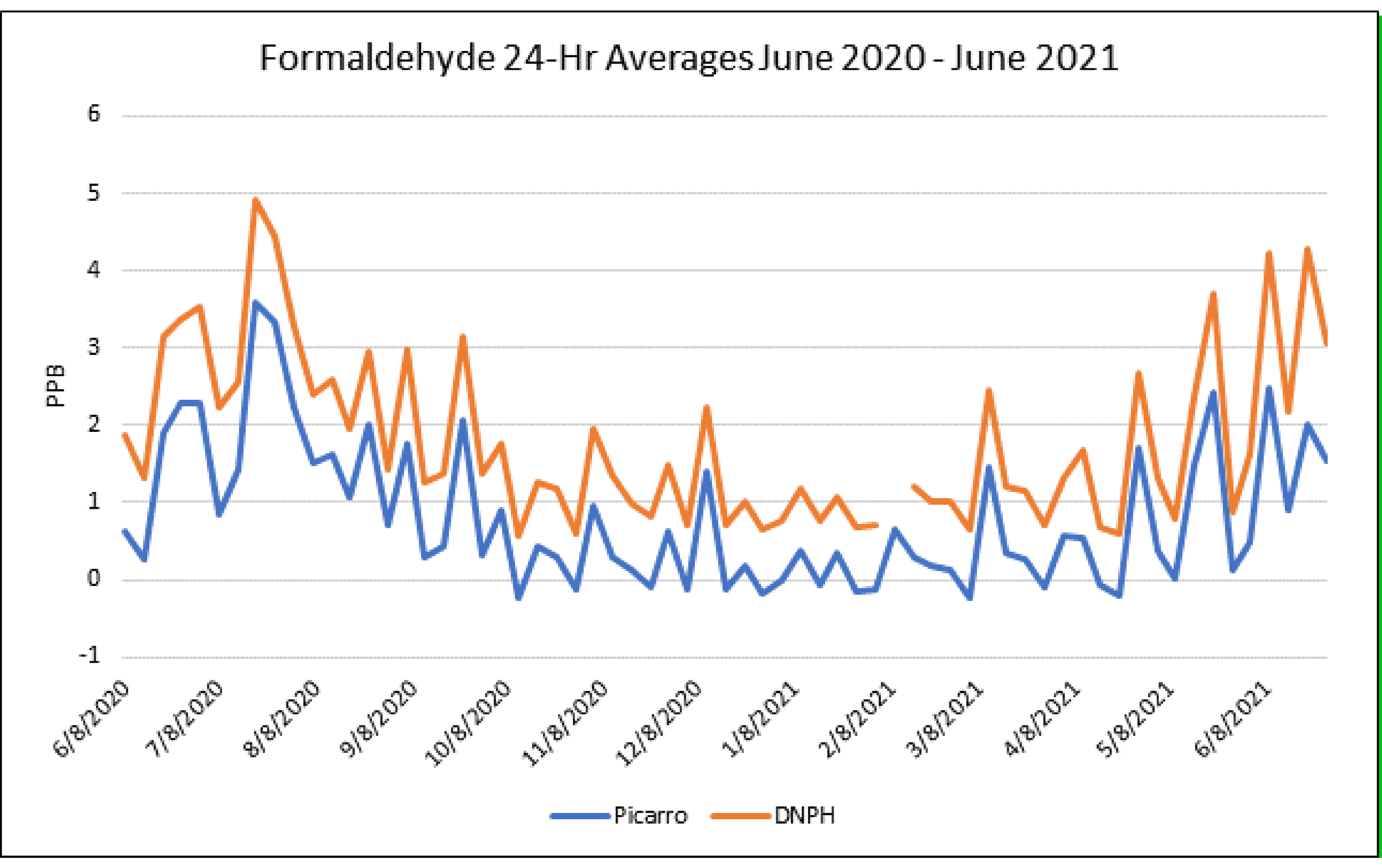
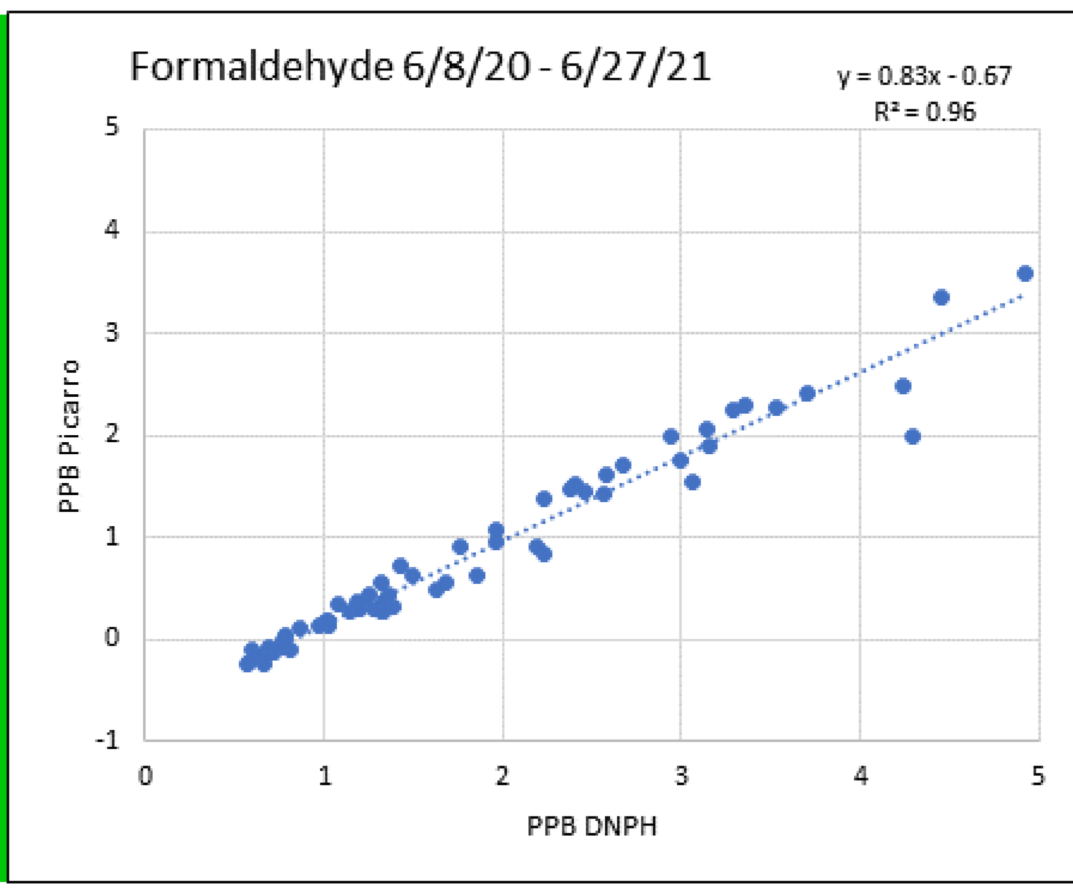


Recent Advances in Real-time, Continuous, Sub-ppb Formaldehyde Measurements at Ambient Air Quality Monitoring Stations



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1. INTRODUCTION

EPA Method TO-11A outlines practices for measuring formaldehyde using the 4,2-DNPH denuder method, subsequent derivatization, and analysis by HPLC. While the DNPH method has been a stalwart of air quality monitoring for decades, it provides only time-averaged exposure estimates (typically 8 or 24-hour), requires offline analysis at third-party labs, and continues to experience suspected bias effects associated with ozone and water vapor. Because values are reported significantly post-hoc, formaldehyde also cannot be integrated into air quality monitoring forecasts. Furthermore, time-averaged values limit the ability of regulators to correlate source regions with real time wind data.

Over the last decade, commercially available formaldehyde instruments have allowed for sub-ppb measurements of formaldehyde, but questions of zero drift and scaling relative to TO-11A have impeded the ability to provide EPA method equivalence. Picarro Inc released its G2307 formaldehyde instrument in 2017, delivering sub-ppb sensitivity. Initial testing within the regulatory community has indicated that the instrument is highly repeatable at span, but that various analytical techniques disagree significantly on scaling, making it challenging to assess the absolute accuracy of the Picarro instrument's factory calibration. Users have also noted that the typical zero drift on order 1 ppb introduces uncertainty to intercomparisons.

We present here advances in providing a zero-reference system for assessing and ultimately correcting out in real time the zero drift of this analyzer. We also present advances in establishing a DNPH-aligned, repeatable "golden instrument" approach for documenting repeatable accuracy between production units, and that allows users to return their instrument to the factory for annual validation or recalibration. Finally, we present real-world intercomparisons performed by members of the air quality community over the past two years showing promisingly high degrees of correlation between the EPA Method and the Picarro instrument, and suggesting some possible shortcomings in the 4,2-DNPH method.

2. G2307 INSTRUMENT DESCRIPTION

Picarro developed the G2307 formaldehyde instrument between 2017 and 2018 in response to a need for stable real-time measurements of H_2CO in ambient settings where 8-24 hour average signals typically range from 0-10 ppb. The G2307 instrument was equipped with an adjacent CH_4 line to enable both real-time CH_4 measurements and an ability to determine laser and system health without needing to directly check/calibrate with H_2CO.

G2307 Instrument (near-IR CRDS)

G2307 Formaldehyde	Typical Performance**	Specifications***
Lower Detection Limit (3σ, 300 sec)	0.18 ppb	0.3 ppb
Zero Drift (72 hrs)* *(peak-to-peak, 50-minute average)*	0.33 ppb	1.5 ppb
Precision (1σ, 2 sec) **Precision** (1σ, 10 sec) **Precision** (1σ, 300 sec)	0.7 ppb + 0.1% of reading 0.31 ppb + 0.05% of reading 0.06 ppb + 0.02% of reading	1.2 ppb + 0.1% of reading 0.6 ppb + 0.05% of reading 0.1 ppb + 0.02% of reading
Measurement Interval	<2 sec	<2 sec
Response Time (0–20 ppb) *(Rise/Fall Time 10–90% / 90–10%)*	<5 sec	<5 sec
Measurement Range	0–30 ppm	0–30 ppm

** Picarro analyzers do not require a zero reference gas or zero catridge to operate or meet specifications.*

*** Typical performance is defined as the median of testing results from ten sequentially built G2307 analyzers in 2019. Results available upon request.*

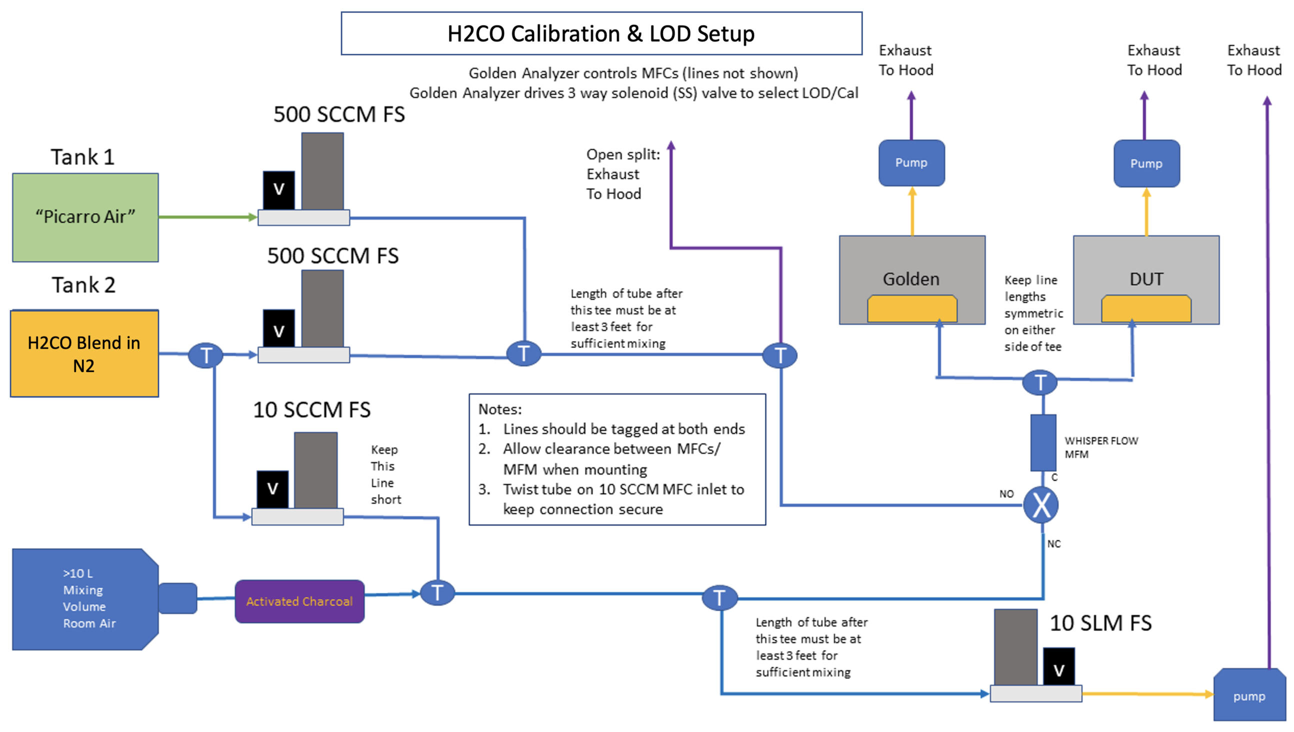
**** Specifications and an instrument-specific testing report (Certificate of Compliance) provided with every analyzer purchase.*

REFERENCES

[1] Saha, S., Barry, H., Hancock, G., N., Ritchie, G.A.D., and Western, C.M.: Rotational analysis of the $2\nu_5$ Band of Formaldehyde, Molecular Physics, 105, 797—805, 2007.

3. METHOD IMPROVEMENTS

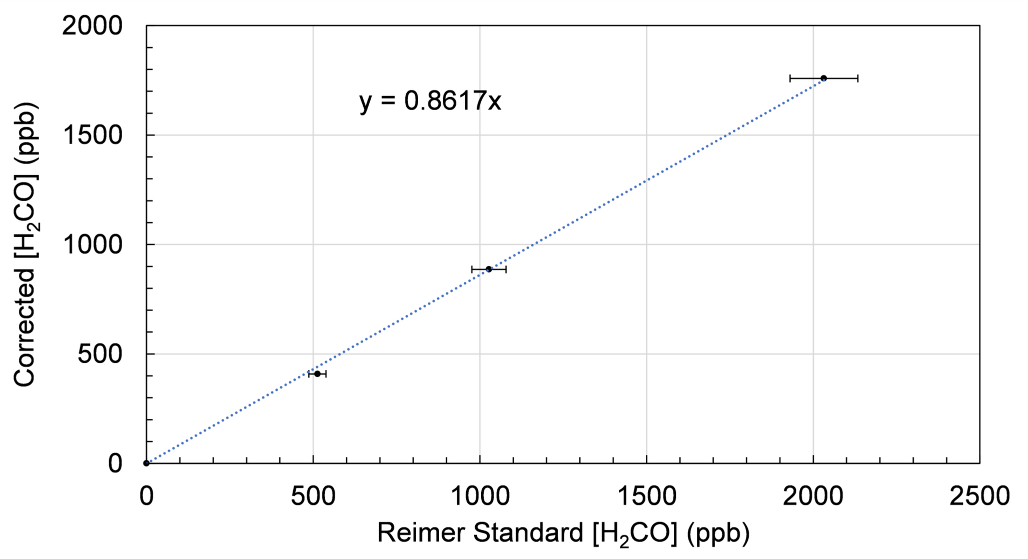
3.a. Golden Analyzer Development



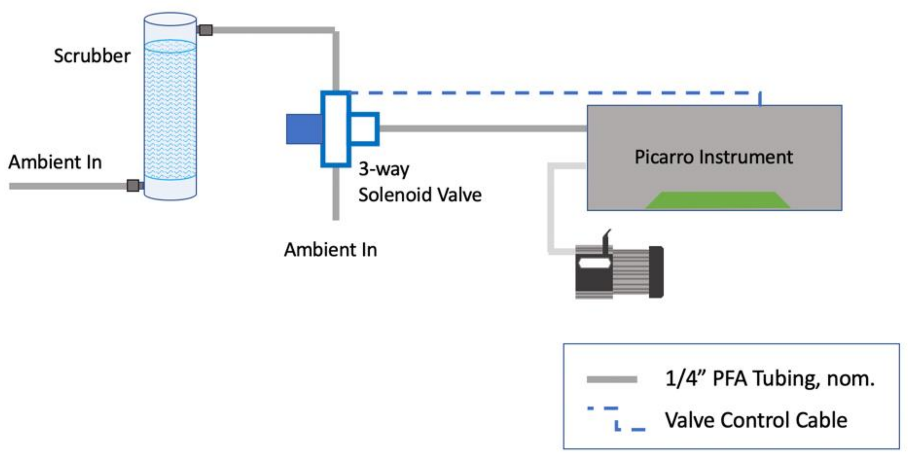
Picarro establishes "golden analyzer" calibration units for species of gas for which primary standards either do not exist because of instability, or which are are hazardous to handle. The instrument serves as an anchor point against which production instruments can be validated and calibrated. The golden analyzer is checked regularly against known surrogate gas standards and trusted primary gas standards to establish any changes to its performance and linearity with time. This approach is only possible because Picarro analyzers overcome long-term drift with wavelength-stabilized cavity ringdown spectroscopy (CRDS).

3.b. Scale Adjustment

Picarro's initial scaling based on the spectroscopy of Saha et al. [2007] and a permeation tube standard reads low relative to an extensive set of DNPH inter-comparisons, and standards from Apel-Riemer, which agree closely. Picarro has decided to use Apel-Riemer standards, in comparison with DNPH records to rescale the current span **by about +15%**.



3.c. Zero Referencing



Picarro has put into place an automated valve switching procedure to track the small zero drift of the analyzer using variably: DrieRite, 4,2-DNPH cartridges, activated charcoal, and zero air. The system utilizes the built-in valve sequencing ability of the instrument to power an external materially-compatible 3-way valve. Zero correction can be automated through DAS programs currently, and Picarro is investigating the possibility of a peripheral which automates these procedures, alongside calibration checks.

3.d. Collaboration & Feedback

New York State Department of Environmental Conservation purchased a total of three Picarro G2307 instruments over 2019 and 2020 with a goal of automating air toxics monitoring for formaldehyde. Initial efforts focused on establishing consistency between instrument results, and reproducibility of calibration and validation checks. Subsequent efforts focused on close intercomparison with existing 4,2-DNPH measurements. The primary source of absolute difference between instruments, and between instruments and DNPH was determined to relate to zero drift, so NYSDEC established a zero reference method to control zero drift on order 1 ppb using zero air produced on site from a zero air generator. Differences at span between instruments and DNPH were found to be consistent, indicating a scaling difference, not span drift. A roughly 1-year record of intercomparisons shows a Picarro/DNPH scaling relationship of 0.83 ppb/ppb. This value is highly consistent with comparisons against standards produced by Apel-Riemer Environmental.

NYSDEC instrument Locations:

- New York Botanic Gardens, Bronx, NY (Source of intercomparison data above)
- Flax Pond Marine Research Laboratory, Old Field/East Setauket, NY
- Goethals Field, Old Place/Staten Island, NY

4. CONCLUSIONS

NYSDEC has provided invaluable feedback on the performance of the Picarro G2307 relative to the TO-11A method, providing insight on scaling, zero drift, and DAS integration. Picarro has worked over the last 1.5 years to adjust the performance of the G2307 to meet the needs of the air quality community by providing a standard of traceability and recalibration; by aligning scaling to the most commonly accepted formaldehyde source material, and in comparison with EPA-method data; and by incorporating auto-zero functionality. Work continues to automate the auto-zero correction more fully, and to identify the most effective and accurate scrubbing medium. **Field-deployed intercomparison work demonstrates excellent overall correlation between DNPH and Picarro G2307 formaldehyde measurements when the above considerations are accounted for, with strong tracking of signals and an R^2 = 0.96.**

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