

## **DFGAS (Difference Frequency Generation Absorption Spectrometer) for the Measurement of Formaldehyde**

As discussed in Weibring et al. [2006, 2007], the DFGAS instrument is a state-of-the-art infrared (IR) spectrometer that operates at room temperature. Liquid nitrogen cooling is thus no longer needed for generating mid-IR laser light and the IR detectors employ thermoelectric cooling. The two papers by Weibring et al. discuss the many other advantages of DFGAS in detecting CH<sub>2</sub>O relative to more conventional liquid nitrogen cooled tunable lead salt diode laser absorption systems (TDLAS), and many of these have in fact been realized during the 2008 ARCTAS and 2010 Venture Class AQ studies. In addition, Weibring et al. [2010] have now demonstrated multi-species detection capabilities employing this same technology.

Figure 1 shows the optical components in the DFGAS instrument as well as the instrument mounted on the NASA DC-8 during the 2008 ARCTAS study. The output of two near-IR room temperature laser sources (one at 1562-nm and the other at 1083-nm) are amplified, combined and focused into a periodically poled lithium niobate (PPLN) non-linear wavelength conversion crystal. The mid-IR difference frequency at 2831.6 cm<sup>-1</sup> (3.53- $\mu$ m) is generated at the PPLN output and directed through a multipass astigmatic Herriott cell (100-m pathlength using  $\sim$  3-liter sampling volume) and ultimately onto IR detectors employing a number of optical elements. A portion of the IR beam is split off by a special beam splitter before the multipass cell and focused onto a Noise Detector (ND) to capture and remove optical noise from various components in the difference frequency generation process. The beam splitter coating is chosen so that the intensities impinging on the Sample Detector (SD) and ND are approximately equivalent. A third detection channel from light emanating out the back of the beam splitter is directed through a low pressure CH<sub>2</sub>O reference cell and onto a reference detector (RD) for locking the center of the wavelength scan to the absorption line center. The mid-IR DFG output is simultaneously scanned and modulated over the CH<sub>2</sub>O absorption feature, and the second harmonic signals at twice the modulation frequency (2f) from the 3 detectors are processed using a computer lock-in amplifier, as described by Weibring et al. [2006].

Ambient measurements are acquired by drawing in ambient air continuously through a heated inlet at flow rates around 9 standard liters per minute (slm), through a pressure controller, and through the multipass Herriott cell maintained at a constant pressure around 50-Torr. For the DC<sup>3</sup> and SEAC<sup>4</sup>RS studies a HIML (HIAPER Modular Inlet) inlet will be employed. This inlet boosts the inlet pressure using ram air, and this in combination with a new large conductance low pressure drop inlet valve will allow us to achieve proper sample flow at high altitudes and high aircraft speeds. In past studies this sampling regime presented problems, which caused in certain cases reduced data coverage.

The DFGAS system probes the same moderately strong CH<sub>2</sub>O absorption feature as all our past measurements using TDLAS. This feature is free of all known spectroscopic interferences with the exception of weak methanol absorption features. These features produce a slight positive interference of 1.2% in DFGAS for equivalent CH<sub>2</sub>O and methanol mixing ratios. This small interference is readily removed by simultaneously fitting out the methanol features, the shapes for which are periodically acquired using an

onboard methanol calibration standard added to the inlet. Alternatively, PTRMS methanol measurements onboard the NASA DC-8 can be employed in removing this small interference. Ambient CH<sub>2</sub>O measurements are acquired in 1-second increments for time periods as long as 60 to 120-seconds (determined based upon instrument stability times), and this is followed by 15-seconds of background zero air acquisition, using an onboard CH<sub>2</sub>O scrubbing unit. The zero air is added back to the inlet a few centimeters from the tip at flow rates ~ 2 to 3 slm higher than the cell flow.

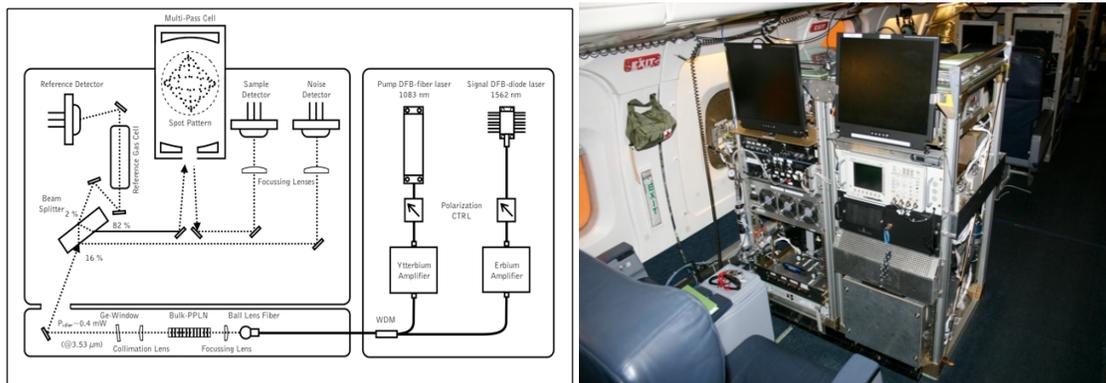


Fig. 1: (Left Panel) Optical schematic of DFG system, which includes WDM (wavelength division multiplexer beam combiner), PPLN (periodically poled lithium niobate non-linear wavelength conversion crystal), Ge (germanium filter). A reference cell containing pure CH<sub>2</sub>O at low pressure precedes the Reference Detector for wavelength locking. **(Right Panel)** DFG system mounted in the cabin of the NASA DC-8 during the ARCTAS mission. The rack to the left contains; calibration and zero air generation systems, along with flow controllers and various power supplies. The rack to the right houses; operator monitor, service oscilloscope, control and data acquisition computer, spectrometer enclosure (lasers and DFG module, fiber amplifiers, multipass cell, detectors), and air-conditioning unit. The entire system, including the rack and vacuum pump weighs 640 pounds.

This frequent zeroing very effectively captures and removes optical noise as well as residual outgassing from inlet line and cell contaminants [Wert et al., 2002]. Retrieved CH<sub>2</sub>O mixing ratios are determined for each 1-second ambient spectrum by fitting to a reference spectrum, obtained by introducing high concentration calibration standards (~ 3 to 11-ppbv) from an onboard permeation calibration system into the inlet approximately every hour. The calibration outputs are determined before and after each field campaign using multiple means, including direct absorption employing the Beer-Lambert Law relationship. The 1-second ambient CH<sub>2</sub>O results can be further averaged into longer time intervals for improved measurement precision, as shown by the high altitude results of Fig. 2 during ARCTAS. This figure represents the typical performance achieved with the DFGAS instrument when flying at constant altitude in clean background air. Here, 1-minute averaged data yields a 1 $\sigma$  standard deviation of 10 pptv over the 18-minute time interval shown while the standard deviation of individual 1-second data over each 60-second measurement interval (error bars on each 1-minute average) average 79 pptv for this interval. As real ambient variability cannot be ruled out here, these performance estimates represent upper limits. Many other constant air mass legs show similar performance, falling in the range of 60 to 80 pptv and 10 to 20 pptv, for respectively, 1-

second and 1-minute of averaging. It is important to note that in all cases the 1-second results are still preserved. This flexibility allows us to further study pollution plumes with high temporal resolution, and at the same time study more temporally constant background CH<sub>2</sub>O levels in the upper troposphere using longer integration times. During the NASA Venture Class –AQ studies in July 2011, very similar performance figures were obtained on the NASA WP-3 aircraft. During these latest studies the optical system was pressure stabilized, which allowed us to achieve such performance independent of aircraft cabin pressure.

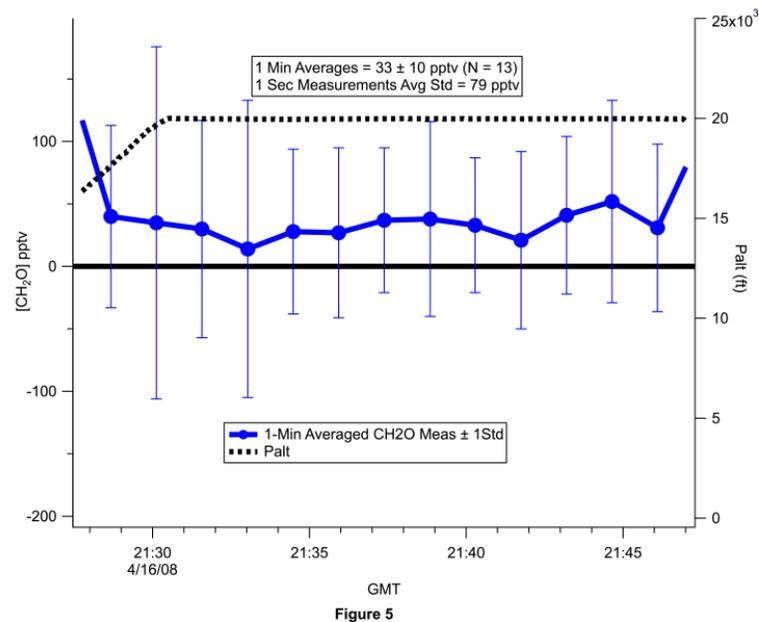


Figure 2: Airborne measurement performance for CH<sub>2</sub>O during one of many constant altitude legs in clean background air at 20,000 feet during the 2008 ARCTAS study.

## References

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