Advances in the Performance Assessment of a Tunable Diode Laser Absorption Spectrometer for Airborne Measurements of CH_2O

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Abstract: An airborne tunable diode laser absorption spectrometer was deployed to measure CH_2O during NASA's 2004 Intercontinental Chemical Transport Experiment. Retrieved time series CH_2O data are analyzed to assess instrument performance, minimum detection limits, and quality of data.

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Formaldehyde (CH_2O) is a ubiquitous intermediate component of the atmosphere formed by the oxidation of anthropogenic hydrocarbons, biogenic hydrocarbons, and methane. In the atmosphere, CH_2O can undergo photodecomposition to form carbon monoxide (CO) or react with the hydroxyl radicals (OH) to form hydroperoxyl radicals (HO_2). Precise measurements of CH_2O are therefore important in our understanding of the global carbon budget, and cycling among odd hydrogen species and odd nitrogen species [1].

To date, measurements of atmospheric CH_2O are at times inconsistent with point/box model estimations of CH_2O in the background atmosphere [2]. Discrepancies in measurement-model comparisons could include errors in the source and sink terms in the models, CH_2O measurement uncertainties, and/or some combination of both. Therefore, it is of importance to assess instrumentally measured atmospheric CH_2O concentration data and determine in-flight aircraft instrument performance. Typically, measuring gas standards of known concentration and determining either signal-to-noise ratios or replicate precisions are used to assess performance, but this is at the cost of reducing available time for measuring ambient air. Therefore alternative methods for frequent performance assessment need to be devised, and this represents the motivation for the present report.

Tunable diode laser absorption spectroscopy (TDLAS) with lead-salt lasers has been demonstrated to be a robust technique for airborne CH_2O measurements and has achieved measurement precisions of 15-50 pptv [3]. Low detection limits ($\sim 10^{-6}$) are achieved using long path optical gas cells at reduced pressures (<50 Torr), wavelength modulation, second-harmonic (*2f*) detection, and zero air background subtraction. Additional improvements include temperature and mechanical stabilization of the optical components, which is significant when operating in an aircraft environment with dramatic changes, in cabin temperature, pressure, acceleration, turbulence, and mechanical vibrations.

Approaches to assessing the performance of TDLAS measurements will be reported that are tailored for *2f* absorption techniques utilizing a long-optical path length gas cell and zero air background subtraction. The TDLAS system has been described in detail in [3], and is only briefly described here. The system consists of a IV-VI double buried heterostructure laser housed in a liquid nitrogen dewar, various transfer optics and an astigmatically compensated Herriott cell (100-meter path length and 3-liter volume), and two InSb detectors (a reference and a sample detector).

The laser is tuned across a CH_2O absorption feature at 2831.6417 cm^{-1} using a 25-Hz triangle waveform producing two spectra per period, which are analyzed separately. The advantage of the triangle waveform is increased usable channels in the scan compared to sawtooth tuning waveforms, which exhibit fly-back due to abrupt tuning changes. A second triangle waveform of 50 kHz is superimposed upon the tuning waveform to rapidly modulate the laser. Lock-in amplifiers sample the output signals from the detectors at twice the modulation frequency (*2f*), which produces 2^{nd} harmonic absorption signals with amplitudes proportional to the concentration of the absorbing species.

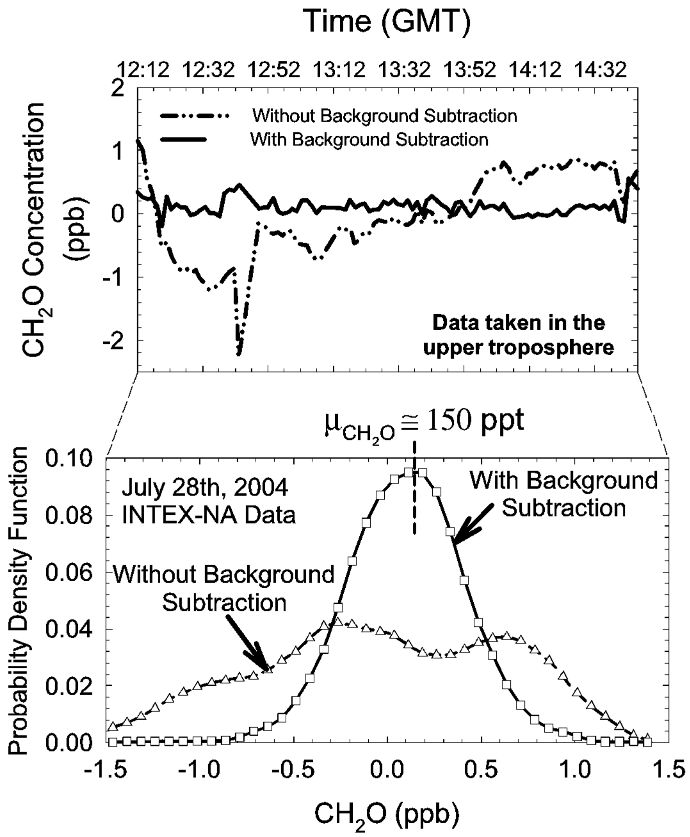

Figure 1. (Top) Time-series plots of CH_2O concentration trend with and without background subtraction performed. (Bottom) Probability distributions of the two concentration trends.

Optical fringes formed from unwanted etalons, arising anywhere in the optical train, are the primary noise source limiting lower detection limits for CH_2O by TDLAS. To reduce the influence of optical fringes in the spectral signal, the background is captured by measuring zero air, i.e._air devoid of CH_2O, and subtracting the background from sample spectra of unknown concentrations. Figure 1 shows a time-series of CH_2O data taken in the upper troposphere, with background subtraction performed and without background subtraction, along with the probability density functions of the two series. As discussed in Ref. 3 and references therein, background subtraction improves the signal and gives a more accurate determination of the distribution of CH_2O in the atmosphere.

Background subtraction is most effective when the background is stable over a measurement cycle (refer to Ref. 3 for detailed description of the measurement cycle for background subtraction). Significant instabilities of the backgrounds can deteriorate the effectiveness of background subtraction. Several statistics are used to assess the stability of the backgrounds over the measurement cycle. For example, background amplitude residuals (BARs) are defined as the average absolute difference of backgrounds between measurement cycles. During the middle of NASA's Intercontinental Chemical Transport Experiment in the summer of 2004, a number of optical components (Herriott cell, cell window, and cell input/output mirror) were mechanically stabilized to minimize subtle alignment changes due to changes in cabin pressure and/or aircraft accelerations and turbulence. Figure 2 shows the effect of these improvements on the distributions of the BAR statistic; confirming that these measures did in fact stabilize the system and reduce fringe movement during various aircraft perturbations.

Additional statistical approaches were used to assess the accuracy and precision in fitting sample spectra of unknown concentration to calibration spectra of known concentration. The effectiveness of using higher-order terms in the fit to account for residual backgrounds over a measurement cycle as well as assessing the performance of varying spectral fitting window sizes is addressed. Figure 3(a) shows an acquired 2*f* spectrum of CH_2O and two possible spectral fitting windows used in a general least-squares routine for determining CH_2O concentrations. Figure 3(b) shows an improvement in the distribution of 1-second replicate precisions (1σ) over 60-second ambient measurement cycles for an entire day of CH_2O time series data, suggesting the larger window size enhanced fitting performance.

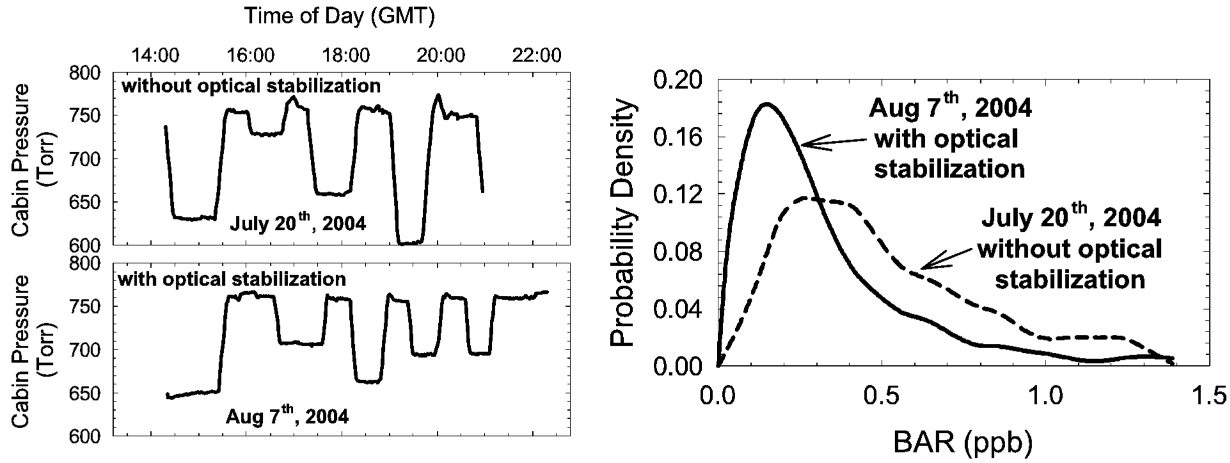

Figure 2. (Left) Time-series plots of cabin pressure taken on July 20th (without optics stabilized) and August 7th (with stabilization) aboard a DC-8 aircraft, both days having large cabin pressures changes. (Right) Plot of the probability distributions for the background amplitude residual (BAR) measure, which show mechanical stabilization of various optical components was able to improve the stability of the backgrounds.

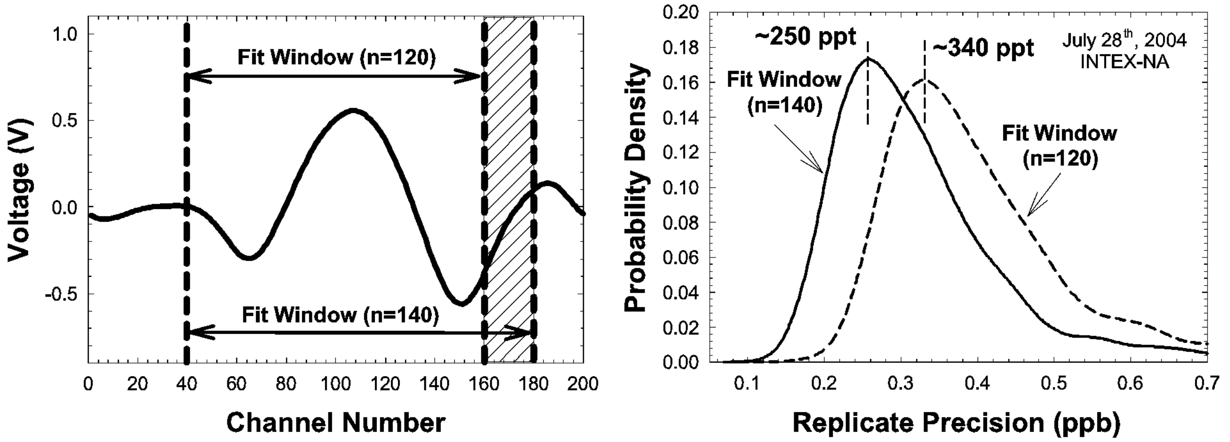

Figure 3. (Left) Plot of 2f CH_2O spectrum and two spectral fitting windows of sizes n=120 and n=140 channel numbers. (Right) Measured 1-second replicate precisions (1σ) retrieved from the two fitting windows for time series CH_2O data taken on July 28th, 2004 during the INTEX-NA mission aboard a DC-8.

Additional statistic measures and their interpretation will be presented. For example, measurement of the average channel standard deviation gives an indication of the best possible minimum detection limit, although this may not be realized due to optical background structure instabilities. All measures must distinguish between real changes in CH_2O concentrations and spurious CH_2O concentrations due to large perturbations of the background structure. Such assessment of noise and performance will reduce some of the discrepancies between predicted CH_2O concentrations determined by models and atmospheric measurements.

References

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