Inter-comparison of Laser Photoacoustic Spectroscopy and Gas Chromatography Techniques for Measurements of Ethene in the Atmosphere

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Laser photoacoustic spectroscopy (LPAS) is highly suitable for the detection of ethene in air due to the overlap between its strongest absorption lines and the wavelengths accessible by high-powered CO_2 lasers. Here, we test the ability of LPAS to measure ethene in ambient air by comparing the measurements in urban air with those from a gas chromatography flame-ionization detection (GC-FID) instrument. Over the course of several days, we obtained quantitative agreement between the two measurements. Over this period, the LPAS instrument had a positive offset of 330 ± 140 pptv (parts-per-trillion by volume) relative to the GC-FID instrument, possibly caused by interference from other species. The detection limit of the LPAS instrument is currently estimated around 1 ppbv and is limited by this offset and the statistical noise in the data. We conclude that LPAS has the potential to provide fast-response measurements of ethene in the atmosphere, with significant advantages over existing techniques when measuring from moving platforms and in the vicinity of emission sources.

Introduction

Volatile organic compounds (VOCs) are known to play a major role in the production of tropospheric ozone and organic aerosols through complex chemical reactions with nitrogen oxides [1, 2]. Ethene ($H_2C=CH_2$) is one of the more abundant and reactive VOCs in the atmosphere and therefore plays a significant role in the chemistry of ozone production, in particular in the vicinity of petrochemical industries. Traditional methods of ambient ethene monitoring involve either canister collection or preconcentration of in-situ samples followed by gas chromatographic (GC) analysis. Neither method is particularly satisfactory, however, for the rapid monitoring necessary when sampling onboard high-speed platforms such as aircraft, nor when sampling near emission sources where the variability is high. Ozone-olefin chemiluminescence techniques are rapid but lack specificity for ethene [3, 4]. Laser photoacoustic spectroscopy (LPAS) is a

technique that is both capable of fast-response (10 s or less) and highly specific to measurements of ethene, and could be ideally suited for atmospheric measurements. It is the purpose of this work to investigate the potential of LPAS to monitor ethene in air at the low- and sub-ppbv (part-per-billion by volume) levels that are typical in the atmosphere, and to evaluate interference from other atmospheric species. Toward this goal, we have inter-compared ethene measurements by LPAS with those from a gas-chromatography flame-ionization detection (GC-FID) instrument, which has been used for atmospheric ethene measurements for many years.

Harren et al. [5] have described the LPAS method in detail. Briefly, the method employs a laser light source, modulated at an acoustic frequency, which is passed through an absorbing medium, in this case ethene in air, thereby exciting the molecules into a higher ro-vibrational quantum state. Depopulation of this state to lower lying states occurs either via fluorescence or via collisions, the latter giving rise to a temperature increase of the gas due to energy transfer into translational energy. This nonradiative relaxation process dominates over the fluorescence decay when the relaxation time can compete with the radiative lifetime, which is generally the case at infrared wavelengths. Modulation of the radiation source at a certain frequency changes the temperature and the pressure also at that frequency, which can be observed as an acoustic signal with a sensitive microphone.

In this work, an LPAS instrument was inter-compared with a GC-FID system for measurements of ethene in urban air. The GC-FID system has been employed in numerous field campaigns onboard aircraft including the North Atlantic Regional Experiment (NARE) in 1993 and the Southern Oxidant Study (SOS) in 1994 and 1995, [6] and at a ground site in La Porte, Texas, during the Texas Air Quality Study (TexAQS) in 2000 [7]. In addition, the instrument was involved in the Non-methane Hydrocarbon Inter-comparison Experiment (NOMHICE), during which it was carefully inter-compared with numerous other VOC measuring instruments [8]. In this work, both the LPAS and the GC-FID instruments monitored ethene in ambient air sampled from outside our laboratory in Boulder, Colorado, and the results were carefully compared. The mixing ratios of ethene during the experiment ranged from hundreds of pptv (parts-per-trillion by volume) to tens of ppbv; in other words, the response of the LPAS system could be verified both in clean continental conditions and for air that was highly impacted by anthropogenic VOC sources.

Experimental Section

GC-FID Instrument. The GC-FID instrument has been described by Goldan et al. [6]. Briefly, C_2-C_6 alkanes, C_2-C_4 alkenes, and alkynes were measured by cryogenically concentrating a 70 STP cm^3 min^{-1} (STP = standard temperature, 273.15 K, and pressure, 1 atm) sample flow during a 5 min sample acquisition for every 15 min cycle of the instrument. The sample acquisition system consisted of a cryogenic moisture removal trap operating at −50 °C, an Ascarite trap for CO_2 removal, and the cryogenic sample trap operated at −160 °C. The sample trap surface consisted of a piece of Al_2O_3-coated, fused-silica capillary tubing that provided quantitative trapping of ethene. Samples were released from the sample trap by heating to 100 °C and transferred to the chromatographic column with a H_2 carrier gas flow of 6 STP cm^3 min^{-1}. Samples were then chromatographically separated on a KCl washed Al_2O_3 column of 50 m in length (J&W Scientific) divided in half to allow back-flushing the first half

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while the separation continued on the second half. This setup allows a complete sample acquisition and analysis every 15 min. Detection was accomplished with a flame ionization detector (FID), and data were collected on a laptop computer, which also controlled the entire instrument allowing unattended operation for up to 6 h (before refilling the liquid nitrogen dewar was required).

A reference standard air mixture was frequently analyzed (every 2−4 h) during the experiments to monitor the sensitivity of the FID, which has proven stable to better than 5% over many years. The gas mixture used has been calibrated against various standards, including NOMHICE intercomparison standards. The overall instrument accuracy for ethene is estimated to be ±10% and the precision ±5%. The detection limit for ethene is approximately 1 pptv.

LPAS Instrument. The Department of Molecular and Laser Physics at the University of Nijmegen, The Netherlands, developed the LPAS instrument for the detection of ethene used in this work. This group specializes in the sensitive and real-time detection of various trace gases emitted from mostly biological samples (9). For the detection of ethene, the group developed a CO_2 laser system with an intra-cavity photoacoustic cell (10). Ethene is an important gaseous plant hormone, and in collaboration with plant physiologists studies have been performed on flowers (orchid, Carnation, citrus petunia, tobacco) (11); dock plants (*Rumex*) adapting to submergence and water logging (12); pollination (13); plant pathogen interaction (14); and ethene−auxin interaction within mutants (15). In human health research, the instrument has been successfully used to follow the emission of ethene in exhaled air, and through the skin as a biomarker of ultraviolet radiation damage (16).

The detection of ethene at the sub-ppbv level requires high laser powers (∼100 W) that are obtained using a CO_2 laser (10). The setup consists of a gas discharge tube to generate the CO_2 laser radiation. At one side of the discharge tube, a grating and a chopper are positioned to select CO_2 laser lines and to modulate the laser beam, respectively. On the other side of the gas discharge tube, a lens ($f = 25$ cm) focuses the laser beam onto the photoacoustic cell and the output mirror (97% reflectivity). Additional control and supply units consist of a stepper motor to control the grating for selecting the CO_2 laser lines, a lock-in amplifier to filter and amplify the photoacoustic signal, and a computer to run the experiment.

The photoacoustic cell was operated at ambient pressure (850 mbar in Boulder) and temperature (293 K). The cell can be operated at other pressures, but the response slowly decreases with pressure. At pressures below ∼100 mbar, the acoustic properties will significantly affect the response of the cell. The cell itself contained a 10 cm long brass tube, which acts as a resonator (diameter 0.6 cm). To be able to excite this acoustic resonator in its first longitudinal mode (at ∼1.6 kHz), the end sections of this resonator are open and coupled to buffer volumes (2 cm diameter, 5 cm long). The total volume of the cell is 35 cm³, and the active volume, that is, the part that determines the photoacoustic signal, is approximately 2.9 cm³. At a typical flow rate of 33 STP cm³ min⁻¹, the response time is thus approximately 5 s. To further improve the response time, the gas flow enters the photoacoustic cell at the center of the resonator and exits at both sides from the buffer volumes. At higher gas flows, the flow itself generates an acoustic signal that adds to the instrument backgrounds and deteriorates the instrument performance.

The CO_2 laser has about 80 laser lines in the 9−11 μm wavelength region divided over four branches. We detect ethene on the 10P14 CO_2 laser line (949.4793 cm⁻¹) where it demonstrates the highest absorption, and the neighboring 10P12 laser line (at 951.1922 cm⁻¹) with a ∼7 times smaller absorption strength (17). The generated photoacoustic signal is proportional to the laser power; therefore, each signal is normalized for the laser power. After this, the normalized signals from the two laser lines are subtracted to correct for interfering absorptions and to calculate the ethene concentration. Interfering absorptions can be generated by the windows of the cell, the wall of the resonator, and other absorbing gases (10). In these experiments, the acquisition of one data point took about 90 s. Much of this time is spent in stepping the laser between the 10P14 to the 10P12 lines: the stepper motor needs time to adjust the grating, and the power meter that monitors the laser power has a slow response. In later designs of the LPAS system, both parameters have been improved, and the measurement acquisition time is reduced to 5−10 s without loss of measurement precision.

The inlet system of the photoacoustic cell contained a CO_2 scrubber (Ascarite). The removal of atmospheric CO_2 is necessary because it absorbs, albeit weakly, at the CO_2 laser lines in the 9−11 μm wavelength region. Furthermore, the photoacoustic signal would undergo a phase shift, due to the combination of the modulation frequency (1.6 kHz) and the slow collisional de-excitation of the absorbed energy by CO_2 (18). In combination with the ethene absorption signal, the overall signal would be lower and could even result in negative (calculated) concentrations. The flow through the inlet system was the same as the flow through the photoacoustic cell. Due to the small flow and the relatively large volume of the inlet system, this led to a reduction of the response time of the system. This situation can be improved easily by passing a higher flow through the inlet and diverting a small fraction to the photoacoustic cell.

The LPAS instrument was calibrated by measuring ethene from a 28.3 ppmv laboratory standard diluted in a flow of zero air to concentrations between 0 (zero air only) and 52.7 ppbv. This flow was also sampled by the GC-FID system, and the concentrations were determined by the GC response which agreed with dilution factors of the laboratory standard to better than 2%.

Inter-comparison. For the inter-comparison of the LPAS and GC-FID measurements of ethene, the two instruments were installed in a laboratory setting, which included (1) a concentration-selectable source of ethene in zero air, and (2) a concentration-selectable source of ethene in breathing air, which also included numerous other atmospheric VOCs, and (3) a source of ambient outside air. Initially, the two instruments sampled the ethene laden zero air to calibrate the LPAS system, and to verify the mixing ratio of the diluted standard mixture by GC-FID. After the LPAS instrument was calibrated, a compressed whole ambient air sample ("breathing air") containing numerous VOCs at concentrations commonly found in urban air was analyzed for ethene by both instruments. This gas stream was analyzed both intact and diluted by factors of up to 10 with zero air. This provided a reproducible sample stream in which any effects of other sample stream components on the LPAS instrument could be observed. Finally, ambient air measurements of ethene by both instruments were compared. Outside air at the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado, was drawn into the laboratory through ³/₈" PFA tubing and analyzed by both instruments. The laboratory's location on the western edge of Boulder at the foot of the Rocky Mountains is ideal for comparison purposes, because both polluted urban air as well as clean mountain air can be sampled from the same location, depending on the direction of the local winds.

Results and Discussion

Figure 1 illustrates the results of the analysis of breathing air described above. Figure 1A shows the time series of both the
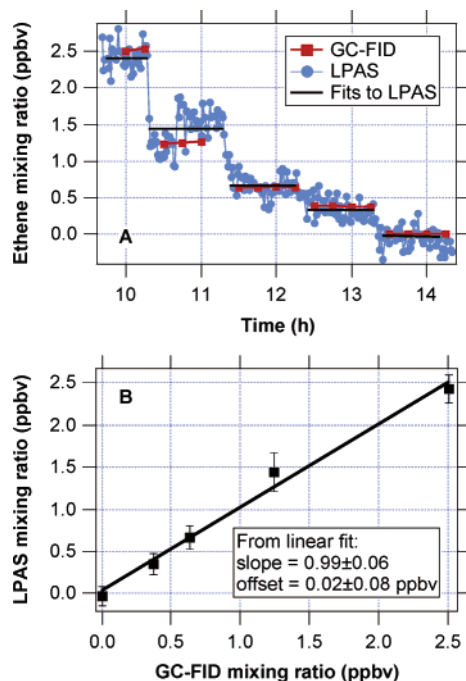
FIGURE 1. Measurement of diluted breathing air by LPAS and GC-FID. Panel A shows the time series of the measurements, during which the breathing air was stepwise diluted in zero air. Panel B shows the scatter plot of the LPAS versus GC-FID results.

LPAS and the GC-FID measurements, as the breathing air was diluted in five steps. Figure 1B shows a scatter plot of the LPAS versus the GC-FID measurement. With the exception of the measurement at ~1.25 ppbv, when the LPAS instrument displayed a sudden shift due to a mode hop of the CO_2 laser, the agreement between both instruments is within the standard deviation of the LPAS signal. Smaller effects of laser mode hops are apparent at several other instances throughout the measurement period shown in Figure 1A, and they limited the precision of the LPAS results. A better alignment and temperature stabilization of the laser should help to alleviate these problems in the future. The scatter plot in Figure 1B indicates that the two instruments are in agreement to within 1% over the measured range of ethene. Error bars on the LPAS data are 1 standard deviation, while 1 standard deviation error bars of the GC measurements are indistinguishable from the symbol. Evidently, the VOCs in the breathing air, which included mainly the C_2-C_5 alkanes plus lesser amounts of the C_6 alkanes, propylene and acetylene (observed by the GC-FID), did not interfere with the measurement of ethene by the LPAS instrument. It should be noted, however, that any oxygenated VOCs such as alcohols and aldehydes were no longer present in the breathing air.

Figure 2 shows the time series of the LPAS and GC-FID measurements of ethene in ambient air outside of the NOAA Aeronomy Laboratory in Boulder, Colorado. The GC-FID instrument was only operated during daytime hours, whereas the LPAS instrument ran continuously. On November 20, 24, and 25, the LPAS results show enhanced ethene mixing ratios in the morning, due to traffic activity around the laboratory. It is seen that the general agreement between the LPAS and GC-FID measurements is good. Both instruments capture the strongly enhanced ethene observed on November 24. The high time resolution of the LPAS instrument allows the observation of several short peaks that are attributed to vehicles in the immediate vicinity of the sampling inlet, for example, around noon on November 21. Because the GC-FID only acquires sample for 5 out of every 15 min, only one of these enhancements, at ~15:00 on November 21, is partially caught by the GC-FID system. Negative responses of the LPAS measurement are observed on November 20, and on November 24 and 25. These were most likely caused by the interference from other species. It is possible that some CO_2 broke through the Ascarite filter, or that laboratory air leaked into the LPAS system. The exact cause was difficult to determine, and these problems point to the need for regular calibrations and background checks of the LPAS instrument in atmospheric monitoring applications.

Figure 3 shows scatter plots of the LPAS versus the GC-FID measurements both on linear and on logarithmic scales. The LPAS data in these plots have been averaged over the 5-min sampling periods of the GC-FID system. Panel A shows that the agreement between the two data sets is good with one notable exception: the highest point in the LPAS measurement on November 21 (around noon in Figure 2) is not reproduced by the GC-FID measurement, probably due to a minor timing issue. Apart from this data point, the correlation between the data sets is high: the linear correlation coefficient, r, was 0.91 ($r = 0.98$ with the outlier from November 21 excluded). The dotted lines in Figure 3 show the 1:1 relationship, and the data points are scattered around that line. A linear least-squares fit was calculated, and the solid lines in Figure 3 show the results. The slope of the line is 0.88 ± 0.04, and the offset is 0.33 ± 0.14 ppbv. Interference to the LPAS measurement from species other than ethene could result in a slope higher than 1. However, the slope is smaller than 1, which may be caused by a drift in the LPAS sensitivity. This points to the need of performing regular calibrations during a measurement to get the best accuracy.
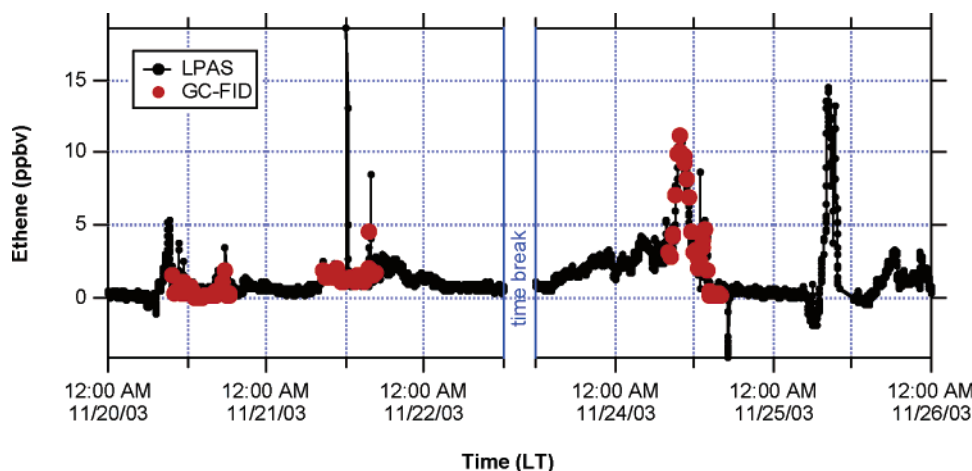

FIGURE 2. Time series of the ambient air measurements by LPAS and GC-FID for two different periods.
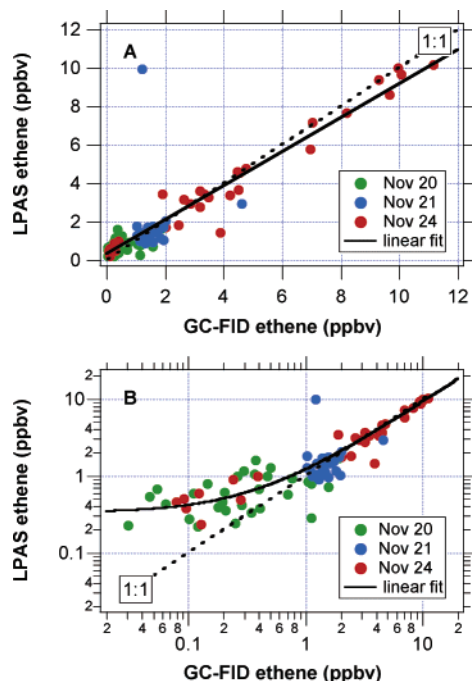
FIGURE 3. Scatter plots of the LPAS versus GC-FID measurements of ethene in ambient air. Panel A shows the data on a linear scale, whereas panel B shows the same data on a logarithmic scale. The solid black lines show the result of a linear fit to data from all three dates (slope = 0.88 ± 0.04; offset = 0.33 ± 0.14 ppbv).
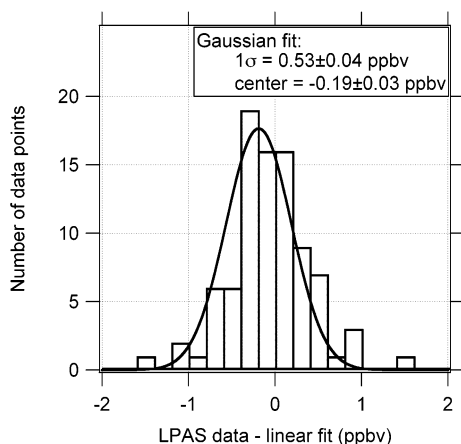

FIGURE 4. Histogram of the differences between the LPAS data and the linear fit shown by the solid lines in Figure 3.

The nonzero offset manifests itself as the curvature in the data points and fit at the smallest mixing ratios in Figure 3B. More work is needed to determine if this offset is due to the baseline determination of the LPAS instrument, or to interference from other VOCs. It is known, for example, that ethanol has some spectral overlap with the ethene absorption line used here and could thus interfere with the ethene measurement. At typical mixing ratios of ethanol in urban air, however, this is not expected to be a significant problem.

The LPAS data generally have more statistical noise than the GC-FID data. To quantify this noise, we have calculated the difference between the LPAS data and the line fitted through the data in Figure 3. A histogram of these differences is shown in Figure 4. It is seen that the distribution can be described by a Gaussian function with a width (1σ) of 0.53 ± 0.04 ppbv. The width depends slightly on the absolute value of the signal: the average difference between the LPAS and GC-FID data points below 1 ppbv was 0.40 ± 0.03 ppbv. We attribute most of this scatter to the limited precision of

the LPAS measurement system, because the precision of these GC-FID measurements is much better (1%). Some additional scatter may be due to actual atmospheric variability and the fact that the two measurements did not perfectly coincide in time. However, previous work has shown that analyses such as these can give useful information on the statistical noise in the data (*19*).

From Figure 3B, it is clear that below 1 ppbv the agreement between the LPAS and GC-FID measurements is poor, and therefore we estimate the detection limit currently achievable to be around 1 ppbv for a single measurement. This detection limit is insufficient for measurements in clean conditions, but in more polluted air and in the vicinity of emissions sources, the sensitivity is easily good enough to detect ethene in real-time, as illustrated by Figure 2.

We conclude from this work that laser photoacoustic spectroscopy (LPAS) can be used to measure ethene in the atmosphere with a time response that is significantly improved over existing methods. Below ethene mixing ratios of 1 ppbv, the LPAS measurement is compromised due to the limited measurement precision and possibly due to interference from other species. More work is needed to determine the cause of the offsets in the LPAS response. Nevertheless, the LPAS instrument tested here has the potential to perform the fast-response ethene measurements that are needed for use on moving platforms and in the vicinity of emission sources.

The LPAS instrument used in this work contained a photoacoustic cell of an older design; newer designs show promise of significantly improved detection limits. Also, the instrument was optimized for biogenic sampling and not for the best ambient air response time. By minimizing the retention time of air in the system, and by optimizing the data acquisition procedure, we expect that response times below 5−10 s can be achieved. Work is in progress to build a compact LPAS sensor that is suitable for use in aircraft measurements and other applications. This sensor will be tested for interference from species such as CO_2, ethanol, and perhaps other olefins. Also, the effects of atmospheric factors such as the humidity on the sensitivity will be studied.

Acknowledgments

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