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Multiple Component Analysis of Cigarette Combustion Gases on a Puff-by-Puff Basis Using a Dual Infrared Tunable Diode Laser System

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ABSTRACT

A dual infrared tunable diode laser system (IR-TDL) has been developed for the simultaneous detection of multiple gaseous components in cigarette smoke. The high spectral resolution (0.001 cm^{-1}) and rapid time response (20 Hz) of the TDL system are ideal for separating the absorptions from the multitude of gas phase components found in this matrix. The combustion products are sampled into a 0.3 liter, 18 meter multiple pass absorption cell with a flow response time of 0.15 seconds, which provides ample time resolution to observe variations within each 2-second puff. Two independent beam paths allow simultaneous detection in two wavelength regions; the first for ethylene and ammonia and the second for formaldehyde. Rapid scan-sweep integration with direct absorption permits absolute gas concentrations to be determined on-line. A non-linear least squares procedure is used for "fingerprint" fitting of up to four gases with each diode. Results demonstrating the instrument sensitivity and time response, along with potential caveats, for several gaseous components will be presented.

Keywords: Infrared Tunable Diode Lasers, Multiple Component Analysis, Cigarette Smoke, and HITRAN Database.

1. INTRODUCTION

The characterization of combustion products from biologically-derived sources, such as coal, oil, natural gas, jet engine fuel, tobacco, etc., is a complex problem due to the multi-component and multi-phasic nature of the products. The combustion of tobacco in a cigarette produces thousands of compounds by pyrolysis, pyrosynthesis, and/or combustion, distributed through gaseous, particulate and aerosol phases. Previous researchers have estimated as many as 2,740 compounds in cigarette smoke, and noted that this matrix may be the most complicated, most varied compositional collection of organic molecules to be found.[1] Cigarette smoke is dynamic and reactive, where species react inter- and intra-molecularly and change phases depending on the cigarette coal temperature, ambient temperature, and local concentration of the species. As such, accurate quantitative methods are required for real time sampling of whole (unseparated) smoke, with high sensitivity (ppt for certain species of interest) and high selectivity (spectral resolution for discrimination). In conjunction with Aerodyne Research, Inc., we have jointly developed a dual beam infrared tunable diode laser system and automated smoke injection system to measure ethylene (C_2H_4), ammonia (NH_3), and formaldehyde (H_2CO).

Previous uses of infrared tunable diode laser (IR-TDL) systems have included such diverse samples as emissions from industrial buildings, landfills, cities, chemical plants, stack gases, automobile exhaust, aircraft exhaust, urban pollution, open flames, and human breath.[2] Beginning in and through the 1980's, Philip Morris laboratories analyzed ethane, hydrogen cyanide, methane, and water vapor in cigarette smoke using a Laser Photonics LS-3 TDL spectrometer with frequency modulation and lock-in amplifier detection.[3,4,5,6] We were intrigued by both the possibility of quantifying multiple species using multiple diodes in the time domain and the use of fitting techniques that could resolve overlapping lines. There have been many technological advancements since the implementation and use of our first TDL, that make fast time domain studies of multiple species possible and make the instrumentation more user-friendly and robust. These advances include metal-organic chemical vapor deposition techniques that produce diodes that operate above liquid nitrogen temperatures (80-120 K) and are single mode over a wider wavelength range; advanced computing power which facilitates real time instrument control,

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data acquisition, and fitting; and optical cell design advances (astigmatic Herriot cells vs. White cell) that mitigate alignment and have higher pathlength to volume ratios (better optical space filling with minimization of fringes). IR-TDL is particularly well suited to complex systems because of its sensitivity, selectivity, and speed. The diode lasers are ~1 mW and coherent, which allows the use of long pathlength cells, in some cases up to 100 meters. Diode lasers have very high spectral resolution, which at low pressures permits the observation of Doppler-limited lineshapes, i.e. the separation of fundamental rotational-vibrational lines. The use of this powerful spectroscopic technique to study cigarette smoke without prior separation and in real time, as opposed to chromatographic techniques which in many cases require multiple cigarettes to be smoked and compounds to be derivatized for detection, will advance our understanding of this combustion process and the factors that affect it. The analytical challenges of this unique matrix also will serve to advance the TDL technique, in terms of quantifying multiple species within the limited single-mode spectral region (~1 cm^{-1}) of a diode and its extension to species which are not at present included in line-by-line spectral databases such as the High Resolution Transmission Molecular Absorption (HITRAN) database.[7]

2. EXPERIMENTAL

2.1 IR-TDL System

The spectrometer was custom designed by Aerodyne for Philip Morris, to be a dual diode system with the capability to expand to a four-color system in the future (i.e. four lasers traversing a single gas cell and then being separated onto four separate detectors). The basic components of the instrument have been described in detail elsewhere.[8,9,10,11] A schematic of the optical design is shown in Figure 1. The centerpiece of the spectrometer is the liquid nitrogen dewar (MN ND-5, Infrared Laboratories) which houses the two diodes and the four detectors. The diodes are 180° apart with space to expand to four diodes on each side to house a total of eight separate diodes. By using spacer bars, the output optics may be incrementally moved to align with the diode of choice, minimizing alignment time. A 10X microscope objective allows one to observe the position of the diode during alignment. A visible trace laser is used to aid in optical alignment, tied to a 200 μm pinhole which is removed during data collection. Schwarzchild reflecting objectives (15x, 0.4 numerical aperture) collect the light from the diodes and create the fist focus at the pinhole location. Reflective optics (flat and spherical mirrors with radii shown in Figure 1) are used throughout the remainder of the optical system. The dewar is equipped with an autofill system (Infrared Laboratories, Inc.) that initiates a liquid nitrogen fill once the temperature in the dewar rises above a specified level and continues filling for a specified time period. The four detectors are placed in a square configuration with the two sample detectors placed high and the two reference detectors placed low indicated by the solid and broken lines, respectively. The detectors are photovoltaic HgCdTe (MCT) elements (MN KV104-1-BM/11, Kolmar Technologies, Inc.) with companion preamplifiers (MN KA01-E6-AG, Kolmar Technologies, Inc.). The elements are all 0.5 mm^2 in size with $D^* \geq 10^{10}$ $Watts^{-1}cm^2sec^{-1/2}$. The preamplifiers have two-stage adjustable gain switches of X1 or X10 and X1, X2, X5, or X10. Each diode is equipped with a laser controller (MN L5830, Laser Analytics, Inc.) to tune the current and temperature and to apply a triangular-shaped current modulation to turn the laser on, sweep it, and shut it off. The diodes were selected to be single mode for a specified wavenumber, 965 cm^{-1} for ammonia and 2815 cm^{-1} for formaldehyde (Laser Components, Inc.). These wavelengths were anticipated to be free from interferences, based on prior knowledge from TDL work on cigarette smoke. Through the use of astigmatic optics, the volume of the 18 m pathlength cell (91 passes, 19.78 cm base) has been reduced to 0.3 L resulting in the sub-second residence times necessary for spectroscopic studies of reactive species. The cell is convertible to 36 m pathlength by rotating and translating one of the mirrors, but because fringing from optical degradation of the mirrors by the accumulation of smoke condensate was expected to be much worse at 36 m than at 18 m, the cell was set at 18 m. The cell has been described in detail elsewhere.[12] A monochromator (MN L5156, Laser Analytics, Inc.) with a 10 μm blaze, fitted with focussing optics designed by Aerodyne, aids in wavelength and mode purity determination. A Ge etalon (MN L5940, Laser Analytics, Inc.) 1.011” in length is used to determine the non-linear tuning rate of the laser, due to switching the laser on and off. The tuning rate (in cm^{-1}/ADC channel) is greatest at the beginning of each scan when the laser is switched on and decreases with time until the laser is switched off.

Data acquisition is based on a rapid sweep integration over the full infrared transition lineshape or group of transitions, by a software package developed at Aerodyne. A current ramp turns the laser on, sweeps it across a single mode wavelength range, and then shuts the laser off. The detector output is digitized by a 300 kHz, 12-bit ADC board (Scientific Solutions). Using a 4th or 5th order polynomial fit to the baseline, the etalon tuning rate equation, the signal intensity at the laser off position, and the known spectral line shapes and positions from the HITRAN database, the integrated area (concentration) is determined by a nonlinear least-squares fitting routine.[13] There are many advantages to using the HITRAN database. The line shapes and positions are known from theory and can be precisely calculated from the temperature and pressure in the cell. This allows one to easily monitor complex and overlapping spectral features. Monitoring several transitions for one species can enhance sensitivity, and is sometimes necessary for spectra with overlapping lines from multiple species or for larger molecules (6+ atoms) where the individual lines are not fully resolved. This fingerprint fitting allows one to monitor multiple species with multiple lines simultaneously, and even allows one to fit unknown lines which overlap the desired spectrum as a method of removing background absorptions. The software is able to fit up to four species on each diode, using up to 45 line definitions from the HITRAN database. The continuous stream of the results of these fits is transferred from the dual DOS-based computers that control the instrument to a second Windows-based computer running the custom smoker program that controls the smoke injection system. The program, described in detail below, converts the stream of concentration data from ppm or ppb data into µg/puff by integrating the 2 sec puff, along with knowledge of the molecular weight of the species and the dilution factor introduced by the flowing system. Reduced pressure sampling is necessary to take advantage of the narrow line width of the laser source. A pressure drop from ambient to 33 torr is obtained by using a critical flow orifice (CFO) of 0.5 mm diameter at the cell inlet and a rotary vane vacuum pump at the back end of the cell. This constantly flowing system minimizes optical degradation from cigarette tar accumulation, reactions among smoke components, and adsorption losses on to the cell walls. The response time of the cell can be calculated using the cell volume, total flow rate, and sampling pressure in the cell, respectively, as follows: 0.3 L/(5.1 L/min * 760 torr/33 torr)* 60 sec./min = 0.15 sec. or 6.5 Hz.

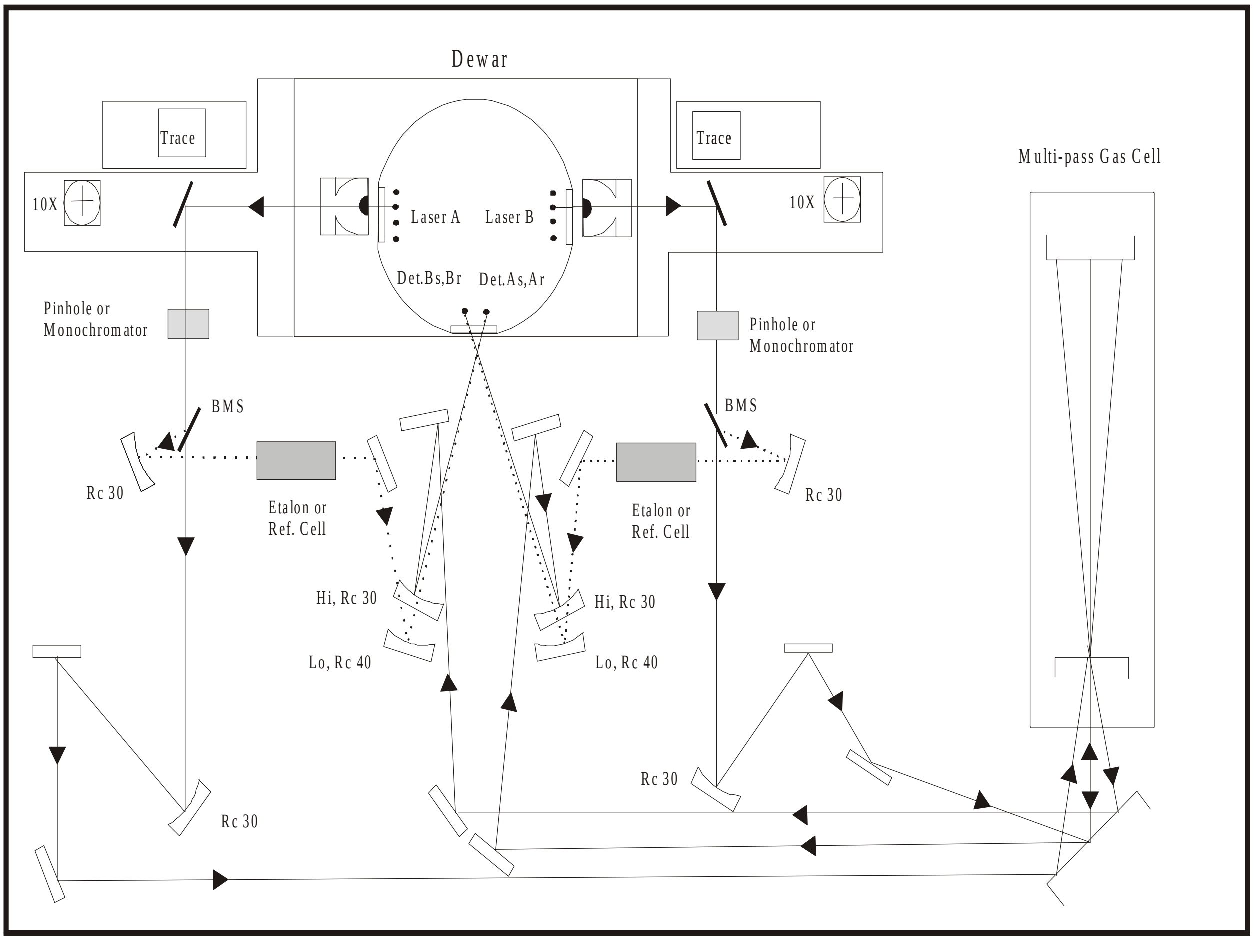

Figure 1. Schematic of the Two-Color Optical Layout.

2.2 Smoke Injection System

The Federal Trade Commission (FTC) specifies the standard conditions under which cigarettes should be smoked as 35 mL puff volume of 2 sec. duration at an interval of 60 sec. with a sine wave flow profile in a conditioned room of 74° F and 60 % relative humidity. Conventional smoking machines utilize a glass or stainless steel syringe into which the smoke is drawn from a cigarette and then expelled, through a switched solenoid, into the analyzer or chemical trap. From past experience, we know that smoke readily reacts with and adsorbs on surfaces, changes composition over time (even during the two second draw), and with sufficient runs deposits enough tar to slow or stop switching solenoids and control valves. In many analytical techniques, a filter pad is positioned between the cigarette and the syringe to collect particulate matter and to protect the switching mechanics and optics, preventing "whole smoke" analyses. Aerodyne has designed and constructed an automated cigarette smoking system that has minimal surface area and no switching solenoids in the smoke stream. The system operates under computer control with software written in Visual Basic (VB). This software controls all aspects of the smoke injection system and provides a convenient user interface for setting the collection parameters and viewing the streaming concentration data. The purpose of this system is to smoke the cigarettes under controlled, reproducible conditions and to quantitatively transfer all of the vapor to the optical absorption cell for analysis. The approach minimizes surface interactions to the greatest extent possible by controlling the flow across the cigarette using mass flow controllers which are upstream from the cigarette. In this way, the flow controlling elements never interact with the cigarette smoke and the cigarette smoke is exposed only to a very small area of inert transfer tubing. A schematic of the smoke injection system is shown in Figure 2.

The cigarette is inserted into a four-way cross, with the opposing port connected to the CFO at the cell inlet. Typically, the pressure in the sampling cell is ~33 torr and the inlet pressure is near atmospheric pressure or ~760 torr. Under these conditions, the flow into the multi-pass cell is linearly proportional to the pressure at its inlet. A piece of tubing connected to the end of the glass CFO directs the smoke over the inlet mirror.

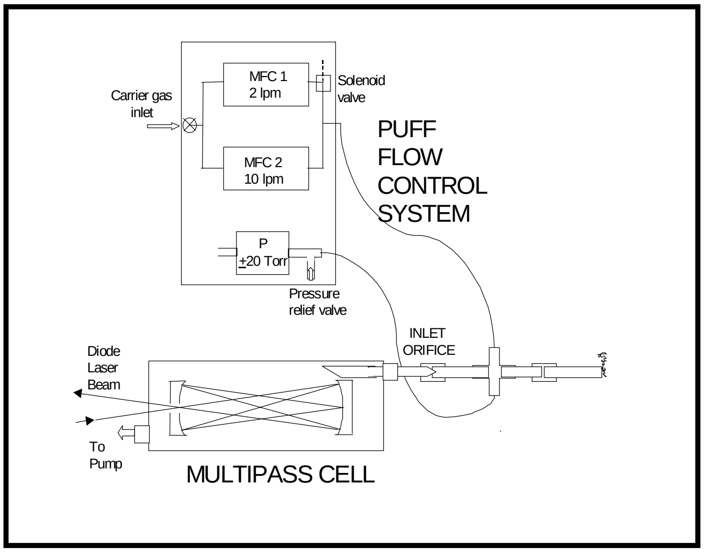

Figure 2. Schematic of the smoke injection system.

The other two ports of the cross are connected to the flow control elements. One port connects to a differential capacitance manometer (20 torr range, MN 223BD-00010AABS, MKS Instruments, Inc.) which measures the pressure difference between the inlet and the room, i.e. the pressure drop through the cigarette rod. There is no flow through this port and it is used only as a sensing element. The fourth port of the four way cross is connected to the outputs of two mass flow controllers (MFC1, MN 1179A14CS15V and MFC2, MN 1179A23CS15V, MKS Instruments, Inc.) which produce flow streams of carrier gas at a selectable flow rate. By varying this flow, the flow of room air through the cigarette rod is controlled. Between cigarette puffs there should be no flow through the cigarette rod, and therefore, no pressure drop across the cigarette rod. This is accomplished by directing the mass flow controllers to provide a flow rate of gas equal to the flow rate generated across the CFO when the inlet orifice is at atmospheric pressure. This flow rate is determined by increasing the carrier gas flow rate until the pressure drop across the cigarette is precisely zero.

Puffs are generated by reducing the carrier gas flow. This could be accomplished by using a single MFC and changing its set point, but can be done more rapidly by using two flow controllers set to fixed rates and switching one of the flow controllers in and out of the flow stream using a three way solenoid valve (PN 009-0737-900, General Valve). The crucial point in the operation of this system is that reduction of the carrier gas flow rate induces a flow across the cigarette which is very nearly equal to the original flow rate. When the carrier flow is reduced, the pressure at the inlet would drop substantially if nothing else changed, but this pressure drop causes a flow across the cigarette which compensates for the reduction in flow. This results from the flow resistance of the cigarette being small (around 9 torr) and the port behaving almost like an open port (negligible flow restriction). An open port does not induce a pressure drop and thus would provide exactly the flow required to keep the inlet flow rate constant. For the FTC-specified smoking regimen, a flow rate across the cigarette of 1050 standard cc/min (sccm) during the puff is necessary. In this case, MFC1 is set to a flow rate of 1050 sccm and MFC2 is set to provide the additional flow required to eliminate any pressure drop across the cigarette, i.e. balancing the flow across the orifice induced by the vacuum pump. Typically this flow rate is ~4000 sccm with the existing orifice size. In the simplest scheme, we would simply divert the flow from MFC1 during puffs and the flow across the cigarette would be approximately 1050 sccm as desired. However, due to the changing pressure drop across the cigarette with consecutive puffs, the actual flow would be underestimated by some amount. We can easily estimate the amount of this error. The resistance of the cigarette is small, but it is not zero. During a standard puff a pressure drop of 9 torr is typical. This means that the pressure at the inlet is not 760 torr as desired, but perhaps 1% less. This implies that the total flow rate across the inlet is also reduced by 1%. The flow across MFC1 will not have changed, so all of the change must arise from the difference between the flow rate across the cigarette and the flow rate of MFC1. Since these flow rates are ~20% of the total flow, it follows that the flow across the cigarette will be 5% less than the flow rate of MFC1 or approximately 1000 sccm rather than the desired 1050 sccm. Even so, this very simple scheme delivers the correct flow rate across the cigarette to within 5% and can be implemented without knowledge of the flow resistance of the cigarette.

A more accurate flow rate may be determined by measuring the cigarette resistance during an initial dry puff, before lighting, and during each actual puff by dynamically recording the pressure drop through the cigarette. Knowing this resistance, the flow rate of MFC2 is set to a slightly lower value during the following puff. For example, its nominal flow rate of 4000 sccm might be reduced to approximately 3950 during the puff. This additional 50 sccm flow reduction will be compensated by extra cigarette draw. In this manner, a standard puff is created by reducing the total carrier gas flow by a total of approximately 1100 sccm. The cigarette responds by adding a flow which is ~95% of this value or 1050 sccm as we desire. This approach is accurate to better than 1% even with only modest knowledge of the resistance to draw of the cigarette. It is important to note that the flow conditions are subject to variation as the cigarette is smoked and that these conditions must be monitored and adjusted for on a puff-by-puff basis. This is facilitated by digital RS485 communication between the smoke injection system and the master VB program. It is also important to realize that the diameter of the CFO may decrease due to gradual tar deposition. The system, therefore, is able to measure and compensate for both the changing pressure drop through the cigarette and for small changes in the CFO diameter which may occur during smoking. These flow and pressure drop values are recorded in real time for the corresponding concentration data.

The present design uses a fast solenoid valve for producing a puff with a “square-wave” profile. Future modifications to the smoker system could incorporate a computer-controlled variable solenoid valve to produce different puff profiles, such as sine, triangular, rectangular, or any user-defined waveform.

2.3 Cigarette Samples

The cigarettes used were Kentucky Reference 1R4F cigarettes, fabricated by the University of Kentucky in 1982. All samples were lit with a match, as opposed to other lighting methods, such as a butane lighter, an electrically-resistive heating element, or a projector bulb with focussing optics. Cigarettes were smoked to a length of tipping paper plus 3 mm, according to FTC convention.

3. RESULTS AND DISCUSSION

Preliminary experiments were conducted on a prototype instrument at Aerodyne to determine the limit of detection for NH_3 in cigarette smoke. These initial experiments used a 3 liter / 100 meter optical cell with a single diode at 928 cm^{-1}, and manual smoke injection by physically toggling the inlet solenoid. The data collection parameters were 15.5 torr sampling pressure, 296° K temperature (the smoke exits the cigarette rod at room temperature), with a total flow rate of 4.9 L/min., resulting in a response time of 0.75 sec. The diode was swept over the range of 928.5-928.9 cm^{-1} for a 200 point scan at a 300 kHz data rate. Coaveraging 500 spectra resulted in 1 data point every 0.3 sec. Single mode laser diode operation over this range was determined by placing sufficient ammonia in the cell so that the lines would saturate. If other modes are present, these saturated lines will not absorb fully to the zero light level. A dual fingerprint fit to C_2H_4 and NH_3 lines within the sweep region was performed. Figure 3 shows a typical data set. Qualitatively, the puff distribution of concentration versus puff number is consistent with previous work. For example, for ammonia the first puff is the smallest and the concentration increases with later puffs as the cigarette rod becomes shorter. Typically, ethylene is present in cigarette smoke at 100 times the concentration of NH_3. Figure 4 shows an expanded view of Puff 6 from Figure 3, where the data have been integrated over the 2 second puff and converted to µg/puff, by using the ideal gas equation at standard temperature and pressure, µg/puff = (PPM_v x M_w x V x P)/(R x T) where Mw is the molecular weight of the molecule in g/mol, V is 0.035 L/puff, P is 1 atm, R is 0.08206 L-atm/mol-K, and T is 298° K .

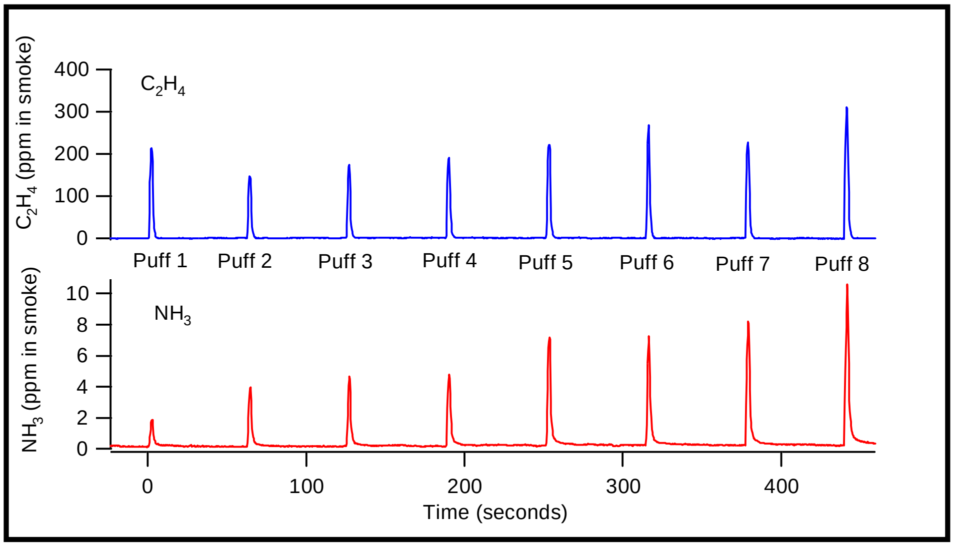

Figure 3. Puff-by-puff data for 1R4F test cigarette collected with the prototype instrument described above.

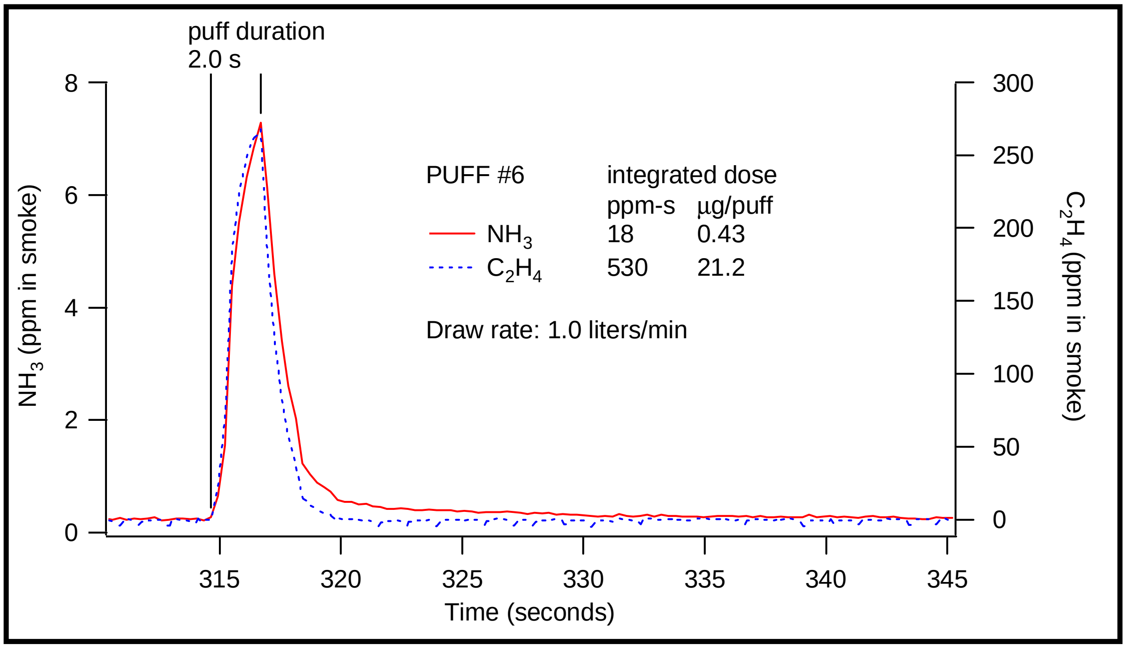

Figure 4. Expanded view of puff 6 from Figure 3, showing limits of integration and results.

If this puff is expanded still further, as seen in Figure 5, a detection limit from the signal-to-noise ratio (SNR) can be determined. The detection limit is defined as three times the SNR. This was calculated using the peak-to-peak noise level and the integration time over the duration of the puff, 3 x 0.015 ppm x $(0.3 \text{ s}/2 \text{ s})^{0.5}$ = 0.018 ppm or 0.4 ng/puff of NH_3. It is interesting to note the trailing edge on the NH_3 trace, while the C_2H_4 trace drops quickly to baseline. This is due to the affinity of NH_3 for surfaces, as compared to the relatively inert C_2H_4.

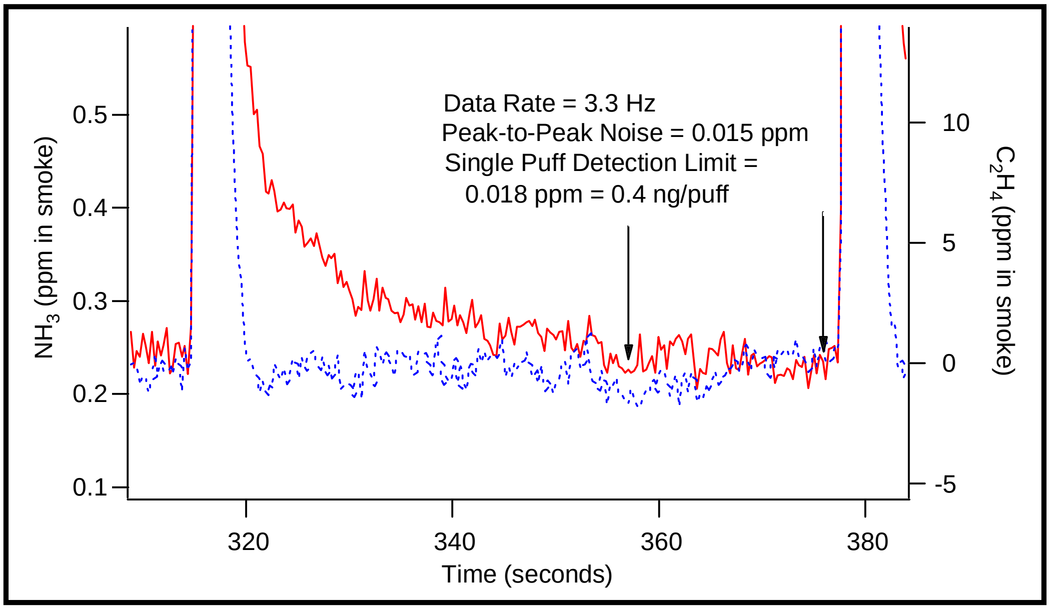

Figure 5. Expanded view of Puff 6 from Figure 4, showing the baseline noise and the detection limit calculation for a signal-to-noise ratio of 3.

In later tests, a 1R4F reference cigarette was smoked on the IR-TDL system described in the Experimental section. The C_2H_4 was fit to the line at 965.459 cm^{-1}, NH_3 was fit to the line at 965.353 cm^{-1}, and H_2CO was fit to the line at 2800.695 cm^{-1}. Figure 6 is a plot of concentration vs. puff number for the three species. In order to make the size of the data files more manageable and since we are normally most interested in the µg/puff delivery, only approximately six seconds of data are saved for each puff (2 sec. before and 2 sec. after each puff). Displaying the data in this way with a non-linear time base, allows us to see the intra-puff variations in concentration. The enhanced time resolution available with the present 0.3 L / 18 m cell, as compared to the 3 L / 100 m cell, is plainly evident in the puff profiles shown in Figures 6 and 4, respectively. The same qualitative trend of puff-by-puff deliveries as was seen in Figure 3 for C_2H_4 and NH_3 is also present. The H_2CO pattern is very distinctive, as previous IR-TDL studies in the Philip Morris laboratories have shown, with the highest delivery on the first puff and much less on subsequent puffs as the species is adsorbed on to tar and water trapped on the cellulose acetate filter. The final 10th puff is a clearing puff where the tobacco column is removed and room air is swept through the filter to draw off volatiles. The increased concentrations for NH_3 and H_2CO in the 10th clearing puff are consistent with their hydrophilicity or tendency to adsorb on surfaces. It is apparent from the shape of puffs 3-8 for H_2CO that the fit has degraded. From later experiments with gases known to be in cigarette smoke, it was found that acetaldehyde, ethane, and methanol all have line transitions in the limited sweep region studied. From FTIR experiments we know that the concentrations of these gases greatly exceed the amount of formaldehyde present, and these gases must either be accounted for in the fitting definition or another formaldehyde region free from interferences must be found. Methanol also was found to absorb in the ammonia spectral region studied, but did not appear to interfere with the fit. Neither acetaldehyde nor methanol are in the HITRAN database. More rigorous quantitative experiments are underway to determine if lines selected for quantitation are free from interferences. These experiments will use certified gas cylinders and permeation devices traceable to National Institute of Standards and Technology (NIST), when available, to ensure that we obtain accurate concentrations from the fit. A multi-component blend of gases at the anticipated concentrations will be analyzed to determine if there are interferences present. To facilitate this, a computerized multi-component gas mixing unit (MN S-2000, Environics Inc.) will be used. This unit takes up to 9 gases of known concentration and dilutes and blends them to produce a single stream with specific gas concentrations. In addition, to generate reactive species not available in gas tanks, a 6-oven permeation device (MN TO-14-B, Kin-Tek) will be used. The output pressure (30 psi) of the permeation device is sufficient to feed into one port of the gas mixing unit in order to produce a mixture containing as many as 13 components, accounting for a nitrogen dilution stream into each of the units.

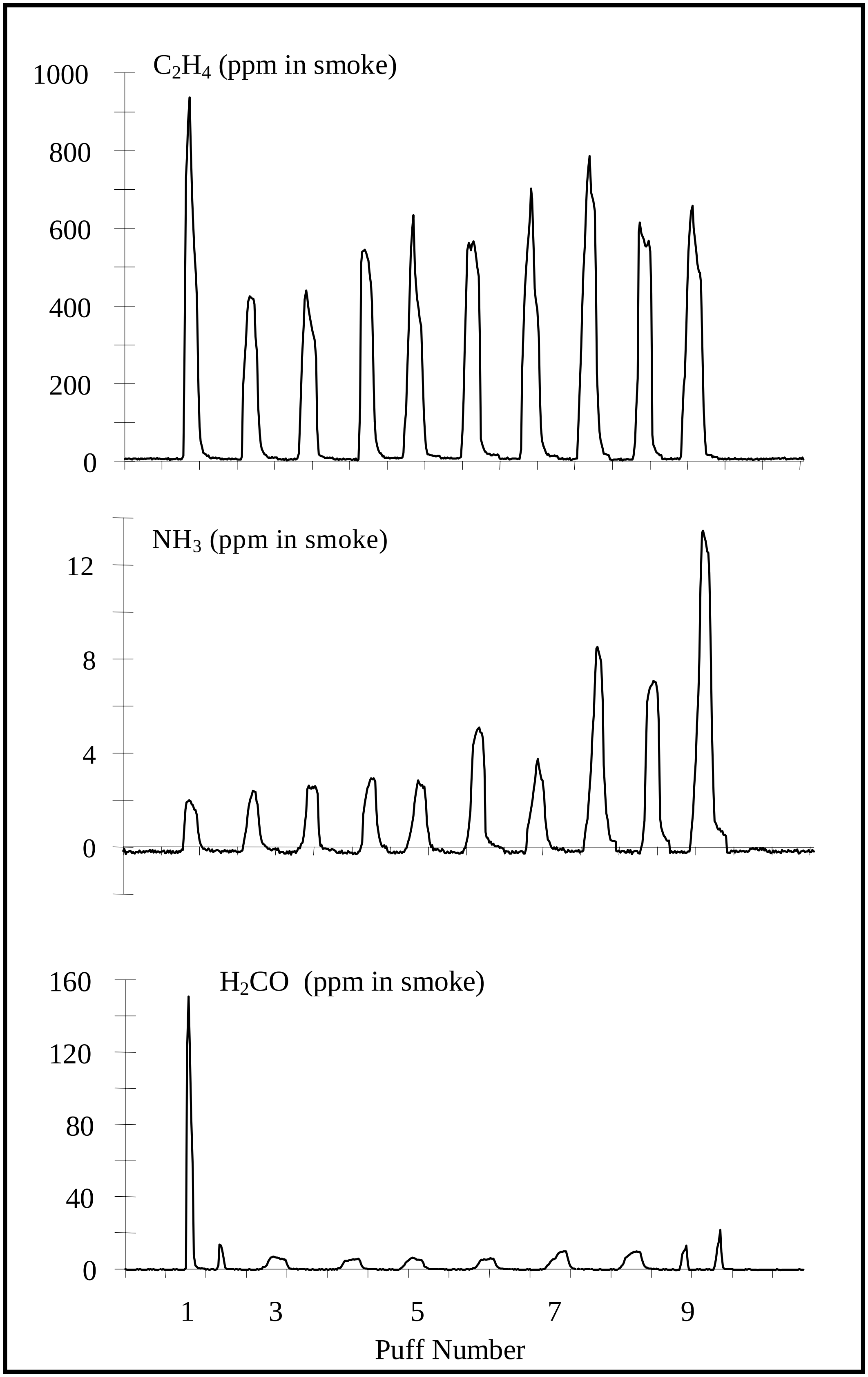

Figure 6. Puff-by-puff data for 1R4F cigarette.

4. CONCLUSION

The capability of the two color IR-TDL to detect three components simultaneously in cigarette smoke with intra-puff time resolution has been demonstrated. Future plans include more rigorous quantitation by using synthetic multi-gas mixtures

that mimic cigarette smoke to test the accuracy and robustness of the fitting parameters. Also, there are many species present in cigarette smoke that are not included in the 39 species that comprise the HITRAN database. We expect it will be necessary

to extend this technique to these other molecules not in HITRAN. Software will be developed to combine a quantitative low resolution FTIR spectrum with a non-quantitative high resolution TDL spectrum to produce a quantitative high resolution spectrum in the HITRAN line format. Additional sensitivity enhancements that are planned include changing the software to perform a combination of rapid background subtraction and spectral signal averaging, either over the entire 2 second puff or over multiple puffs prior to fitting.

5. REFERENCES

1. Michael F. Dube and C.R. Green, “Methods of Collection of Smoke for Analytical Purposes”, *Recent Advances in Tobacco Science* **8**, 42-102, 1982.
2. For an excellent review of instrumentation and applications see: H.I. Schiff, G.I. MacKay, and J. Bechara, “The Use of Tunable Diode Laser Absorption Spectroscopy for Atmospheric Measurements,” in *Air Monitoring by Spectroscopic Techniques*, ed. Markus W. Sigrist, *Chemical Analysis Series V.* **127**, 239-333, John Wiley and Sons, Inc., NY, 1994.
3. G. Forrest and G. Vilcins, “Tunable Diode Laser Measurement of Hydrogen Cyanide in Smoke,” *Appl. Spectrosc.* **34**, 418-419, 1980.
4. G. Vilcins, C.N. Harward, M.E. Parrish, and G.T. Forrest, “Tunable Diode Laser Applications to Cigarette Smoke Analysis”, *SPIE Proc.* **438**, 48-54, 1983.
5. M. Parrish, C.N. Harward, and G. Vilcins, “Simultaneous Monitoring of Filter Ventilation and a Gaseous Component in Whole Cigarette Smoke Using Tunable Diode Laser Infrared Spectroscopy,” *Beitr. Tabakforsch. Int.* **13**, 169-181, 1986.
6. G.T. Forrest, “Tunable diode laser measurement of methane, ethane, and water vapor in cigarette smoke,” *Appl. Opt.* **19**, 2094-2096, 1980.
7. L.S. Rothman, R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A. H. Smith, D.C. Benner, V.M. Devi, J-M Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, “The HITRAN Molecular Database: Editions of 1991 and 1992,” *J. Quant. Spectrosc. Radiat. Transfer* **48**, 469-507, 1992.
8. D.R. Worsnop, D.D. Nelson, M.S. Zahniser, “Chemical Kinetic Studies of Atmospheric Reactions using Tunable Diode Laser Spectroscopy,” *SPIE Proc.* **1715**, 18-33, 1992.
9. D.D. Nelson and M.S. Zahniser, “Air-broadened Linewidth Measurements in the ν_2 Vibrational Band of the Hydroperoxyl Radical,” *J. Mol. Spectrosc.* **166**, 274, 1994.
10. D.D. Nelson, M.S. Zahniser, J.B. McManus, J.H. Shorter, J.C. Wormhoudt, C.E. Kolb, “Recent Improvements in atmospheric trace gas monitoring using mid-infrared tunable diode lasers,” *SPIE Proc.* **2834**, 148-159, 1996.
11. D.D. Nelson, M.S. Zahniser, J.B. McManus, C.E. Kolb, and J.L. Jimenez, “A tunable diode laser system for the remote sensing of on-road vehicle emission,” *Appl. Phys. B* **67**, 433-441, 1998.
12. J.B. McManus, P.L. Kebabian, M.S. Zahniser, “Astigmatic mirror multipass absroption cells for long-pathlength spectroscopy,” *Appl. Opt*. **34**, 3336-3348, 1995.
13. W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, *Numerical Recipes in FORTRAN*, Cambridge University Press, New York 1992.