Airborne Infrared Spectroscopy of 1994 Western Wildfires

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ABSTRACT

In the summer of 1994, the 0.07 cm⁻¹ resolution infrared Airborne Emission Spectrometer (AES) acquired spectral data over two wildfires, one in central Oregon on August 3 and the other near San Luis Obispo, California on August 15. The spectrometer was on board a NASA DC-8 research aircraft, flying at an altitude of 12 km. The spectra from both fires clearly show features due to water vapor, carbon dioxide, carbon monoxide, ammonia, methanol, formic acid and ethylene at significantly higher abundance and temperature than observed in down-looking spectra of normal atmospheric and ground conditions. Column densities are derived for several species at 11. Molar ratios are compared with previous biomass fire measurements. We believe that this is the first time such data have been acquired by airborne spectral remote sensing.

introduction

During late July and early August 1994 hot, dry weather and abundant overgrowth precipitated several wildfires in the Pacific Northwest and California. On the afternoon of August 3, the NASA DC-8 research aircraft was returning to its base at Moffett Field, CA from a flight planned for Synthetic Aperture Radar (SAR) measurements when the flight line was re-directed to make an overpass of one of these fires (some 65 km east of Mt. Hood at latitude 45°19' N; longitude 120°52' W). Accompanying the SAR was the new 0.07 cm⁻¹ resolution infrared Airborne Emission Spectrometer (AES) which succeeded in obtaining a series of spectra (in the 4.5 to 13.5 μm range) beginning at 22:58:24 UT. The AES field of view was locked onto flames of the fire by an interactive video tracker for the 30 seconds that the fire was visible through the viewport installed in the cargo hold of the aircraft. Strong emission lines of water vapor (H₂O), carbon dioxide (CO₂) and carbon monoxide (CO) emanating from highly excited states, indicative of a gas cloud at elevated temperatures, were clearly visible in a preliminary examination of the spectral data. Absorption features due to ammonia (NH₃) were also obvious.

A second series of wildfire spectra was taken on August 15, 1994 in California with the AES on board the same aircraft at 3.8° 41' N, 120° 41' W, about 10 km north-west of San Luis Obispo, CA. This second set of spectra was also obtained as a target of opportunity on a flight with a different primary mission. However, no time was available for three overpasses of the fire line and a total of 90 seconds of spectral data was collected.
directly over flaming areas, as well as from nearby unburned areas. A quick inspection of the spectra from the California fire revealed, as in the data from the Oregon fire, strong H2O, CO2 and CO emission lines— as well as higher levels of saturation in the NJ I3 and CO absorption features than observed for the Oregon fire.

Since these observations were not determined experimentally, there was no other instrumentation to provide in-situ measurements of input verification for a model of the ground and atmospheric state parameters. Nonetheless, we have developed a provisional physical model of the observed fire scene to match our spectral observations. Using this model, and relying on relative spectral features as much as possible, we have been able to quantify the flame temperatures, and the CO, NH3, C31-011 and 1 CO011 column densities. Since H2O and CO2 have a large background abundance, the fit to the spectral features is too model-dependent to give a reliable estimate of the IR excess abundance from the fires.

Emissions from biomass burning are widely recognized as a significant source of pollution affecting atmospheric chemistry, photochemistry, and trace gas concentrations [cf. Crutzen and Andreae, 1990]. The spectral radiative sensing technique holds many advantages for measuring emissions from biomass fires. In general, detectable quantities of gases are higher than those for in-situ sampling; however, many species are above these detection limits in forest fire observations. Due to the difficulties in sample collection, there are few in-situ measurements of emissions factors for reactive species such as methanol and formic acid while a spectrometer can track the abundance of these species in all phases of a fire [Griffith et al., 1991; Yokelson et al., 1995]. Species can be measured simultaneously with none of the uncertainties inherent to the separate handling procedures of in-situ measurements. Ammonia, which has an especially distinct IR spectral signature, can be measured with good precision in contrast to errors as large as 50% for in-situ sampling of NH3 in smoke plumes [Laursen et al., 1992]. Flame temperatures can be estimated and could be useful to other remotely sensed radiometry measurements. Some important species, such as NO and NO2, are difficult to measure with nadir viewing space or airborne spectral remote sensing due to obscuration by atmospheric water vapor absorption, although these species are easily measured in ground-based spectral remote sensing [Griffith et al., 1991; Yokelson et al., 1995]. Other commonly emitted species such as methane and formaldehyde have IR spectral signatures that are not obscured in the nadir view through the atmosphere and were simply outside the frequency ranges in these data.

Fire Descriptions

The August 3, 1994 fire observed at 45° 19' N, 120° 52' W, near the Deslutes river, was one of the many relatively small fires in the area just east of the Cascades range in Washington and Oregon on that day. The best estimate from the Bureau of Land Management [BLM, 1995] was that the fire was on private land with mostly grass, shrubs and sage brush on slopes and a few alder and juniper trees in the lower canyon areas.

The August 11, 1995 observation at 35° 21' N, 120° 41' W was of a large brush fire, designated the 1 Highway 41 fire, that started on August 14, 1994 and moved south-east...
toward San Luis Obispo, CA. This fire was considered the largest California wildfire of 1994, with a total of 45400 acres burned. The Forest Service [Cal. Dept. Forestry, 1995] described this fire as a type 4 heavy brush fire and estimated a fuel load of 20 to 25 tons/acre. A survey of vegetation coverage for the private and public lands burned gave 60% brush (chemise, manzanita), 30% oak woodland, 10% grassland and 1% conifer.

The AES Instrument and Observational Approach

AES is a Fourier Transform spectrometer (FTS) specifically designed to acquire line width-limited (<0.1 cm⁻¹) infrared spectra of the 10 WC atmosphere through a ZnSe window in the underside of an aircraft. Radiation traversing the window is intercepted by a TV-guided 2-axis pointing system. When observing localized targets over land, the pointing system can either be locked onto the source or set into an open-loop rate compensation mode. In the collection of data over burning areas, the flames provided sufficient visible contrast to acquire data. The locked and rate compensation modes allow data sets to be acquired over about 30 seconds (limited by the size of the window) before the system is reset to a forward position. Alternatively, the pointing system can simply be set to a nadir stare mode, in which case, data acquisition is continuous. In any event, the view seen by the 1-m tracking cameras is recorded on a conventional VCR that is time-tagged identically to the infrared data. The same pointing mirror is also used to make frequent (every 3 min or less) observations of on-board black-body radiometric calibrations sources (essential for the retrieval process).

Fig.1 shows optical schematics of the interferometer and the periscope and tracking system. The infrared beam passes via the periscope into the interferometer that is the heart of the 1 'TS'. The interferometer consists of a beamsplitter/recombiner of Ge-coated KBr that divides the beam into two (nominal 50-50), one of which travels to a fixed cube-corner reflector (CCR) and the other to another CCR that moves on a carriage driven by a leadscrew/DC motor combination, thereby imposing an optical path difference between the two arms. Frequency (wavelength) calibration of all 'TS' is unnecessary since the optical path difference is continuously measured by an internal Nd:YAG laser traversing the same optical system as the infrared beam.

Data are acquired with the moving CCR traveling in both directions (2 seconds end-to-end). About 1 second is required to reverse directions. The motion of the CCR impresses an amplitude modulation on the infrared beam that is subsequently sensed and recorded by 4 sets of 1 lnCdTe infrared detectors (each optimized for a different spectral region). Each individual detector set (maintain at 65 K by romping on 1.9 N2 dewars) has 4 adjacent pixels (optically conjugated to two adjacent detectors). Thus 16 interferograms (and therefore spectra) are recorded in parallel on a single digit tape (together with pertinent engineering and navigation data) after being digitized with 16-bit A-D converters. Within each dewar are sets of interchangeable ("on-the-fly") bandpass filters about 200 cm⁻¹ wide whose primary function is to limit the ambient atmospheric thermal background from compromising signal-to-noise ratio. Subsequent data processing is performed off-line. This processing includes converting the interferograms to spectra, phase correcting the spectra, converting the calibration spectra to gain and offset functions and applying the gain and OffSTT to the target spectra.
AES Fire Data

Figures 2 and 3 show the AEROSpectra taken from the Oregon (OR) and California (CA) fires as well as spectra taken from a plume area upwind of the California fire. The spectral bands shown are 950 to 1150 cm \(^{-1}\) (1.7 to 10.5 \(\mu\)m) and 1960 to 2060 cm \(^{-1}\) (4.9 to 5.1 \(\mu\)m). These bands show many of the interesting spectral features due to the fire and the figures represent most of the data used in this analysis. Unfortunately, WC could not use the data in the 1200 to 1400 cm \(^{-1}\) (7 to 8.3 \(\mu\)m) spectral region due to problems with one of the deans. Normally, this is the region where we obtain spectral information for methane, a common emission from fires.

The signals for the spectra shown in Fig. 2 were converted to radiance units using calibration data from the onboard blackbody at temperatures 290 K and 350 K. These calibration data give a gain and offset value at each sampled frequency. The gain has units of data number (DN) per unit radiance (Watts/cm\(^2\)/sr/cm\(^{-1}\)). The offset, which is subtracted from target spectra, is due to the flux contribution from the instrument at ambient aircraft temperature. For most observations, these blackbody temperatures span the range of ground target temperatures, but for the forest fires, this was not the case. Since we did not have a higher temperature calibration point available, we must assume the gain has a linear dependence on temperature and extrapolate to convert to the radiance values observed in the fire spectra. We apply this extrapolated gain to the spectra in the frequency range near 1000 cm \(^{-1}\) (10 \(\mu\)m) where signal levels for the fire views and the 350 K blackbody are comparable. However, this extrapolation is not reasonable for the 2000 cm \(^{-1}\) (5 \(\mu\)m) region shown in Fig. 3 where the fire and the 350 K blackbody signal levels differ by over an order of magnitude and the dependence on radiance is indeterminate. Although uncalibrated spectra will retain the flux contribution from the instrument, that is significant for the view of the unburned area, it contributes less than 10% of the signal level in the fire observation.

The field of view (FOV) in these observations is 3.75” by 1.94 mrad giving a ground footprint of 45 m by 23 m from 12 km altitude. The footprint is therefore likely to be inhomogeneous, i.e. a variety of areas with different surface radiance values, especially in views where the flames were targeted, but did not fill the FOV. Fig. 4 shows a likely scenario for the AES-FOV during fire data acquisition based on the (visible) video recorded during the tracking sequence.

Spectral Modeling and Analysis

In order to quantify the species detected in the fire spectra we have developed three types of physical models for the ground radiance and atmospheric radiative transfer based on the viewing scenario shown in Fig. 4. The models will be referred to as:

1. Smoke plume over unburned ground
2. Embers
3. Flames


Table 1. Model layers and parameters for simulated spectra

<table>
<thead>
<tr>
<th>1. Smoke over unburned ground</th>
<th>2. Embers</th>
<th>3. Flames</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight = 46% OR fire FOV</td>
<td>weight = 49% OR fire FOV</td>
<td>weight = 5% OR fire FOV</td>
</tr>
<tr>
<td>weight = 60% CA fire FOV</td>
<td>weight = 34% CA fire FOV</td>
<td>weight = 6% CA fire FOV</td>
</tr>
<tr>
<td>J km</td>
<td>J km</td>
<td>J km</td>
</tr>
<tr>
<td>500 m</td>
<td>32 m</td>
<td>1.5 km</td>
</tr>
<tr>
<td>100 m</td>
<td>30 m</td>
<td>1.5 km</td>
</tr>
<tr>
<td>20 m</td>
<td>20 m</td>
<td>1.5 km</td>
</tr>
<tr>
<td>0 m</td>
<td>0 m</td>
<td>1.5 km</td>
</tr>
</tbody>
</table>

T = 305 K
H2O, CO2, CO, N2O,
CH4, O3, NH3, OCS

T = 305 K
H2O, CO2, CO, N2O,
CH4, O3, NH3, OCS

T = 325 K
H2O, CO2, CO, N2O,
CH4, O3

T = 330 K
H2O, CO2, (X), N2O,
CH4, O3, NH3, OCS

T = 330 K
H2O, CO2, (X), N2O,
CH4, O3, NH3, OCS

T = 375 K
H2O, CO2, CO, N2O,
CH4, O3

T = 400 K
H2O, CO2, CO, NH3,
CH4, O3, NH3, OCS

T = 400 K
H2O, CO2, CO, NH3,
CH4, O3, NH3, OCS

T = 500 K

Table 1 shows the layers and specified parameters for the three models below 1 km. The three types of models all have the same specifications for J km to 1.5 km and use assimilated temperature and height profiles for these dates and locations, provided by NMC [Gelman, 1994]. We assume a relative humidity of 35% at 1.5 km for the Oregon fire location and 20% at 1.5 km for the California fire location. Above 1 km, we assume abundance levels for CO2 (357 ppm), CO (11.0 ppm), and N2O (312 ppm) based on projecting 1993 values [Dlugokencky et al., 1994; Halpern et al., 1993]. Methane is

For each type of model, the ground temperature and the temperature and abundance profiles for atmospheric gases at prescribed altitudes are specified and a simulated spectrum is generated by solving the equation of radiative transfer [e.g., Goody and Yung, 1989] using the HITRAN 92 molecular line-by-line database [Rothman et al., 1992]. The code used for generating spectra from these models is called SEASCRAPE: Sequential Evaluation Algorithm for Simultaneous and Concurrent Retrieval of Atmospheric Parameter Estimates [Sparks et al., 1991].
included in the models, but does not produce any significant spectral features in the frequency ranges used for this analysis. The CO abundance in the models decreases linearly from 150 ppb at 1 km to 75 ppb at 11 km. Although CO does not have very predictable abundance levels, this appears to be a reasonable assumption based on measurements by Harris et al. (1994).

Because of the inhomogeneity of the scene in our OV, we have no way of uniquely determining the ground temperatures in our models from our spectral radiance. We must therefore set these temperatures to consistent values. We use 500 K for the embers and flames models, based on other fire radiance measurements [Kaufman et al., 1992], and we use 310 K for the unburned ground based on the average brightness temperature of spectra taken away from the fire areas.

The three models are combined with weights that allow a reasonable match to the observed radiances with slightly different species abundance levels in the spectra from 950 to 1,300 cm⁻¹. (The weights must add to 100% and are shown in Table 1). Fig. 5 shows the match of the weighted model combination to the Oregon fire data as we 1 as the individual model components. The combined model spectrum is then scaled (or "decalibrated") to match the spectral data in the 1960 to 2060 cm⁻¹ region. At this point, individual parameters in the models, such as flame temperature or single species abundance can be varied for a best fit to the spectral features in the data. Unfortunately, the species with the largest line emissions, H₂O and CO₂, have a large normal atmosphere abundance and therefore too many model parameters to be varied manually. Quantification of the abundance parameters for these species would require a more sophisticated retrieval technique capable of iterating and optimizing parameters for the three models simultaneously. Although it was not possible to determine uniquely the excess H₂O and CO₂ from the fit in this analysis, our data are consistent with large excess abundances since models with normal atmospheric abundances for these species were clearly inadequate. The H₂O and CO₂ abundance parameters in the models are set to values that give a close enough match to the data so that the estimation of other quantities is not impeded.

No large enhancement in the O₃ abundance was observed and a reasonable fit to the data is obtained with a uniform O₃ abundance of 600 ppb. We do not expect to observe a significantly increased O₃ abundance since O₃ is not produced directly by the fire [Hegg et al., 1990] and our measurements do not include the downdraft fire plume. We also observe CH₃Cl₂ (CH₂Cl₂) and OCS and we can fit the spectral features for these molecules with an abundance of CH₃Cl₂ around 400 ppb and an abundance of OCS around 1 ppb. CH₃Cl₂ has been detected in biomass burning emissions [Hegg et al., 1990], most probably from pollution deposited over time and resuspended by the fire. However, at these low levels, we are not sensitive to an excess abundance in these species over their normal atmospheric abundance.

**Flame Temperature:**

The flame temperatures in the observed fires are determined by varying the temperature and CO abundance in the flame region (0 to 30 m) of the flames model and comparing the resulting spectra to the observed CO emission lines in the 1960-2060 cm⁻¹ region, (see Fig. 3). None of these CO emission features are observed in normal atmospheric spectra and, indeed, some (high rotational quantum numbers in the 2⁻¹ vibrational transition) require temperatures of at least 900 K to populate the relevant energy levels. The
line widths and heights have a dependence on column density as well as temperature and therefore find a range of values in column density and flame temperature that produce a reasonable fit to the spectra. The spectra from both fires can be fitted with a range in CO column density of 20 ppm to 40 ppm over 10 km. The best fit for the Oregon fire data was obtained with a range in flame temperatures of 1050 to 1000 K, while the California fire data required a higher value: 1250 to 1350 K.

**NII3 Abundance:**
Ammonia is a well-known component of forest fire emissions and biomass burning has been shown to be a significant source of atmospheric NII3 [e.g., Hegge et al., 1988 and 1990, Griffith et al., 1991 and Jaques et al., 1992]. NII3 is produced during the smoldering phase of a fire, as opposed to the flaming phase, [Griffith et al., 1991; Yokelson et al., 1995] and dissociates at high temperatures [Hampel and Hawley, 1973]. We therefore expect the highest NII3 concentrations in the embers component of our observations.

Assuming that the mixture of the three models suffices to describe our fire observation, it is clear from Fig. 5 that the preponderance of spectral signatures is also due to the embers component. We therefore obtained estimates of column density for species produced in the smoldering phase by adjusting the thermal contrast and species abundances in the embers model to produce the best fit to the absorption features. Ammonia absorption features are especially useful in determining the appropriate thermal contrast in this model since the NII3 transitions have a similar temperature dependence and some of the strong lines saturate at fairly low abundance, around 50 ppm-m. The ammonia abundance is determined by matching the line strengths of nearly saturated to saturated lines while the radiance signature of the stronger saturated lines provides the thermal contrast for the embers model. Fig. 6 shows the fire data compared to models spectra for some of the ammonia absorption features. The presence of the weaker NII3 lines in the California data indicates a higher ammonia abundance compared to observed in the Oregon fire.

Table II shows the column densities of NII3 in the embers model that gave the minimum residuals in the ammonia spectral regions for the model spectra subtracted from the fire spectra. A good fit to the Oregon data was obtained by adjusting only the embers model NII3 abundance with negligible amounts in the other models. However, the California data required around 100 ppm-m NII3 abundance in models I and III in order to obtain a reasonable match. This affected the uncertainty in the embers (model II) amount for the California fire which is reflected in the NII3 column density error.

**CO Abundance:**
CO is emitted during both the flaming and smoldering phases of a fire, but predominantly in the smoldering phase [Griffith et al., 1991; Yokelson et al., 1995]. We quantify the CO abundance from smoldering processes by using CO absorption lines that have a model signature dominated by the embers model (as opposed to the emission lines which can only be modeled with the flames model). In Fig. 7 we can see that the CO absorption lines are different for the California and Oregon fires. The broader line widths in the California fire data indicate a higher level of saturation. Both fires have significantly wider absorption lines than observed in spectra taken away from the fire area or the embers model spectrum with a background (normal atmospheric) CO abundance. The CO abundances in the first kilometer of the embers model were adjusted to match the absorption line widths and the
resulting column densities are shown in Table II. The first error in the CO column densities corresponds to the statistical uncertainty in fitting the lines, i.e., the changes in abundance that produced no visible change to the model spectrum. The second error is the systematic uncertainty from the background subtraction, which we assumed that the background CO abundance could vary by as much as 50% of the nominal values. This uncertainty is for the entire background column of CO (ground to air plane), since, unlike the other species in Table II, the background CO column has a significant spectral signature. For comparison with the CO values in Table I, the column density for a background level of 150 ppb CO, O to 1 km, would be 0.15e/m² in the embers model.

Our model assumes the standard isotopic abundances: 98.684% 12C16O and 1.108% 13C16O[De Bievre et al., 1984], and we were able to fit to the 13C lines with the model spectrum using the same CO abundance that produced a good model match to the 12CO absorption lines. The 13CO lines were almost undetectable in the embers model with a background CO abundance.

Table II. Estimated column densities for the Oregon and California wildfires

<table>
<thead>
<tr>
<th>Species</th>
<th>1 frequency (cm⁻¹)</th>
<th>column density (molecules/cm²)</th>
<th>column density (gm/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(background</td>
<td>OR fire 3/8/94</td>
<td>CA fire 3/15/94</td>
</tr>
<tr>
<td></td>
<td>subtracted)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2050-2135</td>
<td>3.43±1.18</td>
<td>1.85±0.19</td>
</tr>
<tr>
<td>NiH₃</td>
<td>960-1160</td>
<td>0.041±0.005</td>
<td>0.220±0.044</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>1033</td>
<td>0.083±0.011</td>
<td>0.157±0.024</td>
</tr>
<tr>
<td>HCOOH</td>
<td>1105</td>
<td>0.066±0.011</td>
<td>0.086±0.015</td>
</tr>
<tr>
<td>C₅H₁₀</td>
<td>949.5</td>
<td>detected</td>
<td></td>
</tr>
</tbody>
</table>

Oxygenated organic compounds such as methanol, formic acid, formaldehyde and acetic acid have been previously measured in biomass fire emissions during broadcast burn and laboratory studies [Griffith et al., 1991; McKenzie et al., 1994; Yokelson et al., 1995]. Nonmethane hydrocarbons (NMHC) detected in airborne plume sampling of biomass fires are quantified in Hegg et al. [1990] and Jansen et al. [1992], although ethylene is not among the species listed. Ethylene and other NMHCs are measured in Yokelson et al., 1995. (Formaldehyde, acetone and most NMHCs have their spectral signatures outside the ranges covered in our dataset.) Yokelson et al. [1995], show that these species are clue primarily to pyrolysis and distribution of the embers flame. We do not have enough independent spectral information to distinguish this type of production from smoldering combustion since it also occurs at high temperature and the produced species is smoldering flame. We therefore rely on our "embers" model for quantification of these species and acknowledge that assumed thermal contrast in this model could be different from pyrolysis processes. If our assumed thermal contrast is too high, the 11 species abundances will be underestimated.
To estimate the methanol (CH₃OH) and formic acid (HCOOH) column densities in our data, we apply absorption cross-section data from Hanst and Hanst,[1993], to our radiative transfer model. Methanol has a peak in absorption at 1033 cm⁻¹ which is somewhat obscured by the O₃ band from 1010 to 1070. The spectral signature in the data is therefore more easily seen after subtracting a model spectrum with a reasonable match to the O₃ lines. Fig. 8 shows the data from the Oregon and California fires after subtracting model spectra generated with no abundance of methanol or formic acid. The model signatures for the best fits to these residuals are overplotted and the column densities of CH₃OH and HCOOH are shown in Table II.

Quantifying the ethylene abundance is more problematic. The peak absorbance at 949.5 cm⁻¹ coincides with a CO₂ line and is also on the edge of the optical filter passband, which results in poor radiometric calibration and SNR at frequencies below 950 cm⁻¹. We observe ethylene by noting excess absorption at the 949.5 cm⁻¹ CO₂ line compared to the other nearby CO₂ absorption lines which appear thinner and are reasonably matched by the model spectrum. The depth and width of this excess absorption in the Oregon fire data can be fitted using a model spectrum with an acetic component at 1171 cm⁻¹ with a density around 1.0×17 molecules/cm³. However, this estimate has very large errors due to the unquantifiable uncertainties in (1.) abundance as well as the poor calibration and SNR.

Comparison to other measurements:
Since our data are taken over the hottest regions of these fires, we expect our measurements to be somewhat different from aircraft plume sampling, for example, where gases emitted by the fire are probably sampled after they have moved away from their sources. The more relevant comparison for our results are with ground-based remote sensing data where measurements are conducted fire emissions from their flaming or smoldering sources. Many results are presented in quantities of emission factors (mol/kg fuel) or emission ratios relative to CO. Since we are unable to calculate these quantities from the results, we compare emission ratios relative to CO with other measurements converted to this emission ratio.

For N₁₁−/N₁ⅈ (mol/mol) we measure 0.043 ± 0.016 (OK fire) and 0.042 ± 0.011 (CA fire) in what we assume is smoldering emission. Yokelson, et al.,[1995], using a variety of fuels mixtures in a laboratory combustion chamber, report values giving a range in NH₃/CO ratio of 0.009 to 0.034 (taken from all measurements, using the smoldering combustion only for fires with results quoted for the different fire phases). Lower ratios were found for fuel compositions of only pine needles or sagebrush and higher ratios for more heterogeneous fuel mixtures of dead twigs, pine needles and wood. Field measurements from four broadcast fires in Griffith et al.,[1991] give a ratios of 0.008, 0.017, 0.046 and 0.059 for NH₃/CO with the highest values for brush and grass fires compared to logging waste burns. Heggestad,[1988], report a range of 0.002 to 0.038 with an average of 0.012 ± 0.005 for N₁₁−/N₁ⅈ from aircraft smoke plume sampling. Our best agreement is with the Griffith, et al.,[1991] result for brush and grass fires which we believe to be more similar to the fires we observed than the fires studied by Yokelson, et al.,[1995]. It also seems reasonable to expect different results for the smoke plume ratio compared to the emission ratio directly over smoldering areas.

For methanol, we calculate CH₃OH/CO emission ratios of 0.016 and 0.046 (mol/mol). The results from Yokelson, et al.,[1995] give a range of 0.05 to 0.031, again, with larger
ratios from the fires with heterogeneous fuel mixtures. McKenzie et al., [1994] report a molar ratio of 0.025 for methanol to CO in smoldering combustion of ponderosa pine sapwood.

Our formic acid to CO molar ratios are (0.006 and 0.025) in the fires studied in Yokelson, et al., [1995]. HCOOH was below the detection limit in all but one of the fire set to simulate a "crown" forest fire by using a fuel mixture of Scots pine needles and twigs. Over dry needles and wood, the results from this "crown" fire gave the ratio 0.007 for HCOOH/CO. For smoldering combustion of ponderosa pine sapwood, McKenzie et al., [1994] report a molar ratio of 0.001 for formic acid CO.

Given the large ranges in values for different fires and fuel types, our emission ratios are comparable with previous measurements. We confirm the results of Griffith et al., [1991], McKenzie et al., [1994] and Yokelson et al., [1995] showing a significant presence of methanol and formic acid in biomass burning emissions. Sources of atmospheric concentrations of these species should receive more attention since oxygenated hydrocarbons such as methanol have recently been shown to play an important role in tropospheric photochemistry [Singh et al., 1995].

Unmatched Emission Features:
Although we are fairly certain that we have identified the obvious absorption features in our data, there are emission features that we are unable to match using our three-component model with the 1992 HITRAN database [Rothman et al., 1992], as illustrated in the upper panel of Fig. 9. Based on the features that are modeled, the strong emission lines in our data are from transitions occurring at high temperatures, i.e., in the flames of the fire. This precludes many species from consideration and after comparing our spot spectra in the same frequency ranges [Wallace et al., 1992, 1994, 1995], we conclude that the primary candidates for these emission lines are H2O and CO. A few emission lines in the data also match known high-excitation transitions of CO2. It is not surprising that we do not match all the emission features using the HITRAN92 linelist. The database was intended for terrestrial atmospheric studies at normal temperatures (around 300 K). This results in known defects for H2O within the database applied at high temperatures [Schryver et al., 1995]. A preliminary investigation indicates that many of the emission features in our data can be modeled by extending the spectroscopic database to include high temperature transitions of H2O, CO, and possibly CO2. The bottom panel of Fig. 9 shows a calculation with high-excitation lines of H2O at 2048.33 cm⁻¹ and CO at 2051.076 cm⁻¹ in addition to the HITRAN92 linelist. The identifications are based on assignments given in the solar atlas of Wallace and Livingston [1992] and the parameters in the HITRAN high temperature molecular database [Rothman et al., 1995]. The features were simulated without modification of the HITRAN parameters except for a shift in the position of the H2O line by -0.05 cm⁻¹ to agree with the position reported in the solar atlas.

Conclusions
As a proof of concept, we have shown the utility of the airborne spectral remote sensing technique in measurement of emission from biomass fires. Although we did not have a sophisticated retrieval method for this application, it is obvious that there were large amounts of water vapor, carbon dioxide, carbon monoxide, ammonia, methanol, formic
acid and ethylene emitted by the fires we observed. Increased understanding of the impact of biomass burning emissions, including oxygenated organics, to atmospheric chemistry requires better and more comprehensive quantification of the emitted species. Since many reactive species are difficult to measure with in situ sampling but, in principle, pose no problem for spectral remote sensing, this technique could provide a useful complement to the plume sampling methods normally used for fire measurements.

Our temperature and species abundance retrievals could be dramatically improved with planned experiments over instrumented broadcast burn sites that provide “ground truth” data to verify our physical models. Some commonly emitted species such as methane or formaldehyde were simply outside the spectral range in these observations and would require only minor modifications for detection. We further note that the performance of AIRS has improved considerably since these data were acquired and new fire measurements would have reduced uncertainties.

Acknowledgments

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Figure Captions

Fig. 1. Optical schematic of the Airborne Emission Spectrometer (AES). (The periscope is rotated 90° for clarity). CCR: cube corner reflector; 131, 23 = dichroic beamsplitters; M1, 23, 4 = fold mirrors; IA, 2A, 1B, 2B = detector dewar identifications (with corresponding spectral coverage shown). The interferometer itself is maintained under a low vacuum to protect hygroscopic components and reduce acoustic coupling into the optical path.

Fig. 2. AES spectra from (a) the Oregon fire, (b) the California fire and (c) an unburned area upwind of the California fire. In all the spectra shown in this paper, the instrument view is downlooking with a maximum offset angle of 30°. The overall shape and radiance of the spectrum is dominated by the average ground radiance in the footprint while the sharp features (the spectral lines) arise from molecular transitions in the atmospheric gases along the line of sight. Lines with radiances above the ground radiance are in emission while lines with radiance values below this level are in absorption. Absorption features due to gases released by the fires are labeled in the fire spectra while the features due to species with significant normal atmospheric abundance are indicated in the spectrum of the unburned area. "11" (emission lines in these fire spectra are mostly from hot CO and CO2 and 1120.

Fig. 3. Uncalibrated AES spectra from (a) the Oregon fire, (b) the California fire and (c) an unburned area upwind of the California fire. Although the fluxes in these spectra have not been converted to radiance units, (see text for details), it is possible to compare their spectral features such as the \( \lambda \) of \( \lambda \) emission lines in the firespectra and the lower signal to noise ratio in the spectrum from the unburned area. The labeled emission lines correspond to the CO transitions used for estimating the flame temperatures.

Fig. 4. Likely scenario for the view contained in the AES footprint during fire data acquisition.

Fig. 5. (top) Comparison of the AES spectrum from the Oregon fire to a model spectrum made by combining three simulated spectra generated from models of the different fire regimes contained in the AES footprint. The model parameters for 0 to 1 km altitude are shown in Table 1. (bottom) The spectral contribution from each of the weighted model components. Note that except for emission lines, the "embers" model contributes over 75% of the spectral radiance signature at 1 micron. Is has a weight of 49%.

Fig. 6. Some of the ammonia absorption features present in the fire spectra. (a) Oregon fire data with match to the weighted combination of the three fire model components. (b) California fire data with model match. (c) Simulated ammonia signature. (This spectral region includes the Q-branch, near 965 cm\(^{-1}\)).

Fig. 7. Comparison of CO absorption lines for the California and Oregon fires. On this vertical scale, the background spectrum (taken away from the fire region) would have flux levels around 0.04 (see figure 2). Due to the high signal level and larger CO abundance we can also observe the rarer \(^{13}\)CO isotopic transitions.
Fig. 8. Oregon and California fire spectra as model subtraction. The upper plots show the difference between the Oregon fire data and the best model match that does not include CH$_3$OH or HCOOH. The lower plots show this difference for the California fire data where the fit to the 0 lines was not as good. Methanol and formic acid signatures are clearly seen as the broad (> 1 cm$^{-1}$) N=11 M$_1$ absorption features that produce a negative residual. The sharp positive residual features are due to poorly modeled H$_2$O and unmodeled emission lines. The dotted lines show the model residual: model spectra inducing CH$_3$OH and HCOOH minus model spectra with no CH$_3$OH or HCOOH.

Fig. 9. AIRS data from the California fire compared to model spectra. This spectral range shows two emission features that we are unable to match using only the molecular transitions in the HITRAN92 database (top plot) and the match to these lines when additional transitions are included from the model (bottom plot). The added transitions in the lower plot are H$_2$O at 2048.33 (Q) with a rotational transition (20, 3, 18) to (19, 2, 17) in the 010-000 vibration band and (X) at 2051.076 cm$^{-1}$, the P$_{10}$ rotational transition in the 3-2 vibration band. Note that the same species abundances are used to create the model spectra in both plots and we obtain a reasonable fit to other H$_2$O and CO features that are present in this spectral range.
DETECTOR SYSTEM

PERISCOPE

INTERFEROMETER

ZnSe Aircraft Window

From Scene
AES Footprint

Fire Scenario

smoke and gas plume over unburned material

fire line (flames)

smoldering embers (with gas emission)

4 pixels

1.94 mrad

(23 mat 39000 ft.)