Remote Identification and Quantification of Industrial Smokestack Effluents via Imaging Fourier-Transform Spectroscopy

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Industrial smokestack plume emissions were remotely measured with a midwave infrared (1800–3000 cm⁻¹) imaging Fourier-transform spectrometer operating at moderate spatial (128 × 64 with 19.4 × 19.4 cm² per pixel) and high spectral (0.25 cm⁻¹) resolution over a 20 min period. Strong emissions from CO₂, H₂O, SO₂, NO, HCl, and CO were observed. A single-layer plume radiative transfer model was used to estimate temperature T and effluent column densities q, for each pixel’s spectrum immediately above the smokestack exit. Across the stack, temperature was uniform with T = 396.3 ± 1.3 K (mean ± stdev), and each q varied in accordance with the plume path length defined by its cylindrical geometry. Estimated CO₂ and SO₂ volume fractions of 8.6 ± 0.4% and 380 ± 23 ppmv, respectively, compare favorably with in situ measurements of 8.40 ± 0.03% and 383 ± 2 ppmv. Total in situ NO concentration (NO + NO₂) was reported at 120 ± 1 ppmv. While NO₂ was not spectrally detected, NO was remotely observed with a concentration of 104 ± 7 ppmv. Concentration estimates for the unmonitored species CO, HCl, and H₂O were 14.4 ± 0.3 ppmv, 88 ± 1 ppmv, and 4.7 ± 0.1%, respectively.

Introduction
Optical remote sensing of chemical plumes is a mature field of research and fills an important role in the monitoring of gaseous and particulate emissions from chemical and energy production facilities (1, 2). For example, while in situ continuous emissions monitoring sensors are used to ensure facility compliance with environmental regulations, remote sensing methods can provide an independent verification of emissions compliance. Optical methods also enable sensing over a wide area and are useful in studying plume dispersion and atmospheric transport. Active sensing techniques, which typically rely on a laser tunable over a narrow spectral band to interrogate the source, have been developed and successfully applied to smokestack and flare monitoring (3–5). Active techniques are well suited to detecting and quantifying specific molecules or atoms at concentrations as low as one part per billion volume but are typically limited to interrogation of one or two species due to the limited bandwidth of the laser source. Additionally, active systems tend to have a larger experimental footprint and are often more costly and time-consuming to deploy when compared to current passive sensing techniques. The most common passive technique for smokestack monitoring is Fourier-transform spectrometry (FTS) (1, 6–13). The measurements rely on thermal emissions from effluent gases and particulate material, and the signal strength is a function of both column density and thermal contrast with the background. Since FTS can measure spectral emissions across a wide spectral bandpass at arbitrary (in principle) spectral resolution with excellent efficiency, it is well suited to the identification and quantification problem for multiple effluents. Given that a complete set of calibrated plume measurements can be made in a few hours (including setup and tear-down) by a single operator, modern FTS systems are an attractive option for independent emissions compliance measurements.

Imaging Fourier-transform spectrometers (IFTS) have recently become commercially available and could substantially improve the accuracy of species quantification and enhance understanding of plume phenomenology. At typical stand-off distances (0.1–1 km), the narrow single pixel field-of-view minimizes the effects of averaging over spatial regions which exhibit sizable changes in temperature and species concentrations. This means that simpler models can be used to interpret the spectrum. Furthermore, while temperature and concentration gradients may exist in the plume, spectral imagery of the axi-symmetric plume at the stack exit provide the constraining data needed to successfully use “onion-peeling” tomographic deconvolution methods to determine the plume structure (14, 15). Since radiative transfer models are necessary to accurately extract effluent column densities (9), the ability to simultaneously capture both the plume and background radiation in a single spectral image is advantageous. Spectrally resolved imagery also makes decoupling effluent concentration from plume path length straightforward, and this is useful when a priori knowledge of the stack inside diameter is unavailable. Spectral imagery also affords smart clustering of spectrally similar (though not necessarily adjacent) pixels to increase signal-to-noise ratio (SNR) for trace species identification without complicating the spectral analysis that can accompany simple spatial averaging. Also noteworthy is the DC image that is part of IFTS data due to use of a focal plane array (FPA). While it reduces the dynamic range available for measuring the modulated signal that encodes the spectral information, it is beneficial in the analysis and processing of interferograms collected from turbulent sources (16, 17). Moreover, the ability to visualize and track turbulent eddies in the DC imagery makes possible the estimation of plume flow rates, which when coupled with concentrations could yield total effluent mass flow rates.

In this work, we present the first quantitative midwave (3–5.5 μm) IFTS measurements of a plume from a coal-fired electrical plant. After identifying the species from their spectral signatures, a simple radiative transfer model is developed which enables accurate interpretation of the measured spectra immediately above the smokestack exit using temperature and effluent column densities. Spectral imagery is used to remove plume path length effects, and spectral estimates of effluent concentrations are favorably compared with in situ measurements.

Experimental Section
Instrument Description. The Telops, Inc. (Québec, Canada) Hyper-Cam is an imaging Fourier-transform spectrometer which couples a traditional Michelson interferometer to an...
infrared camera. A sequence of modulated intensity images corresponding to optical path differences are collected on a FPA forming an interferogram cube (i.e., an interferogram at each pixel). Fourier transformation of each pixel’s interferogram produces a raw ultraspectral image. Two internal wide-area blackbody sources maintained at distinct temperatures are used to calibrate the raw spectra at each pixel using established procedures (18). The maximum optical path difference (MOPD) defines the (unapodized) spectral resolution via $\delta \nu = 0.6 / \text{MOPD}$. In this work, spectral units will be expressed in wavenumbers with units cm$^{-1}$ and defined by $\tilde{\nu} = \nu / c$ where $\nu$ is frequency (Hz) and $c$ is the speed of light (cm$^{-1}$s$^{-1}$) in vacuum. The IFTS uses a 320 × 256 pixel Stirling-cooled InSb FPA which is responsive on 1800−6667 cm$^{-1}$. The instrument’s minimum focal distance is 3 m. The integration time of the FPA can be increased from a minimum of 1 μs to adapt to the scene brightness. Each pixel has an instantaneous field-of-view of 0.326 mrad, and a subset of pixels can be read out to improve acquisition rate at the expense of FOV size. The rate at which ultraspectral images can be acquired depends on spectral resolution, FPA integration time, and the number of pixels in the image. The Hyper-Cam’s mean single-pixel noise equivalent spectral radiance (19) for a 1s observation of a 50 °C blackbody at 32 cm$^{-1}$ resolution using a FPA integration time of 5 μs is 4.1 nW/(cm$^2$sr cm$^{-1}$). Additional instrument (20, 21) details can be found in the references.

**Remote Plume Measurements.** Plume emissions from a coal-burning industrial power facility near Dayton, Ohio were remotely observed from a distance of 595 m. Figure 1 presents a schematic of the experimental setup. A commercial GPS receiver provided geodetic coordinates for the measurement site, and georectified imagery from Google Earth was used to estimate the smokestack location. The plant has three smokestacks. Each stack is approximately 76 m tall, and the right stack (northeast) was not operational. The plant has three smokestacks. Each stack is approximately 76 m tall, and the right stack (northeast) was not operational. The plant has three smokestacks. Each stack is approximately 76 m tall, and the right stack (northeast) was not operational. The center stack was operating at full capacity. Continuous emissions monitoring (CEM) is performed in accordance with the Code of Federal Regulations, Title 40 Part 75, as part of the Clean Air Act Acid Rain Program. Three 200:1 dry air dilution probe extractive systems feed standard gas analyzers to continuously monitor sulfur dioxide (SO$_2$), total nitrogen oxides (NO$_x$ = NO + NO$_2$), and carbon dioxide (CO$_2$) emissions. A California Analytical Instruments Model 660D system is used to determine CO$_2$ concentration via a nondispersive infrared absorption measurement. SO$_2$ concentration is measured using a pulsed ultraviolet fluorescence technique with a Thermo Electron Model 43i gas analyzer. Similarly, a Thermo Electron Model 42i gas analyzer measures NO$_x$ concentration through a chemiluminescent reaction with ozone. Each gas analyzer is calibrated daily and all operate with a precision better than 1%. Plume opacity due to particulate material is quantified via a Durag Model D-R 290 which uses a wideband LED (400−700 nm) to measure the fraction of attenuated light. The flue gas flow rate and temperature are tracked with an EMRC gas flow monitor using an in situ S-type pitot sensor. All CEM probes are colocated approximately 24 m below the stack exit, and, as a result, a remotely sensed temperature at the stack exit is expected to be lower than the in situ measurement.

**Results**

**Spectral Imagery.** The top panel of Figure 2 presents a contour plot of the time-averaged radiance at $\tilde{\nu} = 2078$ cm$^{-1}$ corresponding to a CO$_2$ emission feature. The plume structure is clearly evident, and the effect of the prevailing wind is observed by the bending of the plume. At this frequency, selective emission by CO$_2$ is much larger than continuum emission from the smokestack making the latter difficult to recognize. A translucent gray box between horizontal pixels 1−28 and vertical pixels 1−10 is overlaid to indicate the stack’s location. Surprisingly, the radiance at $\tilde{\nu} = 2078$ cm$^{-1}$ initially increases with distance from the stack exit plane and reaches a maximum approximately 1.5 m (7−8 pixels) above the stack. As the plume continues its upward rise, the effects of cooling and expansion into the atmosphere can be observed with the decrease in radiance.

A contour plot of the radiance at $\tilde{\nu} = 2580$ cm$^{-1}$ is provided in the bottom panel of Figure 2. There is no selective emission in this part of the spectrum so the contours indicate variations in the amount of continuum emission. Here the stack is clearly evident as is emission from particulate materials in the plume. Unlike the gaseous plume, the continuum emission decreases with distance immediately from the stack exit.
Analysis of the raw, sequential images in the interferogram datacubes suggested that the center stack plume was not visibly contaminated by emissions from the left stack, indicating that the left stack’s dissipated effluents had likely reached ambient temperature. The prevailing wind direction suggests that these gases would be in the background of the center stack plume. As a result, their contribution to the observed plume emission is expected to be small. To minimize their influence as well as to remove the effects of sky radiance, a line of pixels in row 12 (columns 64–128) were used to define a mean background spectrum which was subtracted from the plume radiance as discussed in a later section.

The spectral imagery reveals information related to the plume fluid dynamics, and a detailed examination of this will be the subject of future work. The scope of the current effort is in the identification and quantification of plume species. In this paper, the spectra from pixels immediately above the stack (row 12) are considered in greater detail. Row 12 is the first row in which the spectrum appear to be pure plume, containing no continuum emission from the stack itself. After first identifying the molecular species by their spectral signatures, a simple radiative transfer model is then developed to quantify the species concentrations. These results will be compared with in situ gas concentration measurements.

**Spectral Identification of Molecular Effluents.** Several diatomic and triatomic species were readily identified by their rotational–vibrational spectral signature. Emission lines will be described using the notation used in the HITRAN spectroscopic database (24). The top panel of Figure 3 presents the complete spectrum after background subtraction for pixel (row, col) = (12, 14). The background spectrum was estimated by averaging pixels (12, 64–128) (see Figure 2). The imaginary component of the spectrum, offset and shown in gray, provides an estimate of the noise level of the instrument. (In a properly calibrated FTS, the signal is contained in the real part and noise is equitably distributed among the real and imaginary parts.) The bottom panel provides the atmospheric transmittance profile for the 595 m path between the plume and instrument based on measured atmospheric conditions.

![Figure 2](image1.png)

**Figure 2.** Top panel: Contour map of the time-averaged spectral radiance at \( \tilde{v} = 2078 \text{ cm}^{-1} \) corresponding to a CO\(_2\) emission line. Bottom panel: Contour map of the spectral radiance at \( \tilde{v} = 2580 \text{ cm}^{-1} \) corresponding to continuum emission from particulates in the plume. The translucent gray rectangle indicates the position of the stack. The horizontal line at row 12 between columns 64–128 indicate the pixels used to estimate the background spectrum.

![Figure 3](image2.png)

**Figure 3.** Top panel: Time-averaged spectrum from a single plume pixel near the stack exit. The imaginary component of the spectrum, offset by \(-0.25 \mu\text{W/cm}^2\cdot\text{sr}^{-1}\cdot\text{cm}^{-1}\), is representative of the approximate noise level. The inset plots provide an expanded view for several regions of interest and several emission lines are assigned. Line identification follows the HITRAN nomenclature. Bottom panel: Atmospheric transmittance profile for the 595 m path between the plume and instrument based on measured atmospheric conditions.
atmospheric transmittance profile along the 595 m path estimated from local meteorological measurements. Nearly all the absorption features are due to atmospheric H$_2$O (1800 ≤ ν ≤ 2160 cm$^{-1}$ and 2600 ≤ ν ≤ 3080 cm$^{-1}$) and CO$_2$ (2280 ≤ ν ≤ 2390 cm$^{-1}$). The observed spectrum is qualitatively similar in both features and absolute radiance to previously published spectra of coal-fired smokestack emissions (1, 25).

Perhaps the most easily recognized spectral features are the P- and R-branch emission lines between 2650 cm$^{-1}$ and 3000 cm$^{-1}$ arising from the fundamental HCl vibrational transition. Lines P(1) – P(10) beginning at ν = 2865 cm$^{-1}$ and decreasing with ν at nearly regularly spaced intervals are observed. Similarly, lines R(0) – R(5) beginning at ν = 2906 cm$^{-1}$ and increasing with ν are recognized despite several of the lines being strongly attenuated by atmospheric H$_2$O and being near the edge of good instrument response. At δν = 0.25 cm$^{-1}$ resolution, it is possible to resolve the H${}^{35}$Cl (taller) and H${}^{37}$Cl (shorter) lines. For each rotational–vibrational transition, the line heights are in proportion to the 76:24 isotopic abundance. The bottom inset plot of the top panel of Figure 3 shows the first few lines from the HCl P- and R-branches. The SNR of the P(4) line at 2798.9 cm$^{-1}$ is approximately 40.

The most prominent spectral features arise from the rotational structure associated with transitions between various CO$_2$ vibrational levels. For example, the large, narrow emission feature at 2395 cm$^{-1}$ arises from rotational transitions involving the asymmetric stretching mode. While most emission lines associated with this mode are subsequently absorbed by atmospheric CO$_2$ along the line-of-sight, the high plume temperature increases the population of higher-energy rotational levels leading to emission outside this opaque region. Similarly, emission is observed on the low-wavenumber edge of this opaque region for the same reason, and various other rotation–vibration transitions thermally accessible at the elevated plume temperature contribute there as well. This pattern of strong CO$_2$ emission on each side of the same CO$_2$ absorption feature is found in many combustion plumes, and the large emission features are often referred to as the red (longer wavelength) and blue (shorter wavelength) spike (26). CO$_2$ is responsible for several other emission features and the top-right and middle-right inset plots in Figure 3 identify them using spectroscopic notation adopted by the HITRAN database (24) and described in ref. 27.

CO and SO$_2$ are also easily recognized in the plume spectrum, and their respective emission bands are indicated in the top-right and middle-right inset panels of Figure 3, respectively. Spectral identification of NO was more difficult with most of its emission lines being strongly or completely attenuated by atmospheric water; the few that were partially transmitted are labeled in the leftmost inset plot of Figure 3. Finally, a large number of emission lines from H$_2$O are distributed through the spectrum. While they are not identified in Figure 3, their presence will be evident when a spectral model is compared to the data in the following section.

Spectral Modeling for Quantification and Interpretation.

Theory. A simple model describing the apparent plume radiance is developed to quantitatively interpret a pixel’s spectral emissivity, and $B$ is Planck’s distribution for blackbody radiation at temperature $T$. The convolution with the instrument line shape function, ILS, accounts for the resolution of the instrument. For a Fourier-transform spectrometer, ILS is defined by the length and symmetry of the interferogram as well as any apodization functions used to attenuate spectral ringing that occurs as a consequence of the finite interferogram length (28). No apodization was applied, and the interferogram symmetrization process (22) yielded the canonical FTS line shape function given by ILS($\nu$) = $2\text{asin}(2\pi a\nu)$ where $a = 2.4$ cm is the instrument MOPD. The spectral emissivity can be expressed as

$$L(\nu) = \int \tau(\nu')e(\nu')B(\nu', T)\text{ILS}(\nu - \nu')d\nu' \quad (1)$$

where $\tau$ denotes the atmospheric transmittance profile between the instrument and plume, $e$ represents the plume’s spectral emissivity, and $B$ is Planck’s distribution for blackbody radiation at temperature $T$. The convolution with the instrument line shape function, ILS, accounts for the resolution of the instrument. For a Fourier-transform spectrometer, ILS is defined by the length and symmetry of the interferogram as well as any apodization functions used to attenuate spectral ringing that occurs as a consequence of the finite interferogram length (28). No apodization was applied, and the interferogram symmetrization process (22) yielded the canonical FTS line shape function given by ILS($\nu$) = $2\text{asin}(2\pi a\nu)$ where $a = 2.4$ cm is the instrument MOPD.

Here, $q_i$ represents the product of the $i^{th}$ species’ volume fraction $\xi_i$ and the path length through the plume $l$, and we denote the quantity $q_i = \xi_i l / \text{the "fractional column density"}. N is the total gas density [molec·cm$^{-3}$] and is related to the plume pressure $P$ (assumed equal to the atmospheric pressure) and temperature $T$ via the ideal gas law, i.e. $N = P/(k_BT)$ where $k_B$ is the Boltzmann constant. Near the stack where the plume geometry can be inferred from the spectral imagery, the path length will be factored out of $q_i$ so that species concentrations $\xi_i$ can be compared with in situ stack measurements. The exponential term represents the total transmittance due to all gas phase plume constituents. The final term $r_p$ represents the transmittance of the particulate material in the plume. Since reflection by the plume is not considered in this work, its emissivity is expressed via Kirchoff’s law as one minus the total plume transmittance.

Spectral emission and scattering characteristics of particulates depend on their intrinsic chemical structure and particle size distribution. This is difficult to know a priori, but in general the emission characteristics change slowly with wavenumber. The particulate material is assumed to be small so that (1) its temperature is the same as the surrounding gas and (2) the scattering of radiation in the midwave infrared can be ignored (29). As described in the next section, spectral fitting is performed in two windows, each less than 500 cm$^{-1}$ wide. For this reason, spectral variations in soot transmittance are ignored and $r_p$ is assumed constant. For the gas-phase molecular species, the phenomenological absorption cross-section $\sigma_i$ [cm$^2$] accounts for all emission lines of molecule $i$

$$\sigma_i(\nu, T) = \sum_j S_{ij}(\nu, T)f_j(\nu) \quad (3)$$

where $S_{ij}$ is the line strength [cm$^{-2}$·cm$^{-1}$·(molec)] of the $j^{th}$ absorption line of molecule $i$ with transition wavenumber $\nu_j$. $S_{ij}$ accounts for both the intrinsic quantum mechanical transition probability and the relative population of the absorbing state. Under the LTE assumption, inelastic collisions occur with sufficient frequency so that the gas kinetic temperature $T$ defines the internal energy state populations according to the Boltzmann distribution (30). The line shape term $f_j$ is a Voigt profile [1/(cm$^{-1}$)] associated with the $j^{th}$ absorption line and depends on several parameters describing the line width and slight shift away from $\nu_j$ in terms of the temperature, pressure, and relative concentrations of gas species. The HITRAN spectral database (24) is a comprehensive collection of the spectroscopic parameters needed to compute the absorption cross section for several molecules including those found in this smokestack plume.
This model represents a substantial simplification of the actual radiative transfer problem and warrants a brief discussion. First, the model neglects sources of radiation behind and in front of the plume. Instead, it is assumed that these effects can be removed via the background subtraction previously described without introducing significant error. Systematic errors introduced by this assumption have not been quantified but are expected to be less dramatic in the 3–5 μm band compared with the 8–12 μm band where plume measurements are often made due to the difference in plume and background temperatures. Second, the model assumes a perfectly homogeneous plume along the line-of-sight of each pixel. Temperature and density gradients may exist within the plume and the corresponding temperature and relative concentrations obtained by fitting may be systematically biased due to the nonlinear way in which T and q_i affect radiance. Finally, the plume is turbulent (the degree to which we have not yet attempted to quantify), and the mean radiance computed at each pixel represents an average over a temperature and density distribution. For large enough temperature fluctuations, this can introduce additional systematic errors again due to the nonlinear relationship between T and radiance (31). A method to overcome this problem has already been proposed (17) but not yet applied to this data set. As a result of these simplifications, the spectral model has few parameters and the fits converge quickly. Moreover, as demonstrated in the next section, the fit results are exceptional and extracted species concentrations are in good agreement with in situ measurements, suggesting that systematic errors resulting from these simplifications are minor.

**Spectral Fitting.** The Line By Line Radiative Transfer Model (32) was used to compute absorption cross sections for CO_2, CO, SO_2, HCl, NO, and H_2O using spectral line parameters from the 2004 HITRAN database (24) at temperatures every 1 K between 300–425 K on the highly sampled (δν = 0.005 cm⁻¹) spectral interval 1750 ≤ ν ≤ 3150 cm⁻¹. Linear interpolation was used to estimate the ν_i’s at intermediate temperatures. The convolution appearing in eq 1 was efficiently computed using a pair of fast Fourier transforms and sampled onto the spectral axis defined by the imaging spectrometer. For each pixel immediately above the stack exit (row 12, columns 4–25), optimal column densities, particulate transmittance, and temperature were estimated by fitting eq 1 via a Levenberg-Marquardt nonlinear minimizer.

Small systematic errors were observed when fitting the full spectrum. Specifically, including the red and blue CO_2 spike resulted in the model overestimating radiance at all of the weaker CO_2 emission bands. Because the fitting routine minimizes the sum of squared errors, the largest radiance features in the data dominate any biasing of model parameters necessary to compensate for systematic errors in the model (e.g., background subtraction errors, exclusion of temperature gradients, etc.). This effect becomes evident in spectral regions containing weaker lines that are modeled by the same (biased) parameters. To minimize this problem, independent fits were performed on Region I: 1890 ≤ ν ≤ 2190 cm⁻¹ and Region II: 2500 ≤ ν ≤ 2980 cm⁻¹ to avoid the large red and blue spikes. In the first region, T, τ_p, and fractional column densities for H_2O, NO, CO_2, and CO were free fit parameters. These quantities were then held fixed, and the fractional column densities for SO_2 and HCl were allowed to vary in Region II. While only about half of the SO_2 emission band falls within Region II, this portion is sufficient to estimate its column density. τ_p was also allowed to vary in Region II to accommodate any wavelength-dependent change in the optical properties of the particulate material.

**Fit Results.** Figure 4 presents the fit results for pixel (row,col) = (12,14). This pixel corresponds approximately with the center of the stack. Panel A shows the spectrum in Region I along with the fit residuals—defined as the difference between the spectrum and model—offset for clarity. The residuals are a small fraction of the observed radiance.
with a root mean-squared (rms) error less than 15.8\,nW/\,(cm^2\cdot sr\cdot cm^-1). Using the imaginary part of the spectrum as a measure of the instrument noise, we note that the rms error is only about 1.5\,times greater than the noise-equivalent spectral radiance (NESR) of 10.7\,nW/(cm^2\cdot sr\cdot cm^-1). The NESR characterizes the noise level of the instrument in radiometric units, and in a properly calibrated IFTS, the imaginary part of the spectrum contains only noise. An estimate of the NESR in each region was made using the rms value of the imaginary radiance. (Refer to gray curve in Figure 3.) It follows that the model accounts for nearly all of the information content in the spectrum. Panel B of Figure 4 presents the emissivities of the individual plume species emitting in Region I. The emissivities have been multiplied by the atmospheric transmittance profile \(\tau\) and the curves are presented on a relative scale for clarity. Despite the substantial attenuation by atmospheric water, several \(H\) are presented on a relative scale for clarity. Despite the fractional column density \(q_i\) presented as a percent (%) or parts-per-million (ppm), and \(l\) is the path length through the plume (cm). The error column reports the half-width of the 95\% confidence interval. Region indicates the spectral window in which each parameter was determined.

As expected, each fractional column density parameter decreased with distance from plume center. This can be seen in the top panel of Figure 5 which presents the average of the normalized fractional column densities \(q_i(x) = q_i(x)/\sum q_i(x)\) denoted \(q_i\) (hat signifies the average). Note that \(q_i\) is peak normalized in Figure 5 for convenient graphical interpretation. The normalization process enables the \(q_i\)'s to be compared on the same scale. Error bars for \(CO_2\) and \(SO_2\) are provided in an alternating fashion and are representative of the statistical uncertainties between 2\%–4\% for all \(q_i\)'s. The differences between the average and individual normalized column densities are shown in gray and demonstrate the degree to which each individual \(q_i\) exhibited the same variation across the plume. Note that each fractional column density \(q_i\) was a free parameter at every pixel, and no a priori information about the plume geometry was included in the spectral model.

If the effluent volume fractions \(\xi_i\) are all assumed constant through the plume, then \(q_i(x) \propto l(x)\). This variation with \(x\) can be used to estimate radius and true center of the plume, and a nonlinear regression yielded \(r = 10.98 \pm 0.17\,\text{pixels}\) = 212.7 \(\pm 3.4\,\text{cm}\) and center pixel location of \(x_0 = 14.42 \pm 0.14\). Note that the estimated plume diameter of \(2r = 425.4\,\text{cm}\) is in excellent agreement with the known inside diameter of 423.7 cm at the stack exit.

Temperature was found to be fairly uniform through the plume as demonstrated in the bottom panel of Figure 5. Excluding the rightmost pixel, the mean temperature was 396.3 K with a standard deviation of 1.3 K. Error bars correspond to the 95\% confidence interval and were on the order of 0.25–0.50\%. Temperature does gradually decrease near the right edge of the plume, and the lack of a similar trend on the left side may be due to the prevailing wind direction. The uniform temperature, expected geometric variation in \(q_i\) with pixel location, and small spectral fit residuals are all strong indications that the single-layer plume model is a reasonable approximation near the stack exit.

Since the path length through the plume has been determined as a function of pixel location, it is possible to estimate the effluent volume fractions via \(\xi_i = q_i(x)/l(x)\). While this can be accomplished using a single pixel, an average over the results for pixels 4–25 and a characterization of the variance there within provides a better estimate of the effluent concentrations and associated uncertainties. The standard deviation of concentrations \(\xi_i\) across pixels was about twice as large as the uncertainty obtained by summing the associated statistical errors in quadrature. Table 2 provides the spectrally estimated concentrations and a comparison with available in situ stack measurements. The \(SO_2\) volume fraction is in excellent agreement with the in-stack measurement, whereas the spectral estimate of the \(CO_2\) volume fraction underestimates the measured concentration by about 8\%. \(NO\) represents the sum of both NO and NO\(_2\), and is quantified without speciation via in situ measurements. The spectral estimate of \(NO\) concentration is less than the in situ NO\(_2\) concentration by roughly 13\%. NO\(_2\) has a vibrational band centered at 2905 cm\(^{-1}\), and this feature was not observed in the plume spectra. Given the noise level in that part of the spectrum, an NO\(_2\) volume fraction of approximately 50 ppm would be necessary for detection at these IFTS measurement settings. Factoring in this detection limit, the remote nitrogen oxides estimate is 104 ppm \(\leq NO\) \(\leq 154\) ppm.

The plume transmittance \(\tau_p\) systematically increased with distance from the plume center but not at the same rate as the plume gases. The transmittances are high enough that nonlinearity found in Beer’s law is not to blame. At present,

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\(a\) The value associated with each molecule \(i\) is the fractional column density \(q_i = \xi_i/l\) where \(\xi_i\) is the volume mixing fraction as a percent (%) or parts-per-million (ppm), and \(l\) is the path length through the plume (cm). The error column reports the half-width of the 95\% confidence interval. Region indicates the spectral window in which each parameter was determined.

\(l(x) = 2\cos\left(\sin^{-1}\left(\frac{x - x_0}{r}\right)\right)\)
the particulate phenomenology and distribution within the plume is not well understood. For the sake of comparison, the in situ and spectrally estimated plume transmittances are provided in Table 2. While they are in good agreement differing by less than 2.5%, it must be noted that the in situ measurement is made using broadband visible-wavelength light, whereas the spectral estimate is made in the midwave infrared. As the optical properties of the particulate materials have not been characterized, we have not attempted to estimate visible transmittance from the infrared measurement.

**Table 2.** Comparison of Spectrally Estimated and in Situ Monitored Effluent Volume Mixing Fractions

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<td>5.31</td>
<td>-</td>
</tr>
<tr>
<td>SO₂</td>
<td>380.23</td>
<td>383.2</td>
</tr>
<tr>
<td>NO</td>
<td>104.7</td>
<td>119.1</td>
</tr>
<tr>
<td>NO₂</td>
<td>-</td>
<td>1 ppm</td>
</tr>
<tr>
<td>HCl</td>
<td>95.2</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>14.7</td>
<td>-</td>
</tr>
</tbody>
</table>

a The in situ measurement for NO₂ accounts for both NO and NO₂, however, only NO was detected spectrally. The spectral estimate error is the standard deviation across plume pixels, and the in situ error is the standard deviation in reported values during the spectral plume measurement time. The spectral estimate for \( t_p \) refers to the center plume pixel and refers to transmittance near 5 \( \mu \text{m} \), roughly an order of magnitude larger than the wavelength associated with the in situ transmittance measurement.

**Discussion**

Passive Fourier-transform infrared spectrometry is a well-established technique for identifying and quantifying smokestack effluents. Imaging Fourier-transform spectrometry has the potential to substantially improve the current state-of-the-art, and this work demonstrates some of the advantages spectral imaging brings to the quantification problem. The high resolution spectra enabled unambiguous identification of CO₂, H₂O, SO₂, NO, HCl, and CO. Moreover, effluent concentrations were accurately quantified as a result of being able to use spatially resolved spectra to decouple path length from column density. Errors of 1% and 8% between in situ and remotely estimated concentrations of SO₂ and CO₂ are good, especially when considering the simple model employed in their retrieval from the spectrum. A more complete radiative transfer model which properly includes the effects of background radiation and its transmittance through the plume is expected to improve the concentration accuracy, especially for CO₂ which has many optically thick emission lines. SNR could have been improved with an increased measurement time and possibly lowered the 50 ppm NO₂ uncertainty driven by the NO₂ detection limit. Nonetheless, these results compare favorably with what has been previously reported for nonimaging FTS measurements of smokestack effluents. For example, in a series of measurements involving eight separate power plants during 1992, Haus et al. reported (9) differences between spectral and in situ measurements of 4.8 ± 3.6% for CO₂, 14.8 ± 13.4% for NO, 11.9 ± 3.0% for H₂O, and 12.3 ± 9.9% for CO. Here the values reported are the mean and standard deviation of the errors reported for each smokestack, except for water as only three stacks provided in situ H₂O measurements. Spectral imagery also provides a means to partially check model assumptions. While the use of a single-layer plume model to retrieve effluent concentrations can lead to systematic errors when the plume structure is more complicated, analysis of the spectral imagery revealed that the single-layer model was an adequate approximation, thus building confidence in the reported concentrations.

This work only partially illustrates the advantages of IFTS over FTS for effluent monitoring. The spectral imagery also reveals information related to the fluid dynamics and effluent dispersion into the atmosphere. In future work, we hope to take advantage of the time-resolved DC-level imagery in which turbulent vortices enable the visualization and possibly quantification of the plume flow rate. The ability to use a single, rugged, and easily deployed instrument to passively estimate total effluent emissions for various compounds of environmental concern could make IFTS an attractive tool for independent verification of reported emissions. Moreover, the ability to persistently monitor a wide field-of-view with good spatial resolution may make IFTS useful for related applications such as the fugitive emissions and fence line monitoring problems where infrared cameras and arrays of FTS instruments have been traditionally employed. For these reasons, the additional instrumentation cost and data analysis complexity associated with IFTS may be justified for certain environmental monitoring problems.

**Literature Cited**


