Passive Fourier-transform infrared spectroscopy of chemical plumes: an algorithm for quantitative interpretation and real-time background removal

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We present a ratioing algorithm for quantitative analysis of the passive Fourier-transform infrared spectrum of a chemical plume. We show that the transmission of a near-field plume is given by $\tau_{plume} = (L_{obsd} - L_{bb\text{-}plume})/(L_{bkgd} - L_{bb\text{-}plume})$, where τ_{plume} is the frequency-dependent transmission of the plume, L_{obsd} is the spectral radiance of the scene that contains the plume, L_{bkgd} is the spectral radiance of the same scene without the plume, and $L_{bb\text{-}plume}$ is the spectral radiance of a blackbody at the plume temperature.

The algorithm simultaneously achieves background removal, elimination of the spectrometer internal signature, and quantification of the plume spectral transmission. It has applications to both real-time processing for plume visualization and quantitative measurements of plume column densities. The plume temperature ($L_{bb\text{-}plume}$), which is not always precisely known, can have a profound effect on the quantitative interpretation of the algorithm and is discussed in detail. Finally, we provide an illustrative example of the use of the algorithm on a trichloroethylene and acetone plume.

Key words: Remote sensing, Fourier-transform infrared spectroscopy.

1. Introduction

Chemically selective remote sensing is a vital technology with wide-ranging applications, particularly in environmental monitoring of effluents. Since every molecule, with the exception of homonuclear diatomics (e.g., N_2, O_2), has a unique infrared spectrum, infrared spectroscopy provides a discriminate technique for molecular remote sensing. In particular, the 8–12- and 3–5-μm regions are well suited for remote sensing because of the relative transparency of the atmosphere at these wavelengths and the presence of uniquely identifying features for a wide range of molecules. In the case of passive spectroscopy of ambient temperature chemical plumes, the 8–12-μm or fingerprint region is especially useful because of the comparatively high photon fluxes produced by sources at terrestrial temperatures (a factor of 30 higher photon flux at 10 μm versus 5 μm at $T = 298$ K).[1] Passive techniques for infrared spectroscopy in this region are desirable because of

their unobtrusiveness and consequent applicability to real-world situations. However, literature reports of passive infrared spectroscopy of effluents are surprisingly rare,[2] although passive infrared techniques are used extensively for atmospheric sounding.[3]

Several difficulties arise when one attempts to measure passively the spectrum of an effluent plume. These include obtaining a significant difference between the plume temperature and the radiometric temperature of the background, removal of the spectral features of the background, correctly accounting for internal emission of spectrometer elements when viewing cold backgrounds, and obtaining quantitative information about the plume. An additional concern lies in determining the quality of data as they are being acquired in order to provide for real-time optimization of acquisition conditions. This optimization procedure requires that processed spectra be provided to the user in real time.

The most significant of these difficulties is that the absolute signal strength is dependent on the difference (ΔT) between the temperature of the plume and the radiometric temperature of the background.[4] If the plume is near ambient temperature, these temperature differences are typically very small (5–10 °C), particularly when one views a plume against the sky at low elevation angles or against an earth background. An optimal signal can be obtained by

viewing the plume against the sky at zenith, which provides temperature differences as high as 100 °C in the best atmospheric windows for cloudless conditions.[5] Nevertheless, these differences are small compared with those used in a standard laboratory absorption measurement, which has the benefit of an artificially generated hot background. In passive spectroscopy, this problem can be overcome only through judicious choice of backgrounds within the limitations of the monitoring situation.

A second problem lies in the dominance of atmospheric features in the background spectrum, which, in the 8–12-μm region, are due principally to water and ozone. The simplest approach to the background problem is digital subtraction of a background spectrum from an observed spectrum with a plume:

$$L_{\text{plume}} \approx L_{\text{observed}} - L_{\text{background}}, \qquad (1)$$

where L refers to spectral radiance. However, the plume and background spectra are not strictly additive because the plume is partially opaque in the spectral regions where it absorbs or emits. If Eq. (1) is used, the background will be oversubtracted in regions of plume absorption.

To obtain the optimal signal in a passive plume-monitoring experiment, it is usually best to use a very cold background ($|\Delta T| = 50–100$ °C) such as the sky at zenith. An issue that becomes significant when using very cold backgrounds is that the internal signature of the spectrometer can dominate the measured signal. In a Fourier-transform spectrometer, the internal signature arises mainly from beam-splitter emission and is generally out of phase with the incoming radiation. Consequently, anomalous effects are seen in the Fourier transform of an interferogram with a significant internal signature because the calculated phase spectrum will be incorrect. This can result in such effects as emission peaks that appear as absorption features. Several approaches to removing the internal signature are discussed in the literature.[6,7] A particularly simple approach involves performing the Fourier transform on a difference of two interferograms, both of which contain the internal signature.[6]

In the ensuing discussion, we present a special ratio algorithm that both applies an improved background removal procedure and simultaneously eliminates the internal signature of the spectrometer. This algorithm uses approximations that usually apply only in ground-based uplooking or low-altitude downlooking experiments that involve near-field plumes—viewing an ambient plume through an ambient temperature uniform medium or viewing a plume of arbitrary temperature through a totally transmitting medium. We show that the special ratio is analogous to the conventional background ratioing technique of absorption spectroscopy:

$$\tau = \frac{L_{\text{observed}}}{L_{\text{background}}}, \qquad (2)$$

where τ is the transmission and L is the spectral radiance. The conventional ratio of Eq. (2) applies to the standard active absorption experiment, in which the background is an intense light source such as a lamp or laser. However, in passive spectroscopy of plumes, the radiometric temperature of the typical background is colder than or very close ($\Delta T < 10$ °C) to the plume temperature. In such a case, the self-radiance of the plume must be taken explicitly into account.

By accounting for the self-radiance of the plume, the algorithm converts the spectra into units of transmission that can be directly related to column density if the absorption coefficient of the molecule is known. Furthermore, the algorithm can easily be adapted to rapid, real-time processing. In Section 2 we present a derivation of the special ratio algorithm, which is followed by a discussion of the effect of the plume temperature on the calculation. We then illustrate the utility of this algorithm in the interpretation of field spectra of acetone and trichloroethylene plumes. Finally, we conclude with a summary of the important results.

2. Special Ratio Algorithm

As has been stated, there are four essential problems that a data-processing algorithm must address. These are removal of the dominant atmospheric background spectrum, conversion of the molecular plume spectrum into units that can be related to molecular column density, elimination of the internal signature of the spectrometer in the case of cold backgrounds, and providing a general method for observing the plume in real time. The key to solving all these problems lies in obtaining a method to solve for the transmission of the chemical plume.

In a typical spectroscopy experiment, concentration or column density is measured using Beer's law[8]:

$$\tau(\nu) = \exp[-k(\nu)cl], \qquad (3a)$$

$$A(\nu) \equiv -\log_{10}[\tau(\nu)] = 0.434[k(\nu)cl], \qquad (3b)$$

where τ is the frequency-dependent fractional transmission of the medium, k is the absorption coefficient of the molecule, c is the concentration, and l is the path length. In Eq. (3b) we define absorbance $[A(\nu)]$, which is useful because it is linearly related to column density (cl). The following analysis shows how the transmission of a chemical plume can be derived from a spectrum containing emission and absorption features from both the plume species and atmospheric species. The plume transmission can then be converted directly to a column density using Eq. (3a), provided that the molecular absorption coefficient is known.

Figure 1 illustrates the approach we use. The atmosphere is divided into two parts: a region beyond the plume (far field) and one between the spectrometer and the plume (near field). When viewing the atmosphere without a plume, the background
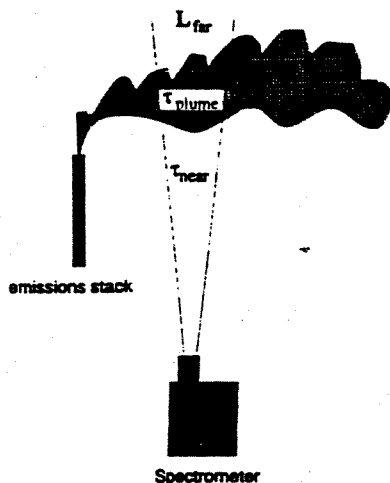
Fig. 1. Schematic of the important regions of a chemical release. The radiometric roles of the background, plume, and near field must be taken into account.

radiance incident on the spectrometer is given by

$$L_{bkgd} = L_{far}\tau_{near} + (1 - \tau_{near})L_{bb-near}, \quad (4)$$

where L_{far} is the spectral radiance of the scene beyond the plume, $L_{bb-near}$ is the spectral radiance of a blackbody at the near-field temperature, and τ_{near} is the transmission of the near-field atmosphere. These and all other radiance and transmission terms are frequency dependent.

The first term in Eq. (4) is due to the far-field atmospheric radiance attenuated by the near-field atmosphere, and the second term is due to the self-radiance of the near-field atmosphere. Equation (4) assumes that the near-field atmosphere is at a uniform temperature. This should be a good assumption if the observation point is relatively close to the plume, such as in a ground-based lookup or a low-altitude lookdown. It is not a good assumption for a satellite or high-altitude aircraft experiment, for which the second term will be considerably more complex. In addition, Eq. (4) neglects the effects of scattering, which can be important for plumes with a high aerosol content, especially in the 3–5-μm region.

After introducing a plume of uniform temperature, the radiance incident on the spectrometer is given by

$$L_{obsd} = L_{far}\tau_{near}\tau_{plume} + (1 - \tau_{near})L_{bb-near}$$
$$+ [(1 - \tau_{plume})L_{bb-plume}]\tau_{near}, \quad (5)$$

where τ_{plume} is the transmission of the plume and $L_{bb-plume}$ is the spectral radiance of a blackbody at the plume temperature. The first two terms in Eq. (5) are analogous to those in Eq. (4) except that the far-field radiance is further attenuated by the plume. The last term is the self-radiance of the plume attenuated by the near-field atmosphere.

Equation (5) can be further simplified if it is assumed that the plume temperature is equal to the near-field temperature. This is generally a good approximation for a typical chemical release because

the plume should equilibrate with the atmosphere quickly by entrainment. In this approximation, Eq. (5) becomes

$$L_{obsd} = \tau_{plume}\tau_{near}(L_{far} - L_{bb-plume}) + L_{bb-plume}, \quad (6)$$

which is similar to an equation derived by Flanigan.[4] Equations (6) and (4) can be combined to eliminate L_{far} and can be rearranged to give

$$\tau_{plume} = \frac{L_{obsd} - L_{bb-plume}}{L_{bkgd} - L_{bb-plume}}, \quad (7)$$

which we refer to as the special ratio. The special ratio differs from the conventional background ratio used for absorption spectroscopy [Eq. (2)] because self-radiance is accounted for through inclusion of the blackbody term. A conventional absorption spectrometer uses an intense light source, which is equivalent to L_{far} being large compared with $L_{bb-plume}$. The conventional ratio can be arrived at by considering only the first terms in Eqs. (4) and (5).

Equation (7) also holds for plumes at temperatures that differ from the near-field temperature when $\tau_{near} \approx 1$. This almost always is the case in the 8–12-μm region for near-field plumes.

Equation (7) suggests a useful method for obtaining spectra in transmission units while in the field. The background radiance can be measured by pointing the spectrometer away from the plume, but against a similar background. If a black plate (emissivity of 1 in the infrared) is kept at the ambient near-field temperature, its spectrum provides a direct measure of $L_{bb-near}$, which is approximately equal to $L_{bb-plume}$. All three radiance components of Eq. (7) can thus be measured in the field, and, because Eq. (7) is a ratio, calibration into absolute radiance is not necessary.

An additional advantage of using this method involves the Fourier-transform infrared spectrometer internal signature, which can have a significant contribution to the radiance measurements involved in Eq. (7). However, since the internal signature is shifted in phase from the external radiation, it is not simply added into each of the measured radiances in Eq. (7). We can take advantage of the subtractions in both the numerator and denominator of Eq. (7) to remove the spectrometer internal signature. Since the internal and external components do add directly into the interferograms, the internal component can be removed by performing both subtractions in interferogram space. The transmission is now given by

$$\tau_{plume}(\nu) = \frac{FFT(\nu, I_{obsd} - I_{plate})}{FFT(\nu, I_{bkgd} - I_{plate})}, \quad (8)$$

where I represents interferograms and $FFT(\nu, I)$ is the fast Fourier-transform operation for a single frequency. Note that Eq. (8) uses no calibration other than the black-plate spectrum. Equation (8) yields an ideal method for real-time processing of data

into a transmission spectrum. With only occasional updating of the background and black-plate spectra to accommodate spectrometer and background drift, it is straightforward to obtain real-time atmospheric background removal.

Typically, the black-plate temperature is not identical to the plume temperature, and adjustments must be made to Eq. (8) for quantitative studies. These require spectrometer calibration and knowledge of both the plate and plume temperature. The plate temperature is typically measured by generating a calibrated plate spectrum and fitting it to a Planck curve. The plume temperature can be assessed either by using a calibrated spectrum to obtain the absolute radiance of an optically thick component of the plume, or by assuming that the plume is at the air temperature. Equation (8) can then be corrected, yielding

of no chemical plume ($\tau_{plume} = 1$). The blackbody spectrum at the plume temperature represents the opposite limit of an optically thick plume ($\tau_{plume} = 0$). The special ratio measures the actual plane transmission, which lies between these two extremes. Its value should be 1, except at frequencies where the plume absorbs. Figure 2 shows the case in which the background is colder than the plume and the chemical spectra appear in emission. If the plume is viewed against a hot background (e.g., the ground), a similar figure can be drawn, except that the background will lie above the blackbody spectrum and the peaks will appear in absorption.

3. Effect of Plume Temperature on the Column Density Measurement

An important systematic source of error lies in the determination of the plume temperature. Analysis

$$\tau_{plume}(\nu) = \frac{\text{FFT}(\nu, I_{obsd} - I_{plate}) + g(\nu)[L_{bb}(\nu, T_{plate}) - L_{bb}(\nu, T_{plume})]}{\text{FFT}(\nu, I_{bkgd} - I_{plate}) + g(\nu)[L_{bb}(\nu, T_{plate}) - L_{bb}(\nu, T_{plume})]}, \tag{9}$$

where $g(\nu)$ is the spectrometer gain curve (converts radiance to spectrometer units) and L_{bb} is the blackbody spectral radiance for a given frequency and temperature. Equation (9) is not typically used for real-time processing but enables a small final correction to be made before the data are interpreted quantitatively.

Figure 2 provides a graphic depiction of the special ratio. A background spectrum represents the limit
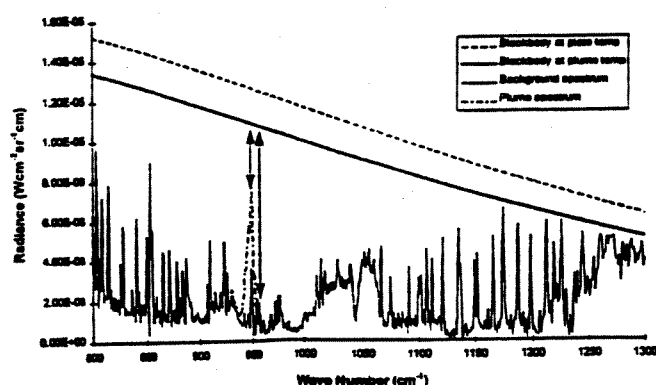
$$transmission = \frac{L_{obsd} - L_{bb-plume}}{L_{bkgd} - L_{bb-plume}}$$

Fig. 2. Schematic illustration of the special ratio method, showing a simulated SF$_6$ emission band seen over an atmospheric background spectrum. The distance between the background spectrum and the $L_{bb-plume}$ curve shows the radiance range available for the experiment (large arrow and denominator in special ratio). As the plume column density gets larger, the plume spectrum asymptotically approaches the $L_{bb-plume}$ curve. The plume transmission for a given wave number is given by the fraction of the available radiance range between the plume spectrum and the $L_{bb-plume}$ curve (small arrow divided by large arrow). For real-time processing, $L_{bb-plume}$ is simulated by a black plate, requiring postprocessing corrections to be made.

of the effect of this error also provides insight into the effects of different magnitudes of instrumental noise and instability. There are several methods for determining the plume temperature. The simplest method, and one that is always true sufficiently downwind from the release stack, is the assumption that the plume is at the air temperature. Unfortunately, as one views the plume further downwind to ensure complete equilibration, signal levels also drop because the plume spreads. Closer to the plume source, the temperature can be measured if a spectral component is optically thick ($\tau_{plume} \approx 0$). The calibrated spectral radiance of the optically thick component can be used to determine the corresponding blackbody temperature, as demonstrated by Solomon et al.[9] There are also iterative methods of finding the plume temperature. One method is to find the plume temperature in Eq. (9), which yields the best atmospheric background removal. Alternatively, the temperature can be adjusted to obtain accurate peak ratios since absorbance ratios in the spectrum of a single molecule should be independent of concentration. Finally, the intensity profiles of rotational structure in molecules can be used to ascertain temperature, as demonstrated by Herget and Brasher.[10]

The ensuing analysis shows the effect of error in the plume temperature on measured absorbance and column density. We show that these effects are highly dependent on the ΔT between plume and background and on the absorbance of the plume. In general, higher magnitude ΔT and a higher transmission mean that error in plume temperature has a reduced effect on column density measurements. Although we often refer to ΔT as a determining factor in experimental sensitivity, the truly relevant quan-
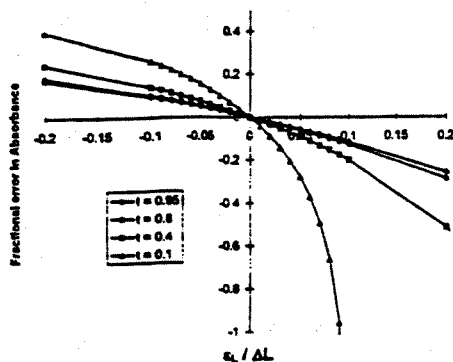
Fig. 3. Fractional error in absorbance and column densities as a function of $\varepsilon_L/\Delta L$ for a variety of transmissions. Note that at transmissions of less than 0.4, measurements of absorbance become sensitive to error in temperature.

tity is ΔL, the difference between the background spectral radiance and the blackbody spectral radiance at the plume temperature. ΔL can be directly related to experimental sensitivity and represents the available radiance range (see Fig. 2) for an experiment. However, ΔT can be directly related to sensitivity only if the magnitude of the two temperatures is known. Therefore, our values of ΔT refer to a fixed temperature, which we choose to be a plume temperature of 25 °C (298 K). In addition we define

$$\Delta T = T_{background(radiometric)} - T_{plume} \qquad (10)$$

such that ΔT is positive for spectra observed in absorption and negative for those observed in emission.

The graphs in Fig. 3 show the effect of errors in the plume radiance on the calculated absorbance. Given an error in plume temperature ε_T, such that

$$T' = T_{plume} + \varepsilon_T, \qquad (11)$$

where T' is the plume temperature used in calculat-

ing the ratio and T_{plume} is the actual plume temperature, we can determine an error in $L_{bb-plume}$:

$$\varepsilon_L = L_{bb}(\nu, T') - L_{bb}(\nu, T_{plume}). \qquad (12)$$

The transmission that will be calculated using an erroneous plume temperature in Eq. (7) will be

$$\tau_{plume}' = \frac{L_{obsd} - L_{bb-plume} - \varepsilon_L}{L_{bkgd} - L_{bb-plume} - \varepsilon_L}$$

$$= \frac{L_{obsd} - L_{bb-plume} - \varepsilon_L}{\Delta L - \varepsilon_L}, \qquad (13)$$

Rearrangement of Eq. (7) to solve for L_{obsd} and substitution into Eq. (13) yields

$$\tau_{plume}' = \frac{\tau_{plume}\Delta L - \varepsilon_L}{\Delta L - \varepsilon_L} = \frac{\tau_{plume} - \varepsilon_L/\Delta L}{1 - \varepsilon_L/\Delta L}, \qquad (14)$$

Equation (14) shows that $\varepsilon_L/\Delta L$ is a useful parameter that relates directly to the introduction of error. We are ultimately interested in the fractional error in the absorbance ($\Delta A_{fractional}$), which is equivalent to the fractional error in the column density:

$$\Delta A_{fractional} = \frac{-\log_{10}(\tau_{plume}') + \log_{10}(\tau_{plume})}{\log_{10}(\tau_{plume})}, \qquad (15)$$

Figure 3 uses Eqs. (14) and (15) to derive the fractional error in absorbance as a function of plume transmission (τ_{plume}) and $\varepsilon_L/\Delta L$. The plots in Fig. 3 are independent of optical frequency and plume temperature. Although $\varepsilon_L/\Delta L$ is a useful parameter, it is not as intuitive as units based on temperature. Therefore, Table 1 gives values of $\varepsilon_L/\Delta L$ for typical values of ε_T and ΔT at an optical wave number of 1000 cm^{-1} and a plume temperature of 298 K. Some important rules of thumb can be drawn from Fig. 3. First, the sensitivity of a column density measure-

Table 1. Obtaining $\varepsilon_L/\Delta L$ from ε_T and ΔT for a Wave Number of 1000 cm^{-1} ($\lambda = 10$ μm) and $T_{plume} = 298$ K[a]

	$\varepsilon_L/\Delta L$						
ε_T	$\Delta T = -100$	$\Delta T = -50$	$\Delta T = -20$	$\Delta T = -10$	$\Delta T = -5$	$\Delta T = 5$	$\Delta T = 10$
40	−0.86	−1.25	−2.65	−5.03	−9.81	9.35	4.56
30	−0.62	−0.90	−1.91	−3.62	−7.06	6.72	3.28
20	−0.39	−0.57	−1.22	−2.31	−4.50	4.29	2.09
10	−0.19	−0.27	−0.58	−1.10	−2.15	2.05	1.00
8	−0.15	−0.22	−0.46	−0.87	−1.70	1.62	0.79
4	−0.07	−0.11	−0.23	−0.43	−0.84	0.80	0.39
2	−0.04	−0.05	−0.11	−0.21	−0.41	0.39	0.19
1	−0.02	−0.03	−0.06	−0.11	−0.21	0.20	0.10
−1	0.02	0.03	0.06	0.10	0.20	−0.19	−0.09
−2	0.04	0.05	0.11	0.21	0.41	−0.39	−0.19
−4	0.07	0.10	0.22	0.41	0.80	−0.77	−0.37
−8	0.14	0.20	0.43	0.81	1.58	−1.50	−0.73
−10	0.17	0.25	0.53	1.00	1.95	−1.86	−0.91
−20	0.32	0.47	1.00	1.90	3.70	−3.53	−1.72
−30	0.46	0.67	1.42	2.70	5.26	−5.01	−2.45
−40	0.58	0.85	1.79	3.40	6.64	−6.32	−3.09

[a]All the quantities are defined in Section 3.

ment to temperature errors increases dramatically when the optical thickness of the plume increases (lowered transmission). Ideally, the plume transmission should be greater than 0.4. Given a transmission of 0.4 or greater and a desired precision of 20% or better, Fig. 3 shows the approximate requirement, $|\varepsilon_L/\Delta L| < 0.1$. From Table 1 this requirement roughly corresponds to an ε_T of 6 °C for a ΔT of -100 °C and an ε_T of 1 °C for a ΔT of 10 °C.

4. Illustrative Example

Figure 4 illustrates different stages of analysis of a spectrum of a trichloroethylene and acetone release taken against a clear-sky background at the zenith angle. We released 15 lb/h (0.11 kg/min) of each chemical, and the spectra were taken approximately 5-m downwind of the release site. Several stages of the processing of a single interferogram are shown. The data were all taken with a 4-cm^{-1} nominal-resolution M21 spectrometer (manufactured by Brunswick), optimized for the 8–12-μm wavelength region. Fourier-transform operations were per-

Fourier Transform

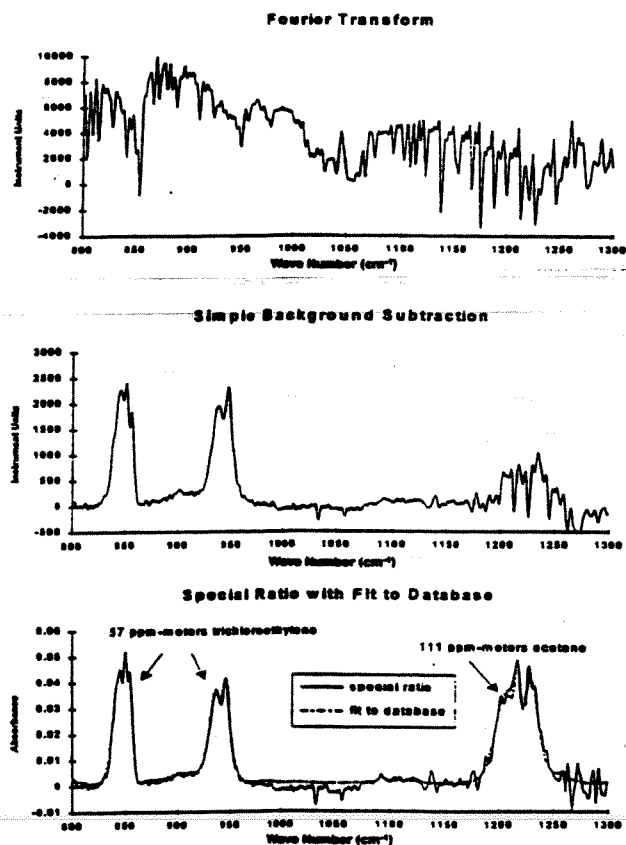Simple Background Subtraction

Special Ratio with Fit to Database

Fig. 4. Three stages of data processing. The simple Fourier transform is dominated by the presence of atmospheric lines and has emission features appearing as absorptions caused by the internal signature of the instrument. The simple background subtraction enables identification of the primary spectral features; however, the area of the acetone peak is severely oversubtracted because of the opacity of the plume to the background. Finally, the special ratio method takes the opacity of the plume explicitly into account and provides a quantitative measure of the plume column density.

formed using a Mertz phase correction, triangular apodization, and a factor of 4 zero filling.[11]

The simplest approach to processing is a simple Fourier transform with no background subtraction. Two problems are immediately evident. The most significant is that the identifying spectral features of acetone and trichloroethylene are totally obscured by the dominant atmospheric background. In addition, the intense out-of-phase internal signature of the instrument is evidenced by the appearance of atmospheric emission lines as absorption features.

The next approach illustrated is a simple subtraction of a background spectrum from the data spectrum. In this case, the data spectrum and background spectrum were transformed separately, and the data spectrum was subtracted from the background. The background subtraction reveals the identifying features of the molecules; however, the line shapes are distorted, and there is considerable leakage of atmospheric features into the acetone spectral features. The simple background subtraction does not take into account the opacity of the plume to the background in regions where it absorbs, resulting in oversubtraction in those regions.

Finally, the special ratio approach of Eq. (8) is illustrated, using no temperature correction. The background removal is greatly improved because the ratioing algorithm rigorously takes into account the opacity of the plume to the background. In addition, unlike the other two examples, the special ratio provides spectra that can be straightforwardly related to column density. The column densities were determined by a least-squares fit to Infrared Analysis database[12] spectra. For each molecule, the only two parameters that are fitted are the baseline of the spectrum and the molecular column density. The results of the fit are illustrated. In this case, the measured column densities cannot be verified independently; however, the measured molar ratio of 1.95 (acetone/trichloroethylene) is within 15% of the released ratio of 2.27.

5. Summary

We have presented a special ratio algorithm for the quantitative analysis of an effluent plume using infrared spectroscopy. The special ratio requires three inputs: a plume spectrum, a background spectrum, and the spectrum of an ambient temperature high-emissivity plate. The algorithm provides for both background removal and elimination of the spectrometer internal signature. This method can be applied to real-time processing for plume visualization, and can be further corrected in postprocessing for more quantitative use. The algorithm uses approximations that usually apply only in ground-based uplooking or low-altitude downlooking experiments— viewing an ambient plume through an ambient temperature uniform medium, or viewing a plume of arbitrary temperature through a totally transmitting medium.

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