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Chemical Detection Using the Airborne Thermal Infrared Imaging Spectrometer (TIRIS)

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ABSTRACT

A methodology is described for an airborne, downlooking, longwave infrared imaging spectrometer based technique for the detection and tracking of plumes of toxic gases. Plumes can be observed in emission or absorption, depending on the thermal contrast between the vapor and the background terrain. While the sensor is currently undergoing laboratory calibration and characterization, a radiative exchange phenomenology model has been developed to predict sensor response and to facilitate the sensor design. An inverse problem model has also been developed to obtain plume parameters based on sensor measurements. These models, the sensors, and ongoing activities are described.

Keywords: organic compounds, chemical warfare agents, drug manufacturing byproducts, imaging spectrometer, plume tracking, infrared, terrain thermal emission, inverse problem, TIRIS.

1. THE PROBLEM

When toxic compounds are spilled, either following an accident in a chemical plant, derailment, trucking accident, etc., toxic plumes may drift or be wind-blown into residential areas. The emergency response of authorities is to evacuate large areas. In some recent cases where uncontrolled fires have burned in chemical plants, residents had to stay out of their homes for several days, as a safety measure rather than due to actual presence of toxic fumes. Such situations point out the need for remote sensing techniques for evaluation of the hazard levels. Similarly, clean up crews can use remote sensing techniques to assess the hazard level before attempting to access the affected area. Presently, they must approach the contained area in protective gear and use gas sampling based sensors (or the canary in a cage method) to detect potential hazardous material. Single point measurements, however, are of lesser value than line-of-sight data for planning strategies of egress or cleanup.

The present state-of-the-art in IR spectral remote sensing is based on open air-path Fourier transform infrared (FTIR) spectrometers. Typically, a monostatic or bistatic arrangement is used where a hot source is located across the field of measurement (bistatic) or adjacent to the sensor with a retrorefletor across the field (monostatic). The source, at temperature much higher than that of the gas plume, emits infrared (IR) radiation allowing the plume to be observed in absorption. When plumes are released from a stack at an elevated temperature, they can be observed by FTIR instruments in emission and there is no need for a IR source. Emission measurements are often performed with the (cold) sky as a background. The sky radiance is typically low relative to that of the hot plume and the signal to noise ratio (SNR) is acceptable for reliable measurements.

In an emergency response situations, however, the placement of retroreflectors or IR sources, or having a specific view angle for the plume is not always practical, considering that the wind directions keep shifting. Moreover, the extent of plume spread is typically unknown and a wide area search may be required to continuously delineate the boundaries of the plume spread. In such situations airborne sensors that operate in the downlooking mode may be useful. The purpose of this paper is to describe the status of an ongoing effort to address the technical challenge of such a detection scheme.

The detection of most organic, organophosphates, and similar high molecular weight compounds is best accomplished in the IR (see typical spectral assignments in Fig. 1). There are several challenges that must be addressed in order to accomplish these airborne IR remote sensing measurements: (i) the intervening atmosphere significantly affects the spectral signatures observed by the airborne sensor, (ii) the plume-to-ground temperature contrast is often very small and may be positive or negative, (iii) the background terrain that acts as an IR source has unknown spectral properties, and (iv) real-time considerations require a short exposure time and fast signal processing.
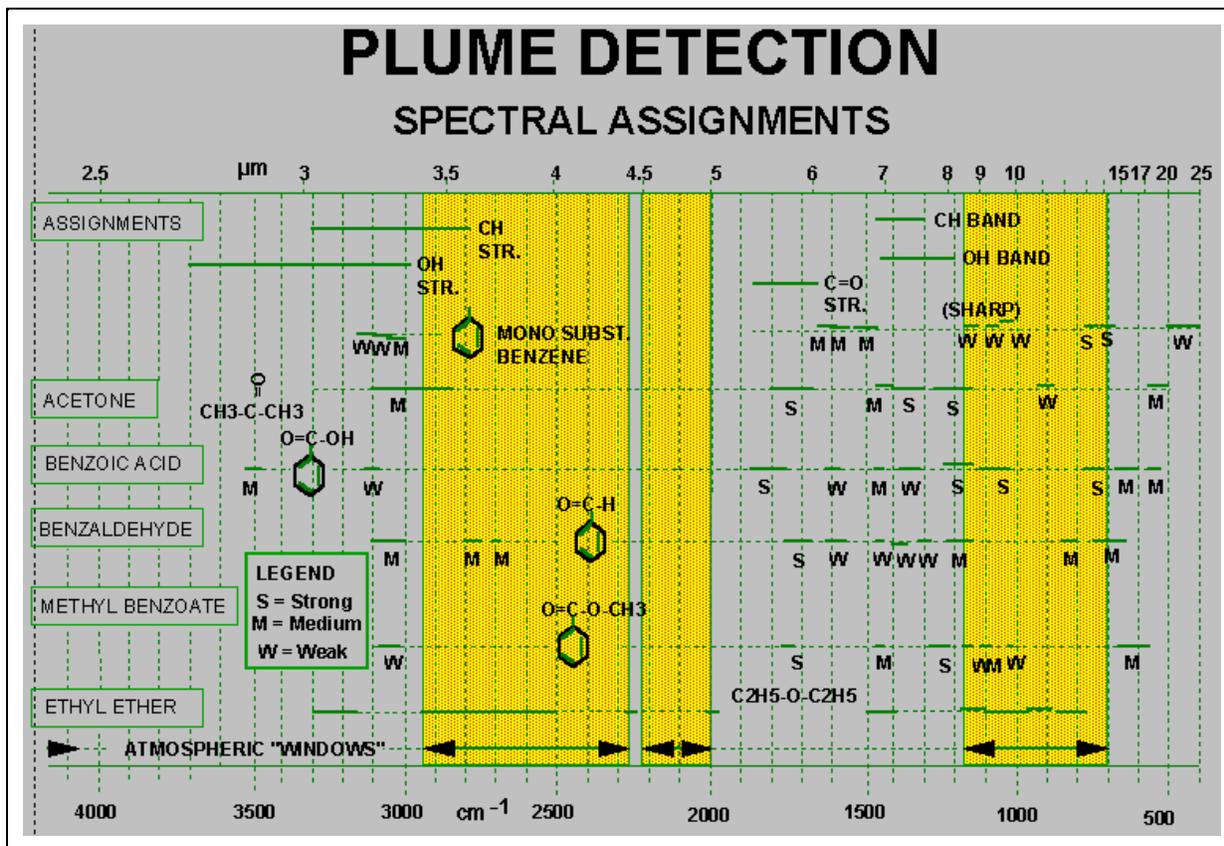

Figure 1. Typical spectral assignments of some organic compounds and the atmospheric "windows."

2. APPROACH

2.1. The Sensor

The approach selected to address these problems is based on a low spectral resolution sensor (relative to FTIR spectrometers) specifically developed for this application. The Thermal InfraRed Imaging Spectrometer (TIRIS) is an airborne instrument under development for emergency response, the detection of toxic compounds, air pollutants, chemical warfare agents, and for tracking their plumes in real-time. The TIRIS operates in 20 spatial and 64 spectral bands between 7.5 to 14.0 µm at $\Delta\lambda \approx 0.1$ µm resolution ($\Delta\nu \approx 10$ cm^{-1} at λ=10 µm), in a down looking mode, and detects / identifies plume composition against the thermal radiation of the background terrain. A laboratory prototype, TIRIS-I was constructed and tested. A field deployable version, TIRIS-II in now under development [1]. Being an imaging spectrometer, the plume is simultaneously characterized spatially and spectrally, and the measurements can be registered to a map location via geographical information systems (GIS).

The benefit of a low spectral resolution, dispersive system, is that it allows the capture of a relatively broad spectral signature (7.5 to 14.0 µm in this case) in a single short-exposure "snapshot." In order to ensure that the resolution of TIRIS is still sufficient to detect target gases, the entire EPA gas phase library of the most hazardous air pollutants (HAPs) was deresolved

from its original 0.25 cm^{-1} resolution to an equivalent 100 nm resolution of the TIRIS. A comparison of one set of original and deresolved spectra, shown in Fig. 2, indicates that although the fine structure of the gas phase spectrum is lost, the overall structure is clearly adequate to detect and in most cases identify the gas.
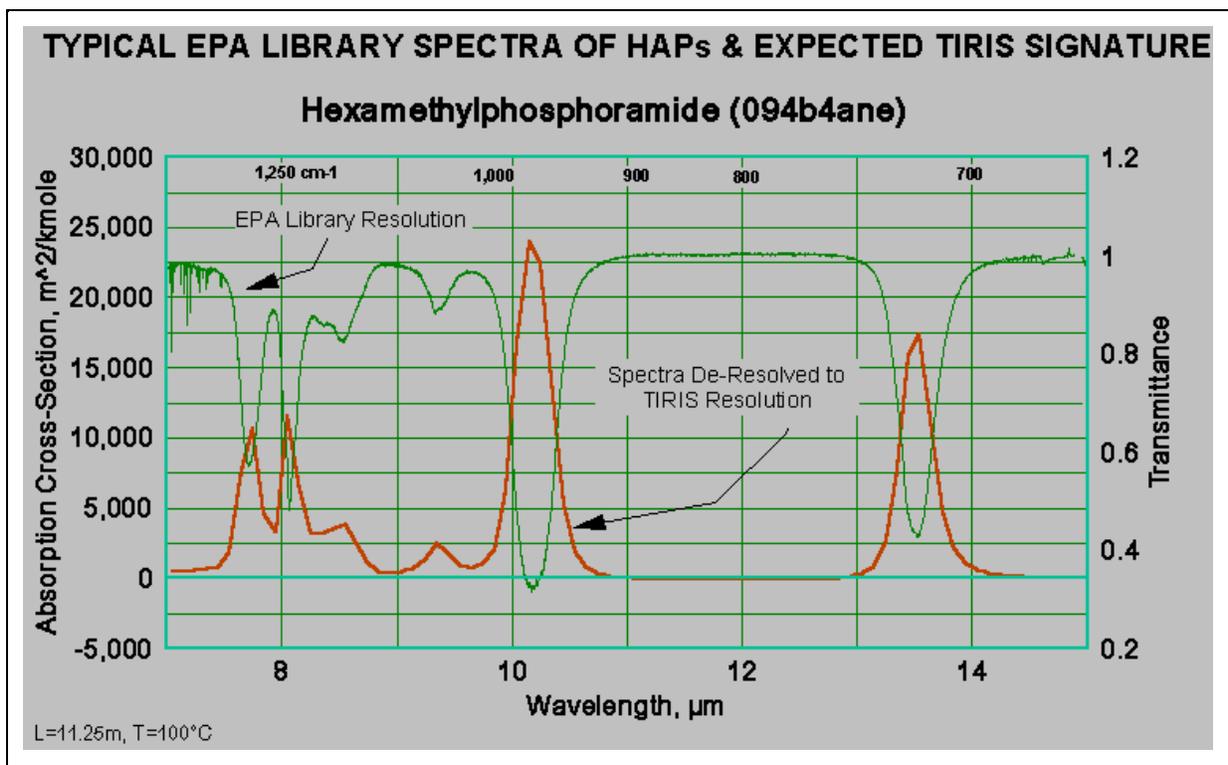

Figure 2. TIRIS resolution is sufficient to characterize IR spectrum. The top line corresponds to transmission measured by an FTIR instrument in a vapor phase cell at 0.1 cm^{-1} resolution. The lower line is the absorption cross section calculated from the transmission data and deresolved to 100 nm, or about 10 cm^{-1} at 10 µm.

2.2. Sensor Model: Forward Solution

A phenomenology model (forward solution) that serves as a sensor design tool has been developed to simulate the sensor response for a better understanding of its operational parameters and limitations. This is a radiative transfer model that accounts for the terrain infrared characteristics, sky radiation, and the plume parameters (Fig. 3). A plume may be observed in absorption or emission depending on the temperature contrast with the background. Several spectral libraries, of organic compounds and of background materials are used to model and predict the sensor response under a prescribed scenario. The libraries used for the modeling include the EPA's HAPs spectral library, the EPA/NIST vapor phase IR library, and the NPIC spectral library of background materials. Other libraries can be incorporated into the model, and the model itself can be adapted to other sensors. A list containing Internet sites of relevant spectral libraries can be found on the WWW[2].

The model, depicted in Fig. 3, shows the various sources of radiation and the exchange of radiation in the measurement environment. The model takes into consideration the terrain spectral characteristics, and any exchange of radiation with other elevated terrain features or sky and clouds. The ground can be assumed to behave as a Lambertian black or gray body source, or a real source based on selected elements from the backgrounds library. The plume is modeled under the thin gas approximation as a mixture of any number of compounds. Their mixing proportions can be specified.

In general, the radiation measured by the sensor along a line of sight to the ground can be described by Eqs. 1 and 2, where the nomenclature corresponds to that in Fig. 3. Eq. 1 expresses the radiation directly emitted by the terrain, plus reflected sky

radiation. Eq. 2 expresses the direct emission from the plume and absorption of terrain radiation as it passes through the plume.

$$N_{\lambda,b} = \alpha_\lambda \cdot 2hc^2 / \{\lambda^5 \, [\exp(hc/\lambda kT_b) - 1] \} + (1 - \alpha_\lambda) \cdot 2hc^2 / \{\lambda^5 \, [\exp(hc/\lambda kT_s) - 1] \} \tag{1}$$

$$N_{\lambda,r} = N_{\lambda,b} \cdot \exp(-k_\lambda L) + B_\lambda(\lambda, T_a) \cdot [1 - \exp(-k_\lambda L)] \tag{2}$$

In these equations, T_b, T_s, and T_a are the temperatures of the background terrain, the sky (e.g., clouds), and the plume, respectively. k is an absorption coefficient (a function of wavelength, λ), and L is the path length through the plume. The emissivity α is also a function of wavelength.

A computer code that incorporates the model with a graphical user interface has been developed and a screen capture is shown in Fig. 4. In this forward solution the user can "create" synthetic mixtures of various library compounds, specify plume, atmospheric and ground parameters. The model calculates and displays various spectra of interest such as the combined absorption cross section signature of the selected mixture (bottom left of Fig. 4), the radiance at the sensor aperture (bottom right), or the sensor output (using the sensor transfer function). All calculations are conducted at 1 cm⁻¹ intervals. Sensor output is given at the specific sensor resolution (100 nm for TIRIS).
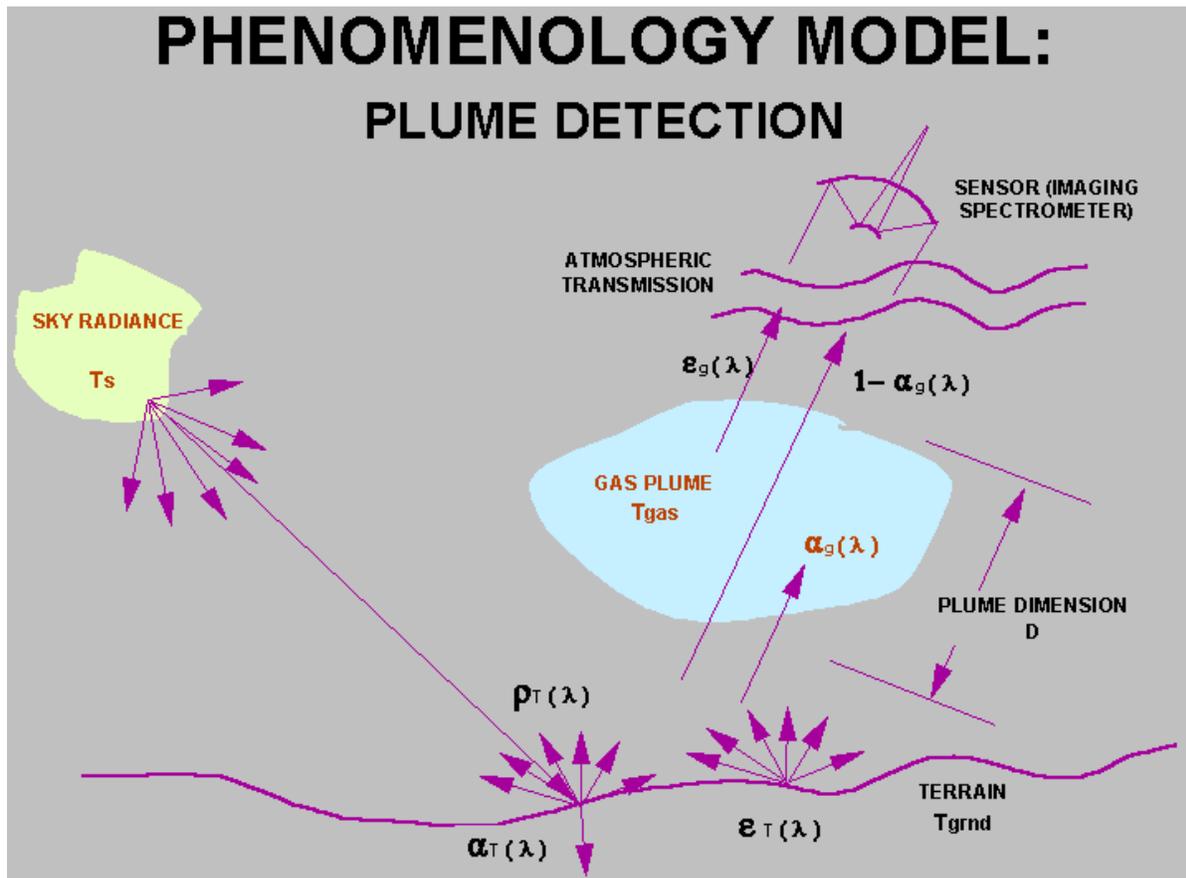

Figure 3. IR radiative exchange model for airborne plume detection.

The spectral signature at the aperture of the sensor is used here to illustrate the effect of the thermal contrast. In this particular case the terrain is warmer than the plume by about 10 °C. The Planck function at the terrain (T_b) and plume (T_a) temperatures are depicted in the figure (bottom right). The radiance at the sensor can be seen confined between these two

curves. As the temperature contrast becomes smaller, the plume signature diminishes to zero at the reversal point. Once the plume becomes hotter than the terrain it reappears this time in emission (still confined between the two curves corresponding to the Planck blackbody at the gas and terrain temperatures).

As depicted in Figs. 3 and 4, and expressed by the term T_b (background temperature) in Eq. 1, terrain background emission is an important factor in the observed signature. Since this is seldom known it has to be estimated from the actual sensor data. To validate an approach for extracting ground emissivity and temperature (addressing the so called ε-T problem), a special experiment was conducted. The ATLAS multispectral scanner, operated by NASA Stennis Space Center, was used to collect IR signatures over Baton Rouge, LA. The spectral signatures from the six thermal IR bands of ATLAS were used then in an iterative procedure to extract ε-T information. A false-color map of the terrain apparent temperature is shown in Fig. 5[3]. The ATLAS technique was found sufficiently accurate and has been ported to the TIRIS sensor environment.
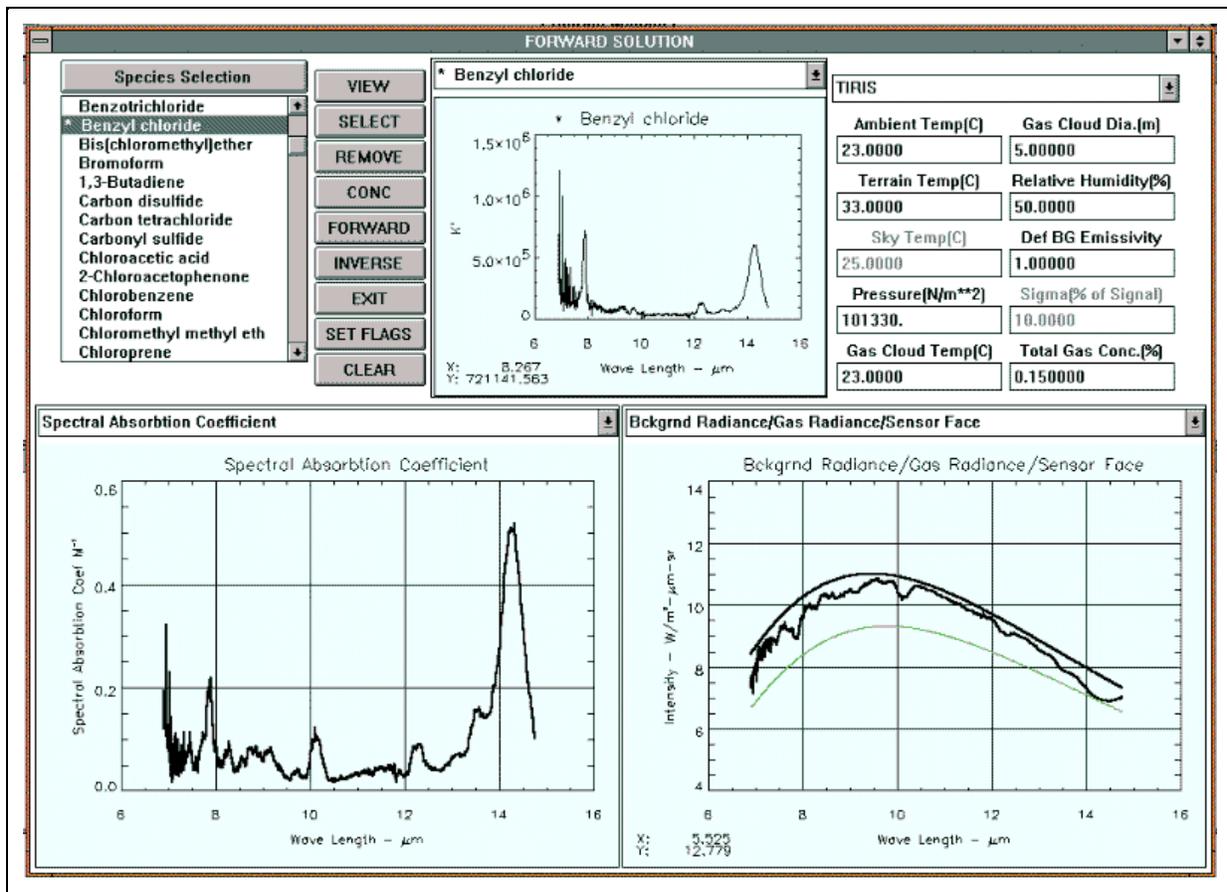

Figure 4. Radiative exchange and sensor response model. The plot on the bottom right shows that the expected sensor signature is located between two curves that depict the Planck blackbody radiance at the ground and the plume temperatures.

The forward solution was written in IDL (interactive data language) that runs on all the popular computing platforms, and can be incorporated into ENVI, a hyperspectral data processing package. Atmospheric correction are obtained via the MODTRAN code that was compiled to run on a PC using the 32-bit version of Microsoft Fortran 90 and MS development studio.

2.3. Sensitivity Estimates

The radiative transfer model discussed above applies to monochromatic radiation only. In attempting to estimate detection sensitivities or reduced broadband absorption spectra to determine species column densities, one needs to know whether

spectrally averaged values of the absorption coefficient k_λ can be used. Such an assumption is *only* valid if the average spacing between the spectral lines in the spectral band being used is less that the typical line width[4]. Spectral line widths are usually about 0.1 - 0.2 cm^{-1} at 1 atmosphere. When these conditions apply (as they usually do for molecules with more than about five atoms at one atmosphere pressure), one can apply the so-called "smeared line model" and use average absorption coefficients. Absorption based upon use of average spectral absorption coefficients will be less than predicted by Eq. 2 if the spectral lines do not overlap.

The smeared line model can also be used in weak concentration limit where $k_\lambda L << 1$ at all wavelengths, including the centers of strong spectral lines. In this case, the spectral lines are all "optically thin" and as a result exponential terms in the radiative transfer equation can be linearized.

Preliminary detection sensitivity estimates in the following paragraphs are based on the smeared-line model where representative values of the average spectral absorption coefficient per molecule in the LWIR bands are needed to estimate species detection thresholds. OKSI used the EPA's HAPs spectral library to obtain average spectral absorption coefficients. The EPA library, obtained using an FTIR spectrometer, is measured in 0.25 cm^{-1} intervals; average values were calculated over relatively broad spectral intervals (100 nm -- corresponding to the TIRIS sensor), and dividing by the column density in the measuring device. The resulting absorption cross-section values range from 200 to 10,000 m^2/kmole for strong bands, corresponding to an absorption cross-section of 3×10^{-21} to 2×10^{-19} cm^2/molecule. These results are in reasonably good agreement with the theoretical band-integrated absorption coefficients (10^{-19} to 10^{-17} cm^{-1}/moleclue) divided by the typical vibration-rotation band width of 10 to 100 cm^{-1} (IR band width tend to fall in a narrow range governed by the temperature and the molecular moment of inertia) which result in a range of LWIR peak absorption cross sections from 10^{-21} to 10^{-18} cm^2/molecule.

Therefore, we assume

$$10^{-21} < k_\lambda / n_i < 10^{-18} \text{ cm}^2 \text{/molecule} \tag{3}$$

for representative LWIR bands, near band center. Note that if the bandpass $\Delta\lambda \approx 100$ nm or $\Delta\nu \approx 100$ cm^{-1} is used for the detection instrument, as with the TIRIS, the average absorption coefficient over the band might be considerably less, since the absorption band would be narrower than the measurement bandpass.

Next we set a detection "threshold" of say $A \approx 5\%$, for high-confidence detection of particular species. Here we define A to be the relative reduction in radiance along the ray path from the surface to the receiver. We will also assume that $T_b - T_a = 10°C$, so that according to Eq. 2,

$$A = [N_{\lambda,b} - N_{\lambda,r}]/N_{\lambda,b} \approx 0.15 \cdot [1 - \exp(-k_\lambda L)] \tag{4}$$

Eq. 2, with minor modifications, can also be used to estimate the value of the factor that precedes the $[1 - \exp(-k_\lambda L)]$ term for other values of $T_b - T_a$. If one sets a minimum absorption threshold at $A = 0.05$, the corresponding required value for the $[1 - \exp(-k_\lambda L)]$ term is $A/0.15 = 0.33$, which requires

$$k_\lambda L > 0.4 \tag{5}$$

for high probability of detection. Now assuming $10^{-21} < k_\lambda / n_i < 10^{-18}$ cm^2/molecule, this implies that the column density $n_i L$ must satisfy the inequality

$$n_i L > 4 \times 10^{17} \text{ to } 4 \times 10^{20} \text{ molecules/cm}^2 \tag{6}$$

If the absorbing species "i" that one hopes to detect is confined to a convective mixing layer near the ground that is 10 meters thick, the corresponding species detection limit would be

$$n_i > 4 \times 10^{14} \text{ to } 4 \times 10^{17} \text{ molecule/cm}^3 \tag{7}$$

Eq. 7 corresponds to species mole fraction in a 0.001% to 1% range, approximately. More accurate estimates of required column densities for detection can be made once the species are defined, temperature difference T_b-T_a are known, and a minimum detection threshold level of **A** required for high-confidence species identification is established. The forward solution computer model is used to generate such estimates.

2.4. Plume Detection: Inverse Problem Solution

The second model (inverse solution) uses the sensor output to determines the composition of organic gases that created the observed IR signature. The inverse solution has two steps. First, the organic compounds library is scanned and reduced to a set of *M* potential end-members that may contribute to the signature, based on detection probability and constant false alarm rate considerations. In the second step, an *MxM* matrix is constructed in which the *M* compounds selected in the first step are incorporated into *M* linear equations, in *M* spectral bands. In practice, *M<< # of bands.* The solution of this system of equations provides an exact solution to the problem rather than the traditional least squares approximation. The key to this approach is the proper selection of the *M* band.
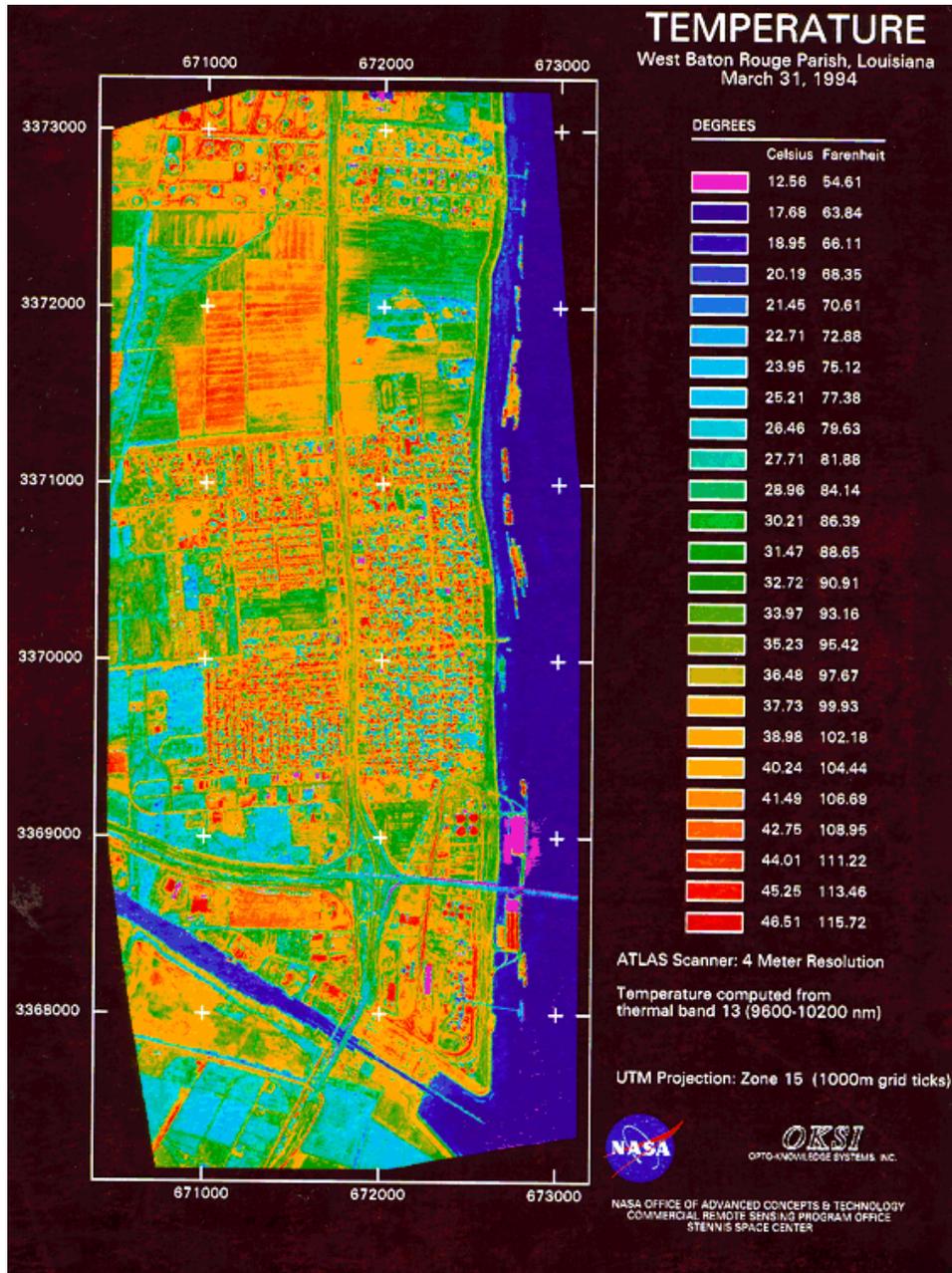
Figure 5. False color terrain temperature map obtained From ATLAS IR imagery.

The validation of the inverse model suffers from the lack of real data with accurate ground truth. While developing the code, synthetic data were produced from the spectral libraries (using the forward solution). These data were then "corrupted" with various models of noise and various levels of SNR. Results of one trial, summarized in Fig. 6, show 100% detection success. Work underway presently with field data will be used to validate these algorithmic paradigms.

PERFORMANCE OF INVERSE SOLUTION		
End-Member	**True Concentration**	**Inverse Solution Estimated**
Benzyl chloride	1.0E-03	1.0003E-03
1,3-Butadiene	0.0E+00	0.0000E+00
2-Chloroacetophenone	0.0E+00	0.0000E+00
Chloroprene	0.0E+00	0.0000E+00
m-Cresol	0.0E+00	0.0000E+00
1,2-Dibromo-3-chloropro	5.0E-04	4.9877E-04
Dichloroethyl ether	0.0E+00	0.0000E+00
1,2-Epoxybutane	0.0E+00	0.0000E+00

Figure 6. Example of Inverse Solution Analysis Results. In this case, synthetic mixtures were created from an arbitrary number of compound in the list. The Inverse solution was able to determine which compounds actually were included and at what composition.

3. LABORATORY VALIDATION

The TIRIS-II sensor is currently set up in the laboratory for calibration and characterization, as depicted in Fig. 7. A vacuum cell with KBr windows was designed to provide the required optical path length. Various vapor phase compounds may be injected into the cell in controlled amounts. The cell temperature may be raised above ambient and the pressure accurately monitored to a subtorr level, from which the column density of the vapor can be calculated. The source of IR background radiation is a blackbody that can vary over a wide temperature range. The combination of background and cell temperature permits observation of gas spectral signatures either in emission or absorption. Background spectra obtained using only the evacuated cell and blackbody can be used to obtain the overall system transfer function (including FPA, various filters, and windows spectral characteristics). The laboratory tests are currently underway to validate both the forward and inverse solutions.
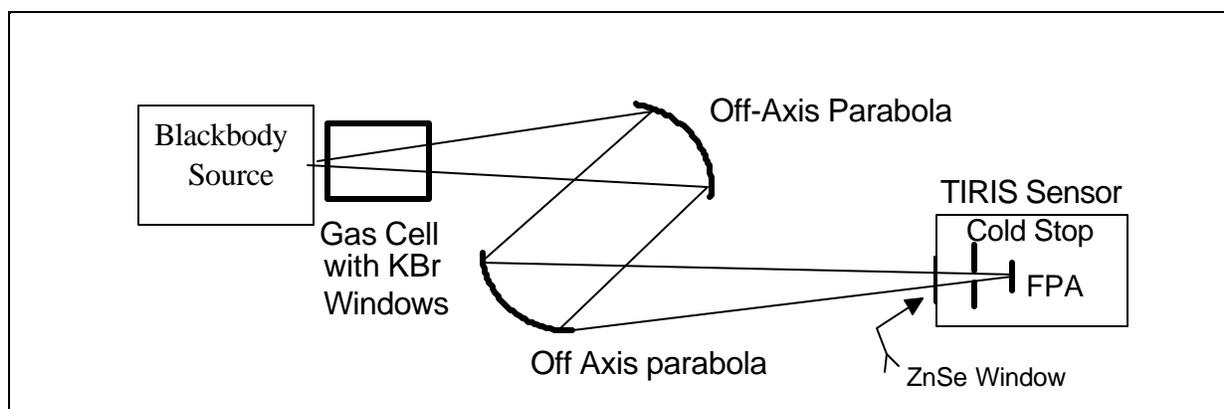

Figure 7. Schematic of Laboratory Setup for the TIRIS Vapor Phase Detection Characterization and Sensor Calibration.

4. SUMMARY

Extensive use of synthetic data was made for the validation of the algorithms. In order to futher validate the approach to data analysis, OKSI is studying spectral signatures collected with an FTIR airborne Atmospheric Emission Spectrometer. These spectra, measured at a higher spectral resolution than the TIRIS, were obtained from an altitude of 5,000 meters, and cover a

plume emitted by a coal burning power plant and of the terrain in the vicinity of the plant. Data processing is currently underway, aided by extensive ground truth that are available for this data set.

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