Passive Fourier Transform Infrared (FT-IR) Monitoring of SO₂ in Smokestack Plumes:
A Comparison of Remote Passive Spectra of an Actual Hot Plume with Emission Spectra Collected with a Heatable Cell

C.T. Chaffin, T.L. Marshall
AeroSurvey, Inc.
Manhattan, KS

R.J. Combs, R.B. Knapp, R.T. Kroutil
U.S. Army Edgewood Research, Development and Engineering Center
Aberdeen Proving Ground, MD

W.G. Fateley, R.M. Hammaker
Kansas State University
Manhattan, KS

ABSTRACT

In the interest of developing practical methodologies for remote passive FT-IR analysis of sulfur dioxide in heated smoke stack plumes, infrared spectra have been collected in a number of relevant experiments. Field data includes passive remote FT-IR spectra collected at a coal-burning power plant for which plume conditions were characterized by in-stack continuous emission monitors (CEMs), spectra collected of a controlled plume from a model stack device, and spectra collected with a heated cell filling the field-of-view (FOV) of the spectrometer, into which controlled levels of sulfur dioxide could be introduced while the spectrometer viewed sky backgrounds similar to those behind the actual power plant plume. An extensive spectral data set has also been collected in the laboratory under controlled target and background conditions using a heated cell. Typical spectra are presented and the potential for characterizing many of the important factors involved in remote passive FT-IR analyses through controlled-condition experiments such as these is discussed.

INTRODUCTION

Passive remote FT-IR monitoring of smokestack emissions has been investigated for many years and the feasibility has been demonstrated through the collection of passive spectra containing the infrared emission signature of plume constituents.[1,2,3,5,6,9] Also, progress in instrumentation is gradually improving the practicality of such techniques. However, while the theoretical aspects of remote passive FT-IR analysis of sulfur dioxide in heated plumes have been fairly well established[1-6,9], a generalized methodology for performing remote analyses of smokestack plumes has yet to be developed. Reducing spectral field data to quantitative information is significantly more complicated in analyses involving emission data than in field analyses based only on absorption phenomena.

Many parameters affect the infrared spectral signature of a heated plume containing infrared-active analytes as viewed through the open atmosphere. In general, these parameters include:

- the temperature and composition of the plume
- the temperature and composition of the background
- the ambient atmospheric conditions and distance to the plume
- the temperature-dependent spectral characteristics of the plume constituents
- the unique response characteristics of the sensor

Methods have been developed to characterize the instrument response function[7,13]; this work is primarily aimed at producing a robust data set that can be used to address the other parameters listed above. Characterizing the effects of these parameters will be required if a methodology is to be developed for deriving quantitative information from the plume's spectral signature as it is recorded by an infrared sensor.

Toward this goal, infrared spectra have been collected in the field at a coal-fired power plant for which CEM data was made available for comparison. With these spectra of an actual characterized plume as a point of reference, spectra have been collected under more controlled conditions, both in the laboratory and in the field in the interest of determining the potential of characterizing the parameters listed above in an efficient manner through controlled experiments. The controlled field data collected includes spectra collected at the power plant with a cell that filled the FOV of the spectrometer and for which temperature and sulfur dioxide levels could be controlled, as well as spectra collected of a plume generated in the open atmosphere by a model stack device that allowed sulfur dioxide loading in the plume to be controlled. Controlled laboratory experiments have also been performed with the heated cell in which the temperature of both target and background was known.

EXPERIMENTAL DETAIL AND RESULTS

All spectra discussed and presented in this paper have been collected with Midac M2400-series field spectrometers (Midac Corporation; Irvine, CA). Although four separate instruments were used, all of the spectrometers were equipped with liquid nitrogen cooled MCT detectors and provided good response in the 8-12 micron window. Ten-inch aperture collection telescopes providing a 3 mrad FOV have been used in the collection of all outdoor field data.

Much of the work to be presented involved the use of a heated cell purchased from International Crystal Laboratories (Garfield, NJ). The stainless steel cell has a 10 cm optical path, a 1.5" clear aperture, and it's temperature can be controlled from ambient to 250° C. The cell has been modified to feature two valved ports to allow flow-through operation during spectral data collection and/or static sample loading. Sodium chloride windows were used in this work. Custom cell holders were manufactured which allowed the heated cell assembly to be mounted directly to the front windows of the spectrometers. The presence of the cells did not occlude the spectrometer's FOV and did not interfere with the use of the 10" aperture collection telescopes during the collection of field data. The spectrometers without their collection telescopes were mounted on custom data collection plates for the laboratory experiments.

A mixture of sulfur dioxide in nitrogen (Scott Specialty Gases) was used as the source of the sulfur dioxide gas samples. The calibration gas was certified at 10,100 ppm; lower concentrations were obtained by diluting the calibration gas with pure nitrogen, using a reference gas generator with two mass flow controllers to meter the relative flow rates of the gases being mixed.

The data has been collected at a variety of resolutions. Various collection times have been used, all 1 minute or less. Much of the data collection was performed in the Spectracalc (Galactic Industries; Salem, NH) software environment. A great amount of data, however, has also been collected while using the "Collect" program written by R. T. Kroutil and others (U.S. Army Edgewood Engineering, Research and Development Center; APG, MD). Over 120,000 single-scan interferograms have been collected in this particular effort in the field and in the

laboratory with the Collect program to date.

Field data collection at a coal-fired power plant

Passive remote FT-IR spectra have been collected on numerous occasions at a coal-burning power plant. Concurrently-collected CEM data have been made available to the passive FT-IR researchers and provide a valuable point of reference for interpreting the spectral data collected at this site.

Typically, sample spectra have been collected of the plume radiance from a distance of approximately 600 to 1000 m and background spectra of the sky background 3 to 4 plume widths upwind of the plume have been collected from the same monitoring location. Alignment to the plume is accomplished with a coarse visual alignment followed by fine adjustment to maximize the infrared energy impinging on the detector, as evidenced by intensity in the interferometric signal. A typical difference spectrum is presented in Figure 1 and has been created with a simple subtraction of the sky background spectrum from the plume sample spectrum. Figure 2 presents a series of spectra collected within a few minutes of one another at various spectral resolutions, from 0.5 cm-1 to 32 cm-1. Thirty-two coadded scans were used in all cases, with collection times varying from approximately 50 seconds for the 0.5 cm^{-1} spectra to less than 3 seconds for the 32 cm^{-1} spectra. Although the subtraction coefficient was manually adjusted to result in the flattest baseline, the subtraction coefficient was usually between 0.98 and 1.0.

Data from the in-stack CEM monitors collected concurrently to the collection of these spectra indicated sulfur dioxide concentrations of approximately 100 ppm and a temperature of 95° C, measured at a location halfway up the 330 m stack. Based on these values and an inner diameter of approximately 8 m, a value of 665 ppm*m sulfur dioxide can be estimated for the plume exiting the 27' diameter stack, corrected to 25° C. The difference in plume temperature between the CEM sensor location and the area of FT-IR measurement immediately above the top of the stack is not known.

The difference spectrum shown in Figure 1 was collected when the sky background consisted of low, dense clouds. Ambient temperature was approximately 21° C with a 1 to 2 m/s north wind present. The spectrometer was looking at the plumes in profile, from a position estimated to be approximately 640 meters from the top of the smokestack and at an angle of elevation of approximately 15 degrees. Humidity was high, partly due to weather conditions (a thunderstorm was brewing) and partly due to the presence of nearby cooling structures that were producing large steam plumes which appeared to be occasionally entering the field of view of the instrument during the collection of both sample and background spectra.

Figure 3 presents a typical difference spectrum collected while the instrument was viewing cloudless sky at approximately 15° elevation above the horizon through the heated cell at 120° C. In this difference spectrum, the sample and background spectrum were collected with the same FOV but with different cell contents. For the collection of the sample spectrum, a 1,010 ppm*m sample of sulfur dioxide filled the FOV of the spectrometer. and was created by flowing the 10,100 ppm SO_2 certified reference gas mixture through the 10 cm cell at 0.1 L/min. For the background spectrum, nitrogen gas was flowed through the cell at 0.1 L/min.

Field data collection with a scaled-down stack model

A field device to generate heated plumes containing sulfur dioxide in the open atmosphere has been constructed. The device produces a heated combustion plume from a 150,000 Btu/Hour propane heater, with the plume being directed out of an 8" diameter stack by a 550 cfm fan at temperatures ranging from 150° C to 300° C. Currently, fine control over analyte introduction rate and coarse control over temperature and stack flow rate exist. Temperature is monitored with a thermocouple at the stack exit. Analyte introduction rates up to 10 L/min are possible; the rate is controlled by a mass flow controller.

A preliminary data set has been collected to evaluate the potential of this device as a controllable stack model. Figure 4 presents a series of passive spectra collected with the model stack device over different pathlengths.

Laboratory data collection with a heated cell

Infrared emission spectra have been collected in a controlled laboratory environment to characterize the spectral emission characteristics of sulfur dioxide. For the collection of the laboratory data, various concentrations of sulfur dioxide were loaded into a heated cell which filled the FOV of a spectrometer viewing an ambient-temperature background. Six data sets were collected using six different concentrations of sulfur dioxide and one data set was collected when the cell contained only nitrogen. Each of the seven data sets contains spectra collected with the cell at 50° C, 80° C, 120° C, and 150° C. A second set of spectra have been collected with various concentrations of sulfur dioxide in the cell, with the cell temperature held constant at 100° C. In all cases, background spectra have been created with only nitrogen in the cell at the appropriate temperatures.

The concentrations of sulfur dioxide within the cell were validated with a second spectrometer. The validation spectrometer viewed a 1500 K background and, therefore, produced traditional transmission spectra displaying the absorption bands of sulfur dioxide with high signal-to-noise ratios. These transmission spectra were used to create absorbance spectra from which accurate quantitative information concerning the cell's contents could be derived. Initially, only the concentration of the certified gas mixture was known accurately; the concentrations of the diluted cell samples were determined by spectroscopic comparison to the 10,100 ppm cell sample.

The cell holders were configured to allow easy and rapid transfer of the heated cell from one spectrometer to the other. Both spectrometers used in the collection of the laboratory heated cell data were mounted on similar custom calibration plates, placed side-by-side on a laboratory bench.

Figure 5 presents a series of difference spectra, all collected with a cell temperature of 100° C but using various concentrations of sulfur dioxide. Figure 6 presents a series of difference spectra, all created with 1,010 ppm*m sulfur dioxide but at various temperatures.

DISCUSSION

The actual plume spectra presented in Figures 1 and 2 illustrate a number of phenomena associated with remote passive FT-IR emission spectra. Most obvious (and important) in the spectra is the P and R structure of three emission bands centered at 1152 cm^{-1}, 1064 cm^{-1}, and 960 cm^{-1}. The P and R bands centered around 960 cm^{-1} and 1064 cm^{-1} are hot bands of carbon dioxide and provide a means of determining plume temperature as previously described by other researchers.[11,12] (The calculation was not performed in this work.) The band centered at 1152 cm-1 is the ν_1 fundamental of sulfur dioxide.

Considering that a significant infrared energy difference was detected in the plume radiance as compared to the surrounding sky radiance, one might expect that straightforward subtractions of sky background spectra from plume sample spectra would have produced difference spectra with severely skewed baselines. This, however, was not found to be the case. Apparently, the increased radiances are primarily due to the emission bands of the plume's molecular constituents, seen clearly in the difference spectra, with the plume being essentially transparent at surrounding wavelengths. As the power plant monitored is a relatively new and modern facility, it is not uncommon for the plumes to be invisible if non-condensing atmospheric conditions exist and operation can only be verified by detection of increased infrared radiances emanating from above the stacks as compared to the surrounding sky. Particulate loading may be much higher in other plumes and previous work by other

researchers suggests such loading can significantly affect a plume's infrared signature. Simple subtractions of sky background spectra from plume radiance spectra when particulate loading is high may not produce flat baselines due to increased opacity and other more subtle effects.[9]

Although the optically dense and thermally homogenous clouds present during the collection of these spectra might be considered an optimum background, the spectrum in Figure 1 has been found to be fairly typical of spectra collected under vastly different atmospheric conditions at this site. The most important factor in achieving relatively flat baselines in the difference spectra collected at this site has seemed to be the amount of time between the collection of the plume spectrum and the collection of the sky background spectrum. The difference spectra shown in Figure 1 was created from sample and background spectra collected within 10 minutes of one another.

It should also be noted that no effort has been made in these spectra to remove the effects of the instrument itself. Careful determination and removal of instrumental contributions could further improve the flatness of the baselines, especially if the instrument response function is varying over time.

Figure 2 illustrates the expected increase in signal-to-noise ratio (SNR) for the broad ν_1 fundamental band of sulfur dioxide centered at 1152 cm^{-1} as spectral resolution is decreased. If the effects of atmospheric attenuation due to the much sharper water lines can be accounted for computationally (perhaps through the use of databases such as HITRAN), future methodologies for performing remote passive analysis of sulfur dioxide in heated plumes may be able to capitalize on the higher SNR, increased data collection efficiency, and simplified instrumentation associated with lower resolution FT-IR spectra.

Figure 3 presents a difference spectra collected at the power plant, while the spectrometer was viewing a cloudless sky background at approximately 15° elevation above the horizon through the cell containing a 588 ppm*m sample of sulfur dioxide at 120° C. The most significant difference in this spectrum compared to the difference spectra collected of the actual smoke stack plume is the appearance of the ν_3 fundamental band of sulfur dioxide at 1350 cm^{-1} that is not seen in the remote passive spectra of the actual plume. The spectra in Figure 4, which were collected with the model stack, illustrate the increasing attenuation of the 1350 cm^{-1} emission band as atmospheric pathlength is increased. Apparently, atmospheric attenuation of the plume radiance by water is practically complete in this region over the 640 m pathlength used to produce the spectrum in Figure 3. The model stack may be useful in future work to validate predictions of atmospheric attenuation models.

From the spectra in Figure 5, it has been determined that the band intensities (defined as band height above baseline at 1163.1 cm^{-1}) are, to a first approximation, linearly related to cell concentration with an R^2 value greater than 0.98. The spectra in Figure 6 suggest a non-linear relationship between band intensity and temperature, as would be expected if the sample molecules obey the Boltzmann distribution.

CONCLUSIONS

The spectral data collected to date indicate that many of the factors that affect the spectral irradiance on an FT-IR remote sensor viewing a heated plume through the open atmosphere can be characterized efficiently through a variety of controlled experiments. Specifically, laboratory heated cell data can be used to determine the temperature- and wavelength-dependent emission characteristics of analytes while atmospheric models can be validated and improved through the use of controlled plumes. Prototype methodologies for performing remote analyses of sulfur dioxide in heated plumes can be tested and developed at power-plant sites for which stack conditions are known.

REFERENCES

1. Low, M.J.D., Clancy, F.K.; Environmental Science & Technology, 1967, 1, 73-74.
2. Prengle, W.H., et al; Environmental Science & Technology, 1973, 7, 417-423.
3. Barnes, H.M., Jr., Herget, W.F., Rollins, R.; Analytical Methods Applied to Air Pollution Measurements, Ann Arbor Science, 1974
4. Griffiths, P.R.; American Laboratory, 1975, March, 37-45.
5. Herget, W.F., Brasher, J.D.; Applied Optics, 1979, 18(20), 3404-3420.
6. Herget, W.F.; in Proceedings of the 1981 International Conference on Fourier Transform Infrared Spectroscopy, Volume 289, 449-456, 1981.
7. Vastag, B.J., Horman, S.R.; in Proceedings of the 1981 International Conference on Fourier Transform Infrared Spectroscopy, Volume 289, 74-79, 1981.
8. Solomon,P.R., et al; Applied Spectroscopy, 1986, 40(6), 746-759.
9. Herget, W.F.; Applied Optics, 1982, 21(4), 635-641.
10. DeBlase, F.J., Compton, S.; Applied Spectroscopy, 1991, 45(4), 611-618.
11. Medvecz, P.J., et al; Applied Spectroscopy, 1991, 45(8), 1350-1359.
12. McNesby, K.L., Fifer, R.A.; Applied Spectroscopy, 1991, 45(1), 61-67.
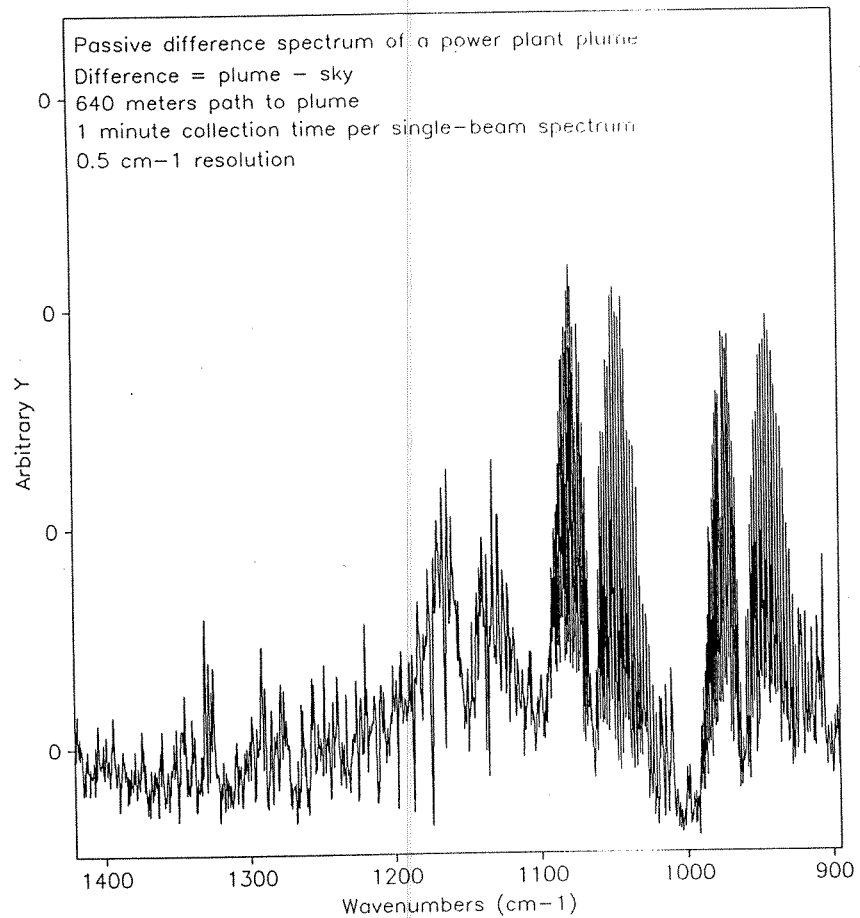13. Lindermeir, E., et al; Applied Optics, 1992, 31(22), 4527-4533.

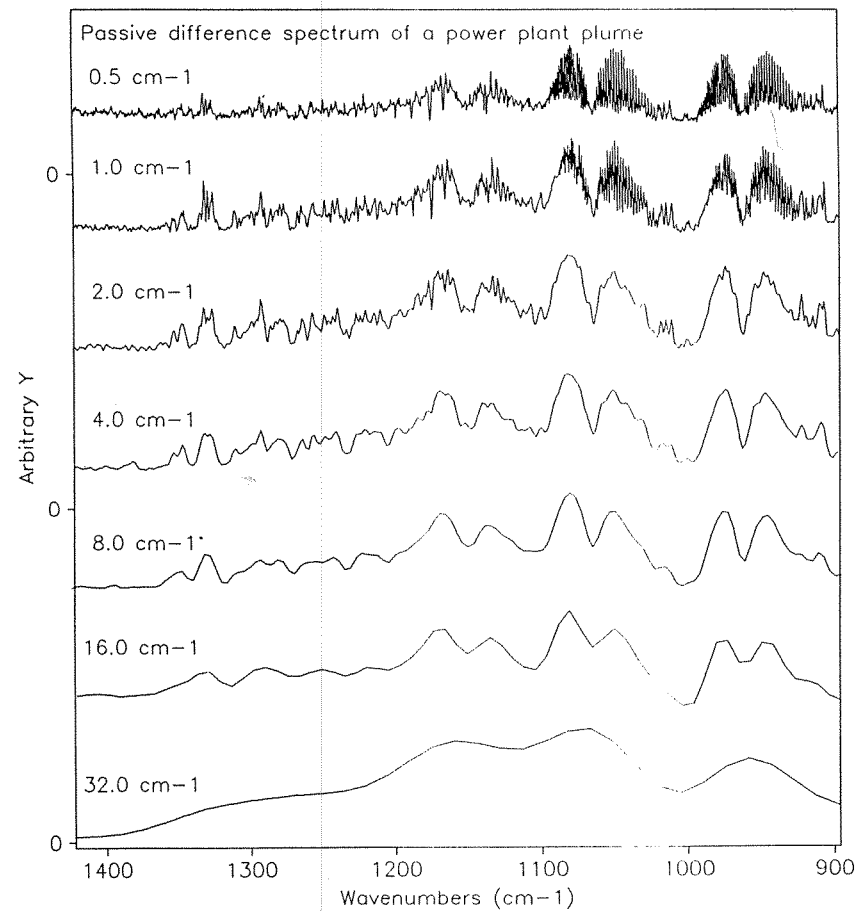Figure 1. *Typical difference spectrum of a power plant plume.*

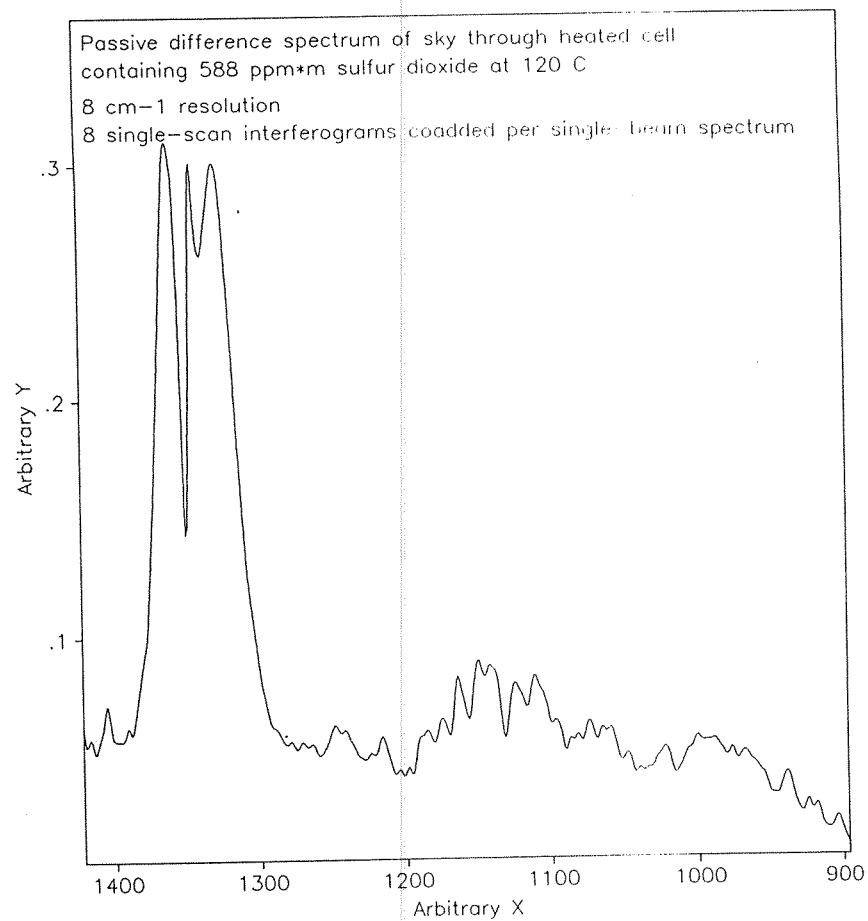Figure 2. *Difference spectra of a power plant plume at various resolutions.*

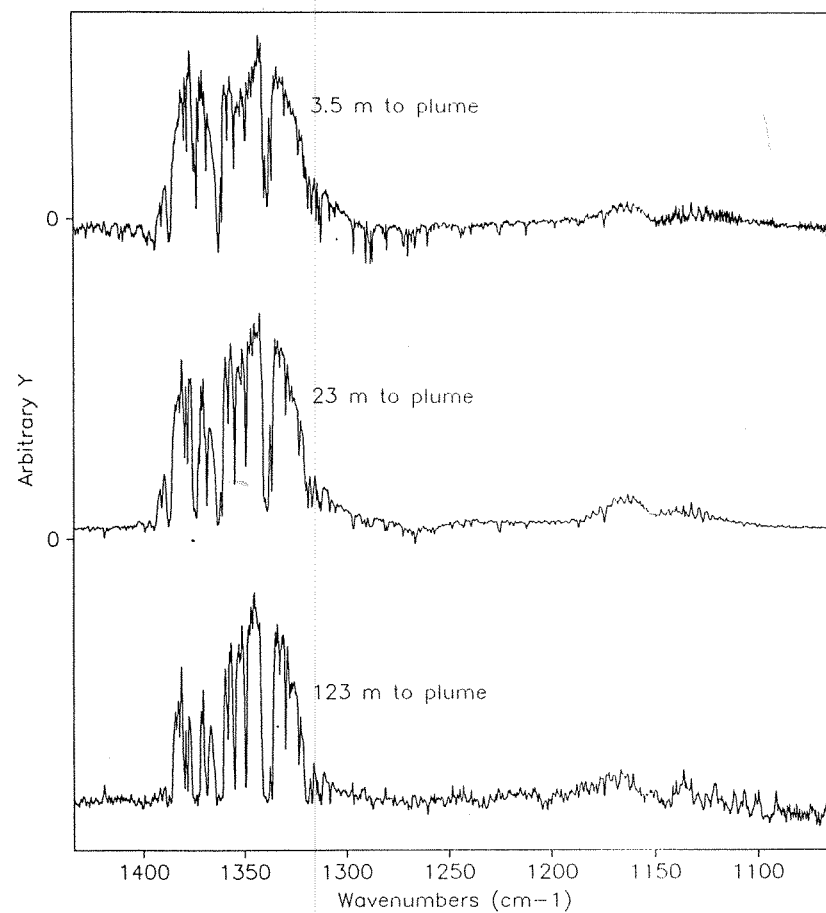Figure 3. *Difference spectrum produced while viewing a sky background through a heated cell.*

Figure 4. *Difference spectra collected of a model stack plume over various distances.*
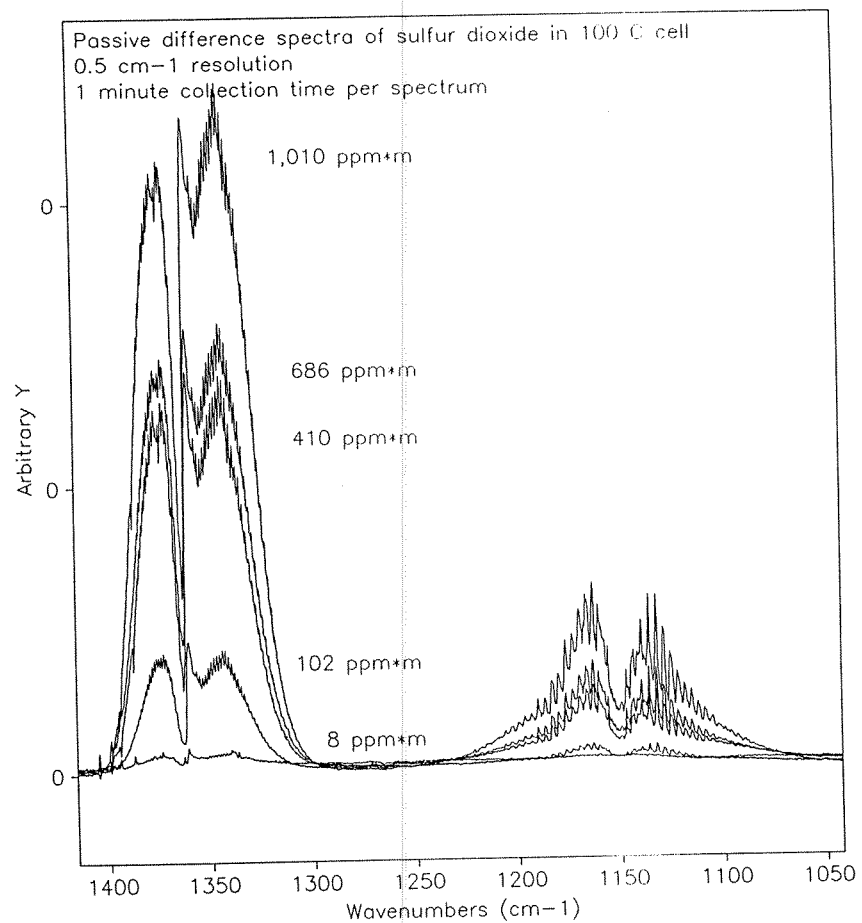
Figure 5.   *A series of difference spectra collected of a cell containing various concentrations of sulfur dioxide in a 100° C cell with an ambient temperature background.*
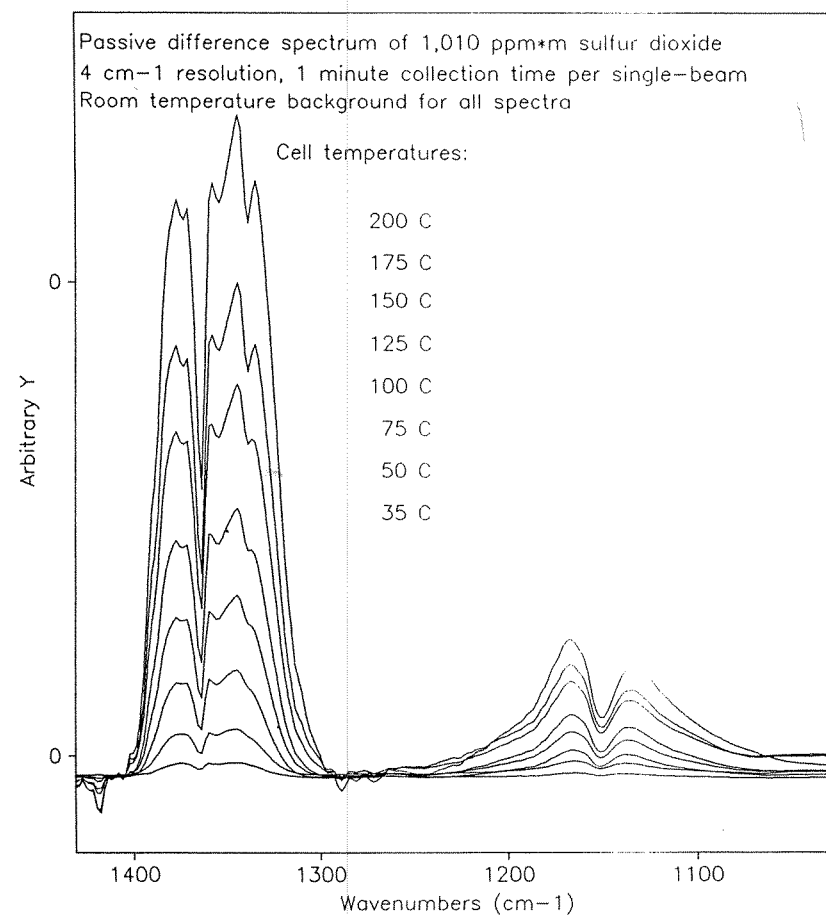

Figure 6.   *A series of difference spectra collected of a cell containing 1,010 ppm*m sulfur dioxide in nitrogen at various temperatures with an ambient temperature background.*