ANL/CMT-ACL/CP--83191

Detection of Emission Sources Using Passive-Remote Fourier Transform Infrared Spectroscopy*

Conf-9502097-

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to be published in the Proceedings of the
Fourth International Symposium on Field Screening Methods
For Hazardous Wastes and Toxic Chemicals
February 22-24, 1995
Las Vegas, NV 89193-3478

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*Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38.

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ABSTRACT

The detection and identification of toxic chemicals released in the environment is important for public safety. Passive-remote Fourier transform infrared (FTIR) spectrometers can be used to detect these releases. Their primary advantages are their small size and ease of setup and use. Open-path FTIR spectrometers are used to detect concentrations of pollutants from a fixed frame of reference. These instruments detect plumes, but they are too large and difficult to aim to be used to track a plume to its source.

Passive remote FTIR spectrometers contain an interferometer, optics, and a detector. They can be used on tripods and in some cases can be hand-held. A telescope can be added to most units. We will discuss the capability of passive-remote FTIR spectrometers to detect the origin of plumes. Low concentration plumes were released using a custom-constructed vaporizer. These plumes were detected with different spectrometers from different distances. Passive-remote spectrometers were able to detect small 10 cm on a side chemical releases at concentration-pathlengths at the low parts per million-meter (ppm-m) level.

INTRODUCTION

Passive-remote FTIR spectrometers are an excellent tool for detecting toxic chemicals released in the environment. Their portability allows them to be used to determine the source of the chemical release. We will discuss the potential of passive-remote FTIR spectroscopy in terms of detection levels and the effects of using the instrumentation under real field conditions. Data were collected using trees, grass, low sky, and brick wall backgrounds both with and without telescopes and with different field-of-views.

The detection of environmentally hazardous chemicals is also possible with open-path and fixed-point methods, such as open- path FTIR spectroscopy and canister collection followed by gas chromatography/mass spectroscopy (GC/MS). However, these methods only detect chemical plumes; they cannot trace them to their source. It is important to discover the origin of a plume to determine responsibility for the release and to repair the cause of the leak. Source detection is especially important for fugitive emissions, unknown leaks, and for evaluating environmental compliance. Light, mobile instrumentation with real-time data analysis methods is essential for tracking a plume to its source.

Passive-remote FTIR systems are light and transportable. Data analysis can be performed in real time. The basic system consists of an interferometer, focusing optics, and a detector. The instrumentation uses ambient energy as its infrared source. Data are transmitted directly to a laptop computer. The systems discussed are either transportable or can be hand carried to facilitate detection of the plume source.

Open-path and passive-remote FTIR should be considered as complementary techniques. Open-path systems will provide semiquantitative data for emission levels from a fixed area over extended periods of time. Open-path units function best in a fixed position because they are large and require aiming. After an open-path unit detects a plume, passive-remote units can be used to track it to its source.

Passive-remote instrumentation was used to detect a low ppm-m concentration-pathlength releases. A 1 ppm-m release corresponds to a 1-part per million (ppm) chemical release that has a width of one meter. This release would be identical to a 10-ppm release with a width of 0.1 m. These releases were performed using a specially designed vaporizer with a 10- x 10-cm orifice. The spectrometers detected plumes of this size from distances in excess of 50 m. Plumes can be detected from open windows and other low-volume sources. Larger passive-remote units mounted on a tripod or a moving vehicle can be used to initially detect a plume. After detection, smaller units can be used to determine the origin.

Experimental

Data were obtained using passive-remote spectrometers from Midac (Midac, Costa Mesa, CA), Bomem (Hartmann-Braun, Montreal, PQ), and Designs and Prototypes (Nashua, NH) Data were collected at 4 cm^{-1} as files of single scans using software provided by coauthor J. Ditillo. Scans were coadded post-run for data analysis. Dimethyl methylphosphonate (DMMP), 97% purity, and methanol (MEOH) (high purity) were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Small-scale chemical releases were performed with a vaporizer constructed at the Argonne National Laboratory. The vaporizer was built to convert liquids into vapors at the ppm level. The unit consists of a blower motor connected to a main tube possessing a sidearm. The main tube contains the primary air flow at ambient temperature. The sidearm flow, approximately 10% of the total, is heated and evaporates the liquid release. Air traveling through the sidearm is heated to 135°C before reaching a Sono-tek ultrasonic atomizing nozzle, which converts the liquid into an aerosol. The aerosol vaporizes when it contacts the hot air in the sidearm. Liquid flow is monitored by a syringe pump. The exact flow is calculated from the volume displacement in the syringe. The nozzle is capable of atomizing the liquid to a particle size of 15 µm. The warm air and vaporized solvent enter the main tube and are mixed with air at ambient temperature. The mixture passes through a baffle system in the 10- x 10-cm square exit pipe, to ensure thorough mixing and even flow throughout the chamber. At the orifice, the air exits at an average velocity of 165 cfm (4.7 m^3/min) and at 34 to 40°C, depending on ambient temperature. The variation in flow was measured at nine different places at the orifice of the vaporizer to determine the average release velocity. The square orifice provided a constant path length. The release was calculated in concentration-pathlength units of ppm-m.

Results

Passive-remote FTIR systems use ambient energy as their energy source. Hence, the energy available for detection is a function of the temperature of the background and the temperature of the release. The larger the difference in temperature (ΔT), the larger the peak. The vaporizer commonly released chemicals at 37°C ± 3°C. This temperature would increase on very hot days. When the background temperature is greater than the release temperature, an absorption spectrum is obtained. When the background is cooler than the release, an emission spectrum is obtained.

Background temperatures vary widely. Grass and tree backgrounds are normally approximately equal to the ambient temperature. Low blue sky backgrounds are very cold. The greater the angle from the horizon, the lower the temperature. Even 10-20° angles are below 0°C. Higher angles rapidly approach -40°C, which is the limit of our pyrometer. The primary problem with low sky backgrounds is occasional large concentrations of ozone. Cloudy low sky backgrounds are much warmer but show a great deal of temperature variation. Brick wall backgrounds heat and cool slowly and are, therefore, quite stable. The slow change does provide a reasonably stable blackbody background. They also absorb a large amount of heat. We have measured brick walls as hot as 80°C in the sun.

Our first objective was to determine the detection levels under ideal laboratory conditions. This information can be used to determine applicable scenarios. Obviously, detection levels in the field would be less than those determined in the laboratory. The laboratory data would provide a benchmark for the feasibility of potential uses. Two chemicals were selected for release: Methanol (MEOH) is typical for solvents that could be escaping into the environment and DMMP is a safe surrogate for phosphate-based pesticides such as malathion and parathion.

Laboratory Data

Detection levels for MEOH and DMMP are at the low ppm-m level. Figure 1 shows transmission spectra of methanol releases that vary in concentration from 4.0-19.4 ppm-m. The spectra were obtained using a 50°C blackbody and a release temperature of 37°C (ΔT=13°C). The signal-to-noise (S/N) ratio is greater than 20. DMMP showed even more sensitivity. In Figure 2, the absorption spectra of four concentrations of DMMP are shown. The 1 ppm-m absorption has a S/N greater than 20.

The effect of changes in temperature is shown in Figure 3. The top spectrum shows the absorption spectrum when ΔT is positive by 16°C and for the bottom spectrum ΔT is negative by 15°C. The amplitudes are virtually identical. The closer that ΔT approaches zero, the smaller the absorption or emission. However, the background temperature is never constant, and even though some scans will not show analyte, the compound can be detected when multiple scans are collected.

Field Data

Releases were performed directly in front of the spectrometer with the spectrometer aimed at different backgrounds. The intensity of the band is a function of ΔT. The change in temperature was largest for the low sky background. The trees were in the sun and considerably hotter than the grass, which was in the shade. In Figure 4, the spectra for methanol releases and their integrated peak areas are presented for data collected using low sky, trees, and grass backgrounds. The low sky spectrum was inverted to facilitate comparison.

Ozone absorption may be quite high when low blue sky backgrounds are collected. In Figure 5, the ozone bands are clearly visible around 1100 cm^{-1}. However, even with the interference the methanol bands are clearly visible.

Field Data Using A Telescope

A telescope is essential for locating chemical plumes. Most vendors sell more than one power telescope, which provides flexibility in selecting a field-of-view. The Midac telescope would focus on the 10-cm release area at approximately 25 m from the vaporizer. The farther the instrument is from the release, the greater the area observed and the larger the more non-sample background in the spectrum. The effects are relatively minor with a stable temperature background such as a brick wall. In Figure 6, the methanol spectra obtained 50 and 60 feet from the release are shown. The peaks are easily recognized.

Grass background is less stable and the effect of baseline shifting is more apparent. Methanol was released 50 feet from the telescope at concentrations of 5.3 and 19.4 ppm-m, as shown in Figure 7. The peaks are still discernable, but there is more noise and variation.

Low sky provides a very difficult background. Although ΔT is large, the amount of ozone and the variation in temperature is very great, which causes an unstable background. In Figure 8, the spectra of 5.3 and 19.4 ppm-m methanol releases are shown. Data were collected 60 feet from the release. The changing low sky temperature causes the large slope in the background. The ozone is also readily discernable.

Hand-portable FTIR spectrometers can be easily carried to the source. One instrument tested, Designs and Prototypes miniFTIR, is very versatile. Its sensitivity is lower than larger units, but its portability can compensate for the reduced sensitivity. In Figure 9, a spectrum obtained using this instrument with a 19.4 ppm-m release in front of a 50°C blackbody is shown.

CONCLUSIONS

The data clearly show that passive-remote FTIR spectrometers have the sensitivity to detect low ppm-m releases in the environment. Different environmental backgrounds have particular advantages and disadvantages. Brick buildings provide a stable background, while low blue sky provides the highest ΔT but the least stability. Once a release is detected, smaller units can be used to discover the origin.

Improved real time data analysis is needed. Edgewood Research, Development, and Engineering Center (ERDEC) is currently developing and testing detection algorithms. As they become available for use, we can expect increased usage of passive-remote FTIR spectrometers.

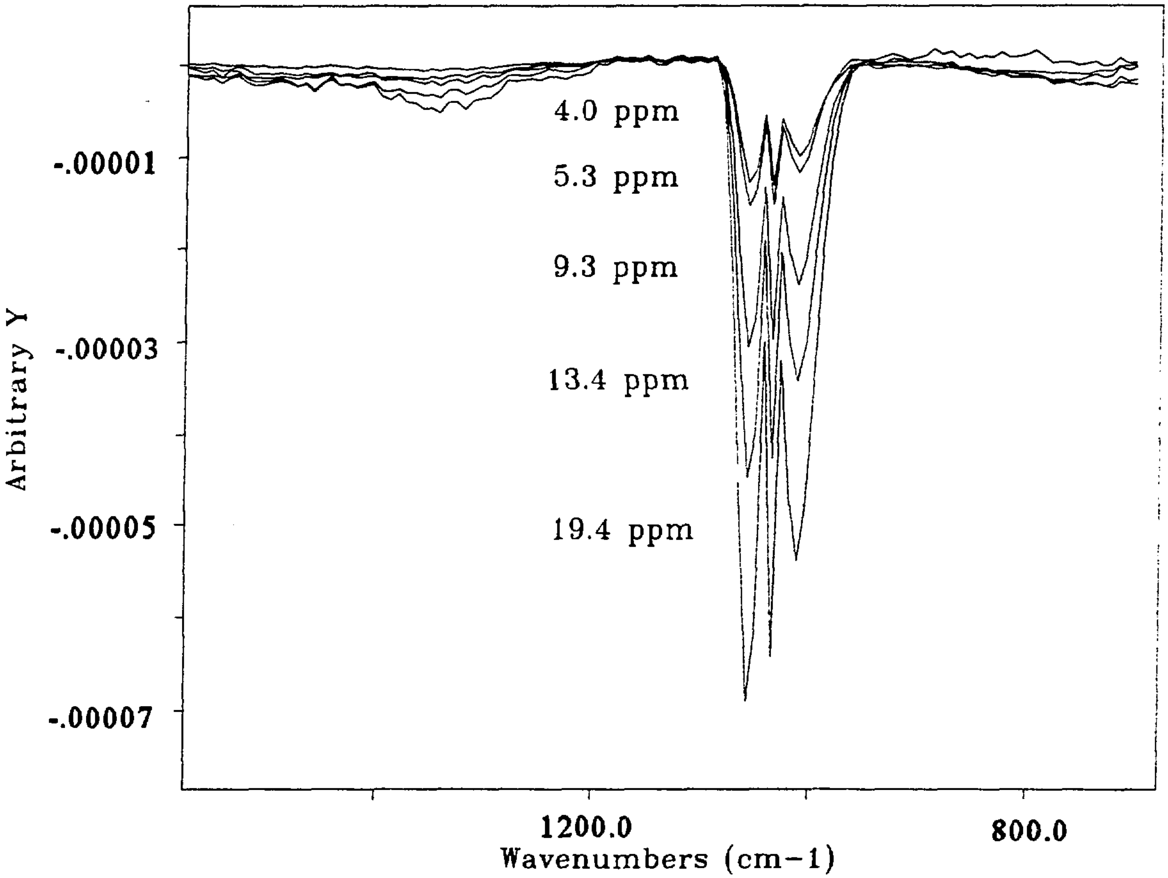

Figure 1. Transmission Spectra of Methanol Releases at 37° against a 50°C Blackbody.

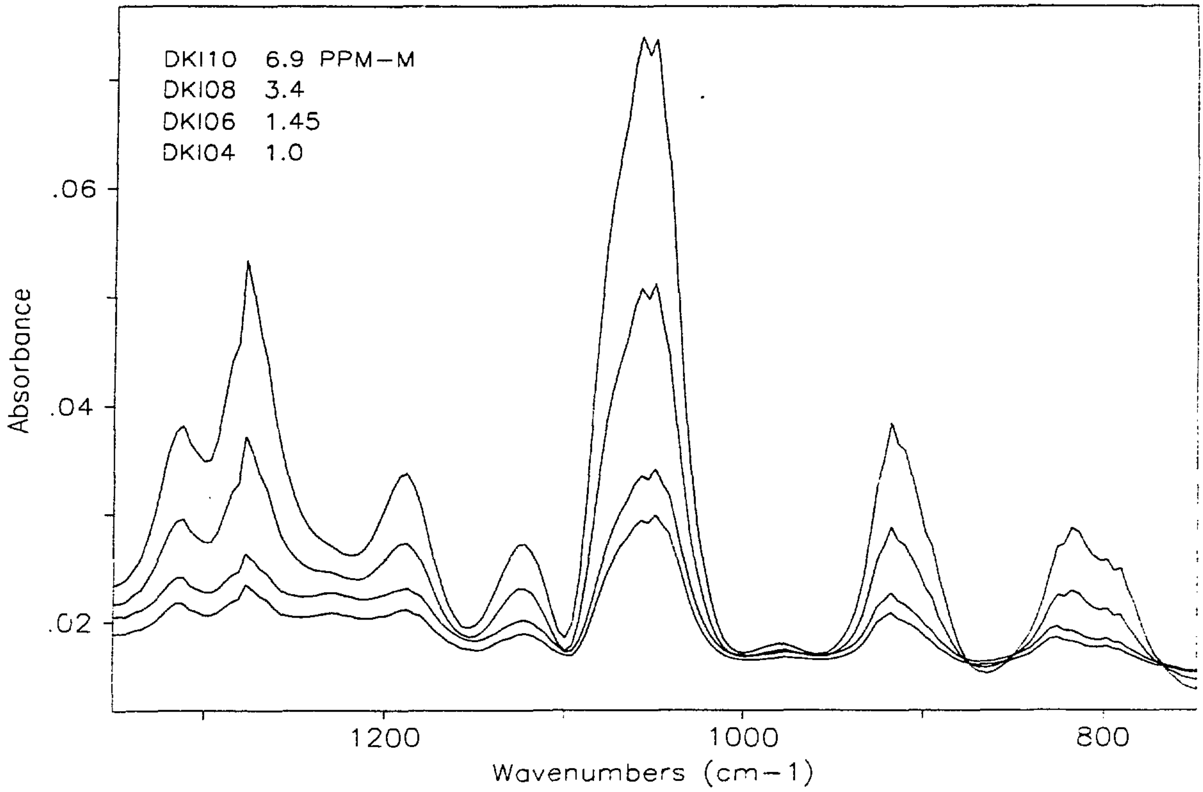

Figure 2. Absorption Spectra of Four Concentrations of DMMP Release Against a 50°C Background.

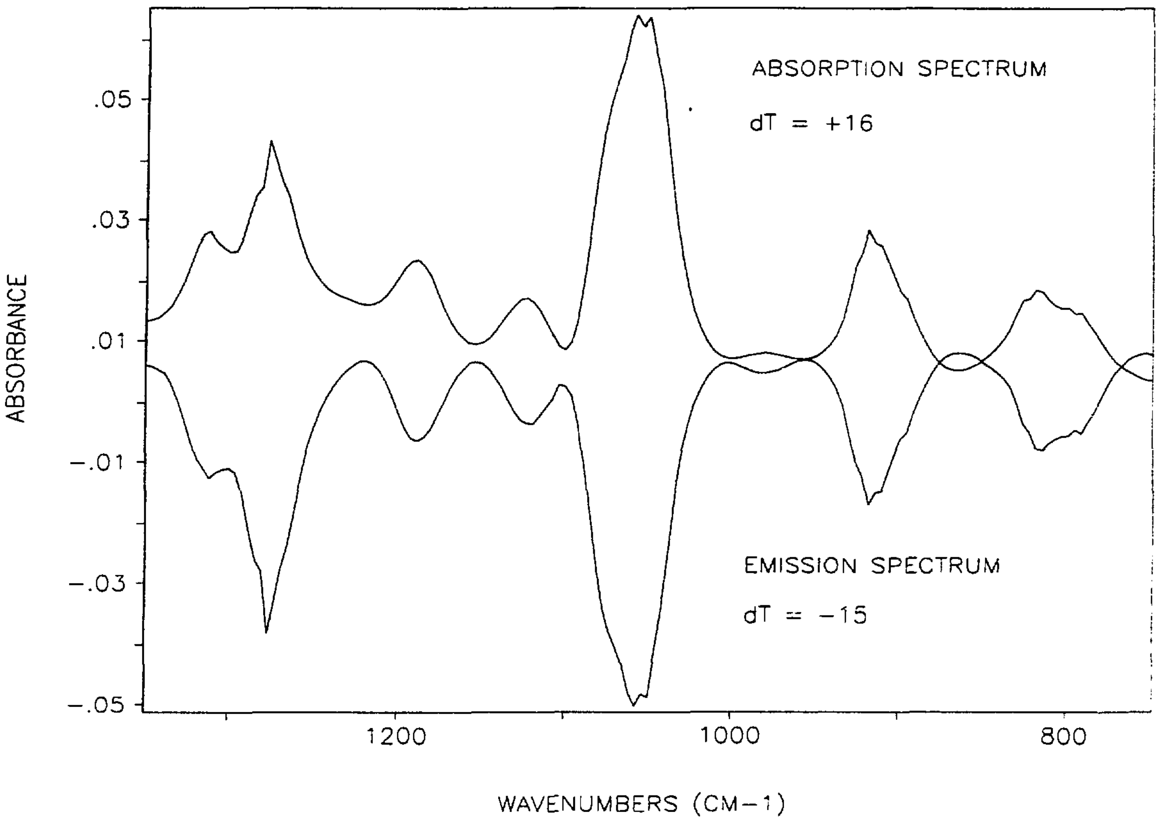

Figure 3. Comparison of Absorption and Emission Spectra of DMMP Caused by Changes in Temperature

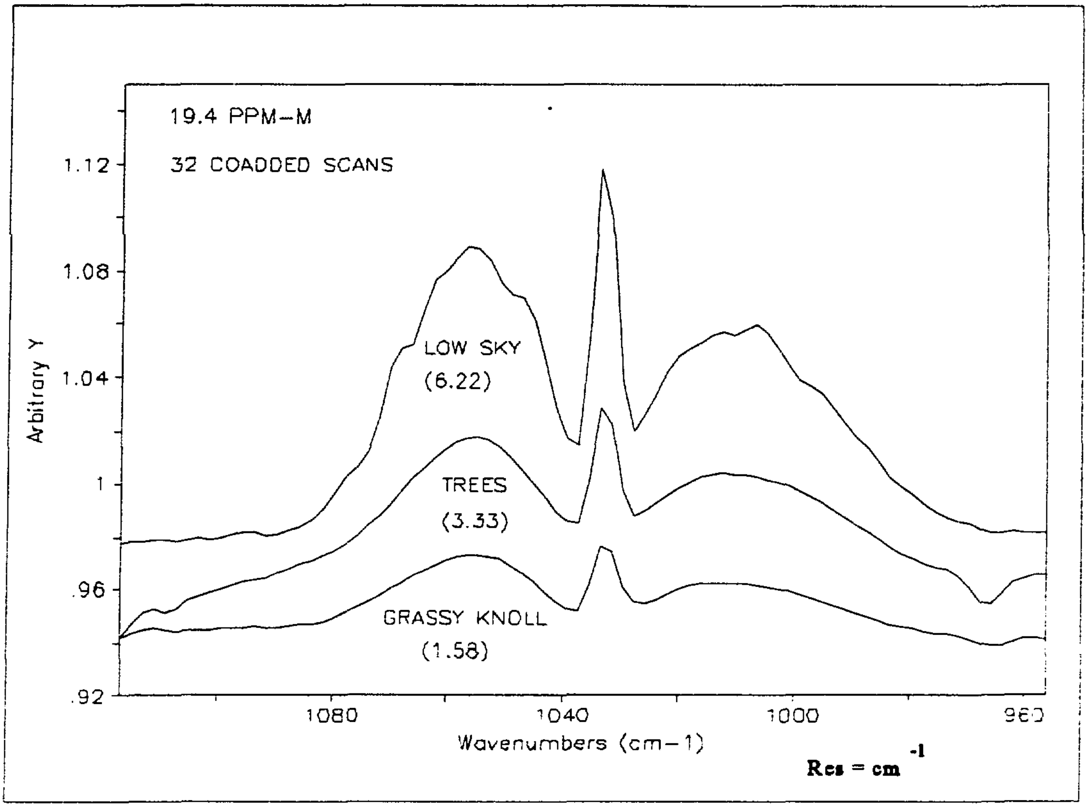

Figure 4. Spectra of Methanol Releases with Different Environmental Backgrounds.

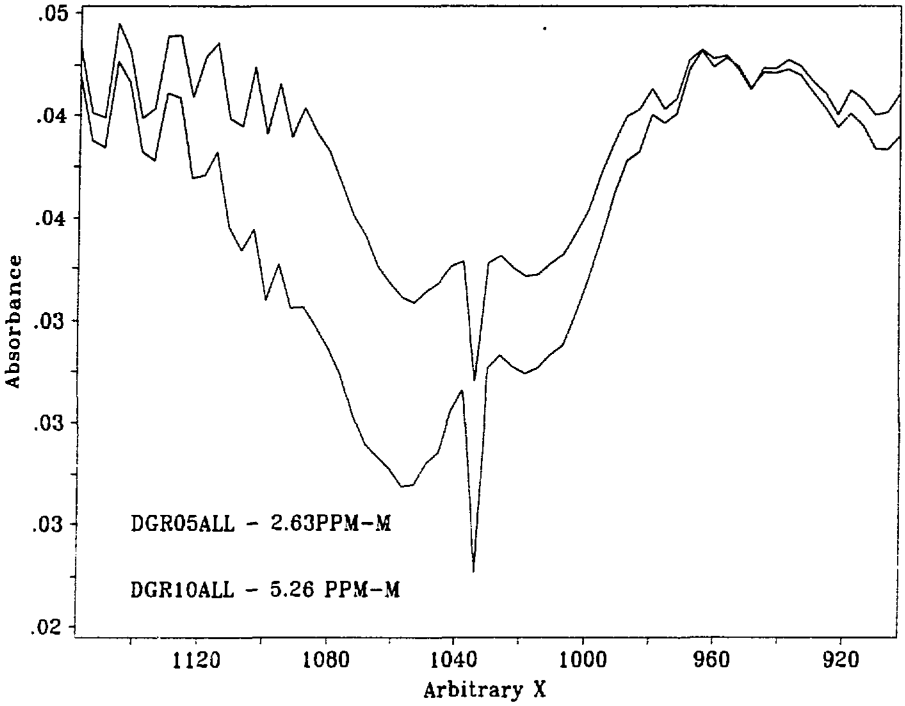

Figure 5. Methanol Release in Front of a Low Sky Background.

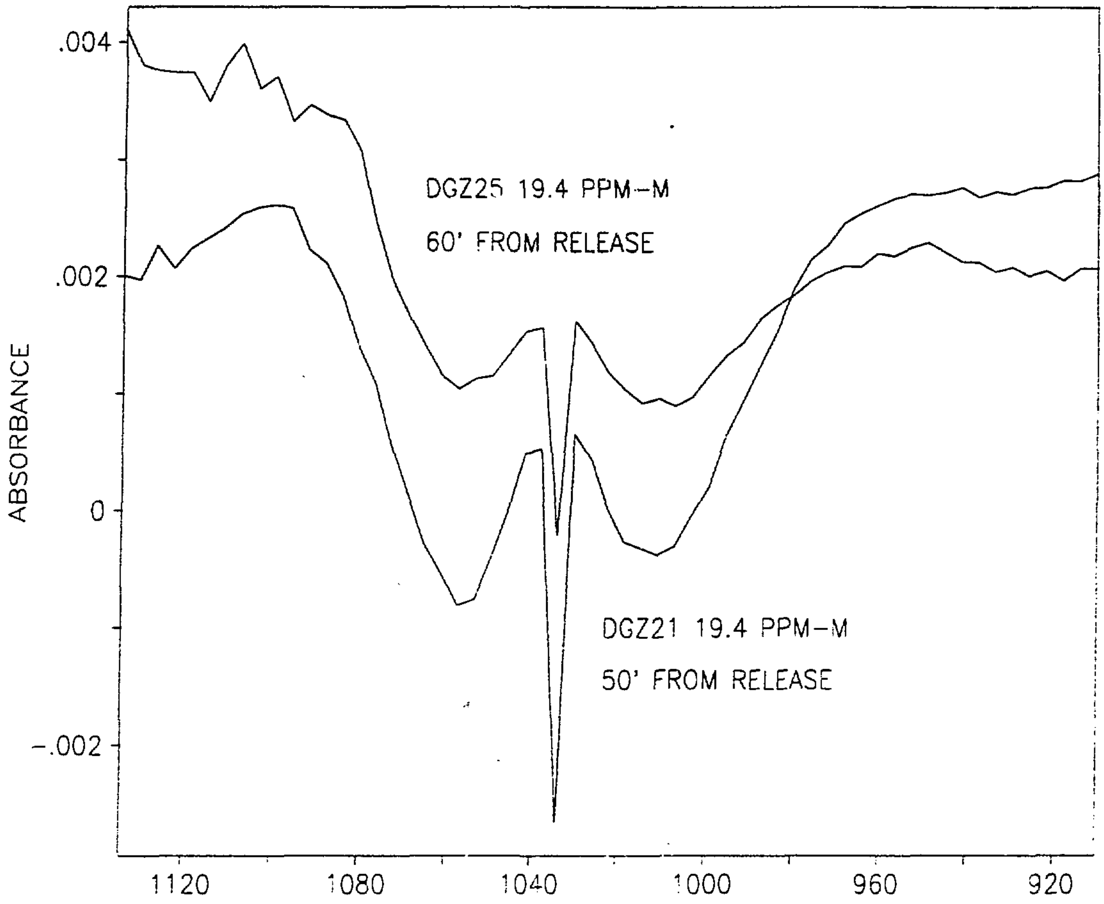

Figure 6. Methanol Release in Front of a Brick Wall Background.

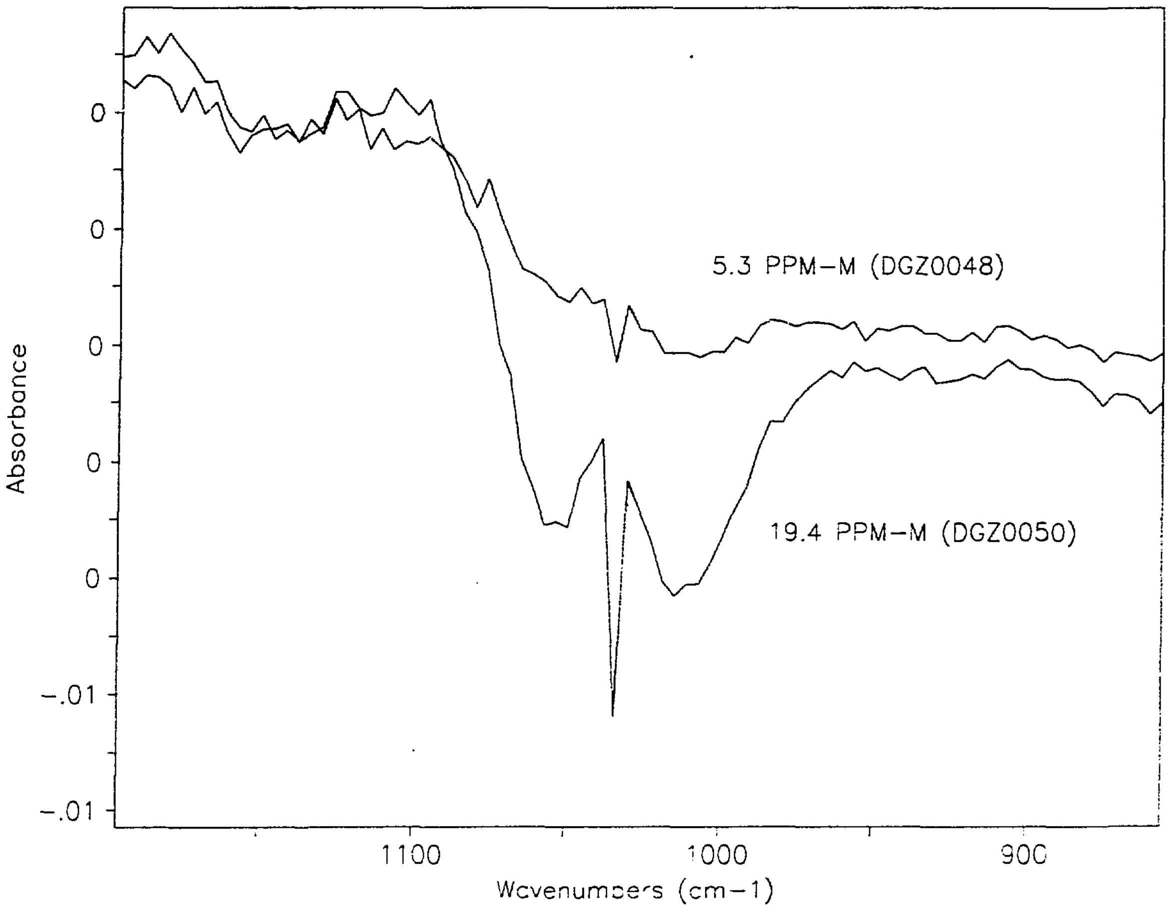

Figure 7. Methanol Release in Front of a Grass Background.

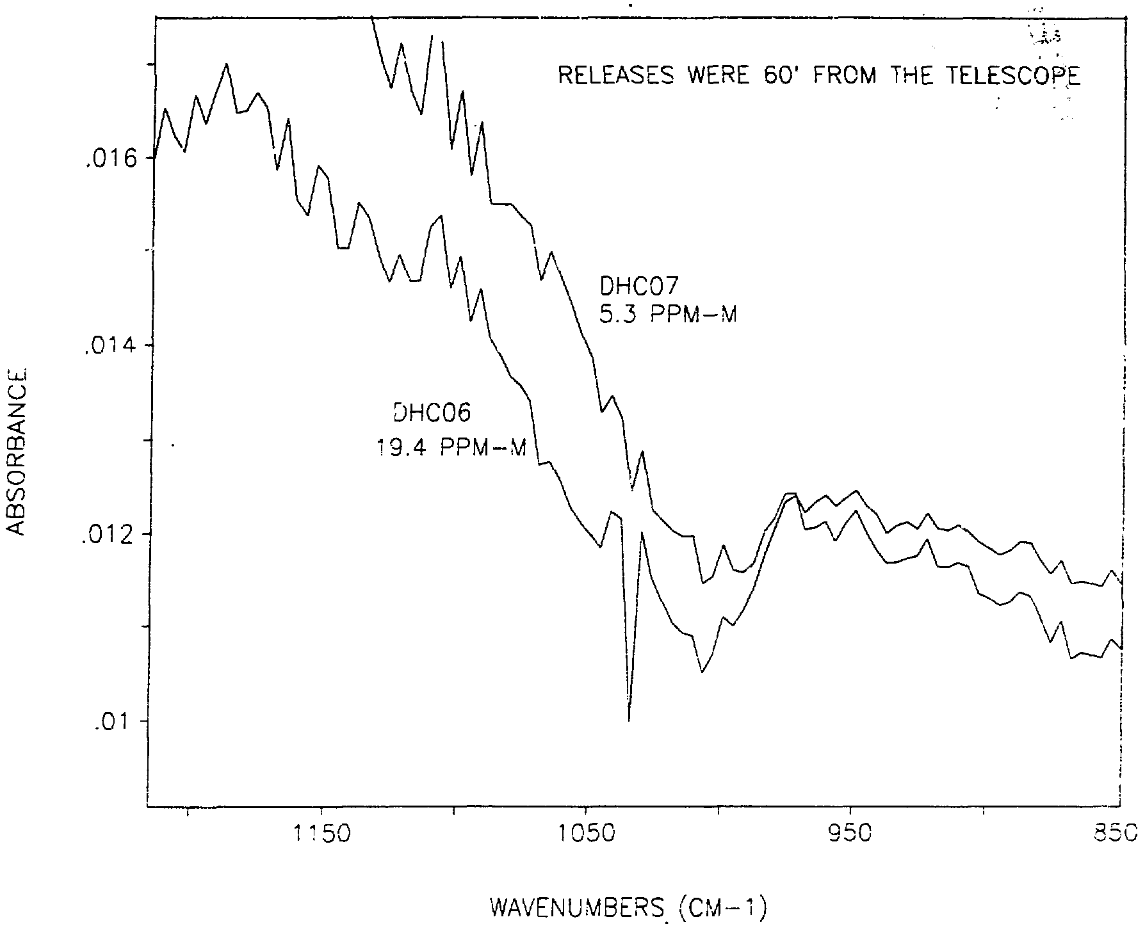

Figure 8. Methanol release in Front of a Low Sky Background.

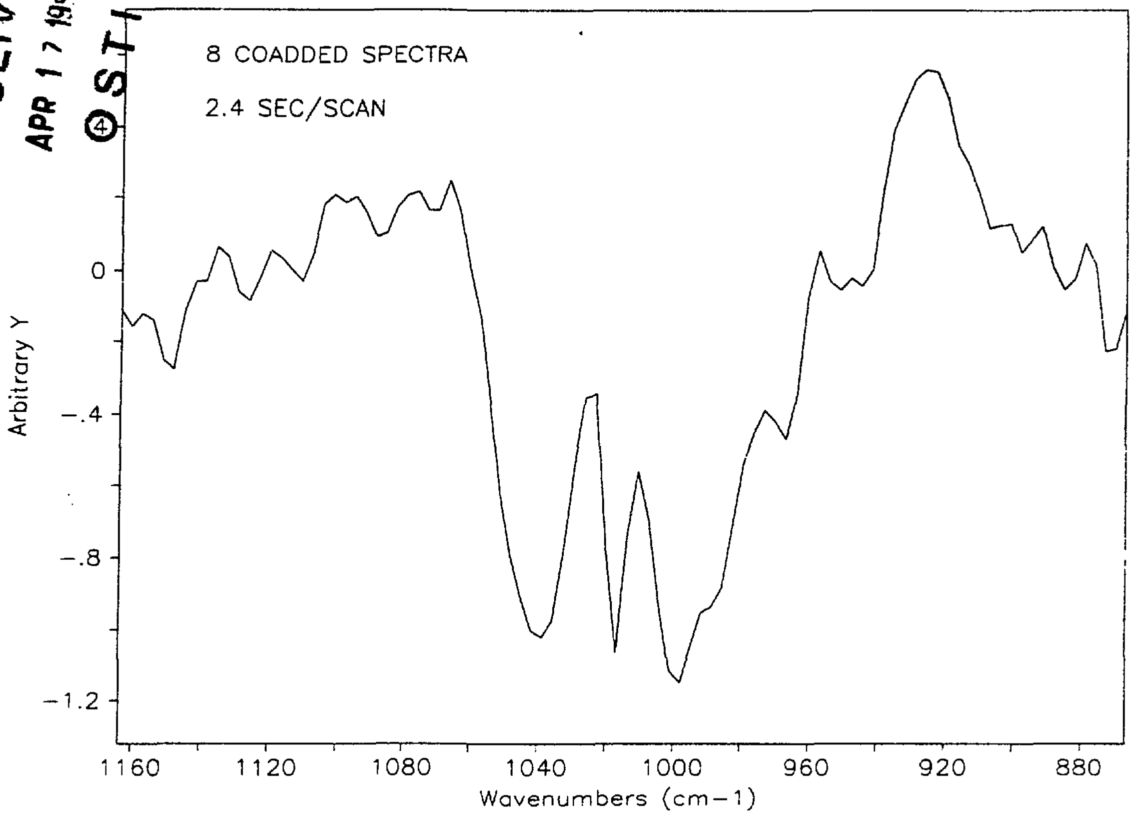

Figure 9. Infrared Spectrum of a Methanol Obtained Using a D&P MiniFTIR.