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SAMPLING AND ANALYSIS OF ORGANOPHOSPHORUS COMPOUNDS ON A THERMOELECTRIC COLD PLATE USING FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY

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13. ABSTRACT (Maximum 200 words)

This report documents findings of work performed under U.S. Army Chemical Research, Development and Engineering Center (CRDEC) Contract No. DAAA15-86-0020, by contractor personnel in conjunction with CRDEC scientists. This research addressed the sampling of organophosphorus compounds from the air and their detection using Fourier transform infrared (FTIR) techniques with computer-aided pattern recognition. Vapor samples from a thermoelectrically-cooled plate, typically used as a liquid aerosol collector, were examined to determine the feasibility of recording infrared emission spectra directly from the plate. A comparison of this method was made with gas chromatography/infrared (GC/IR) spectroscopy analysis of samples that were first removed from the plate. It was found that a thermoelectrically-cooled mirror can be used as the collector to offer four advantages: (1) sample loss due to evaporation is minimized; (2) sample loss due to reaction is minimized; (3) the sample can be observed directly by infrared emission as a sample pre-screening technique; and (4) the sample can be readily removed for subsequent analysis by GC or GC/IR analysis.

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PREFACE

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SAMPLING AND ANALYSIS OF ORGANOPHOSPHORUS COMPOUNDS
ON A THERMOELECTRIC COLD PLATE
USING FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY

1. INTRODUCTION

1.1 Statement of the Problem.

Sampling of organophosphorus compounds from air and their detection in the collected samples using computer aided pattern recognition of infrared (IR) spectra is addressed in this report. This report will evaluate the utility of a cold-plate liquid-aerosol collector for preserving volatile organophosphorus compounds for IR analysis. The feasibility of directly recording IR emission from the sampler will be evaluated. A comparison of this method will be made to that of removing the sample from the cold plate for gas chromatography/infrared (GC/IR) spectroscopy analysis.

1.2 Scope of Investigation.

This report examines the sampling of organophosphorus compounds on a thermoelectrically cooled mirror and subsequent analysis based on emission measurements using a Fourier transform infrared (FTIR) spectrometer and by GC/IR spectrometry for comparison. For the purpose of this study, 2,2-dichlorovinyl phosphate (DDVP, 93%) and 0,0 dimethyl-S-(dicarbethoxyethyl) dithiophosphate (malathion, 95%) were used.

These are complex compounds whose IR spectra exhibit the signatures of many common organic functional groups including the phosphorus-oxygen-carbon group (P-O-C) characteristic of organophosphate poisons. The 2,2-dichlorovinyl phosphate contains the phosphorus oxygen (P=O) group, carbon-halogen (C-Cl), and alkenyl group (C=C). Malathion possesses the phosphorus-sulfur groups (P=S, P-S-C) and the carbonyl group (C=O). Measurements are made on the pesticides cygon (0,0-dimethyl-S-methylcarbamoylmethyl phosphorodithioate) and phorate (0,0-diethyl-S-ethylthiomethyl phosphorodithioate).

1.3 Background Review.

Organophosphorus compounds are commonly used in pesticide formulations and are potent central nervous system (CNS) poisons. Sampling and analysis for this class of compound in the environment is complicated by the ease with which these compounds undergo hydrolysis and by their low but non-negligible volatility.

Organophosphorus compounds readily hydrolyze to produce phosphoric acid or corresponding phosphoric acid derivatives. This hydrolysis is catalyzed by various metal ions including Fe(III), which is a common component of the earth's crust and wind blown dust. A sampling scheme is proposed to minimize loss of organophosphorus compounds due to volatility or hydrolysis.

Once collected, an aerosol or vapor sample must be classified as containing or not containing this class of compound. Infrared spectroscopy is a powerful tool for the detection and recognition of organic compounds by chemical class. Modern IR spectrometers are either dispersive instruments or interferometers (Fourier transform spectrometers). The dispersive instruments use a grating or prism to separate IR light from a high temperature source (typically 1000 °C) into narrow wavelength or frequency windows. The dispersive element is placed between the sample and the detector with the sample between the dispersive element and the source. In this configuration, the sample is exposed to a considerable flux of near-IR radiation. Interferometer-based IR spectrometers are similarly designed; however, the dispersive element is missing. In the dispersive element's place, there is a two-beam interferometer between the source and the sample. The interferometer typically uses a germanium coated beamsplitter that offers an additional bonus of filtering out the near-IR radiation from the source.

Conventional grating spectrometers lack the optical throughput available in Fourier transform spectrometers and, aside from signal-to-noise considerations, grating instruments also, in exposing samples to a higher flux of near-IR radiation, heat the sample more than Fourier transform spectrometers. Heating the sample may cause considerable loss of anlayte through evaporation[1] or thermal degradation. Previous efforts have demonstrated microgram detection capabilities of IR absorption[1] and emission spectroscopy.[2-4]

1.3.1   Sampling.

Atmospheric sampling for organic vapors usually involves pulling large volumes of air at ambient temperature through tubes containing adsorbents such as activated charcoal or activated alumina. The adsorbent material is then heated to drive off the trapped material, or it is extracted with organic solvents to recover the analytes of interest. This technique exposes the sample to large quantities of reactive gases such as ozone, nitrogen oxides, sulfur oxides, and of course, water vapor. Ozone is a natural component of the earth's atmosphere and is also a pollutant formed in urban air along with oxides of nitrogen and sulfur. Some organic compounds are known to react with these gases during sampling. In particular, oxidation and hydrolysis reactions may be important in the sampling of organophosphorus compounds.

An alternative sampling scheme is applicable for aerosol droplets such as those that may be generated in the application of organophosphorus compounds.

The sampling method uses a jet impact collector[5] that separates dry dust particles that have not been activated as condensation nuclei from liquid droplets on the basis of differences in aerodynamic flow. The collector design exhibits a sharp cutoff with near zero collection efficiency for particles smaller than 2 um in diameter and near unity collection efficiency for particles greater than 5 um in diameter.[5] The lighter and smaller dust particles follow the airstreams around the impactor. The larger and heavier liquid droplets, on the other hand, impact a collection surface and are captured. In the original design, the impactor surface consists of a Teflon roller to remove the liquid and divert it to a collection tube. This design is illustrated in Figure 1.
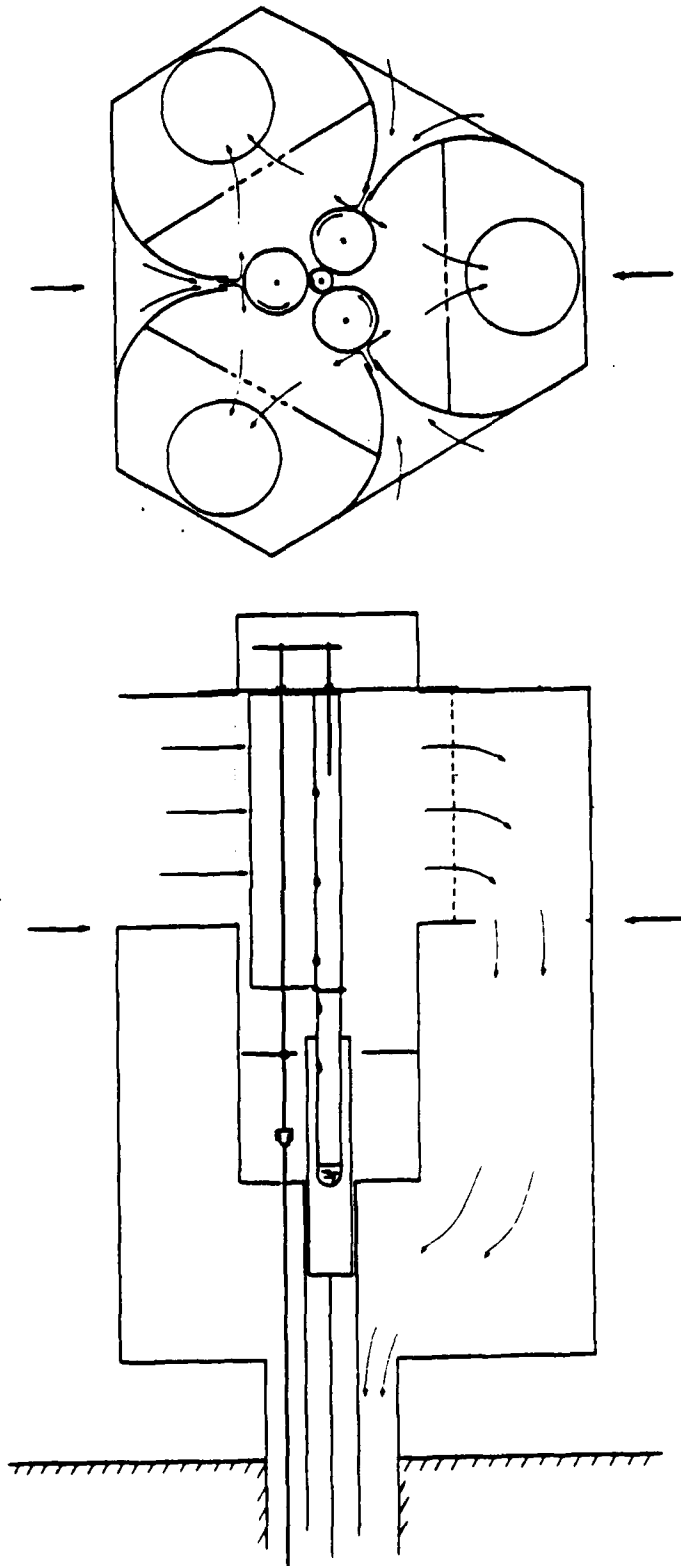
Figure 1. Schematic of Katz Cloud Water Collector

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1.3.2   Infrared Emission.

Infrared emission spectroscopy has not been extensively used outside the domain of remote temperature sensing. The main reasons are derived from the poor optical throughput of dispersive spectrometers compared to Fourier transform spectrometers. Generally, the sample is heated to induce emission, and for organic samples in particular, this may result in degradation and/or volatilization.

The literature on IR emission spectra of organic compounds is rather sparse until recently.[6-8] There are several advantages in IR-emission spectrometry such as in shorter sample preparation time and where sample scattering may be a problem[6] as in transmission measurements. The main disadvantage of emission spectroscopy is loss of sample from evaporation or decomposition. This may be especially severe with dispersive instruments because with their lower optical throughput, higher sample flux and hence higher sample temperature is required.[6] Emission measurements are normally not as sensitive as absorption measurements due to the performance properties of IR detectors. For very weak absorbers, emission measurements may be as sensitive as reflection-absorption measurements.

Kirchoff's[9] law gives the emission of IR radiation from a compound at local thermodynamic equilibrium.

$$L(v,T) = n(v)B(v,T) \tag{1}$$

Where $L(v,T)$ is the emittance at frequency v and at temperature T, $B(v,T)$ is Planck's law, and $n(v)$ is the emissivity at frequency v. The emissivity is approximately given by the absorbance spectrum.

The energy $E(v,T)$, seen by the spectrometer's detector, is $L(v,T)$ plus contributions from the background within the field of view, $L_b(v,T_b)$, and emittance from spectrometer components, $L_s(v,T_s)$, all modified by the instrument response function $f(v)$:

$$E(v,T) = f(v)[L(v,T) + L_b(v,T_b) + L_s(v,T_s)] \tag{2}$$

An emittance measurement can be manipulated to give the emissivity of the sample. This emission spectrum, like the corresponding absorbance spectrum, can be used for sample identification and quantification. It is preferable, but not necessary, to perform the correction because the broad background emittance and the sample emittance can be discriminated by taking the second derivative.[10] The second derivative of the spectrum in effect is a spatial filter that reduces the signature of slowly changing functions, such as the Planck function that represents background emittance, while accentuating rapidly changing features such as the narrow band spectra of the sample emittance.

The possibility of exciting gaseous organic molecules into emission using lasers has been explored. A number of pollutants have absorption coefficients at carbon dioxide laser wavelengths.[11,12]

The intense IR field from a laser involves many if not all the vibrational modes of polyatomic molecules.[13,14] Laser induced IR emission of microgram quantities of gaseous organic compounds has been reported using dispersive instruments and simple filter photometers. Robinson[2,3] demonstrated the detection of airborne organics using a continuous carbon dioxide laser and a dispersive spectrometer. Ambient levels of organic molecules (estimated at about 1 $\mu g/m^3$) were detected nonspecifically, using laser-excited emission with detection by a mercury-cadmium-telluride detector.[4]

Infrared laser irradiation of liquids and aerosols results in rapid heating and evaporation.[15,16] The initial rate of temperature rise is given approximately by:

$$\left[\frac{dT}{dt}\right] = \frac{\alpha I_0 P - UH}{mc} - L(v,T) \tag{3}$$

where $\dfrac{dT}{dt}$ is the initial rate of temperature rise, α is the fraction of energy absorbed, I_0 is the incident energy, P is pressure, m is the sample mass, U is the rate of evaporation, H is the enthalpy of evaporation, and c is the sample specific heat capacity. Decomposition of the sample may result at relatively low incident energy from an IR laser.[15]

1.3.3 Pattern Recognition.

Once a sample has been collected and a spectrum recorded, it is necessary to interpret the spectrum identity chemical classes of interest. In this case, it is desirable to ascertain whether phosphorus-oxygen-carbon (POC) compounds are present in the sample matrix. A characteristic of POC and phosphorus-sulfur-carbon (PSC) compounds is a prominent absorption near 1000 cm^{-1}. It is difficult to distinguish between POC and other compounds based on the 1000 cm^{-1} band alone. In fact, many oxygenated organics exhibit an absorption near 1000 cm^{-1} due to C-O stretching.

Computer aided classification of IR spectra, based on peak positions[17,18] encoded as a binary pattern, is applicable to the classification of sample spectra. For the classification of binary IR spectra, it is assumed that the peak positions are statistically independent, which they are not. The class conditional probabilities are estimated from the average occurrence of peaks in some wavelength interval j for a set of representative spectra for the class and for all such wavelength intervals:

$$p_{ji} = \sum \frac{x_j}{m_i} \tag{4}$$

where x_j is 0 or 1 for the absence or presence of a peak in interval j for spectra of class i and m_i is the number of spectra used to learn class i.

The joint probability for the occurrence of peaks in spectrum X for class i is:

$$R_i = \pi p_{ji}^{x_j} \qquad (5)$$

and the joint probability for the absence of peaks is given by:

$$Q_i = \pi [1-p_{ji}]^{(1-x_j)} \qquad (6)$$

The maximum likelihood estimate that x belongs to class i is then:

$$T_i = R_i Q_i \qquad (7)$$

From equations 5-7, it is evident that if the spectrum X is not that of a single substance then the classification will fail. That is, T_i will vanish if the spectrum X contains more peaks than occur for class i even though the additional peaks may arise from adulterants present with the analyte of interest.

Cross-correlation spectroscopy[19] has also been used to detect the presence of a learned pattern in a sample spectrum. Cross correlation is less sensitive to the presence of additional peaks in the sample spectrum. The dot product of the absorbance spectrum of the sample and a comparison spectrum are taken. The comparison spectrum may be either individual members of a class [to identify the specific component(s)], or it may be an average spectrum for the class. The correlation may be done either over binary encoded spectra or with full digital spectra. In the same manner, the second derivative of the spectra may be used in place of absorbance spectra. This often eliminates the need for background corrections.[10]

2.   MATERIALS AND METHODS

2.1   Materials Used.

O,O-diethyl-S-ethylthiomethylphosphorodithioate (phorate), cygon, DDVP (93%), and O,O-dimethyl-S-(dicarbethoxyethyl) dithiophosphate (malathion, 95%) were obtained from PolyScience Corporation (Niles, IL).

Hanovia liquid bright gold (Newark, NJ) was used to produce the mirror for the thermoelectric chip.

The thermoelectric module used was a Model 1023 thermoelectric chip (Materials Electronic Products Corporation, Trenton, NJ). The mirror-thermoelectric chip was powered with a DC power supply (Radio Shack #277-1016).

The carrier gas used for the gas chromatograph, (GC) was chromatography grade helium (Airco, Inc., Santa Clara, CA). The GC column was a 30 m wide-bore capillary DB-5 column (Supelco, Inc., Bellefonte, PA).

2.2   Methods.

A gold mirror was fabricated from a microscope slide cover slip. The cover slip was cleaned in ammonium persulfate-sulfuric acid solution, rinsed in distilled water followed by an acetone rinse, and then air dried. Hanovia liquid bright gold was diluted 1:1 in toluene, and a drop was placed on the prepared cover slip. The cover slip was then air dried for 1 hr. The coated cover slip was baked for 1 hr at 480 °C to produce a gold finished mirror.

The mirror was cemented to the thermoelectric chip, and this assembly was cemented to an aluminum block to serve as heat sink and to mount the mirror within the aerosol collector intake. In this design, the rollers in Figure 1 have been replaced with the thermoelectrically cooled plate.

This modified collector provides for a simpler mixture for analysis by rejecting dust particles. Also, by sampling onto a refrigerated plate, two additional advantages may be realized; the hydrolysis reaction may be substantially slowed and evaporative losses reduced.

Power is provided to the chip to chill the mirror prior to sampler operation. The sample collected on the thermoelectric plate may be removed and analyzed by conventional methods such as GC or IR spectroscopy. Alternatively, the sample may be analyzed directly on the thermoelectrically cooled plate by IR emission or reflection-absorption because the plate is also an IR mirror.

The flow rate of sampled air is controlled by a calibrated bleed valve between the blow fan and the collector head. The air flow rate is then calibrated as a function of pressure drop. This calibration is shown in Table 1.

Table 1. Flow Calibration of Collector Assembly

ΔP cm-H_2O	Q m^3/min
25	.44
20	.39
25	.33

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Samples were prepared for GC by diluting standard samples of DDVP and malathion dithiophosphate in benzene 1:1000 by volume to prepare a stock solution. These stock solutions were diluted again 2:1000 for the working solutions. This gave a DDVP solution of 284 ng/μL and a malathion solution of 246 ng/μL which were used for quantitative measurements.

Gas chromatography/FTIR analysis was performed using a Sigma 300 GC (Perkin-Elmer Corporation, Norwalk, CT) equipped with a wide-bore capillary column and interfaced to a model 1800 FTIR (Perkin-Elmer Corporation) equipped with a mercury-cadmium telluride (MCT) detector (Infrared Associates, New Brunswick, NJ). The chromatograph was operated with an injector temperature of 220 °C. The detector temperature was 250 °C. The oven temperature was 220 °C. The carrier gas was helium at a linear flow rate of 20 cm/s.

Samples for IR emission measurements were prepared in two ways. One method used the stock solution prepared for GC analysis. In some instances, the dilution solvent was observed and time was allocated for the solvent to evaporate at room temperature with the risk of also losing analyte. In two instances the analyte was applied neat.

3.   RESULTS

3.1   Infrared Emission Measurements.

Initially for the emission measurements, a thin film of the pesticide phorate was tested for its room temperature emission intensity on aluminum foil. Approximately 1 μL of phorate was placed on a coupon of aluminum foil using a microsyringe. To record the spectrum, after a thin smear of the pesticide is placed on aluminum foil, the foil is placed in the spectrometer at the location normally occupied by the hot-wire IR source. A helium-neon laser provided a rough alignment reference to center the sample in the instrumental field of view.

The spectrum, shown in Figure 2, was then recorded using a liquid nitrogen cooled MCT detector with a measurement time of about 1 s. The spectral features around 1000, 800, and 650 cm^{-1} clearly are identifiable as due to phorate. A second more convenient means of obtaining IR emission spectra was also tried. This involved placing the pesticide on a flat aluminum mirror placed in the sample compartment of the spectrometer. The mirror was rotated approximately 45° and translated so as to half block a white-light alignment lamp used for sampling accessories. In this manner, with the normal IR source turned off, about half the radiation emitted from the sample was passed backwards through the spectrometer and was modulated by the interferometer. A portion of the modulated radiation is passed forward to the detector past the sample that is translated to block only half the normal sample beam.[16] This is obviously not optically efficient but does provide a quick and convenient means to record emission spectra in a purged environment. The spectra collected in this manner were identitical to the previous spectra on foil at the source location but were of lower intensity. No attempt was made to correct this spectrum for either the beamsplitter or the substrate emission in this trial experiment.
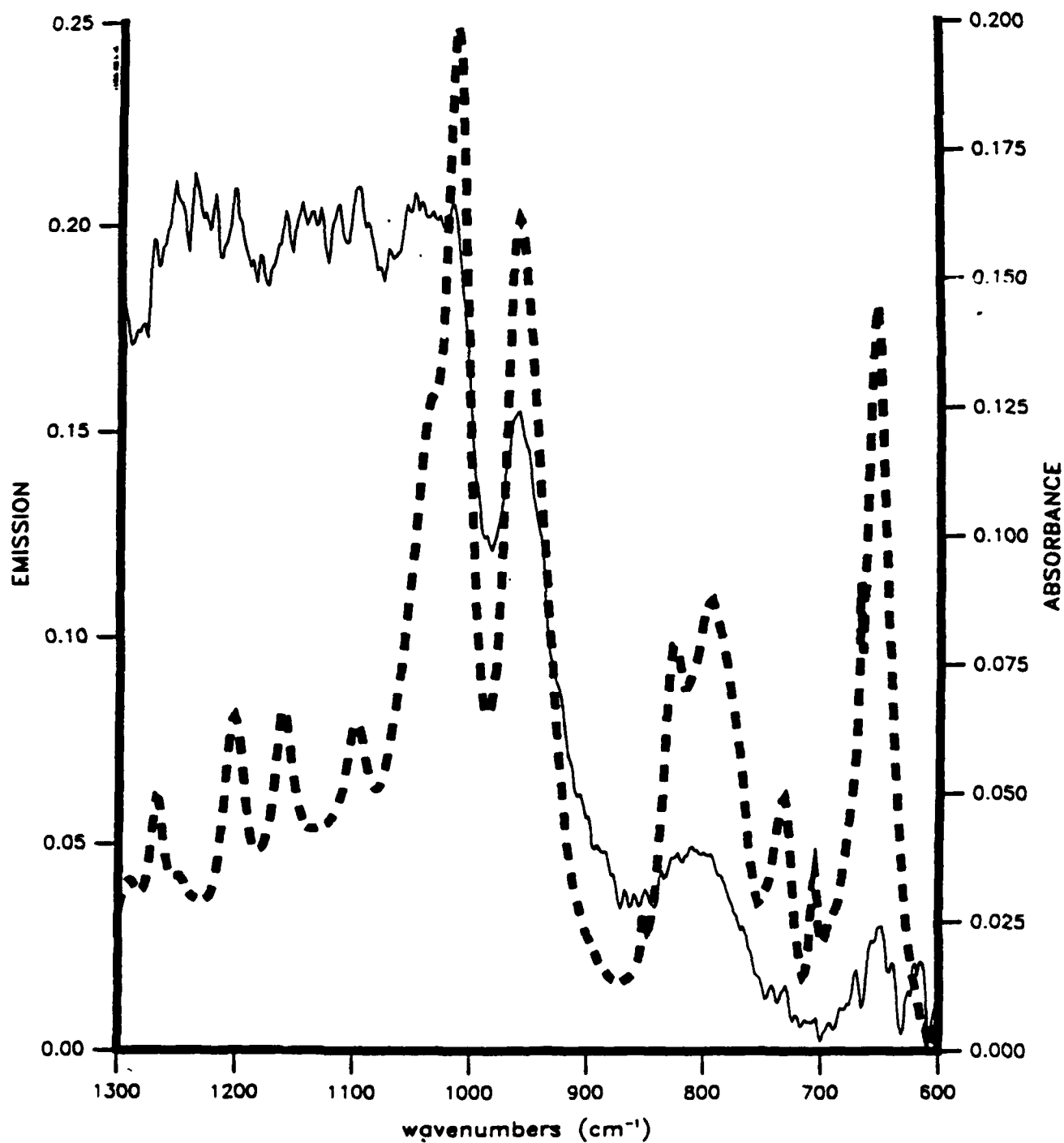
Figure 2. Infrared Emission (Solid Curve) and Absorbance (Dashed Curve) Spectra for Phorate

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A simple correction was applied to subsequent spectra using:

$$\epsilon = \frac{I_s - I_b}{I_R - I_b}$$ (8)

where I_s, I_R, and I_b are the emission intensities of the sample, substrate, and beamsplitter, respectively.[8] The subtractions are performed on the interferograms rather than spectra. This presents an operational difficulty for commercially available FTIR spectrometers. These instruments are manufactured for routine analytical chemistry and frequently are not designed to allow use in interferogram studies. The Perkin-Elmer 1800 used in this study allows for interferograms to be downloaded to the computer, but software support for reading the information in the files is lacking. Short ($\sim$ 8-16 cm^{-1}) interferograms can be downloaded to the spectral memory regions of the Model 1800 for manipulation. Application of equation 8 in this mode did not offer any particular advantage. Equation 8 has the effect of diminishing the featureless blackbody Planck function that is convoluted with the emittance spectrum. This correction scheme was applied to the spectrum of cygon shown in Figure 3. Background emission correction is not necessary for many pattern recognition algorithms. Phase correction for instrumentation errors is more important and more difficult as will be seen later.

Measurement of IR emission induced by irradiation with an IR laser was performed by illuminating a sample of cygon on a coupon of aluminum foil with a continuous carbon dioxide laser at 10.6 µm. The resulting emission spectrum is shown in Figure 4 along with the observed laser emission spectrum. Emittance from the cygon sample constitutes the smaller peaks between 1200 and 600 cm^{-1} convoluted with a blackbody profile according to equations 1 and 2. The three prominent peaks in the upper spectrum arise from instability in the laser output. The output laser frequency wandered over a large wavenumber range due to temperature fluctuations in the coolant water supply. Improvements in the coolant supply improved the short-term stability, but long-term stability required for signal averaging remained poor. The emission from the sample can be attributed wholly to scattered laser radiation and thermal heating of the sample and substrate. The heating from the laser results in sample loss by evaporation and eventually severe charring of the sample. There does not appear to be any benefit from laser excitation to induce emission. Sample loss from evaporation and charring mitigate against laser excitation for condensed samples. A difficulty also occurs with the use of the MCT detector for such emission measurements. Serious phase errors occur with the Mertz phase correction software used in commercial instruments. The Mertz algorithm depends on a distribution of energy across the spectral window. The very low energy levels above 2000 cm^{-1} interfere with the phase correction, and the problem is made worse with intense laser radiation in narrow spectral windows. For these reasons, active (laser stimulated) emission measurements were abandoned in favor of passive emission measurements arising from the difference in temperature between the sample and the detector.

The spectral features observed in Figures 2 and 3 are consistent with those seen elsewhere.[7,20] Notably, the peak locations in emission coincide with
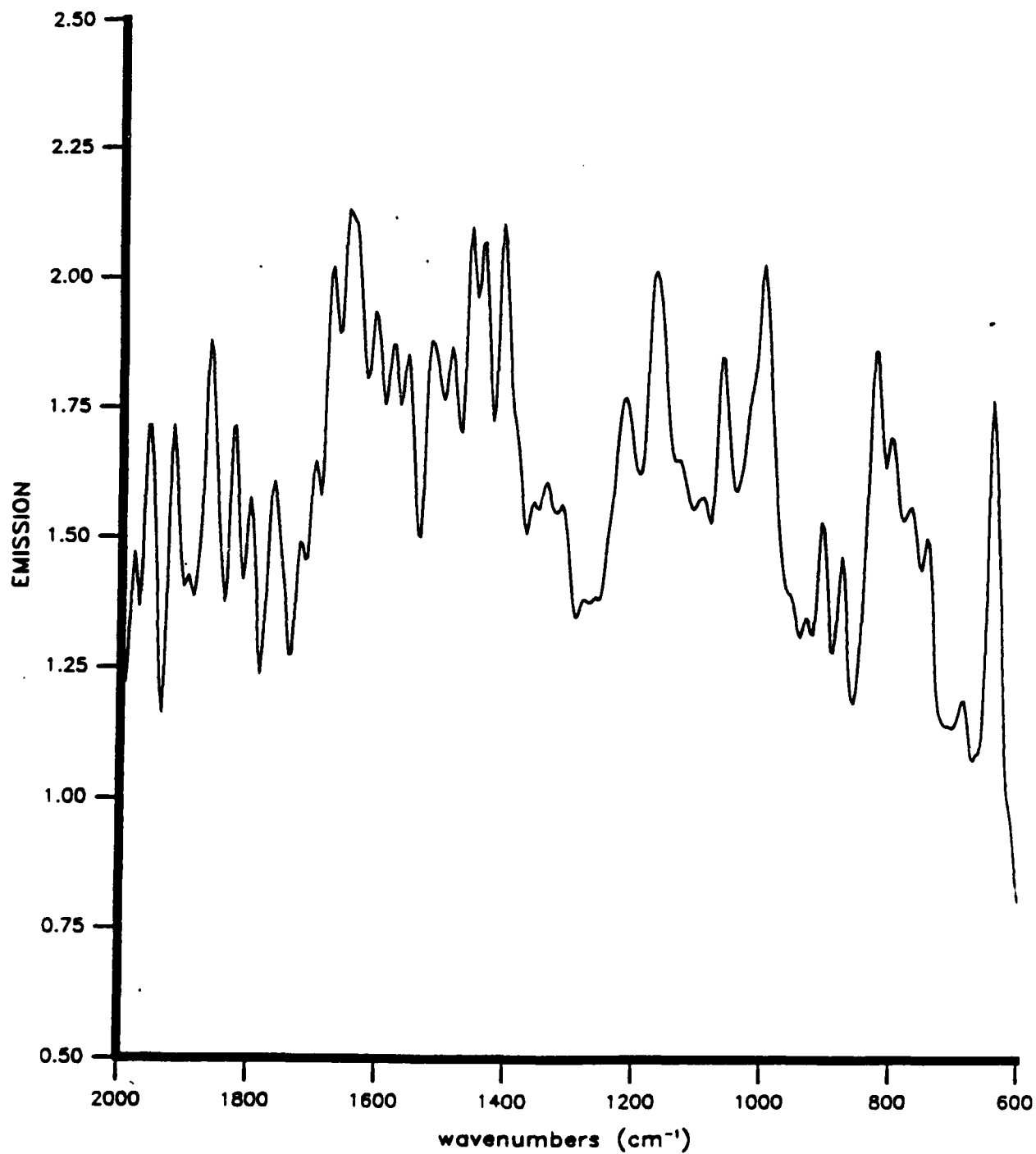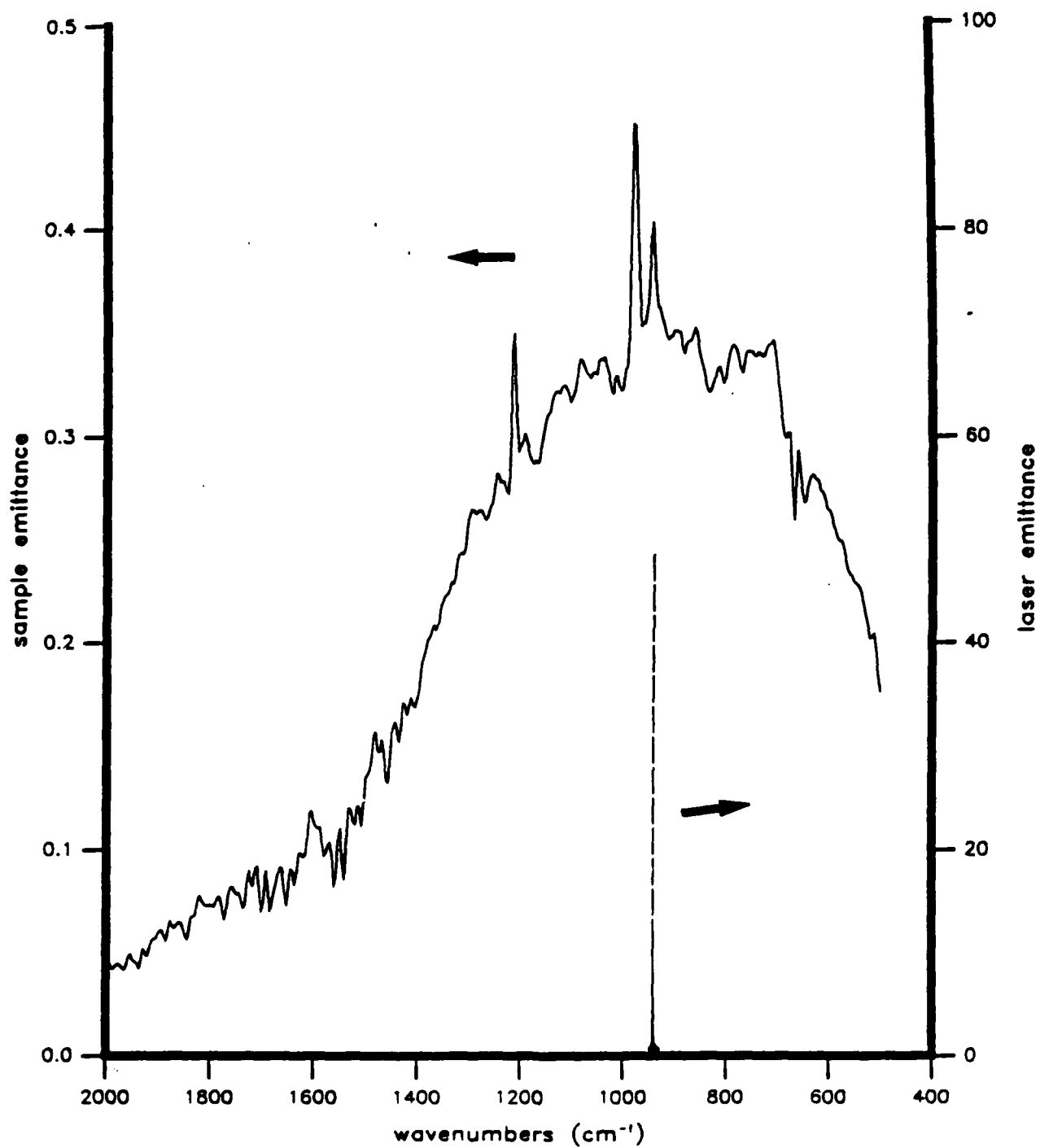
Figure 3.   Infrared Emission Spectrum for Cygon

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Figure 4.   Infrared Emission Spectrum for Cygon Illuminated with a Carbon
Dioxide Laser

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those observed in absorption spectra, but relative peak intensities may differ as a consequence of the Planck function at the effective sample temperature (equation 1).

The preceding spectra illustrate the capability of recording IR emission spectra with sufficient spectral contract to recognize the compounds. An improvement for making IR emission measurements is presented by Low.[21] In a variation of Low's device, the sample holder is placed outside the interferometer at the normal source location and is mated to the interferometer housing with a flexible gasket to provide a gas tight seal. The cold mirror sample is placed in the device that is then purged briefly with dry nitrogen.

Figure 5 shows the emittance spectrum of the cell and cold (0-5 °C) mirror described above. The emittance of the cell with and cold mirror with a sample of DDVP is shown in Figure 6. The ratio of Figure 6 to Figure 5 is presented in Figure 7 and shows the emittance of the pesticide DDVP. Approximately 14 µg of DDVP was placed on the cold mirror with a microsyringe. Superior spectra are obtained in this manner as seen in Figures 7 and 8 for DDVP and malathion, respectively. Maximum sensitivity is dependent on the angle of the mirror to the optical axis. Size constraints limited the range of angles to about 40-60°, with maximum sensitivity expected near 80°.

The application of the background correction schemes, as discussed previously, may not be necessary for spectral identification because second derivative techniques can also discriminate between the sharp band spectra of analytes and the broad Planck function. The second derivative IR emission spectrum of DDVP is shown in Figure 9. Note that in this form the background contribution from blackbody radiators is eliminated and the narrow band features of the DDVP are enhanced. Similar results are obtained with malathion as shown in Figures 10 and 11.

The emittance of DDVP using the apparatus described above (Figure 7) represents about the best sensitivity within the experimental constraints imposed on the mirror angle. This does not compare favorably with other IR techniques such as GC/IR shown in Figure 11. The GC/IR chromatogram is shown in Figure 12. As little as 4 ng of DDVP could be identified by GC/IR.

The sensitivity advantage of GC/IR over emission measurements is expected, and whereas this is still not the most sensitive method for instrumental analysis, it provides for a high degree of specificity not found in some more sensitive methods.

Given the superior detection limits of GC/IR over the emission measurements, the collector assembly may be better suited as a sampling device for GC/IR [or for that matter, gas chromatography/mass spectrometry (GC/MS)] analysis. Accordingly, the sample collector was tested as a sampling device for GC/IR analysis.

The thermoelectrically cooled mirror of the collector assembly produces temperatures between 0 and 5 °C. A sample of DDVP diluted in benzene was placed on the cooled mirror. The sample, 20 µL, froze immediately. After 15 min at the maximum air sampling rate, most of the benzene had sublimed and was lost. With the air flow off, the power was disconnected to the sampler's cooled mirror assembly. When the sample melted, a 0.5 µL aliquot was removed
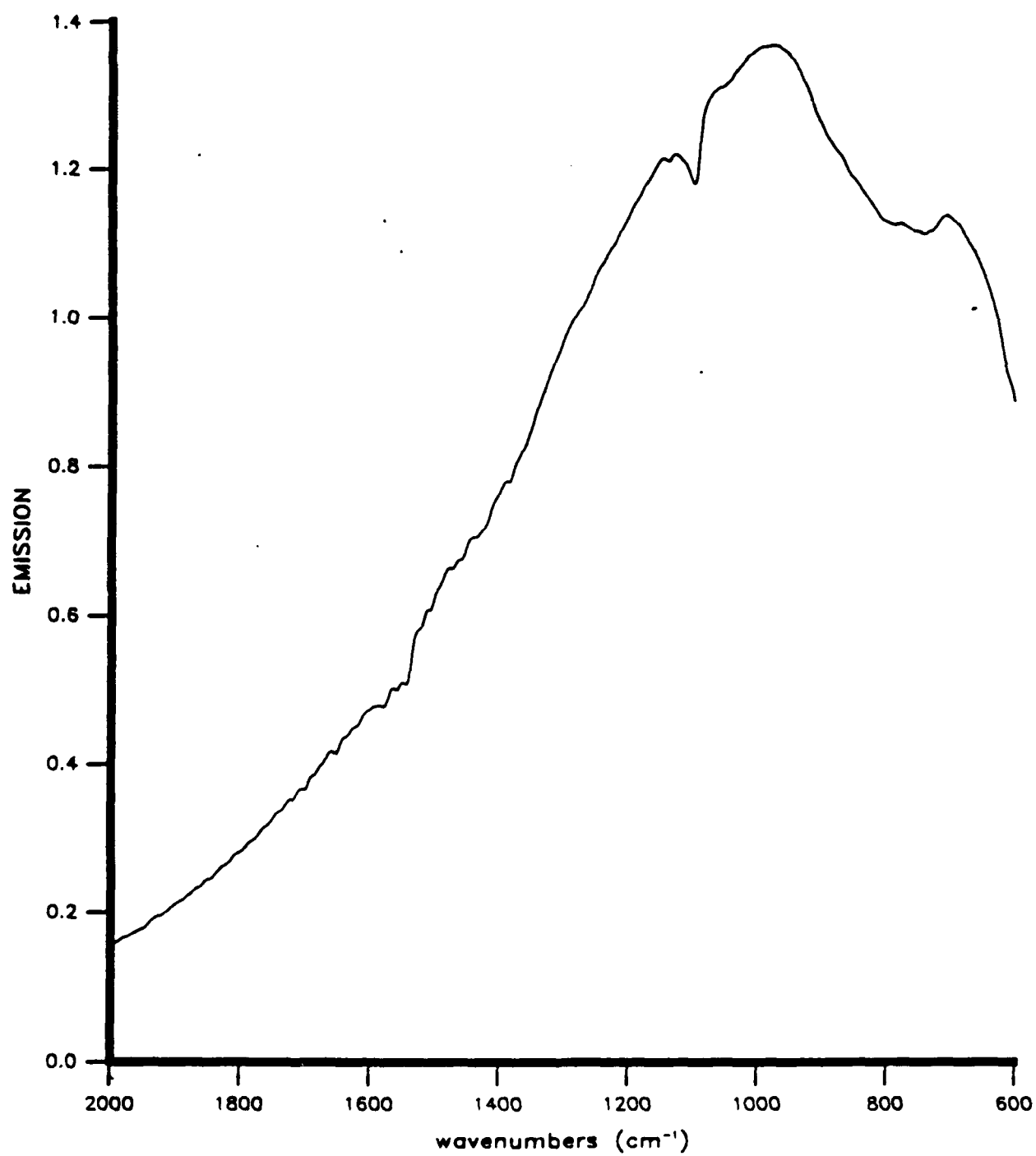
19   (Text continues on page 28.)

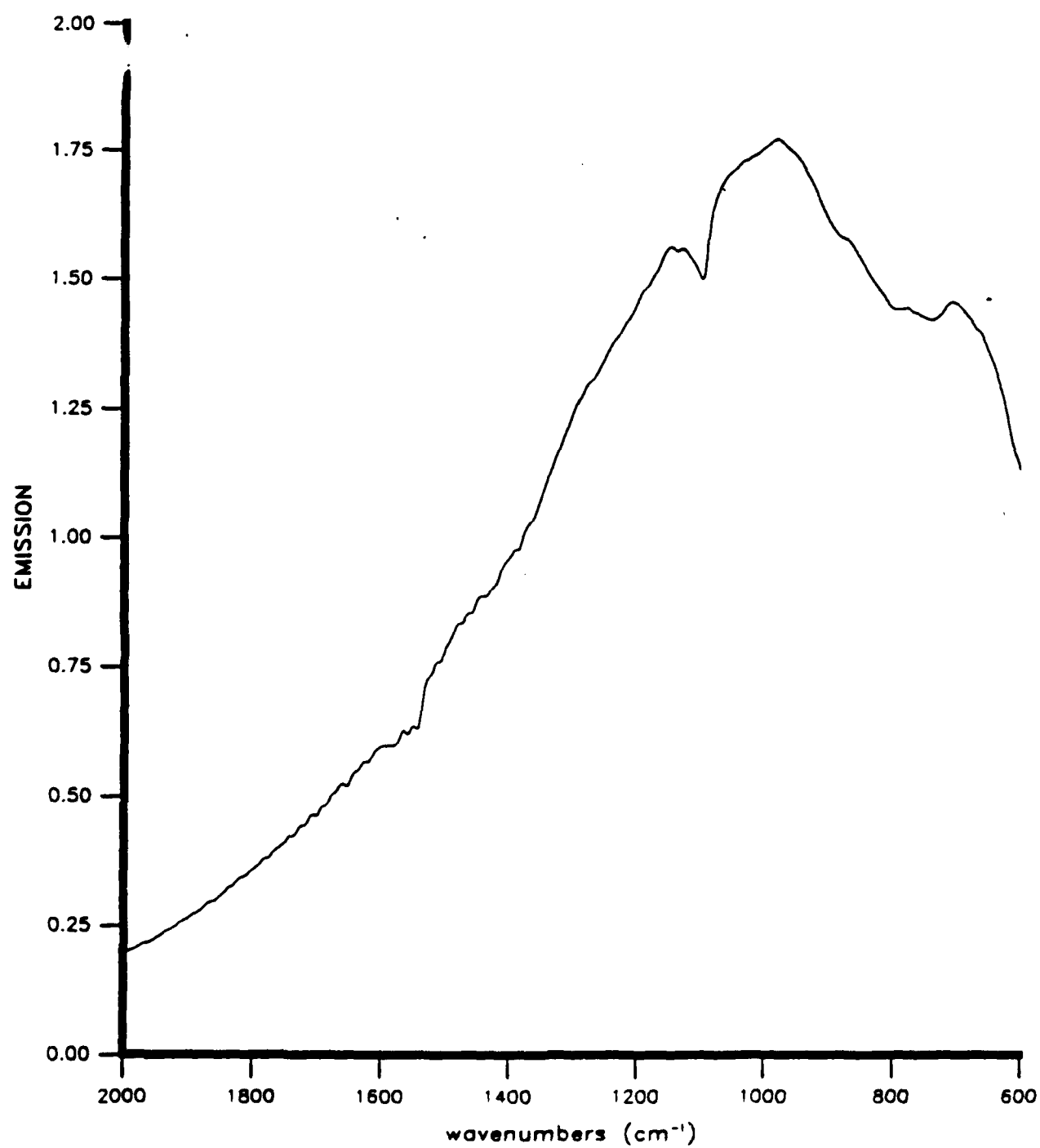Figure 5. Infrared Emission Spectrum of the Empty Emission Measurement Cell

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Figure 6. Infrared Emission Spectrum of DDVP Measured in the Emission Measurement Cell of Figure 5
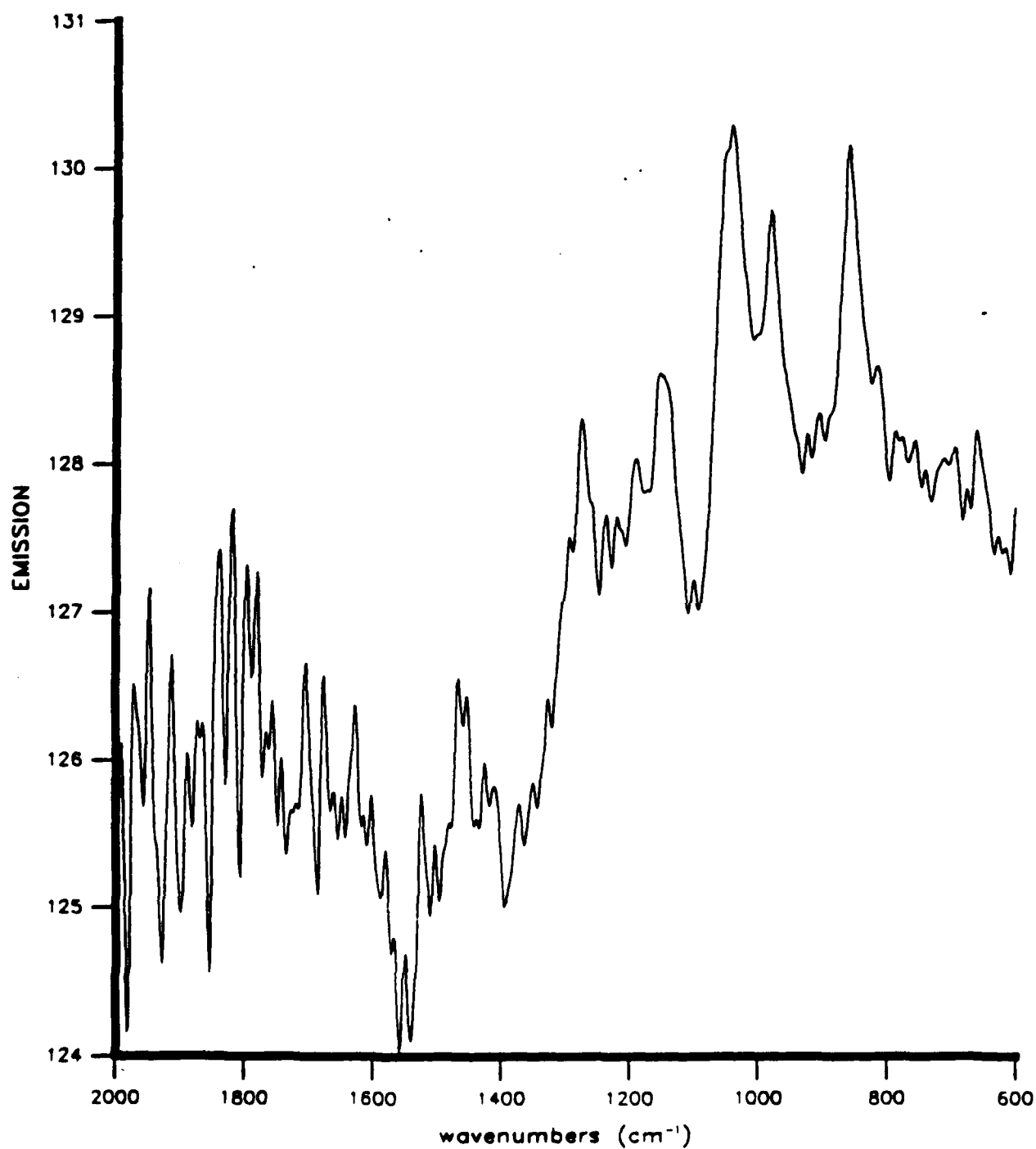
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Figure 7. Infrared Emission Spectrum of Cold DDVP Measured in the Emission
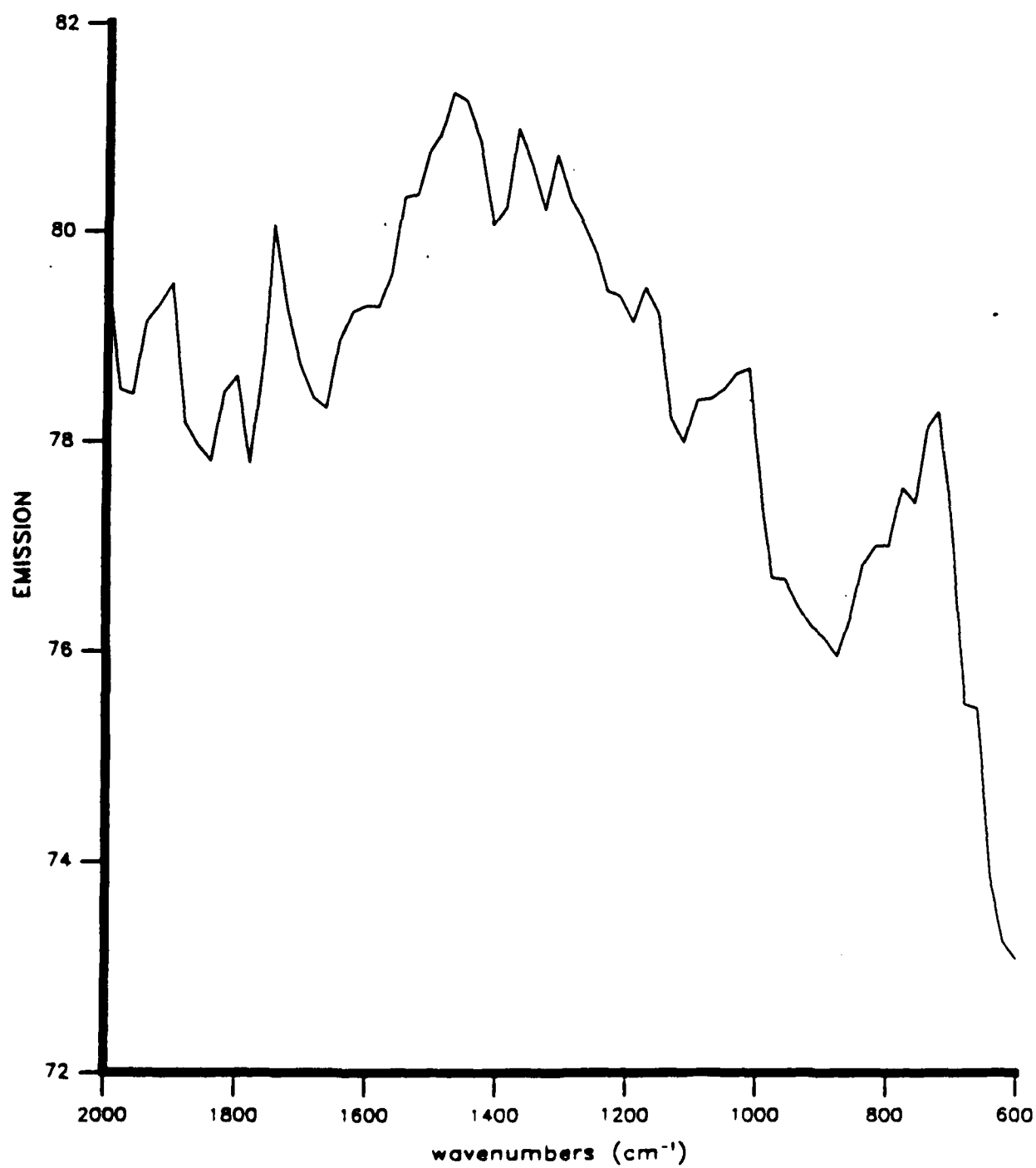Measurement Cell

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Figure 8.   Infrared Emission Spectrum of Cold Malathion Measured in the
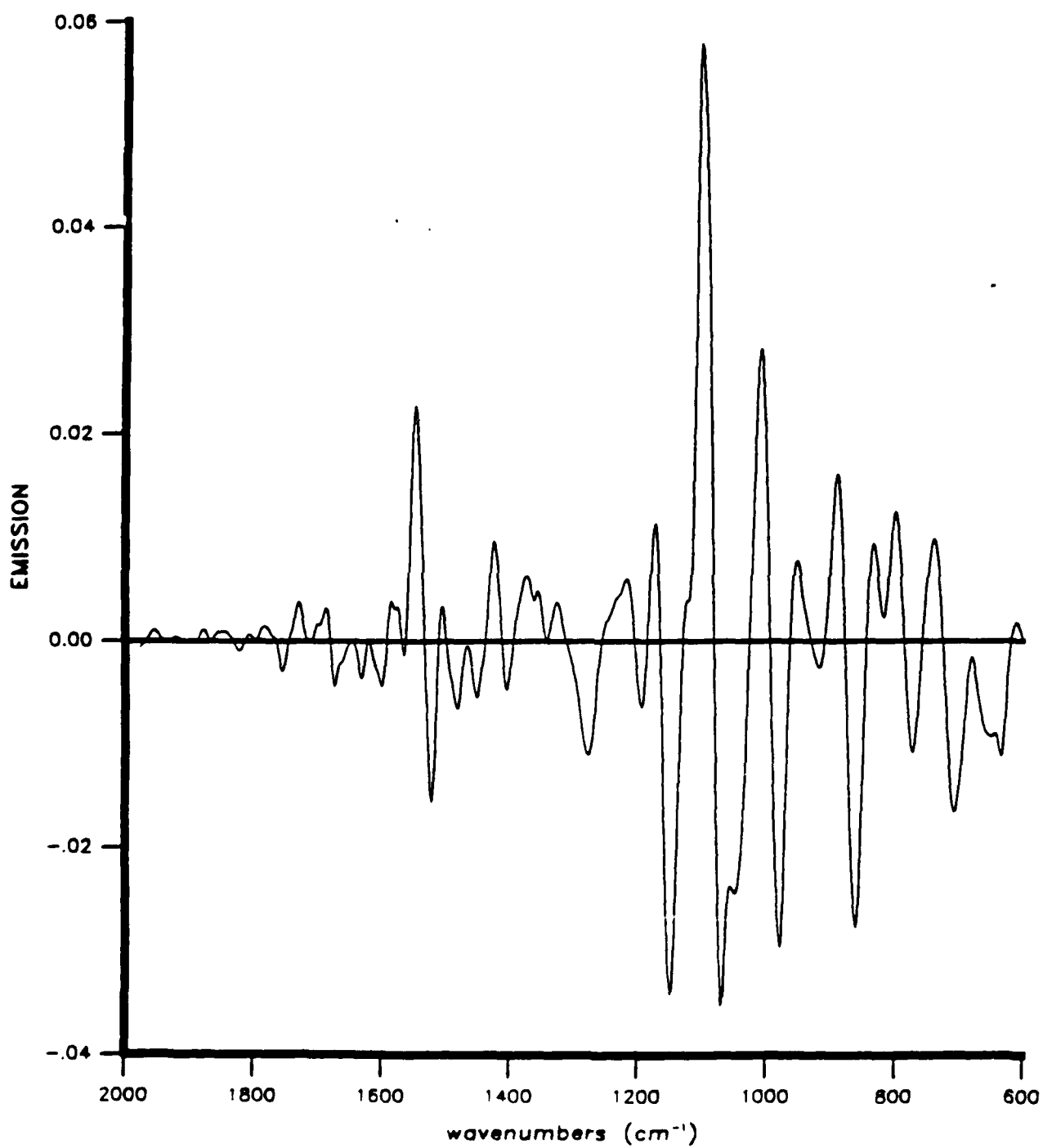Emission Measurement Cell

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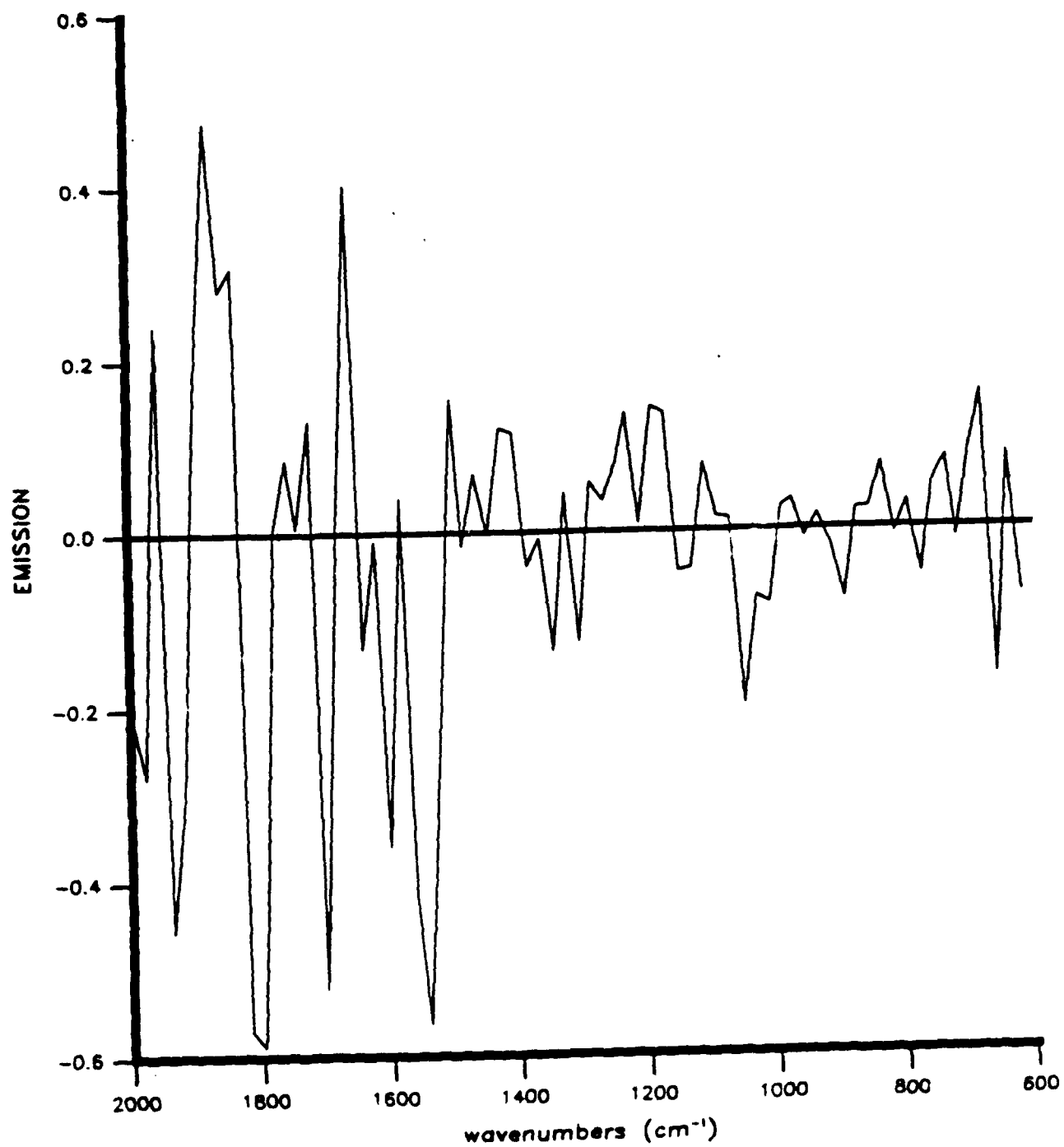Figure 9. Second Derivative of the Emission Spectrum of DDVP

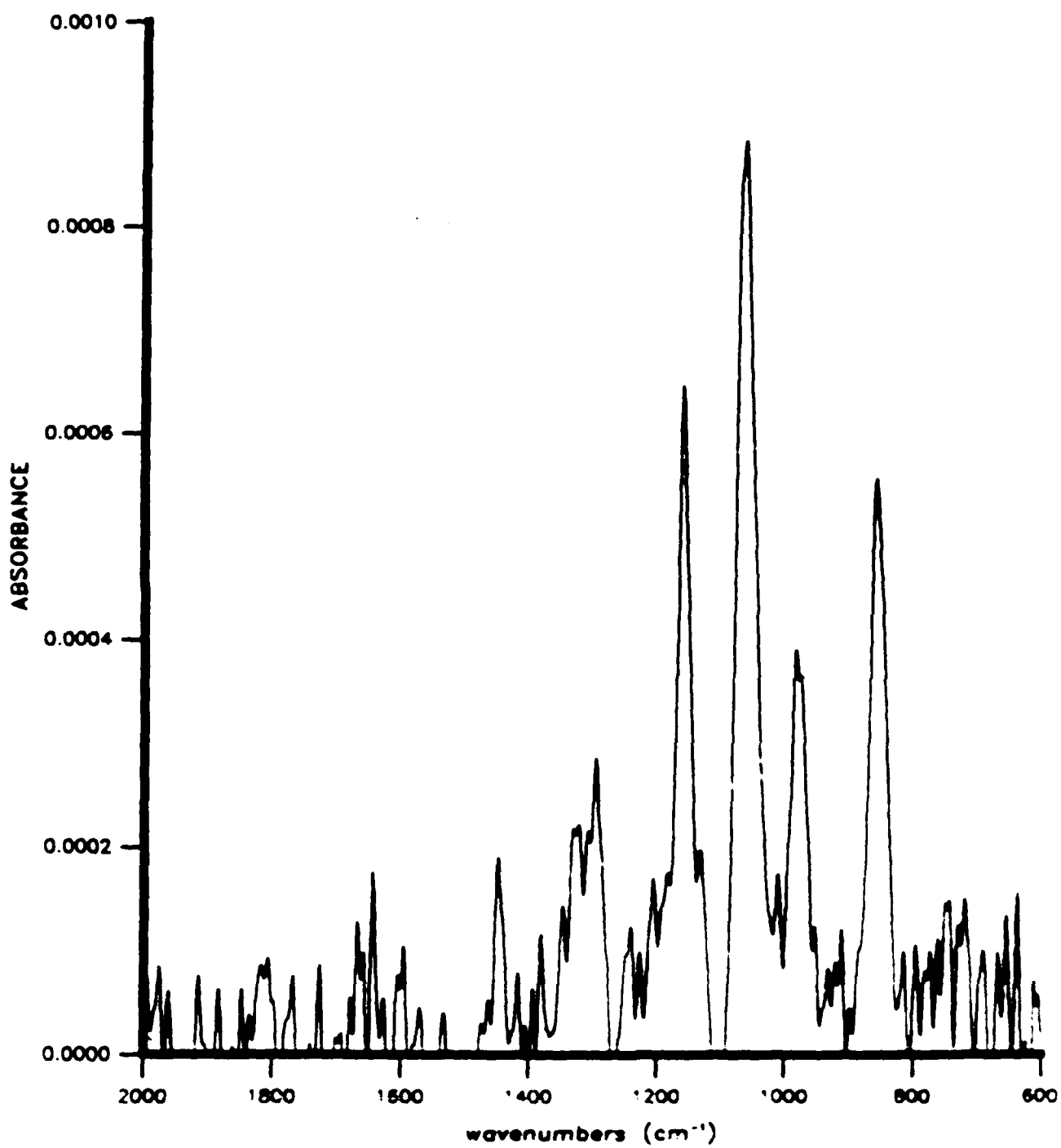Figure 10.   Second Derivative of the Emission Spectrum of Malathion

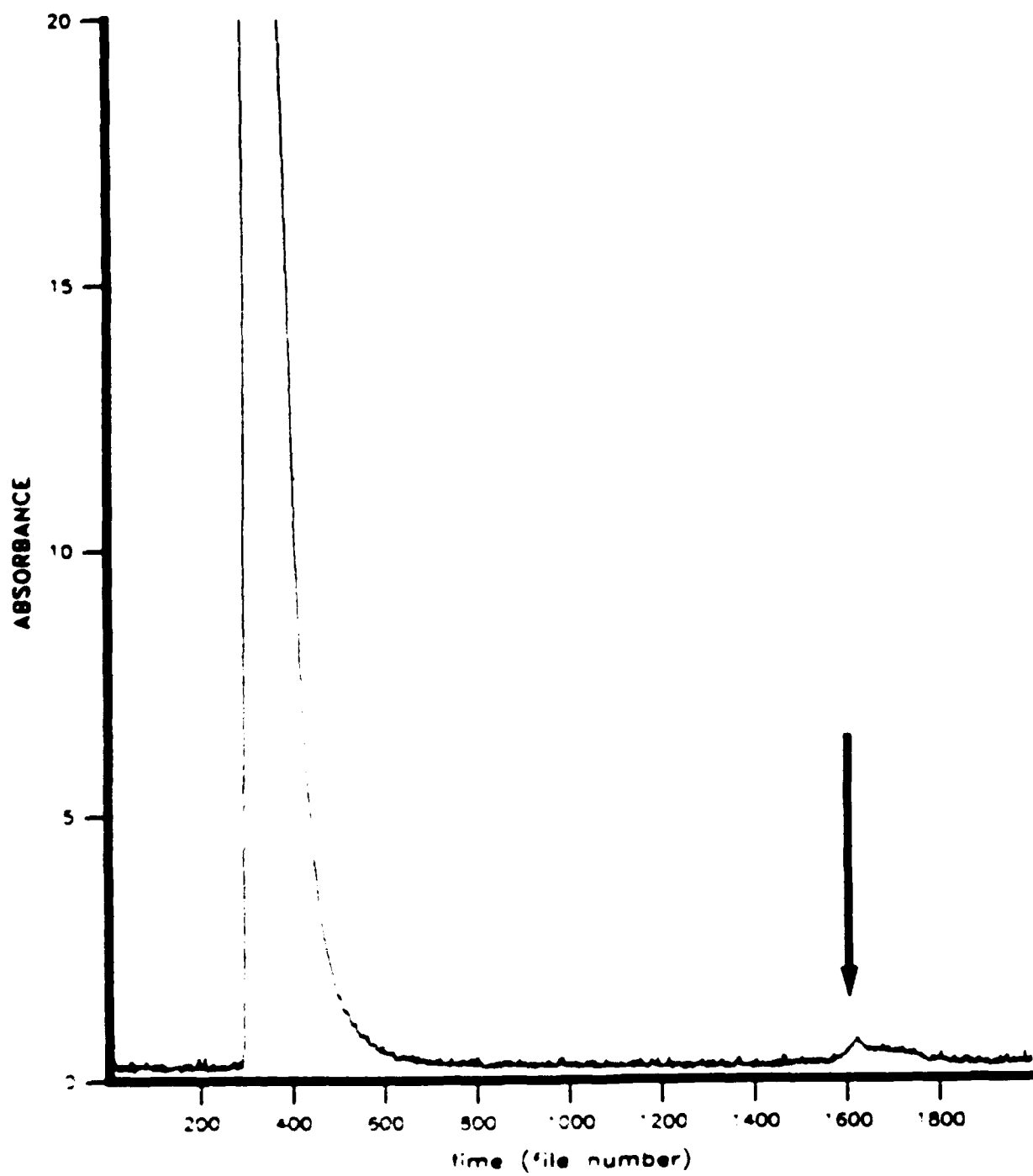Figure 11. Infrared Transmittance Spectrum of 56 ng DDVP Measured by GC. :ρ

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Figure 12. GC/IR Chromatogram of 56 ng DDVP

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by syringe. This sample was immediately chromatographed on the GC/IR system. Figure 13 presents the chromatogram of an "aged" sample on the thermoelectrically cooled mirror. Examination of the IR spectral data revealed that the principal solvent was now water. A trace of benzene elutes just after the water peak and the DDVP (4 ng) elutes at its normal retention time. The spectrum of DDVP at about 4 ng is shown in Figure 14. It is interesting to note that there were no observed decomposition products from the DDVP. The low temperature of the sampler may have inhibited the hydrolytic decomposition of the DDVP.

The use of the sampling device for direct detection using emission from the cold sample is limited due to poor sensitivity. However, there are also limitations to GC/IR or GC/MS detection. Figure 15 presents the chromatogram of malathion processed in an identical manner as the DDVP sample. In this case, there is severe thermal decomposition in the GC injector. This illustrates a pitfall of techniques that rely on chromatography. The necessary chromatography conditions are not always known in advance, and there may not be sufficient sample for repeat trials. Although there was decomposition of malathion, some survived for identification and some of the identification products might be useful to the inferrance of this class of compound.

3.2   Pattern Recognition.

Several algorithms were evaluated for pattern recognition.

A traditional method for pattern recognition is employed in many commercial and public domain library search programs. This involves computing the sum of the difference spectrum of the unknown and each library entry. In some instances, the sum of the square of the differences is computed. This requires that the known and the unknown both be of defined (typically unit) magnitude and that both be single substances, that is, relatively pure. This approach is not appropriate here where the analyte of interest is expected to be the minor component in the sample.

The cross correlation of the unknown with reference spectra is a more reliable means of detecting the reference spectral pattern in the spectrum of the sample. In this way, it is possible for the magnitude and purity of the sample to be compensated. The cross-correlation algorithm is given in equation 9:

$$S = \frac{\Sigma[I_{s,j}I_{r,j}]^2}{\Sigma I^2_{s,j}I^2_{r,j}} \tag{9}$$

where $I_{s,j}$ and $I_{r,j}$ represent sample and reference spectra, respectively, and S is the sample score. The largest scores represent the greatest similarity between the sample and the reference spectrum. As noted earlier, $I_{s,j}$ and $I_{r,j}$ may be replaced by the second derivative of the spectra. This has the effect of weighting the narrow spectral bands over the background. Equation 9 has historical significance in signal detection and works quite well but is costly in computation time. Additionally, it is sensitive to the quality of the data and may fail at low signal-to-noise ratio. Restricting the spectral data to a
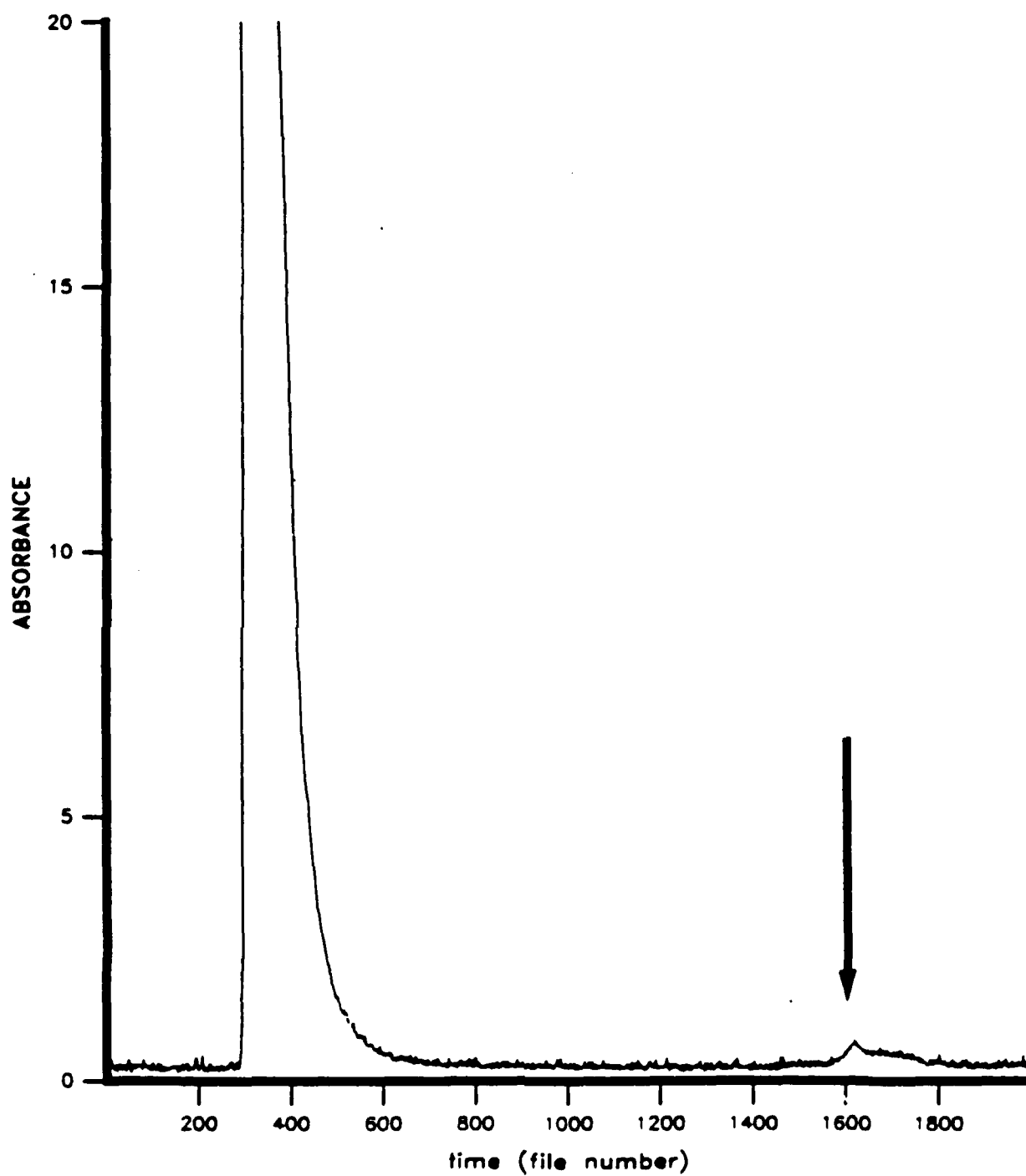
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Figure 13. GC/IR Chromatogram of "Aged" DDVP Removed from the Cold Mirror of
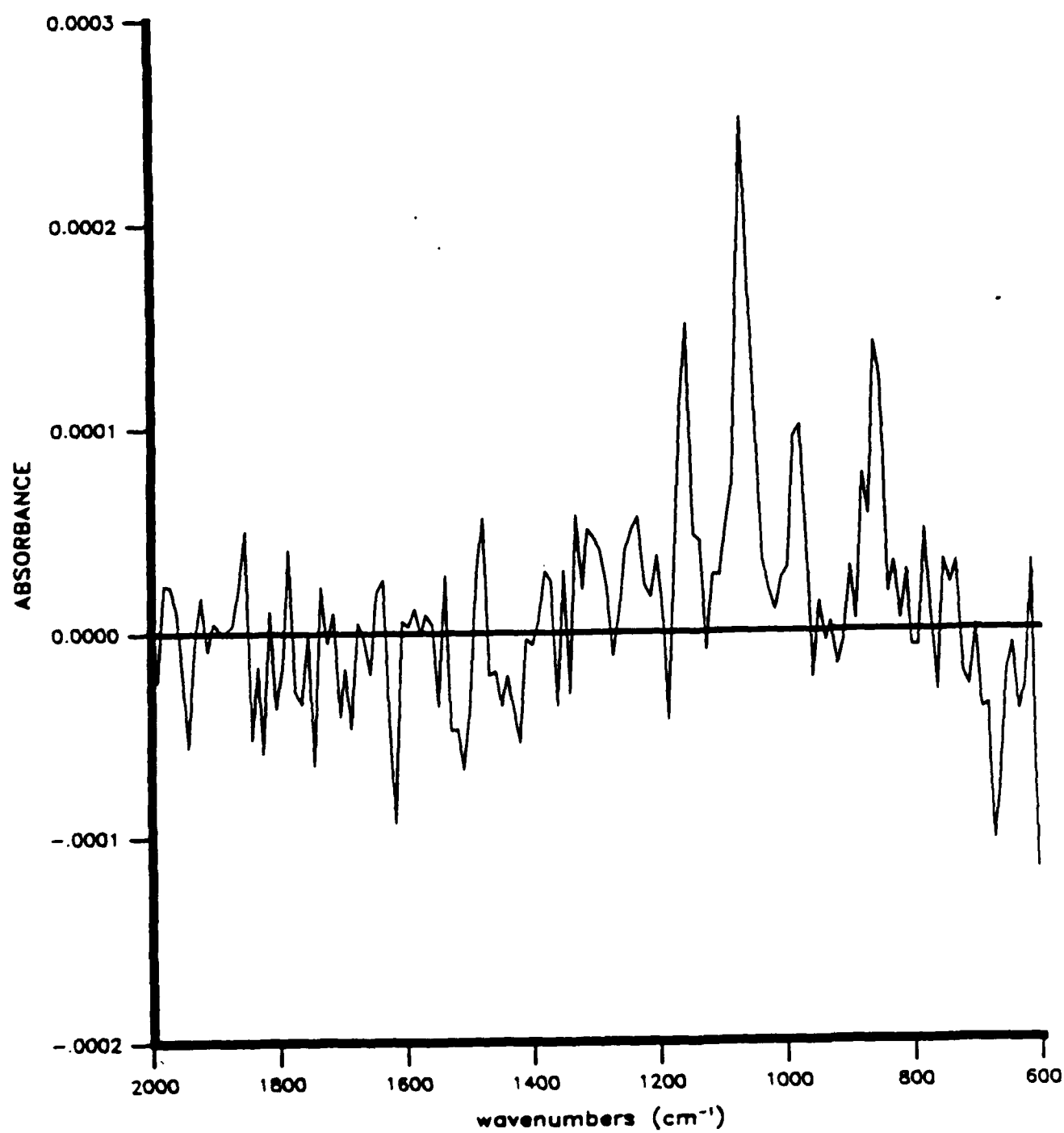the Sample Collector Assembly

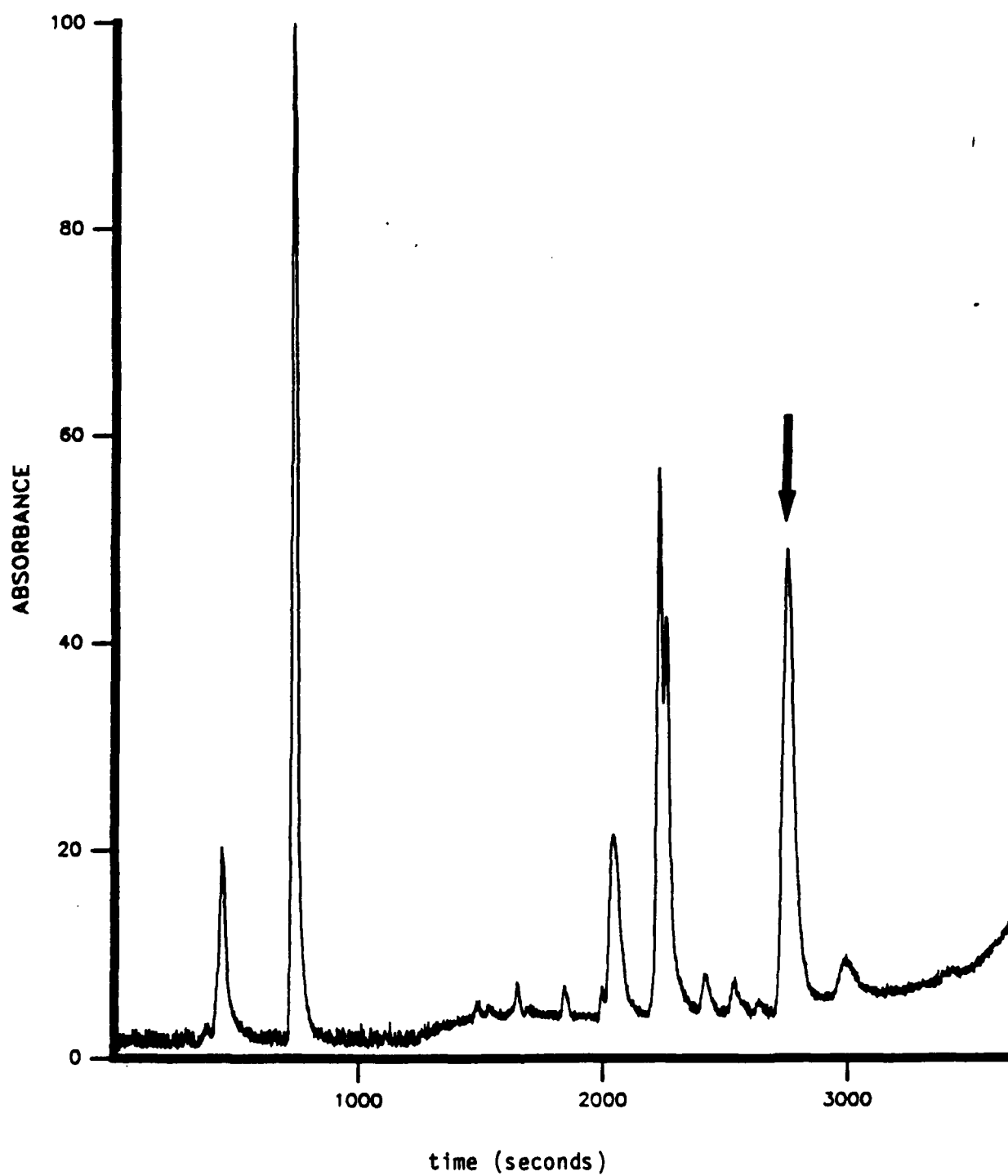Figure 14.   Infrared Transmittance Spectrum of 4 ng DDVP Measured by GC/IR

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Figure 15.   GC/IR Chromatogram of Malathion

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narrow range, such as 1300-600 cm^{-1}, improves the performance. Table 2 presents
the application of this algorithm to the recognition of DDVP.

Table 2. Identification of DDVP by Cross-Correlation

First 4	DDVP Sample Size, Nanograms (Correlation Value)	
Matches	56	4
1 (best)	DDVP(349)	DDVP(147)
2	phorate(60)	ethion(35)
3	ethion(46)	malathion(26)
4 (worst)	malathion(31)	phorate(9)

A drawback of cross correlation is the need for extensive search
libraries. The larger the library the more likely the unknown will be found or
at least that some chemical classification may be inferred from the search
results, but also the larger the search library the slower the search.

Algorithms have been presented for chemical group classification based
on peak probability density functions (equations 4-7). These algorithms demand
a relatively pure sample to function correctly and will fail completely if the
analyte of interest is a relatively minor component in the sample. A simple
modification to equations 5 and 6 is proposed to remove this limitation. In
the modified algorithm, equation 5 is evaluated only when x_j is non-zero, and
equation 6 is evaluated only when x_j is zero. In this manner, the unknown, X,
may have more peaks than specified in the class definition without penalty.
That is, the score (equation 7) now reflects the joint presence of class defini-
tion peaks in the class being tested and in the unknown spectrum without regard
to additional peaks in the unknown sample spectrum. The classes with the
highest scores are indicated to be probable descriptors for the unknown sample.
If the class has more peaks than the unknown then a zero score is computed. A
very careful selection of peak thresholds is required for selecting peaks from
the unknown spectrum. Ideally, peak selection would be based on the signal-to-
noise ratio of the unknown's spectrum. Table 3 presents the test results for
this algorithm. Because the class definitions (equation 4) require a statistical
amount of data to be valid, a library of prerecorded spectra was used in place
of the few pesticide spectra.

Table 3.   Pattern Recognition of Chemical Class

Sample	class						
	p,o,s,c	p,o	p,s	barbits	sugars	cocas	canabs
DDVP	0.001100	1	0	0	0	0	0
DDVP (4 ng)	0.000900	1	0	0	0	0	0
ethion	0.000038	0	1	0	0	0	0
malathion	1.000000	0	0	0	0	0	0
phorate	0.000250	0	1	0	0	0	0
barbituate	0.000000	0	0	1	0	0	0

p,o,s,c - phosphorous, oxygen, sulfur containing organism
p,o   - phosphorous, oxygen containing organism
p,s   - phosphorous, sulfur containing organism
barbits - barbiturates
cocas   - cocaine derivatives
canabs - canabinol derivatives

4.   DISCUSSION

Infrared emission measurements can be made with a commercial Fourier transform spectrometer with the emission sample placed in the usual spectrometer source location or even in the normal sample compartment. Useful IR spectra are obtained with the sample slightly above or below room temperature. Emission from a sample deposited on a mirror placed in the sample compartment is more difficult to detect. Not only is this arrangement not optically efficient, but the emission intensity is angle dependent. Theoretically, the maximum emission should be observed at an angle near 80°, but measurements from the sample compartment require the mirror to be near 45° to the optical axis of the interferometer.

Illumination of thin films of pesticide with a carbon dioxide laser did not produce enhanced IR emission. The carbon dioxide laser used radiates at 940.5 cm^{-1} (10.6 μm). Molecules containing P-O-C and C-O groups typically absorb IR radiation between 1050 and 1000 cm^{-1}. It was originally thought that a carbon dioxide laser would promote enhanced IR emission because of absorbance by the transition corresponding to the P-O-C stretch. Although the peak of the absorption band would not be centered on the laser line frequency, there would still be appreciable absorption from the overlap of the band shoulder at the laser line frequency. Evidence for this has been observed in the irradiation of gas phase organic molecules containing C-O groups in particular.[2-4] For the case of gas phase irradiation with a carbon dioxide laser, the mechanism for emission may involve processes other than simple heating by the laser. For liquid films, the effect of the IR laser appears to only heat the sample, producing the same emission spectra as if the supporting mirror itself was simply heated. In this study, the laser intensity and frequency were difficult to control. This leads to spurious artifacts in the observed emission spectra, sample loss from evaporation, and sample charring. With better control of the

laser intensity and frequency stability, detection of a weak enhancement in emission promoted by laser irradiation might be possible. If such an enhancement exists, it is not likely to compensate for the disadvantages of using a laser to excite emission. There are sound theoretical reasons to expect laser excitation to produce normal appearing emission spectra for large polyatomic molecules and certainly for liquids.[13,14] However, substrate heating, sample evaporation, and decomposition are likely to remain as severe disadvantages.

Excellent emission spectra can be measured from samples at or near room temperature. All matter emits IR radiation at any temperature above absolute zero. When an IR emission spectrum is recorded, the difference in temperature between the source and the detector generates the signal. The larger this temperature difference the larger the observed signal. For this reason, IR emissions have classically been measured by heating the sample and detecting the emitted radiation with a cooled detector.

Aside from the expense of cooled detectors and the inconvenience of using cryogenic fluids, there are other disadvantages to this approach. There are special phase correction problems that occur in conjunction with the use of liquid nitrogen cooled MCT detectors for weak emission measurements. This problem is addressable through software modifications, although not conveniently. Sample heating presents a more difficult obstacle for organic samples such as pesticides.

In the case of volatile organic compounds, the sample heating caused by the usual IR source used for an ordinary transmittance measurement can present problems. When dispersive spectrometers pass so near IR radiation, they volatilize and even char the sample. Fourier transform IR spectrometers employing a Ge-KBr beamsplitter filter out most of the near IR radiation before it reaches the sample. However, sample heating still occurs and is problematic for labile or volatile samples. As seen in Figure 16, enough sample heating occurs to present an analysis problem for volatile samples. The spectra shown in Figure 16 are standard transmittance spectra of DDVP made with a Perkin-Elmer Model 1800 FTIR spectrometer. A thin film of pesticide was deposited on an IR transparent salt window and placed in the spectrometer's sample compartment. All three curves shown in Figure 16 are of the same undisturbed sample recorded at successively later times. The evaporative loss of DDVP is clearly evident; DDVP has a vapor pressure of 1.6 Pa at 20 °C.[22] Sample volatilization is an especially difficult problem when dealing with trace amounts of analyte.[1]

As seen from Figures 7 to 10, acceptable emission spectra can also be obtained when the sample is cooled and the detector is heated. In this instance, the sample is conveniently cooled to 0-5 °C on a mirror, and the detector is a common room-temperature DTGS pyroelectric IR detector. The detector actually operates at 10 °C above room temperature due to waste heat from the electronics in the spectrometer console. Cooling the mirror is conveniently realized by cementing it to a thermoelectric refrigeration chip. However, as one side of the thermoelectric chip becomes cold, the opposite side becomes hot and must be attached to an adequate heat sink or heat exchanger.

Useful emission spectra are obtained in the 2000-5000 cm^{-1} range that encompasses the so-called "fingerprint" region. The emission spectra of P-O-C containing pesticides obtained in this manner are suitable for identification purposes; however, the sensitivity is poor.
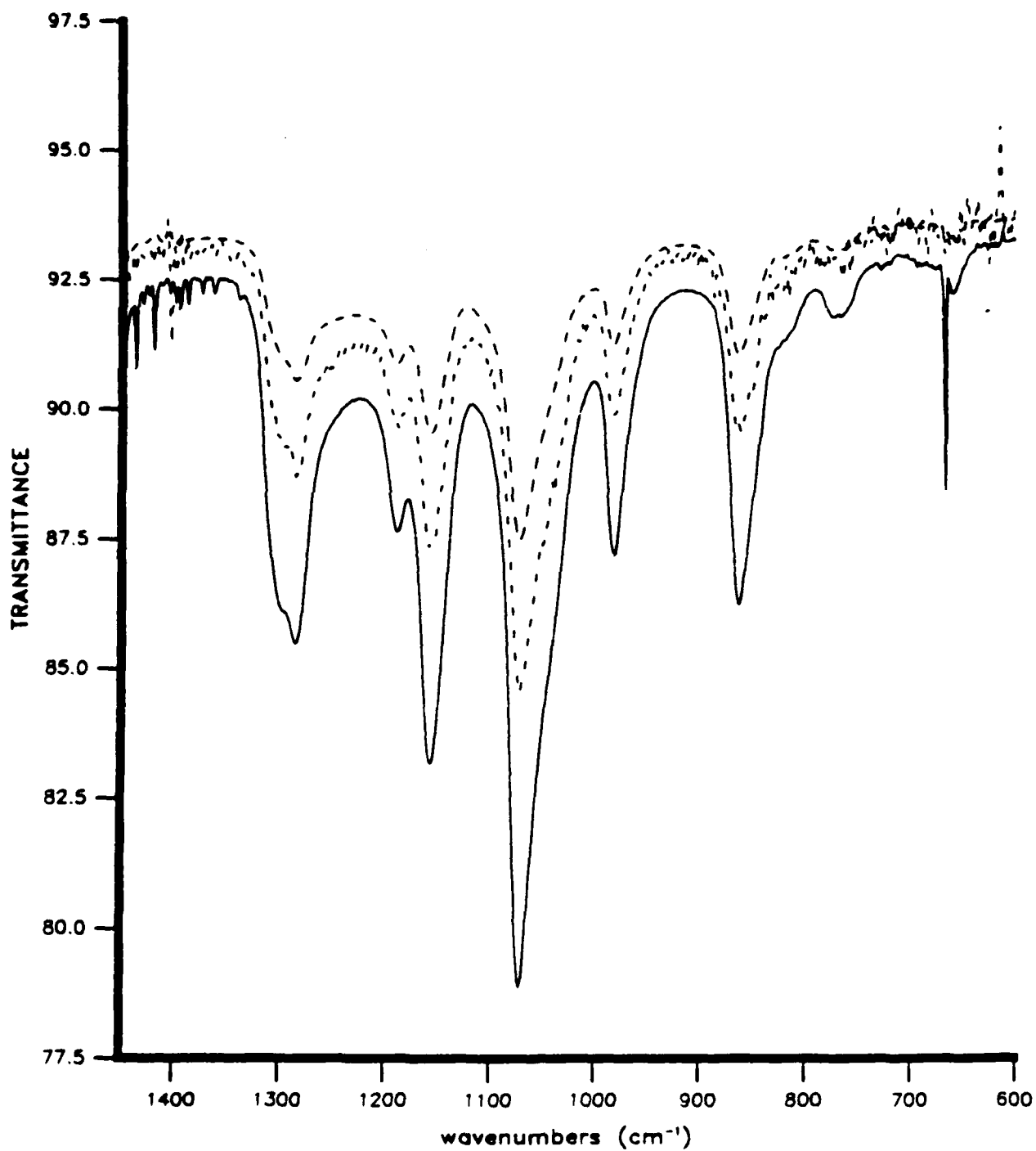
Figure 16. Evaporation of DDVP During Infrared Transmittance Measurement

In this study, recognizable emission spectra required 100 µg of pesticide. Two factors limited the sensitivity in this study. Signal averaging was limited to about 5 min (~ 100 scans) due to waste heat build-up at the hot junction of the thermoelectric chip used to cool the mirror. (Plain mirrors, chilled in a refrigerator, were also used but had insufficient thermal mass to keep the sample cold for very long). The physical const.uction of the sample collector assembly was a limiting factor that did not permit optimization of the mirror angle relative to the optical axis of the spectrometer. The optimum angle for observing emission from a thin film coating on a gold mirror is near 80°. Infrared emission spectroscopy has been compared to reflection-absorption spectroscopy in sensitivity. If this is true, then substantial improvement in the detection limit should be realized with a design that permits longer signal averaging times and adjustment of the mirror angle.

Despite the poor sensitivity, IR emission measurements from cold samples offer three distinct advantages:

● sample loss from decomposition and evaporation is minimized,

● there is no sample preparation step, spectra may be collected directly from the collector assembly mirror, and

● IR spectra provide a high degree of specificity in sample identification.

These advantages are preserved when the sample collector assembly is used in conjunction with GC/IR analysis and the detection limit is greatly improved. Deposition of the analyte on the cold mirror of the collector assembly provides some protection of the sample from evaporation and chemical reactions such as hydrolysis. Removal of sample from the cold mirror presents difficulties. Moisture condensation subjects the sample to water when the sample matrix is thawed. Fortunately the matrix can be left frozen until immediately before the actual analysis. The rate of hydrolysis is slowed by the low temperature preserving the DDVP as seen in Figures 13 and 14. Quantitative removal is difficult with the prototype device, but this is essentially a design problem with several possible solutions.

Infrared spectra, whether from emission measurements or from GC/IR measurements, must be interpreted to be of value. Continuous analyzing for airborne poisons generates a large amount of spectra. The presence of organophosphorus compounds should be determined by a skilled technician. However, the sheer volume of data involved necessitates the use of computer pattern recognition to reduce the number of spectra that need individual human attention.

Two classes of algorithms were considered for this aspect of the project. Specific compound recognition using cross correlation and a chemical class recognition algorithm were evaluated.

Cross correlation requires a library of reference spectra, and a sample can be tested only for those compounds in the library.

It is often enough to simply detect an analyte of interest using sensitive but nonspecific instrumentation. Often it is essential to identify the compound specifically or at least classify it by chemical groups present.

5.   CONCLUSIONS

A liquid aerosol collector, using a thermoelectrically cooled mirror as the collector impaction surface, offers four advantages:

- sample loss due to evaporation is minimized,

- sample loss due to reaction is minimized,

- the sample can be observed directly by IR emission as a sample prescreening technique, and

- the sample may readily be removed for subsequent analysis by GC or GC/IR analysis.

The disadvantages include the requirement of the sampler for electrical power and ice formation on the cold mirror of the sampler.

Infrared emission spectra may be recorded directly from the cold mirror. Infrared spectroscopy is an established tool for qualitative analysis with particular value in examining unresolved mixtures. By recording emission spectra from a cold sample, it is possible to avoid heating the sample that normally occurs in transmittance IR spectroscopy. Because the sample is not heated, losses due to reaction or evaporation are minimized for labile or volatile analytes. The principal advantage is the ability to examine a sample without altering it. The main disadvantage is poor sensitivity that is at least 1000 fold less sensitive than GC/IR analysis. No advantage is found in irradiating the sample with an IR laser; on the contrary all the disadvantages of sample heating are observed.

The maximum utility of the sample collector is gained when used in conjunction with GC/IR analysis. Greatly improved sensitivity is gained over emission measurements without giving up the superb analytical power of IR spectroscopy. Similarly, the collector may be used advantageously for GC/MS analysis. The main disadvantage is in quantitative removal of the sample from the cold mirror.

There are many algorithms used to identify IR spectra. This study considered two different approaches. The use of IR spectroscopy in conjunction with the sample collector can generate large amounts of data. The resulting spectra are of no value until they are interpreted. The final interpretation of IR spectra should be performed by a skilled technician. However, using pattern recognition to tag spectra eliminates much of the work that may indicate the presence of the compounds of interest. The two approaches considered in this project were cross correlation, a compound specific and computer intensive method, and chemical class recognition, a faster but less specific method.

Automated pattern recognition of IR emission spectra or transmittance spectra from GC/IR analysis provides a practical means of surveying large

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numbers of spectra for compounds or compound classes of interest. Best results should occur with GC/IR spectra due to the simpler spectra obtained when mixtures are resolved into single components. Specific compound recognition by cross correlation of the unknown spectra against a collection of known reference spectra may be applied to complex mixtures. Careful selection of the spectral correlation window leads to correct compound recognition when the compound contributes significantly to the spectrum. Disadvantages to cross correlation are:

- the requirements of a reference library,

- the results are not meaningful if the sample is not in the reference collection, and

- the computer time required to perform the correlation.

A faster, though less precise, alternative is chemical class recognition. An algorithm that does not penalize for extraneous peaks in the spectrum of a sample mixture can classify the sample as having or not having a specified chemical class present. An advantage to this approach over cross correlation is the elimination of the required reference library of possible candidates to identify the unknown. Chemical class recognition is also much faster in computing algorithms. There are two major disadvantages to chemical class recognition. Information is lost by ignoring extra peaks in the sample in comparing it to a class description. If the sample has undergone GC/IR (or GC/MS) analysis to resolve the mixture, then this requirement may be removed. The second disadvantage is that to achieve a statistically valid class description, a large number of training spectra are required.

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