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I am submitting herewith a thesis written by Harry O'Neil Brotherton, Jr., entitled "Fourier Transform Infrared Spectroscopy of Selected Polycyclic Aromatic Hydrocarbons Using Conventional Sampling Techniques." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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FOURIER TRANSFORM INFRARED SPECTROSCOPY OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS USING CONVENTIONAL SAMPLING TECHNIQUES

A Thesis

Presented for the

Master of Science

Degree

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ABSTRACT

Fourier transform infrared spectra of polycyclic aromatic hydrocarbons were obtained in four types of matrices (potassium bromide pellets, liquid solutions, mineral oil mulls, and deposited films examined by attenuated total reflectance). The peak positions and identification of the polycyclic aromatic hydrocarbons as components of a mixture were examined.

Studies of reproducibility, detection limits, and Beer's law adherence were made on selected compounds in potassium bromide pellets and liquid solutions, and possible applicability of the sampling techniques to quantitative analyses was determined.

Qualitative analyses were determined to be feasible using potassium bromide pellets, liquid solutions, or ATR with simple mixtures (four or five components). For quantitative studies, the liquid solutions seemed most promising of the four sample matrices examined, yielding the lowest detection limits and linear Beer's law behavior over the widest concentration region.

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CHAPTER I

INTRODUCTION

A. BACKGROUND

The identification and quantitative analysis of polycyclic aromatic hydrocarbons (PAH) in the environment have become analytical problems of increasing concern. PAH have been found to play an important part in the carcinogenicity and tumor-initiating activity of atmospheric pollutants in urban areas (1). Their low concentration in the atmosphere (usually less than 0.1% by weight (2)) requires very careful sample collection and handling as well as very sensitive instrumentation for accurate analysis. Furthermore, the presence of many different polycyclic compounds having similar properties in real samples makes the characterization of polyorganic matter an exceedingly challenging analytical problem.

Several techniques have recently been used in an effort to develop fast and accurate methods of analysis for PAH in low concentrations. Ultraviolet absorption spectroscopy (2-4), luminescence spectrophotometry (5), and mass spectrometry (6, 7) (used in conjunction with gas or liquid chromatography) have all been used with various degrees of success. Until now, infrared (IR) spectroscopy has been almost totally ignored in the investigation of PAH (8), for reasons to be discussed in subsequent paragraphs.

Infrared spectroscopy is capable of producing a large amount of information in a relatively short analysis time. Virtually all PAH exhibit intense infrared absorption spectra. Each spectrum shows a number

of sharp absorption bands (9) which are characteristic of that molecule and may conceivably be used to identify individual PAH (9-12).

Conventional (i.e., dispersive) infrared spectroscopy has several important shortcomings which make it virtually useless for analysis of low concentrations of PAH. Conventional infrared spectroscopy is not sufficiently sensitive to be used for trace analysis. The detection limits of infrared spectroscopy performed with grating and prism instruments are not low enough to study the PAH at concentrations that would be found in samples collected from the environment. Spectra acquired from samples of high concentration cause difficulties when attempting quantitative studies. Quantitative analysis by infrared spectroscopy is based on Beer's law, for which it is assumed that the solute molecules in the system do not interact with each other. In concentrated samples, interactions between the solute molecules do occur, thereby rendering Beer's law invalid for the system. Problems also arise due to solvents or matrices not being transparent throughout the infrared region. These difficulties, along with the fact that the spectrum of a mixture of more than a few PAH would be very complex and almost impossible to analyze manually, have discouraged most workers from attempting to use infrared spectroscopy in the analysis of PAH (8).

Orr and Thompson (13) and Cannon and Sutherland (14) are among the few investigators who have attempted to use infrared spectroscopy in the study of PAH. Their studies covered the spectral region from 5 to 15 μm (2000 to 650 cm^{-1}). Solution concentrations of almost 1.0 molar were required to obtain adequate signal-to-noise ratios in the spectroscopic

measurements. A large number of infrared absorption spectra of PAH were reported, but no attempts were made to study the spectra of mixtures of PAH.

Many of the problems in the use of conventional infrared spectroscopy for the analysis of PAH can, in principle, be minimized or eliminated by the use of Fourier transform (FT) infrared spectroscopy. The principal optical component in a FT spectrometer is an interferometer, rather than a prism or grating monochromator. Use of the interferometer allows the entire spectral range to be observed simultaneously, whereas, in a grating or prism instrument, the detector receives a signal only within a narrow frequency band at a given time (15-19). The "multiplexing" capability of the FT-IR spectrometer results in a significant increase in signal-to-noise ratio over that obtained with a conventional instrument; under ideal conditions, the signal-to-noise ratio is enhanced by a factor equal to the square root of one-half the number of resolution elements, $\sqrt{N/2}$ (20). This signal-to-noise ratio enhancement should permit samples of lower concentrations to be examined by FT-IR. The interferograms (the actual data recorded) are transformed to spectra by a small digital computer which performs a fast Fourier transform (FFT) algorithm on the interferogram (21). The computer can also be used for a variety of data-handling processes, such as storing spectra for future use, or subtraction of the spectrum of the matrix background or of a known compound from the recorded spectrum of the sample.

Four basic sampling techniques have been used in the conventional infrared analysis of solid materials: potassium bromide (KBr) pellets,

liquid solutions, mulls, and attenuated total reflectance (ATR). A brief discussion of each of these techniques follows.

1. Potassium Bromide Pellets

The potassium bromide pellet technique is one of the most widely used sampling techniques for infrared spectroscopy of solid samples. The KBr matrix has no absorption bands throughout the conventional mid-IR region (2.5 to 25 μm). Solids which are not soluble in a solvent suitable for IR analysis may be studied by suspending them in a KBr pellets (10, 11, 22-25). Potassium bromide pellets produce lower scattering losses, better homogeneity of samples, and result in greater ease for examining small samples than mull techniques (24).

The details of spectra obtained by using KBr pellets may, however, be difficult to reproduce. In order to obtain reproducible results, the sample particles must be of a uniform size and homogeneously dispersed in the matrix. The grinding and mixing techniques make true homogeneity very difficult to achieve. Potassium bromide is very hygroscopic and care must be taken to prevent the absorption of water by the matrix during the preparation of the sample. The preparation of KBr pellets requires more time than the preparation of mulls; a special apparatus is required to press KBr into a clear disk (11, 23, 24). In general, KBr pellets have proven very useful for obtaining spectra for qualitative analysis, but are virtually never used for quantitative IR analyses.

2. Liquid Solutions

The spectra of solid samples dissolved in solution are usually very reproducible. Longer pathlengths used for dilute solutions are easily reproduced and compensation for the absorption of the solvent can be made by using a matched cell, which contains the solvent, in the reference beam (10, 11).

Most liquid solvents have strong absorption bands in different infrared regions. While solvent absorption can often be subtracted from the sample spectrum in FT-IR, this factor ultimately limits the cell thickness which can be employed for acquisition of solution spectra. Best results can be obtained by carefully choosing two different solvents which have optimum transmittance in different infrared regions, obtaining the spectra of the samples of interest in both solvents, and then "piecing together" the two spectra so that the sample spectrum can be viewed over the entire infrared region. The possibility of interaction between the sample and solvent must be considered as well as the fact that many organic solvents are volatile and tend to evaporate (23, 24), thus making the preparation of solutions of accurately known concentrations difficult.

3. Mulls

The preparation of mulls (dispersions of finely ground sample in heavy oils) is fast and rather simple, which is an advantage of mulls over KBr pellets (26). However, mineral oil, or "Nujol," which is normally used in the preparation of mulls, has broad absorption bands in parts of the infrared region (1140, 1375, and 723 cm^{-1}) which can

obscure those of the sample. The particle size is very difficult to control, often causing excessive scattering of light and broad spectral bands (23, 24).

4. ATR

The ATR samples are prepared by the evaporation of a solution from the surface of an internal reflectance crystal. The result is a thin deposit of sample on the crystal surface. Spectra obtained by ATR are independent of the sample thickness on the internal reflectance crystal (25). The depth of penetration of the radiation through the crystal face and into the sample is only a few μm. Such a slight penetration through the crystal face requires that the sample preparation result in an intimate contact between the sample and the reflectance crystal surface. Multiple reflections within the crystal are often used to ensure that the radiation comes into adequate contact with the sample. Uneven sample deposits on the crystal surface can also result in a large loss of intensity due to light scattering, as can scratches on the crystal surface (11, 22, 25). Unless a uniform sample thickness, reproducible for each experiment, is achieved, quantitative analysis is very difficult to perform by ATR.

5. Matrix Isolation

"Matrix isolation is a technique for trapping species as isolated entities in an inert solid, or matrix, in order to investigate their properties" (27). Matrix isolation has become of increasing interest in the infrared region, although essentially no analytical use of the

technique has been reported. The isolation of solute molecules in an inert matrix reduces intermolecular interactions and results in sharper spectral bands which in turn allow higher resolution and wavelength precision in the spectra obtained (28, 29).

B. PROPOSED PROBLEM

The purpose of this thesis is to study several PAH using FT-IR spectroscopy, employing each of the four sampling techniques previously discussed (potassium bromide pellets, liquid solutions, mulls, and attenuated total reflectance). The four sampling techniques are compared with respect to quality of the spectra obtained, detection limits of selected compounds, and applicability to quantitative analysis.

CHAPTER II

EXPERIMENTAL

A. MATERIALS

1. Anthracene

Anthracene, $C_{14}H_{10}$, "analytical grade" was obtained from Matheson, Coleman, and Bell, Cincinnati, Ohio. Before use, the compound was recrystallized in ethanol, and vacuum sublimed at about 65°C in a Kontes vacuum sublimator (Catalog Number 855600). The melting point of the sublimed anthracene was 216 to 217°C (29).

2. Benzo (a) Pyrene

Benzo (a) pyrene, $C_{20}H_{12}$, was obtained from B. Pauric, Philadelphia, Pennsylvania. The stated purity of the compound was 99.99% and the compound was used without further purification.

3. Carbazole

Carbazole, $C_{12}H_9N$, was obtained from James Hinton, Columbia, South Carolina. The stated purity of the compound was "zone refined," and the compound was used without further purification. For the purpose of this study, carbazole is considered a PAH.

4. Chrysene

Chrysene, $C_{18}H_{12}$, was obtained from James Hinton, Columbia, South Carolina. The stated purity of the compound was "zone refined," and the compound was used without further purification.

5. Phenanthrene

Phenanthrene, $C_{14}H_{10}$, was obtained from Eastman Organic Chemicals, Rochester, New York. The stated purity of the compound was 90%; the material was a light brown granular substance. Vacuum sublimation at about 64°C and recrystallization in ethanol produced a white granular substance. This white granular substance contained crystals of two distinctly different melting points. One set of crystals melted at 99 to 100°C, characteristic of phenanthrene, and the other crystals melted at 216 to 217°C, characteristic of anthracene. Due to a difference in the rate of dissolution of phenanthrene and anthracene in acetone, the phenanthrene was dissolved and separated from the anthracene by rinsing the crystals twice with acetone. The acetone was then evaporated, and vacuum sublimation of the residue at 60°C produced spectrally pure phenanthrene (all bands in the infrared spectrum were matched with bands in the Sadtler spectrum of phenanthrene (30); no other bands were present).

6. Pyrene

Pyrene, $C_{16}H_{10}$, was obtained from B. Pauric, Philadelphia, Pennsylvania. The stated purity of the compound was 99.9% and the compound was used without further purification.

7. Matrices and Solvents

Potassium bromide and acetone were obtained from Fisher Scientific Co., Fair Lawn, NJ. Carbon disulfide was obtained from Baker Chemical Co., Phillipsburg, NJ. These three compounds were stated to be of analytical

grade and were used without further purification. Mineral oil (pharmaceutical grade) was obtained from Revco Drug Stores. The spectrum of the pure mineral oil closely resembled that of Nujol (23). The mineral oil was used without further purification.

B. APPARATUS AND PROCEDURES

The infrared spectormeter used in this research was an FTS-20 Spectrometer (Digilab, Inc., Cambridge, Mass.).

A teletype (ASR 33) is used to enter the necessary commands and parameters into the minicomputer, a Data General Nova 1200, which operates the spectrometer. Parameters which are most often varied include:

1. Resolution (RES); values of 16, 8, 4, 2, 1, 0.5, 0.25 and 0.125 cm^{-1} may be used. A resolution of 2.0 cm^{-1} was used for most of the spectra obtained in this work.

2. Number of Scans (NSS); the number of scans chosen should be made by considering both the signal-to-noise ratio desired and the time required for the collection of the data. In this work, 100 scans of a given spectrum were normally averaged.

3. Range to be plotted in cm^{-1} (STP, ENP); the starting point and the endpoint (in cm^{-1}) of the abscissa are chosen so that the desired portion of the spectrum is plotted by the digital plotter (DP-1 Complot, Houston Instruments, Inc., Austin, Texas).

4. Height to be plotted in percent transmittance (MXY, MNY); the maximum and minimum values on the ordinate scale are chosen so that the bands of the plotted region are on scale.

5. Number of cm^{-1} plotted per inch of chart paper (XSL); this parameter can be chosen to show peak separations more clearly by expanding the wavenumber scale.

6. Actual length of the ordinate scale in inches (YSL) over which the spectrum is spread. Maximum and most frequently used value is 10 inches.

Other parameter values are changed infrequently and will not be discussed here.

A 256K (1K = 1024 words) fixed head disk (Alpha Data, Inc., Canoga Park, CA) is used for the storage of programs and files of data which have been collected (up to 27 files collected at a resolution of 2.0 cm^{-1}). A much larger storage capacity is provided by a Digital Magnetic Tape Recorder (Model 9700, Kennedy Corporation, Altadena, CA). Each reel of magnetic tape can store over 150 8K (resolution = 2.0 cm^{-1}) files. The option of observing the contents of any one file without the necessity of plotting the spectrum is provided by a Tektronix Type 561 oscilloscope (Tektronix, Inc., Beaverton, OR) which is used as an accessory to the FTS-20 system.

The principal optical component of the system, a Digilab Model 496 interferometer, is a single beam instrument. The optical unit and sample compartment may be evacuated to eliminate any interference in the spectrum due to atmospheric water or carbon dioxide. A germanium-coated potassium bromide beamsplitter is used in the mid-IR region, 4000 to 400 cm^{-1}, and a heated nichrome filament is used as the mid-IR source. A TGS (triglycine sulfate) pyroelectric bolometer is used as the detector.

In usual practice, a reference spectrum was first collected and stored in File Two of the disk. The reference spectrum was recorded by placing the apparatus required (with no solute present) for the sampling technique to be used in the sample chamber and collecting the data under the conditions for which the sample spectrum was to be subsequently collected.

The sample was then prepared and its spectrum collected and placed in File One. A ratioed spectrum, computed by point-by-point division of the sample and reference spectra, was then calculated by the minicomputer and plotted. The sample spectrum was obtained following sample preparation by one of the techniques discussed below.

1. Potassium Bromide Pellets

Potassium bromide pellets were prepared by grinding about one milligram of sample with about one gram of potassium bromide (amounts were varied according to the desired mole ratio of sample to matrix) in a mortar. Sample preparations were usually carried out in a hood, using gloves. For carcinogenic samples (chrysene and benzo (a) pyrene), all manipulations were performed in a drybox. The resulting fine powder was either placed in a die and subjected to a pressure of 16,000 psi for five minutes or placed in a Mini-Press KBr Pellet Maker (Wilks Scientific Corporation, South Norwalk, Conn., Part Number 4032) for one minute.

The mini-press was very convenient for quantitative analysis. The mini-press, containing the pellet, could be placed in the sample beam; after the spectrum had been recorded, the pellet could be removed from

the mini-press and weighed. Since the entire pellet was in the sample beam, the amount of sample in the beam was calculated using the weight and mole ratio of the original sample, assuming that a uniform mixture was achieved when mixing the sample and potassium bromide. At low concentrations this assumption may not be valid since, at low concentrations, sample preparation may result in uneven mixing of the very small amount of sample with the matrix. Pellets prepared from different parts of a low concentration mixture can result in spectra which show large deviations in the individual spectral peak heights.

2. Liquid Solutions

In preparing samples for solution spectra, a small amount of sample (one to four mg) was weighed out, and the appropriate quantity of carbon disulfide was then added using a pipet. The solution was placed in a Barnes leakproof amalgam sealed cell (Barnes Engineering Company, Stamford, Conn.) by using a syringe which locks into the Barnes Universal Holder (Barnes, Part Number 0004-002). Both 8 µl (Barnes, Part Number 0004-671) and 64 µl (Barnes, Part Number 0004-674) cells were used.

3. Mulls

Mulls were prepared by adding six drops of mineral oil (pharmaceutical grade) to a few crystals of sample (2 to 4 mg) which had been ground into a fine powder in a glazed mortar. The mixture was then ground until a uniform dispersion was obtained, then placed between two silver chloride plates in a "mini-cell" (Wilks, Part Number 4041). Consistent sample thickness was difficult to achieve.

4. Attenuated Total Reflectance

The ATR sampling accessory (Wilks, Model 9 Single Beam Internal Reflection Attachment) was first aligned using a Perkin-Elmer 257 Infrared Spectrophotometer. The white light from the source was directed onto the KRS-5 crystal face with a pair of mirrors; a second pair of mirrors was adjusted to transmit a maximum signal. The ATR sampling accessory was then placed in the sample compartment of the FTS-20 spectrometer. A small quantity (0.2 to 0.4 ml) of a solution of the sample in a volatile solvent (acetone) was placed on a KRS-5 internal reflection crystal (Wilks, Part Number 6001). The solvent was allowed to evaporate, leaving a thin coating of sample on the crystal. The crystal was then placed in the ATR sampling accessory and the spectrum was recorded.

CHAPTER III

RESULTS AND DISCUSSION

A. PRELIMINARY STUDIES

Spectra of two PAH in the mid-IR region (3500 to 500 cm^{-1}), shown in Figure 1, indicate the presence of very little information in the region from 3500 to 1500 cm^{-1}. For this reason, the region from 3500 to 1500 cm^{-1} is not shown in most of the spectra presented in this study. The region from 1500 to 500 cm^{-1}, which contains the most useful analytical information for PAH, will be the region of primary interest.

Spectral data for this study were generally collected by scanning the sample and reference 100 times. A comparison of two spectra collected at a resolution of 1.0 cm^{-1}, one using 100 scans and requiring 28 minutes, and one using 5000 scans and requiring approximately 1400 minutes, shows no significant differences between the two spectra (Figure 2). In an enlargement of two regions of the spectra, from 1500 to 1200 cm^{-1} (Figure 3) and from 900 to 600 cm^{-1} (Figure 4), it can be seen that no significant enhancement of the signal-to-noise ratio was produced by averaging 5000 scans. Spectra collected using less than 100 scans show higher noise levels, which decrease as the number of scans approaches 100. It was concluded that, in terms of time required versus improvement in the signal-to-noise ratio, the average of 100 scans yields the most satisfactory results; many additional scans resulted in no detectable improvement in the spectra. The reason(s) for the

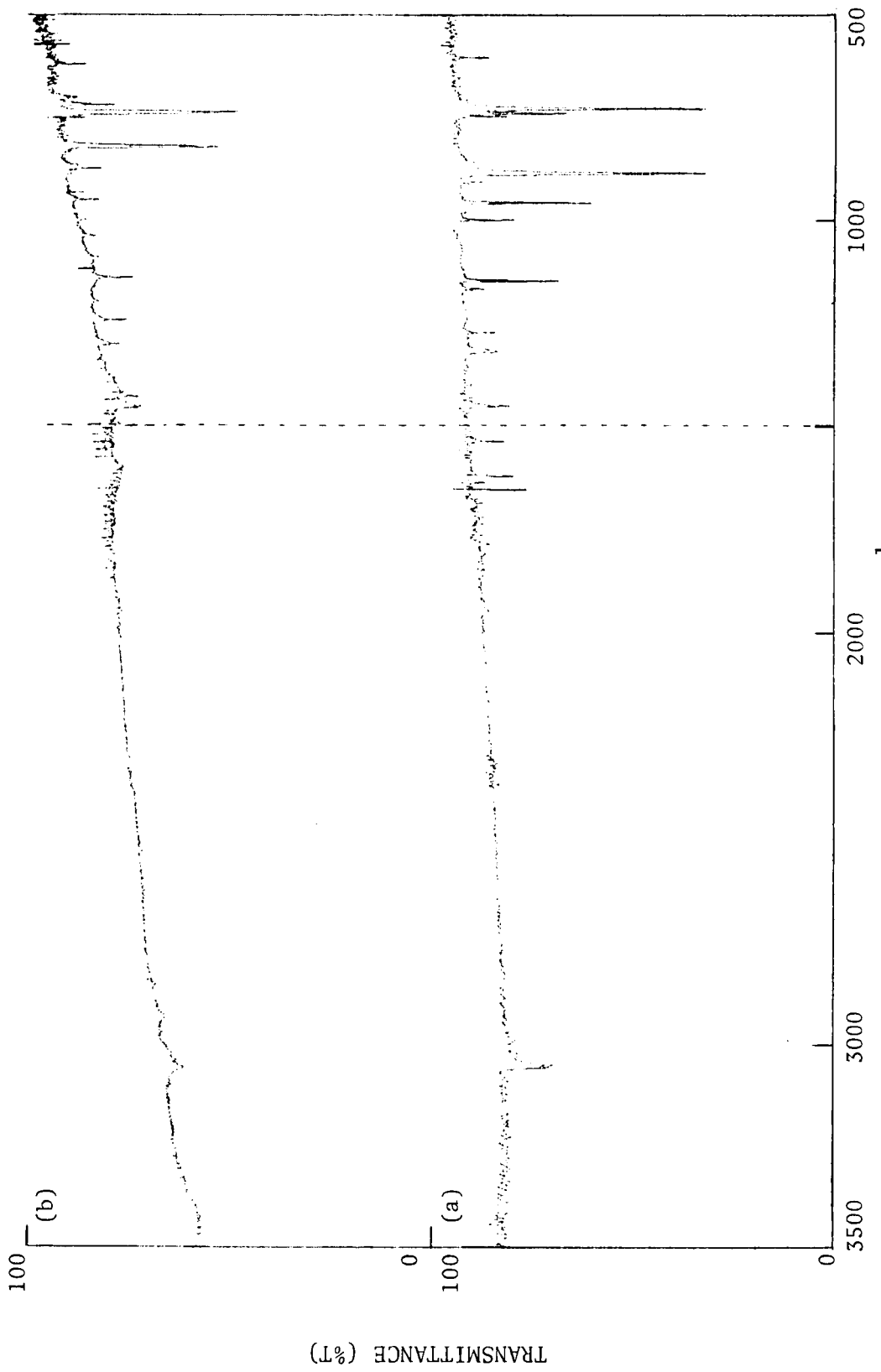


Figure 1. FT-IR spectra of (a) anthracene and (b) phenanthrene in KBr.

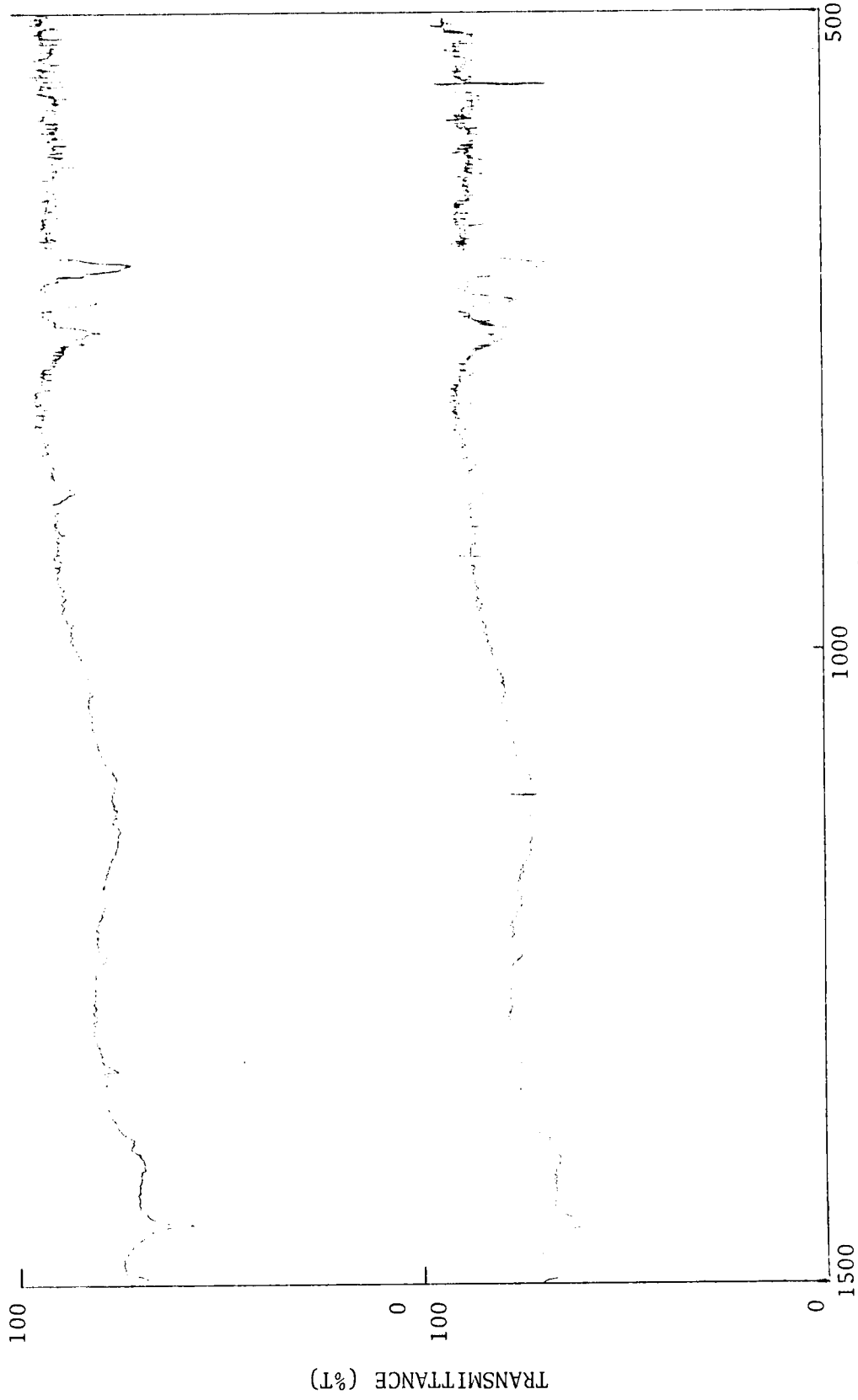


Figure 2. FT-IR spectra of carbazole in KBr at (a) 100 scans and (b) 5000 scans (1500 to 500 cm^{-1}).

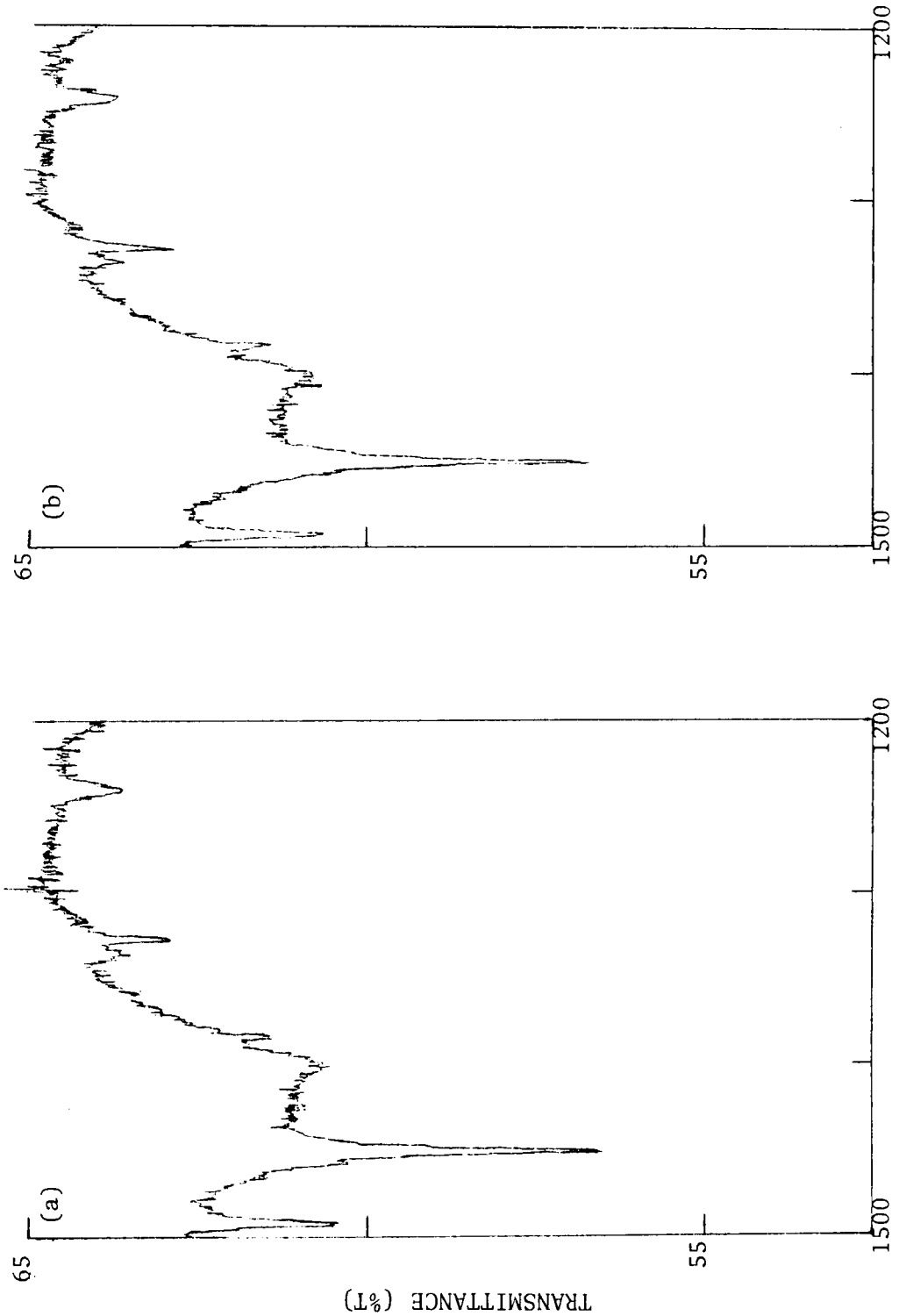


Figure 3. FT-IR spectra of carbazole in KBr at (a) 100 scans and (b) 5000 scans (1500 to 1200 cm^{-1}).

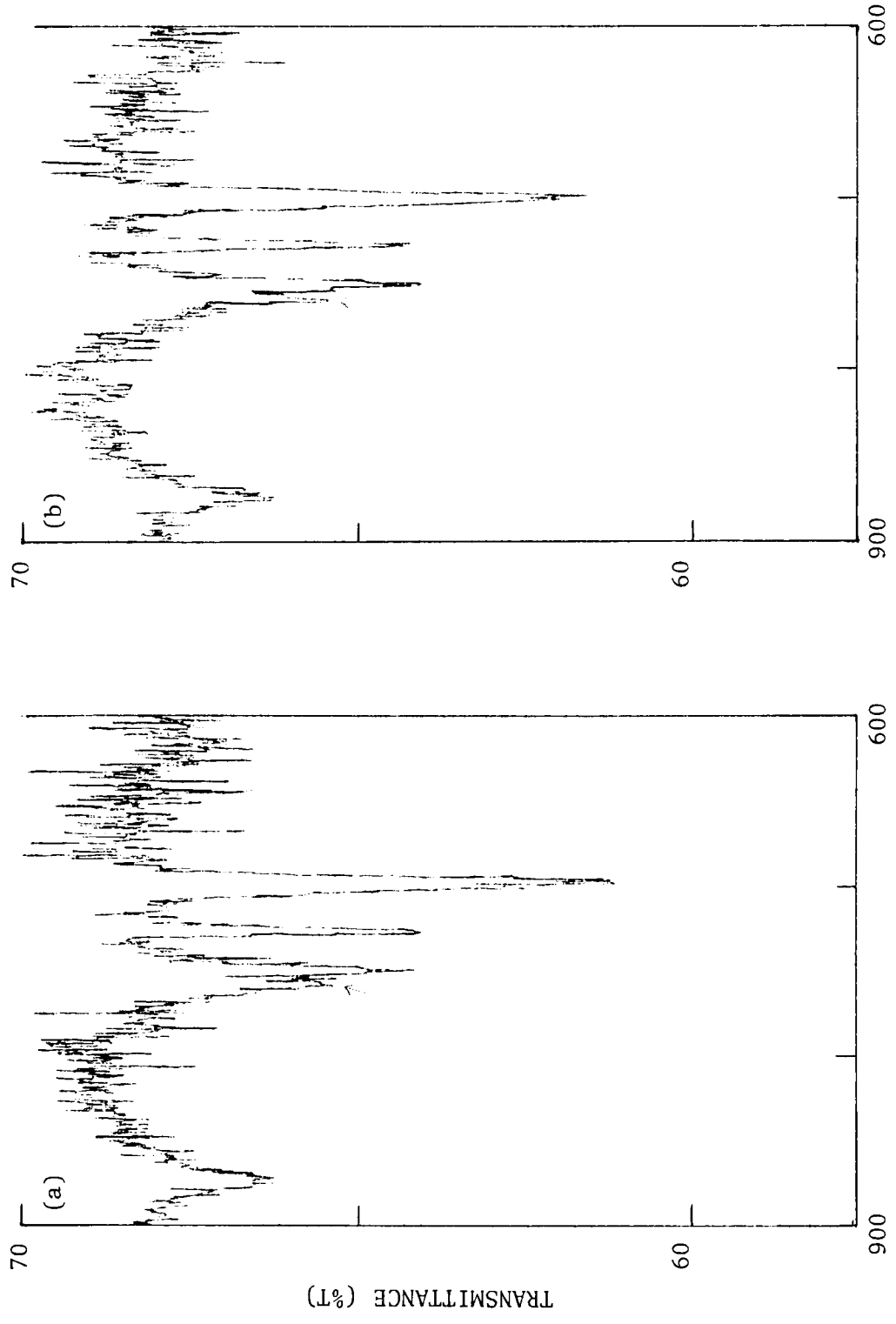


Figure 4. FT-IR spectra of carbazole in KBr at (a) 100 scans and (b) 5000 scans (900 to 600 cm^{-1}).

departure of these data from conventional "signal averaging" theory is unclear.

Figures 5 and 6 show spectra of anthracene at resolutions of 1.0 and 2.0 cm^{-1}, respectively. There are no major differences in the relative peak intensities (small narrow spikes, such as the ones appearing at 570 and 752 cm^{-1} in Figure 5, begin to appear at resolutions higher than 2.0 cm^{-1} and require additional signal averaging to eliminate), and the bandwidths at half maximum are 4.5 to 5.0 cm^{-1} for the major bands at 727 and 884 cm^{-1} in both spectra. It was, therefore, concluded that 2.0 cm^{-1} resolution was normally adequate for the purposes of this study.

B. QUALITATIVE STUDIES

1. Potassium Bromide (KBr) Pellets

A spectrum of each of six PAH (anthracene, phenanthrene, pyrene, chrysene, benzo (a) pyrene, and carbazole) was recorded using a 1:1000 mole ratio of PAH to KBr (about 1.0×10^{-6} moles of PAH per pellet). The six spectra are shown in Figures 6 through 11. A list of the absorption bands of each compound in KBr between 1500 and 500 cm^{-1} is given in Table I. Each compound exhibits strong absorption bands in the region between 700 and 900 cm^{-1}.

A mixture containing 2 mg of each of four PAH (anthracene, phenanthrene, pyrene, and carbazole) was prepared. A spectrum of a 1:1000 gram ratio of this mixture to KBr (a 1:6000 mole ratio for anthracene and phenanthrene, 1:7000 mole ratio for pyrene, and 1:5600

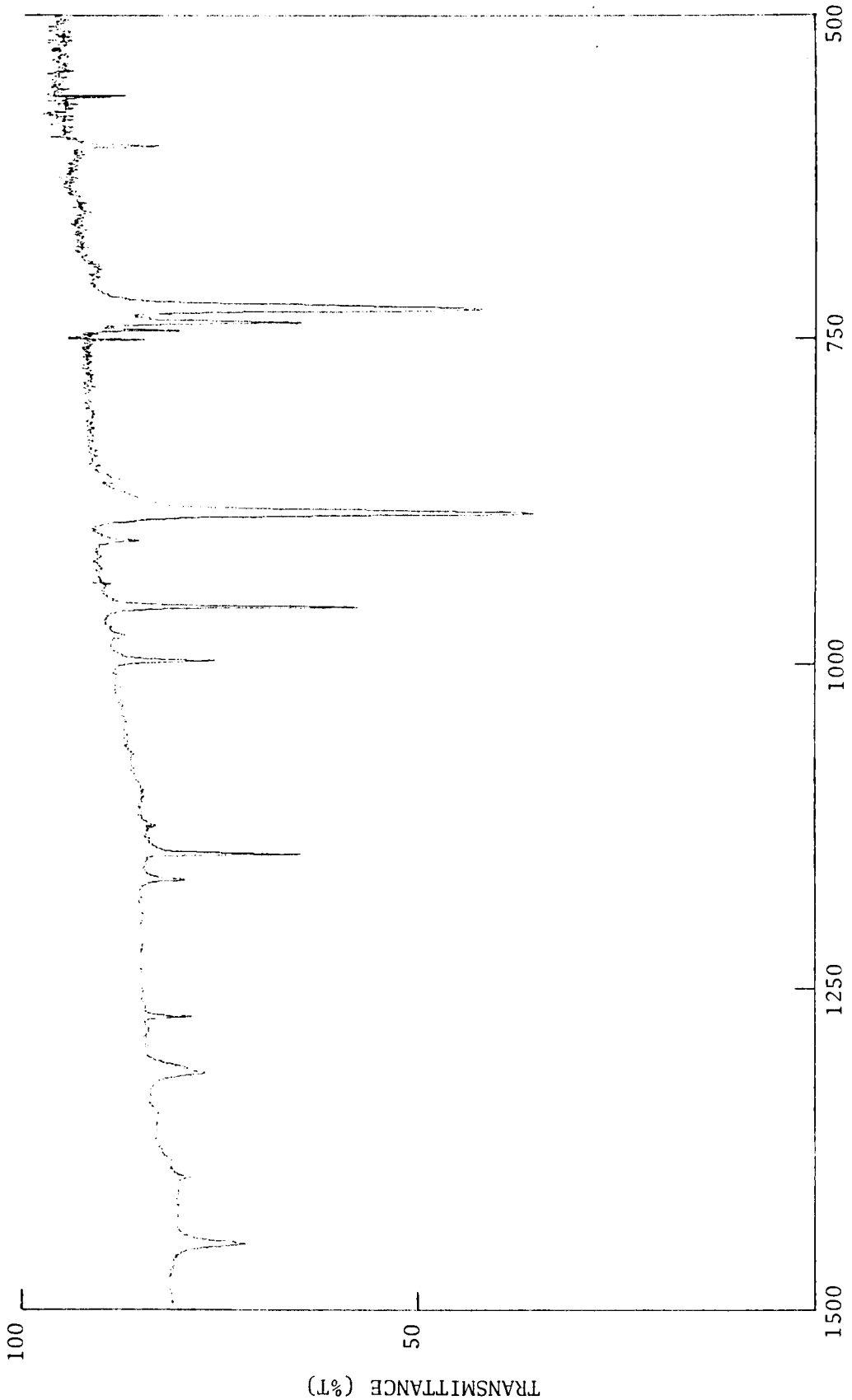


Figure 5. FT-IR spectrum of anthracene in KBr using 1.0 cm^{-1} resolution.

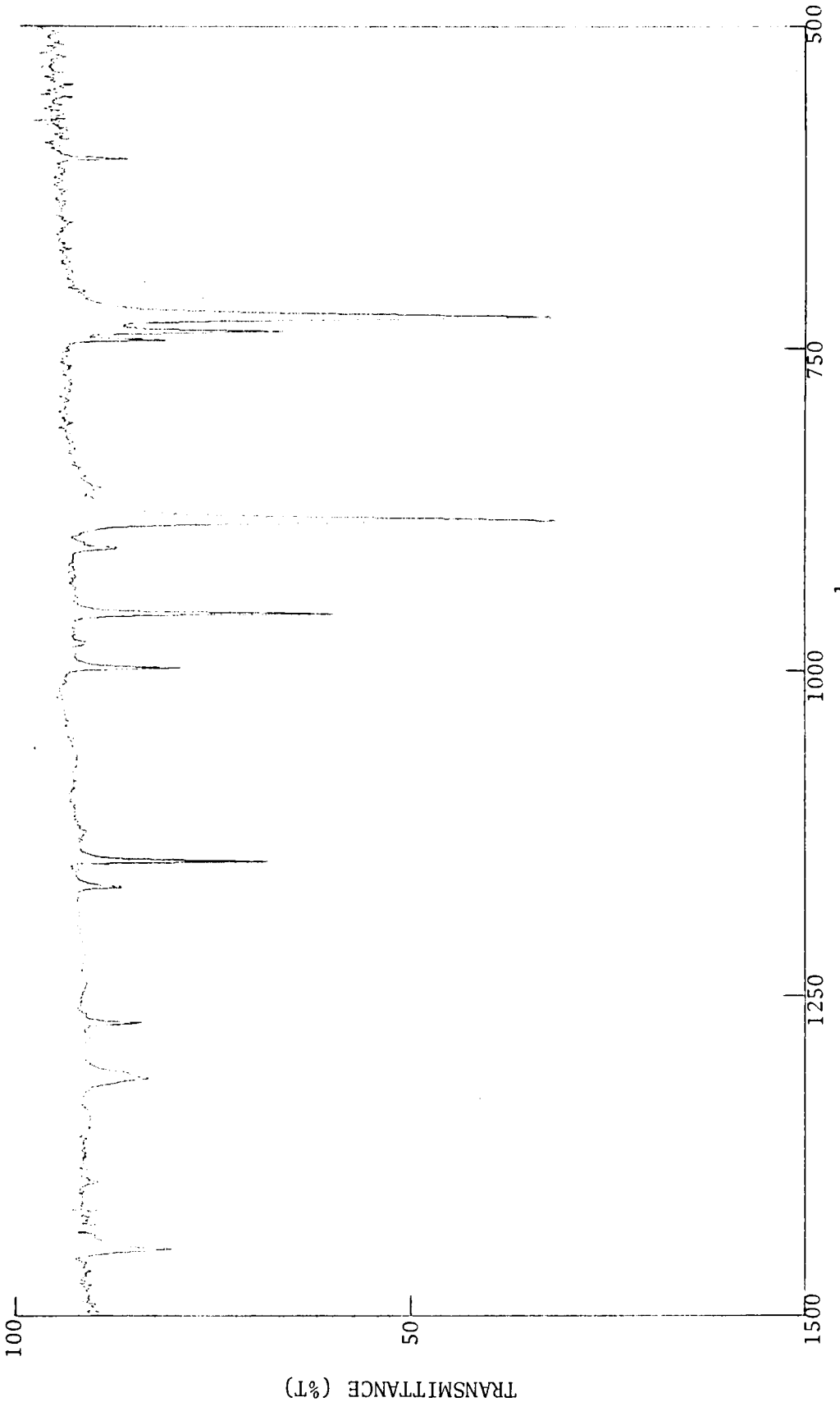


Figure 6. FT-IR spectrum of anthracene in KBr 2.0 cm^{-1} resolution.

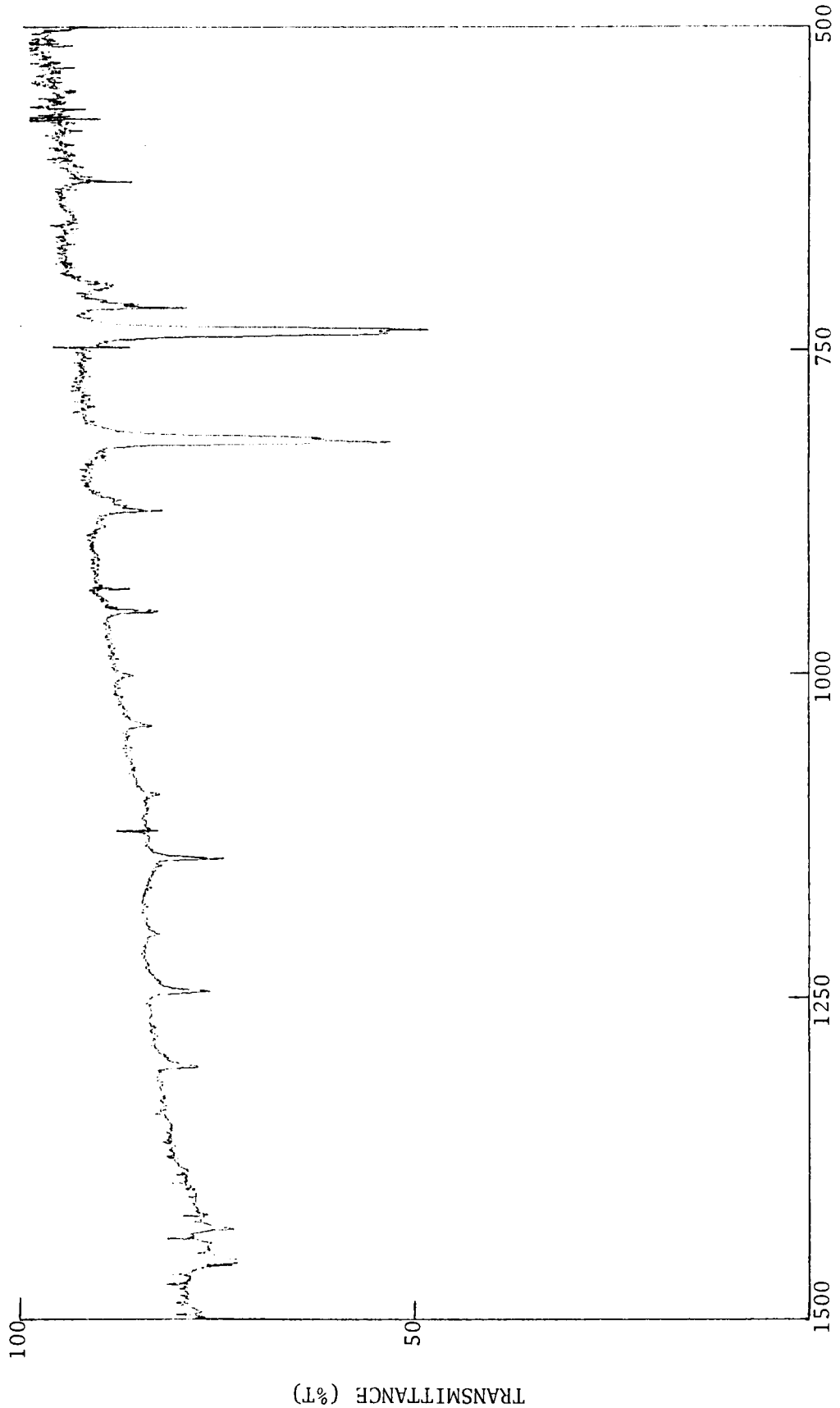


Figure 7. FT-IR spectrum of phenanthrene in KBr.

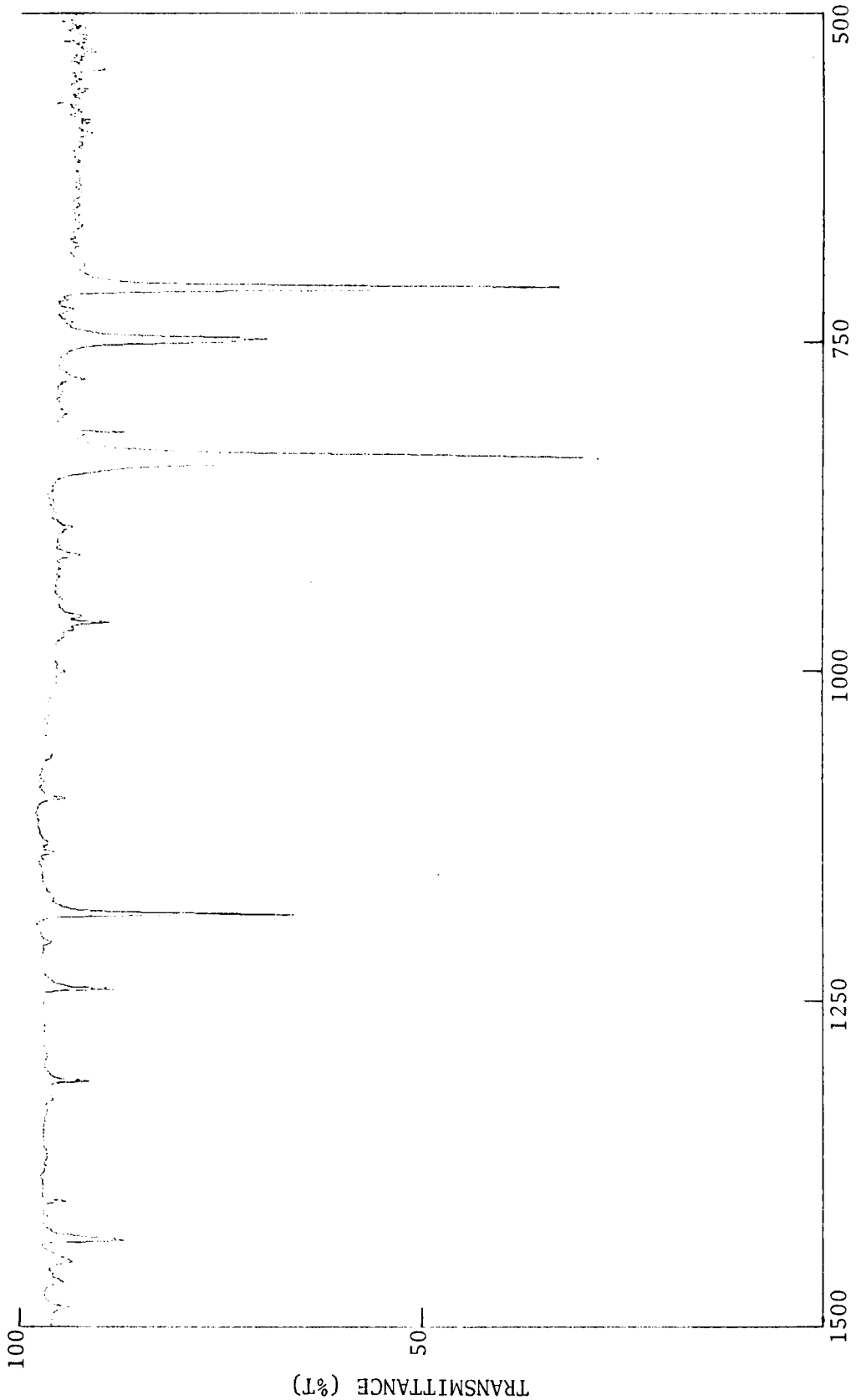


Figure 8. FT-IR spectrum of pyrene in KBr.

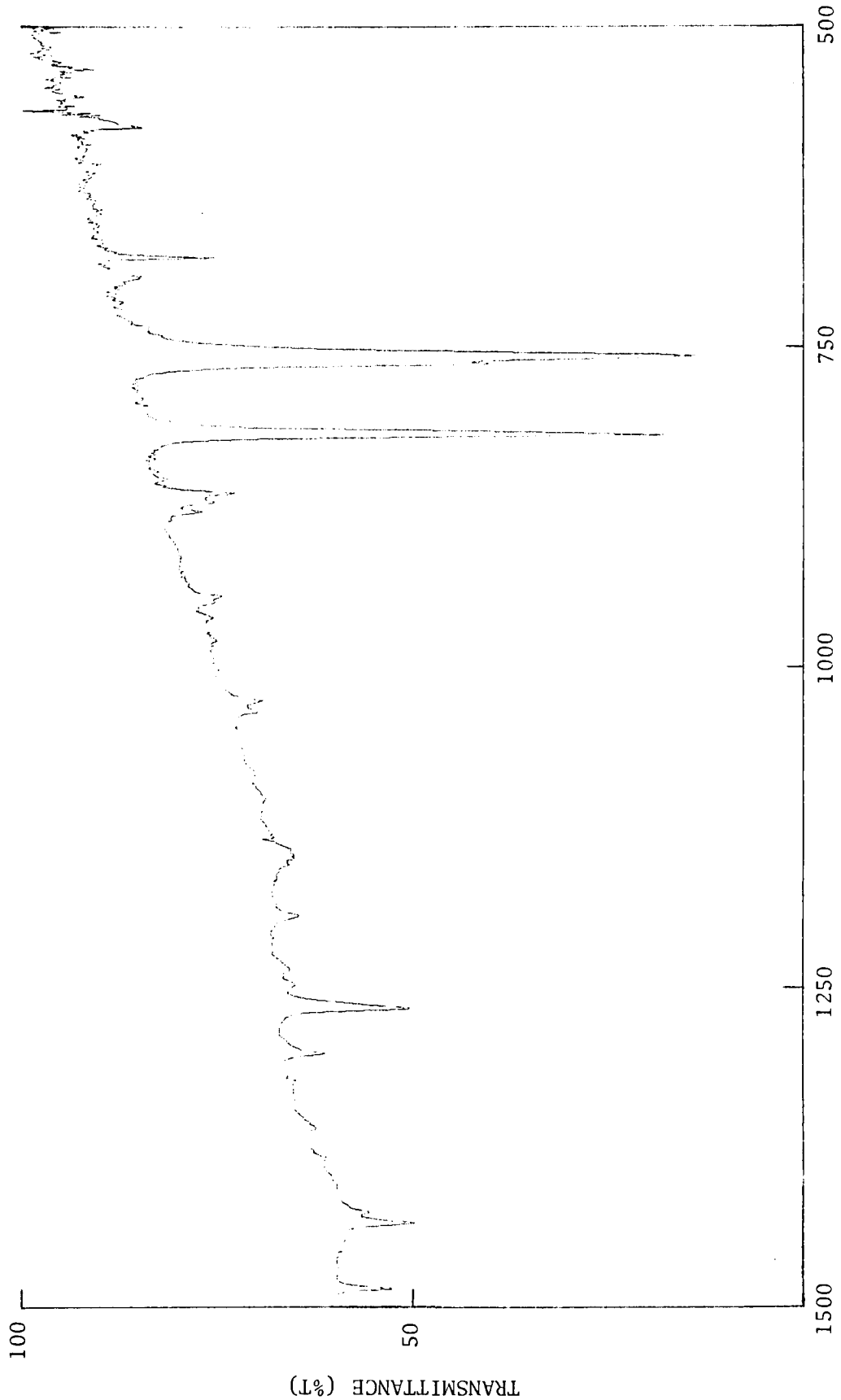


Figure 9. FT-IR spectrum of chrysene in KBr.

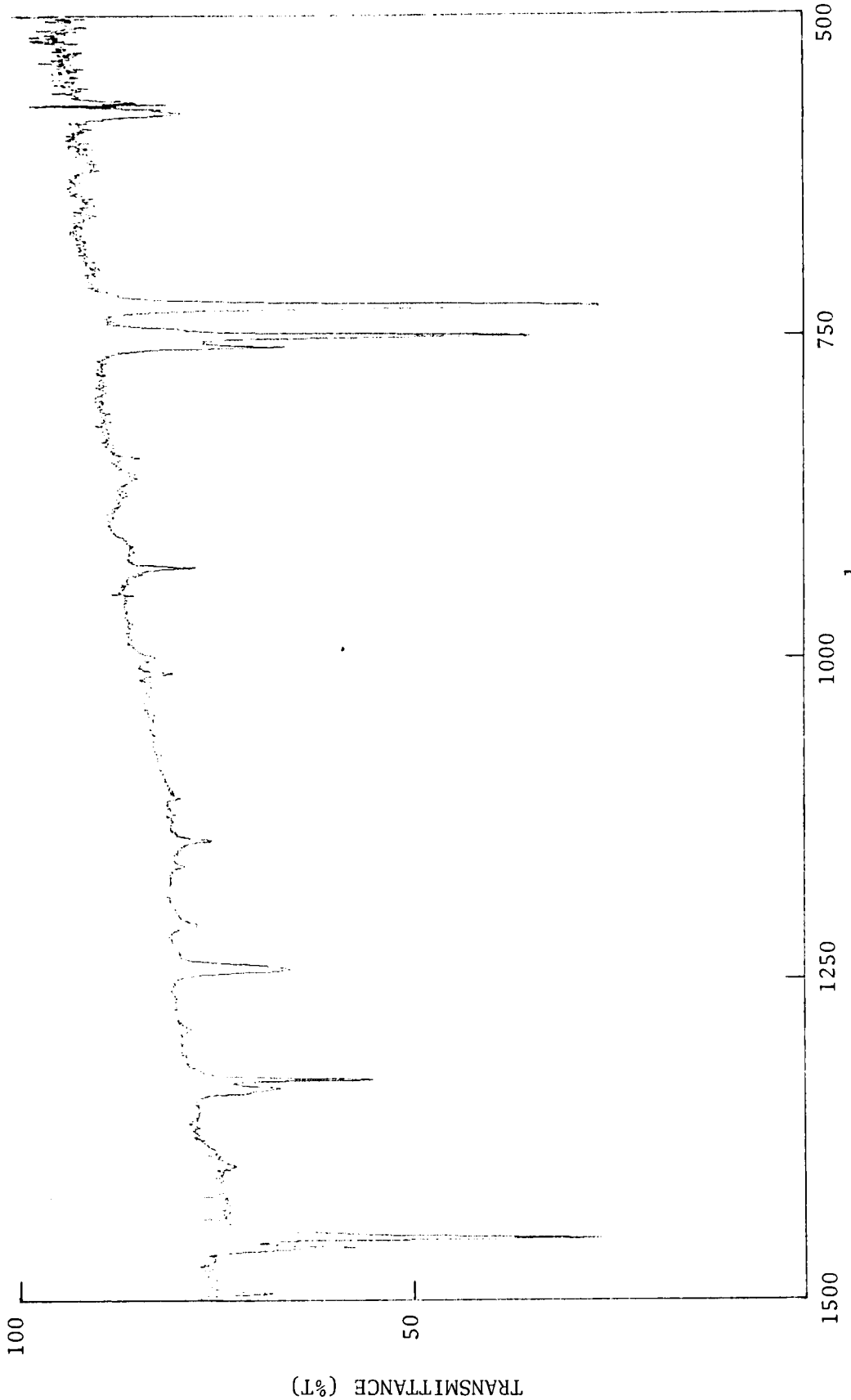


Figure 11. FT-IR spectrum of carbazole in KBr.

TABLE I

BANDS PRESENT BETWEEN 1500 AND 500 cm^{-1} FOR PAH
IN KBr (1 TO 1000 MOLE RATIO)

PAH	Band Positions (cm^{-1})								
Phenanthrene	617	715	819	948	1038		1244	1302	1429
		732	872	999					1455
			885						
Anthracene	602	727	884	957		1148	1273	1323	1449
		738		998					
		744							
Pyrene		709	840			1185	1242	1313	1434
		748							
Carbazole	575	726	843	928	1010	1140	1206	1328	1451
		748				1161	1240	1334	1458
		757						1390	1494
Chrysene		757	818				1264		1434
Benzo (a) Pyrene	689	742	823						
		756	837						
		762	848						
			875						

mole ratio for carbazole) was recorded (Figure 12). The bands in this spectrum were easily assigned to the respective PAH using the frequency maxima from the reference PAH spectra (Table I). Bands from different PAH which contributed to a single band in the mixture are indicated in Figure 12.

In the mixture spectrum, the region between 760 and 725 cm^{-1} contains a number of bands for different constituents which are difficult or impossible to resolve. For example, the carbazole and anthracene bands at 726 and 727 cm^{-1}, respectively, are indistinguishable at a resolution of 2.0 cm^{-1}, and the resulting band overlaps with the phenanthrene band located at 732 cm^{-1}. A spectrum of the same mixture was recorded averaging 100 spectra at 0.5 cm^{-1} resolution and the region between 900 and 600 cm^{-1} was compared with that observed in the 2.0 cm^{-1} resolution spectrum (Figure 13). There is very little additional separation of bands at 0.5 cm^{-1} resolution.

Two-component mixtures of anthracene (1:800 mole ratio in KBr), with carbazole (1:750 mole ratio in KBr) and phenanthrene (1:800 mole ratio in KBr), respectively, were prepared to determine if the peaks in the 732 to 726 cm^{-1} region could be distinguished in simpler mixtures at 2.0 cm^{-1} resolution. For each spectrum, the region from 900 to 600 cm^{-1} is shown in Figure 14. The carbazole and anthracene bands at 726 and 727 cm^{-1}, respectively, appear as one band; all other bands are well resolved. The phenanthrene band at 732 cm^{-1} falls between the two anthracene bands at 727 and 738 cm^{-1}; the resulting overlapped band is very broad. It is concluded that the broad band at 727 cm^{-1} in the

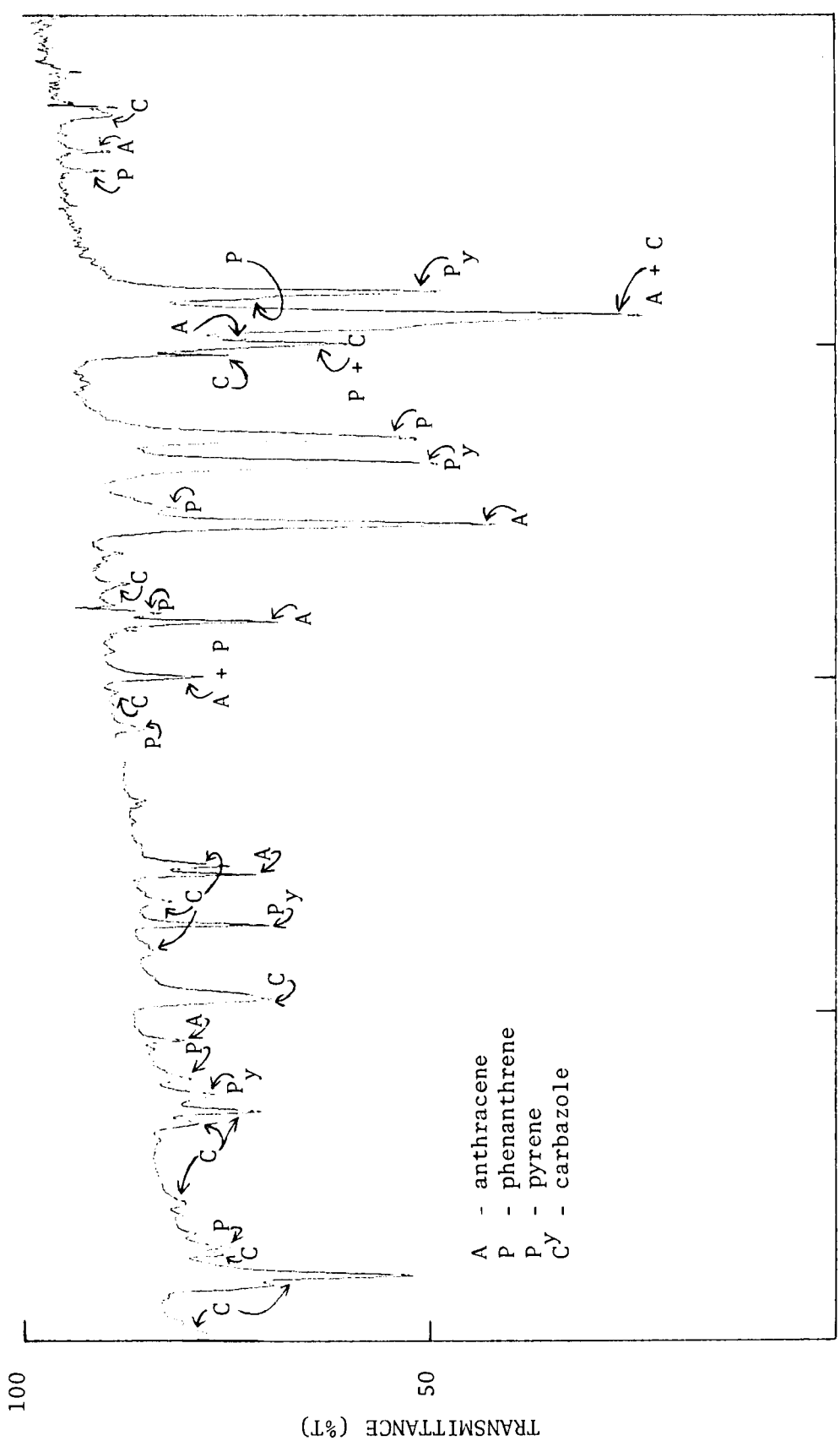


Figure 12. FT-IR spectrum of anthracene, phenanthrene, pyrene, and carbazole mixture in KBr.

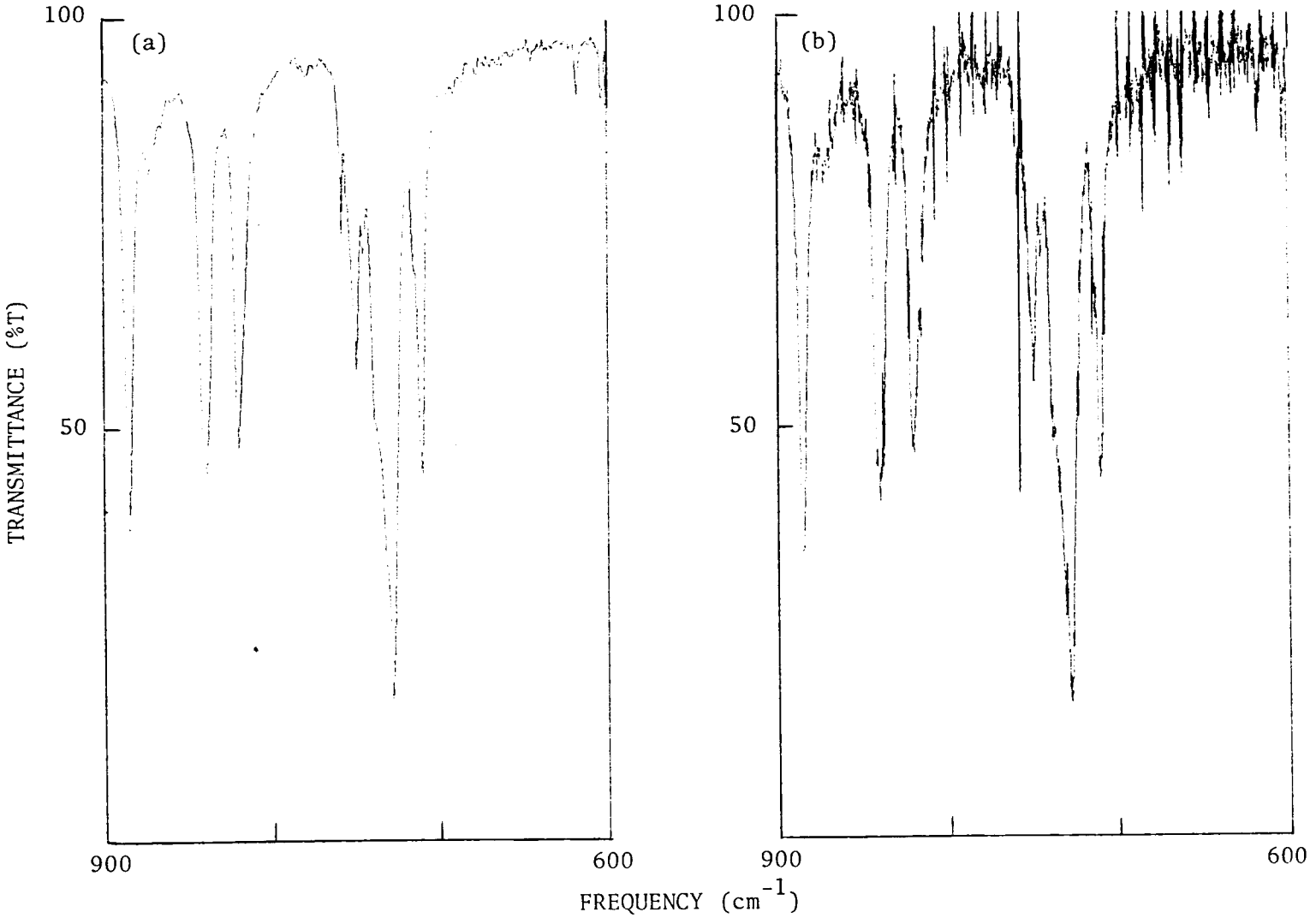


Figure 13. FT-IR spectra of anthracene, phenanthrene, pyrene, and carbazole mixture in KBr at a resolution of (a) 2.0 cm^{-1} and (b) 0.5 cm^{-1}.

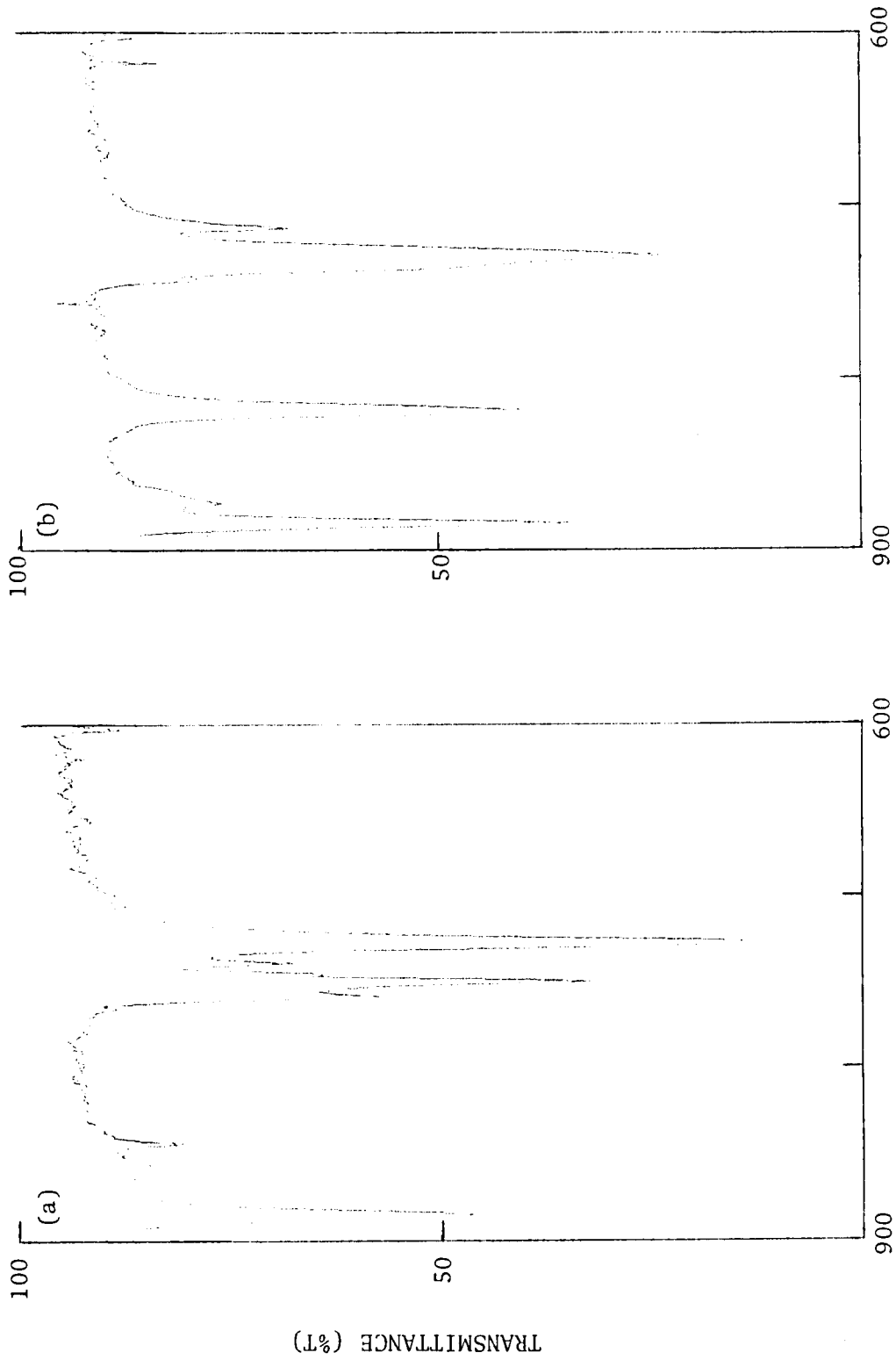


Figure 14. FT-IR spectra of (a) anthracene-carbazole and (b) anthracene-phenanthrene mixtures in KBr.

four-component mixture spectrum (Figure 12, page 30) actually consists of four bands, the 732 cm^{-1} phenanthrene band, the 726 cm^{-1} carbazole band, and the 727 and 738 cm^{-1} anthracene bands, and that these bands cannot be resolved, even at a resolution of 0.5 cm^{-1}.

Even though all bands between 760 and 725 cm^{-1} cannot be separated and assigned to specific sample constituents, all components of the mixture can be identified from other bands present in the 1500 to 500 cm^{-1} region. However, introduction of additional bands into the spectrum by attempting to study more complex mixtures will cause increased difficulty in positive identification of the bands of the various PAH present.

2. Liquid Solutions

A spectrum of each of six PAH was recorded using a 5.7×10^{-3} M solution of PAH in carbon disulfide (CS_2). The spectra, recorded in an 8 µl cell, are shown in Figures 15 through 20. The absorption bands of each compound in CS_2 in the 1400 to 500 cm^{-1} region are listed in Table II (a strong absorption band of CS_2 obscures the region from 1500 to 1440 cm^{-1}). Only the stronger bands are observed in each spectrum, due to the small quantity of each PAH employed (4.6×10^{-8} moles). Nevertheless, each of the compounds exhibits at least one band between 760 and 725 cm^{-1}. The most noticeable difference between the solution and KBr spectra, for any individual compound, is the absence of the two weaker bands at 738 and 744 cm^{-1} in the anthracene solution spectrum. The wavenumber positions of bands of each compound are shifted from

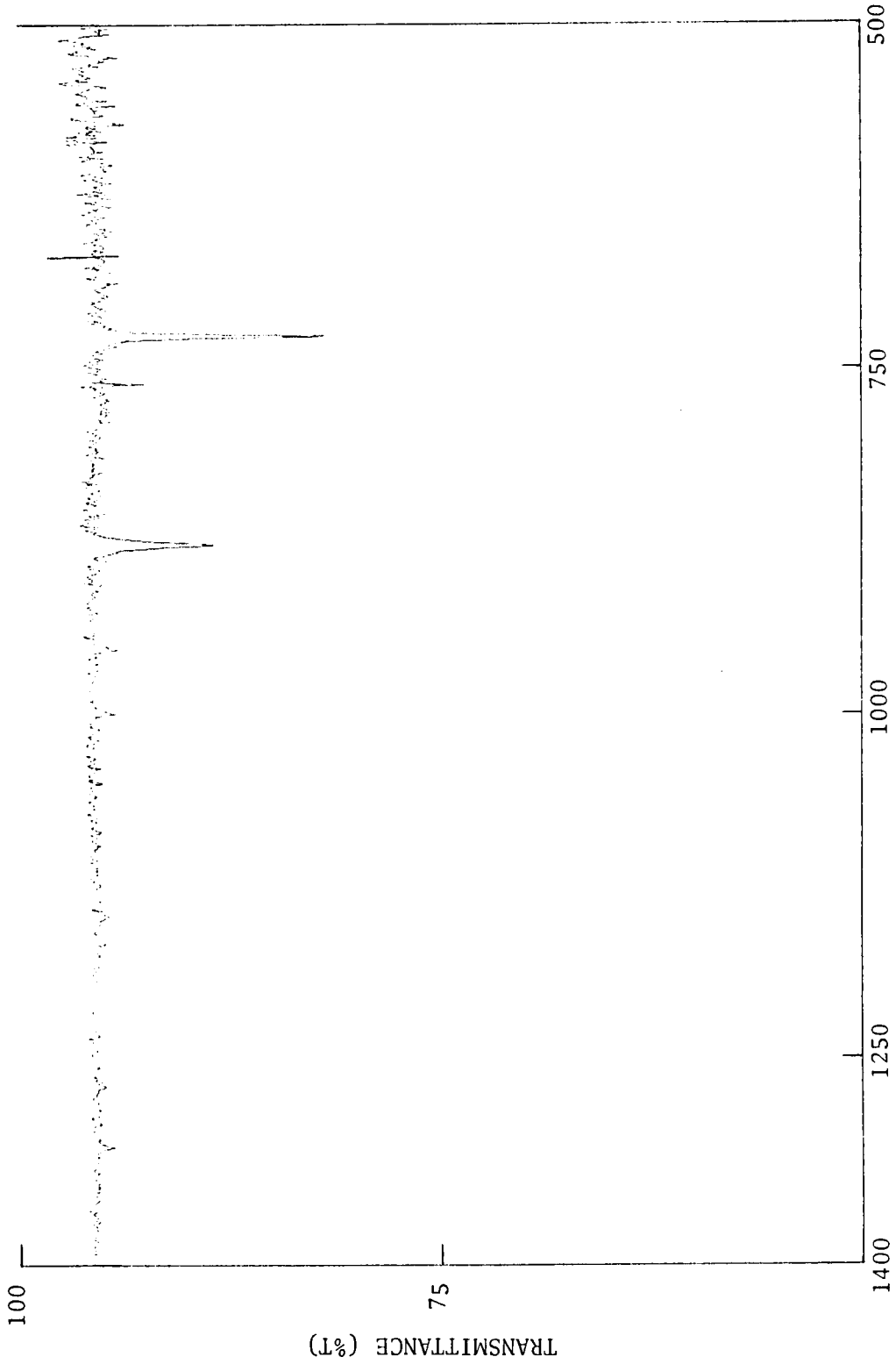


Figure 15. FT-IR spectrum of anthracene (5.7 × 10^{-3} M)in CS_2.

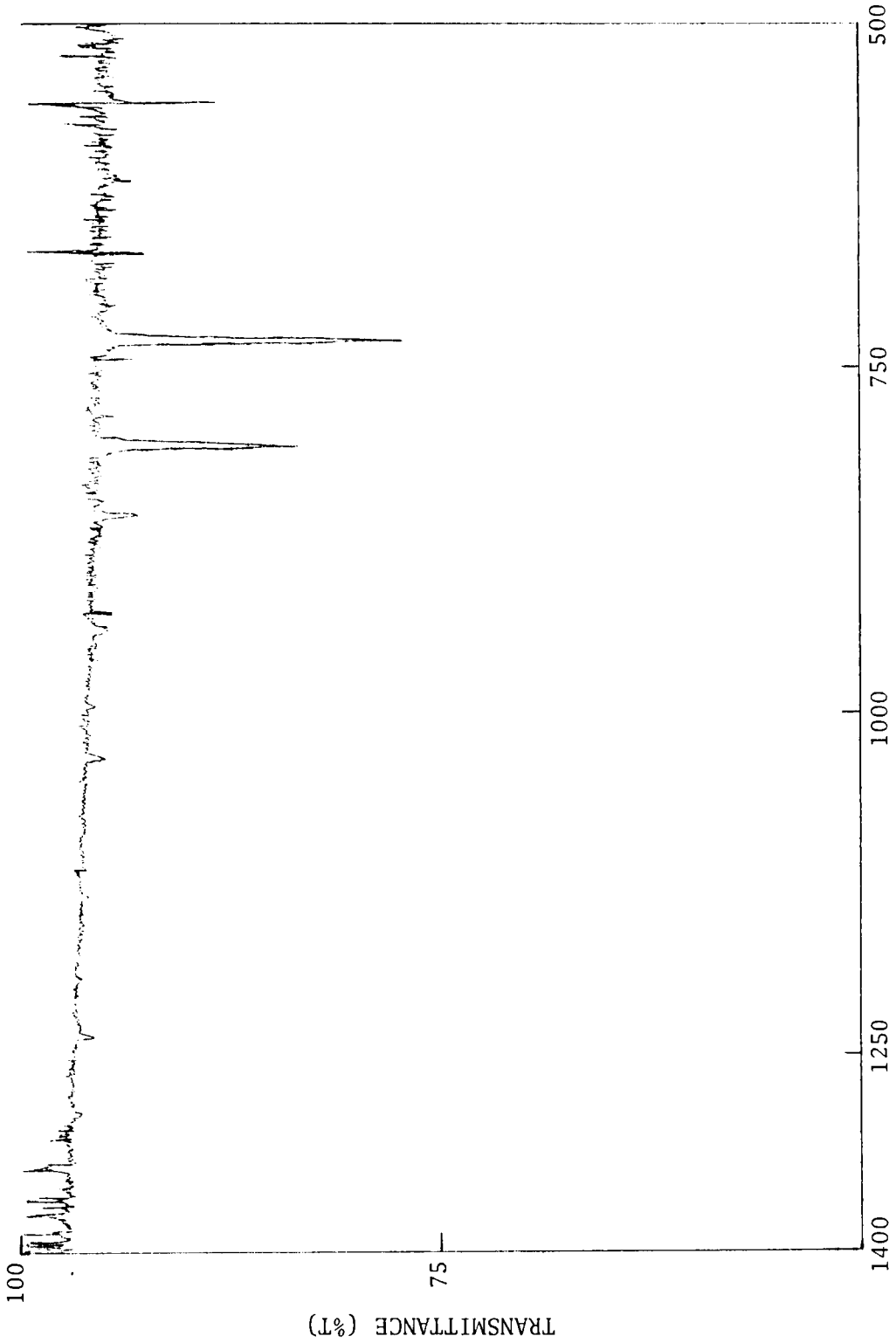


Figure 16. FT-IR spectrum of phenanthrene (5.7 × 10^{-3} M)in CS_2.

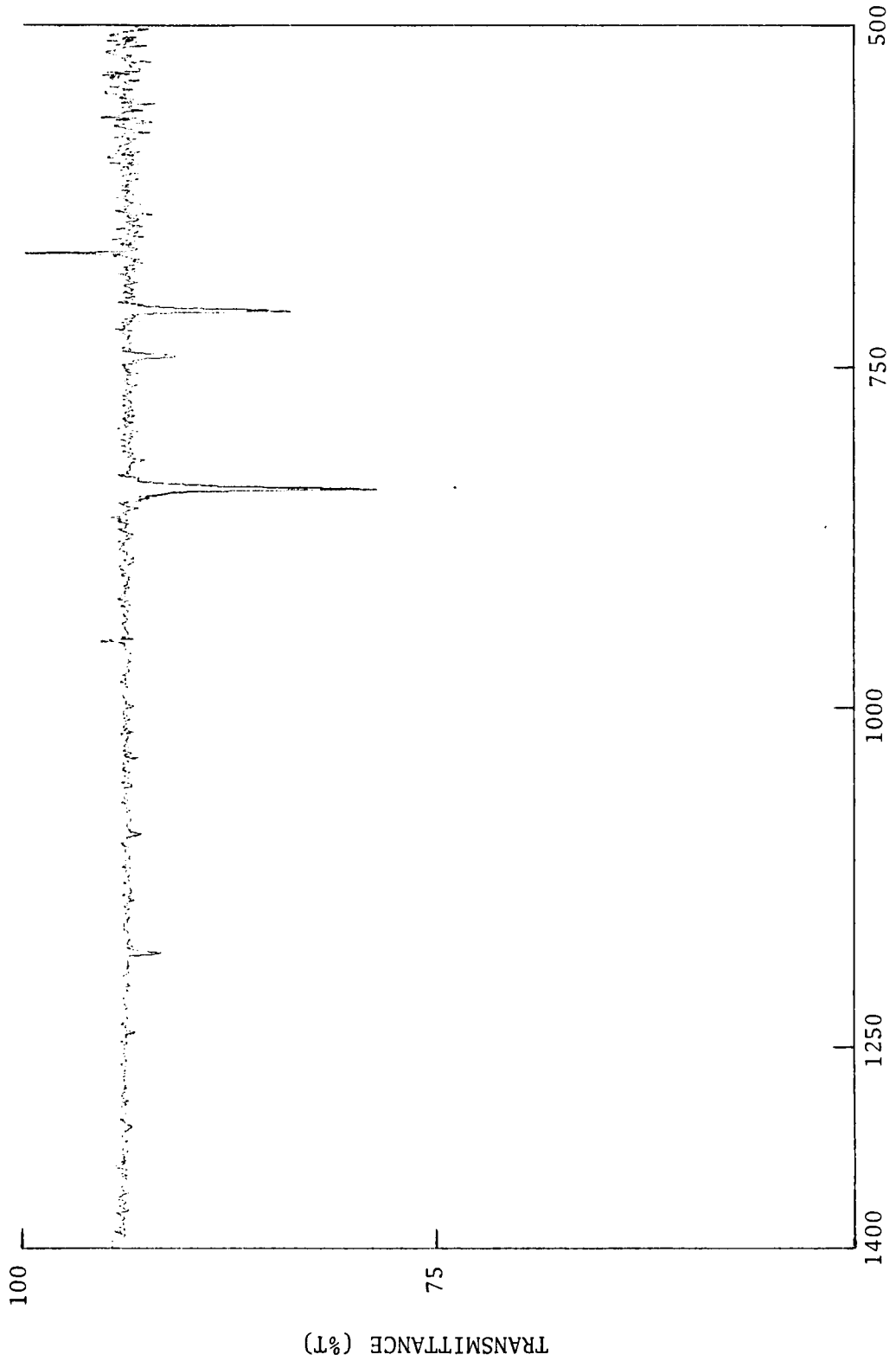


Figure 17. FT-IR spectrum of pyrene (5.7×10^{-3} M) in CS_2.

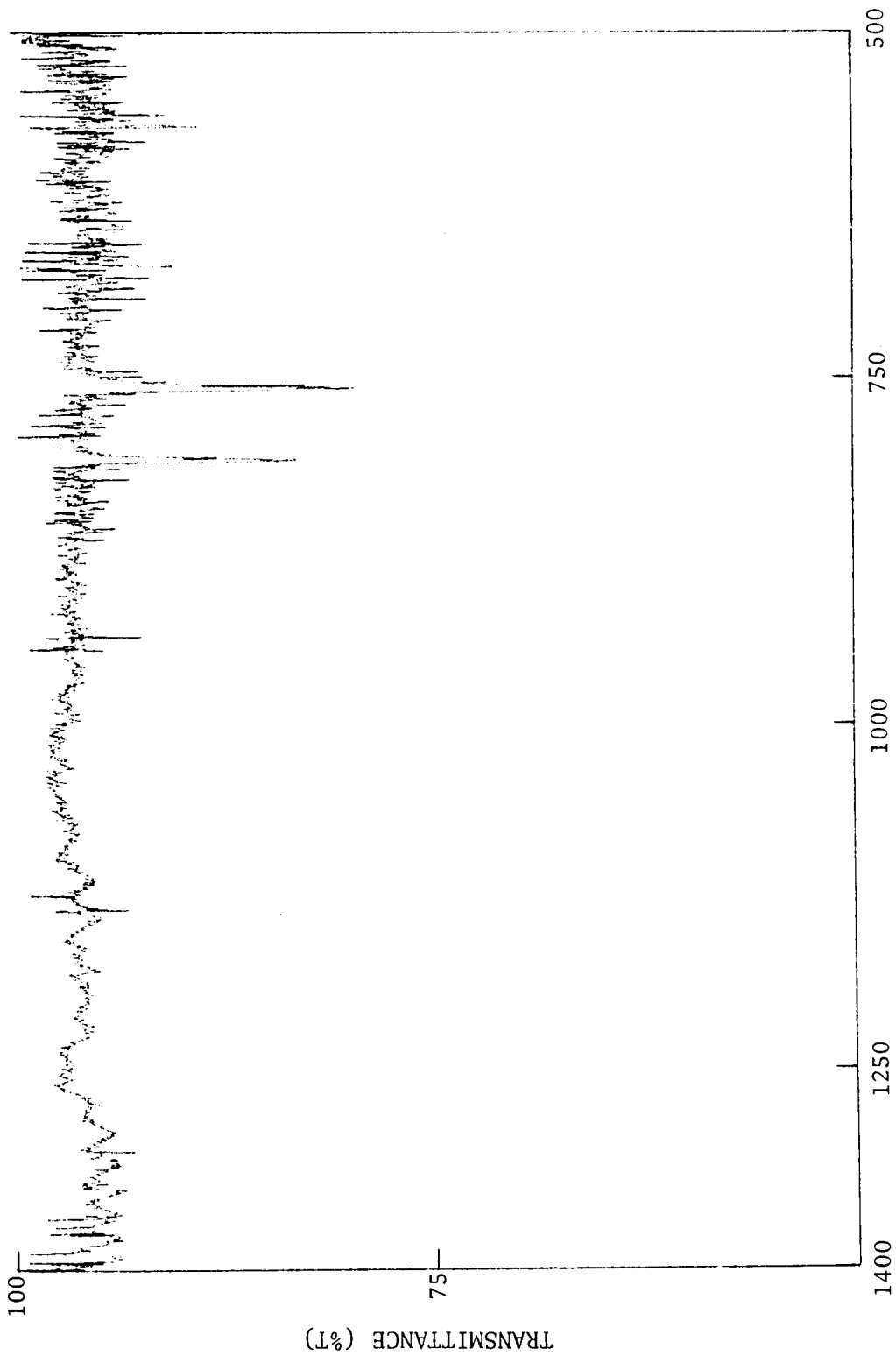


Figure 18. FT-IR spectrum of chrysene (5.7×10^{-3} M) in CS_2.

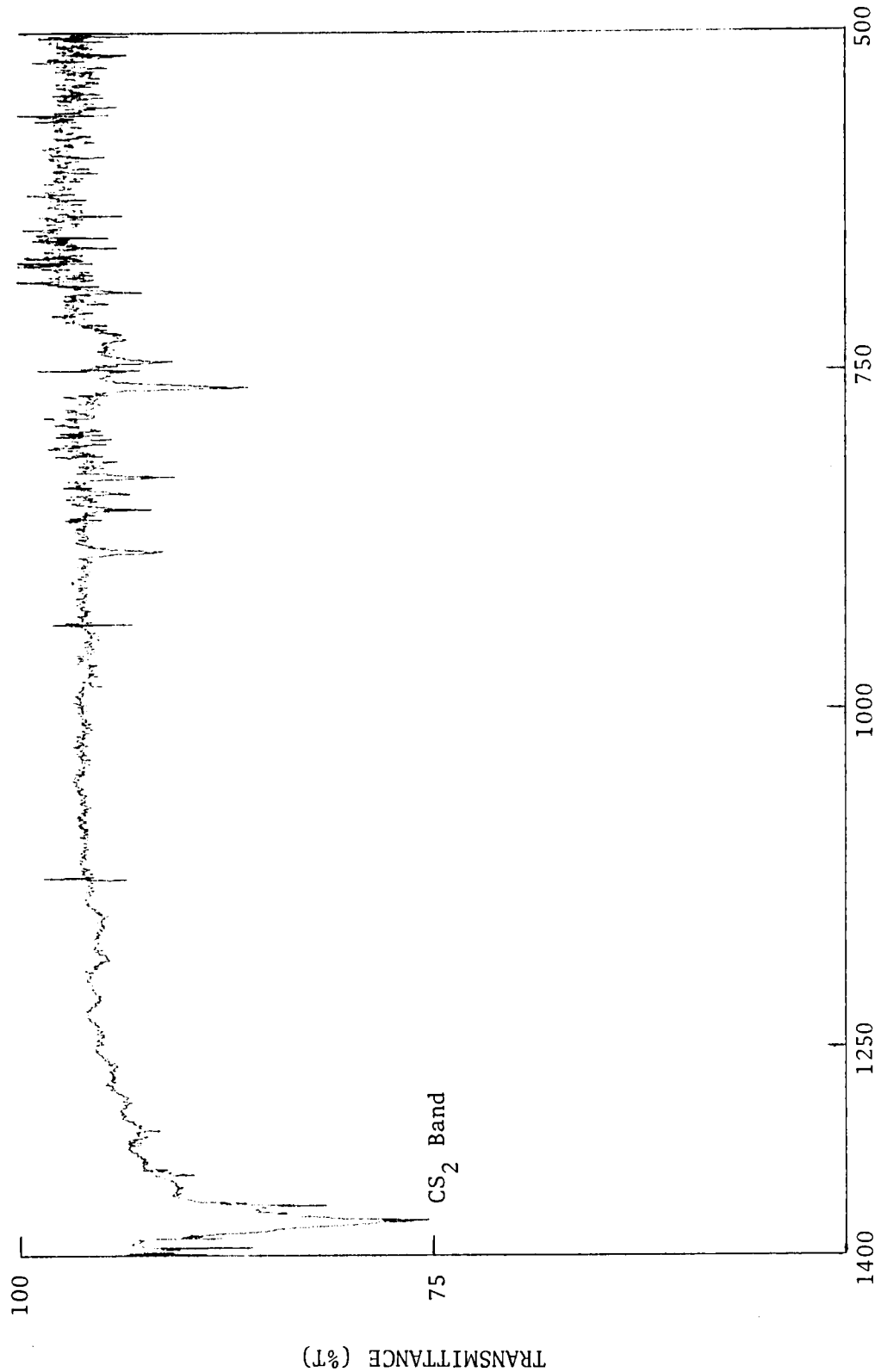


Figure 19. FT-IR spectrum of benzo (a) pyrene (5.7×10^{-3} M) in CS_2.

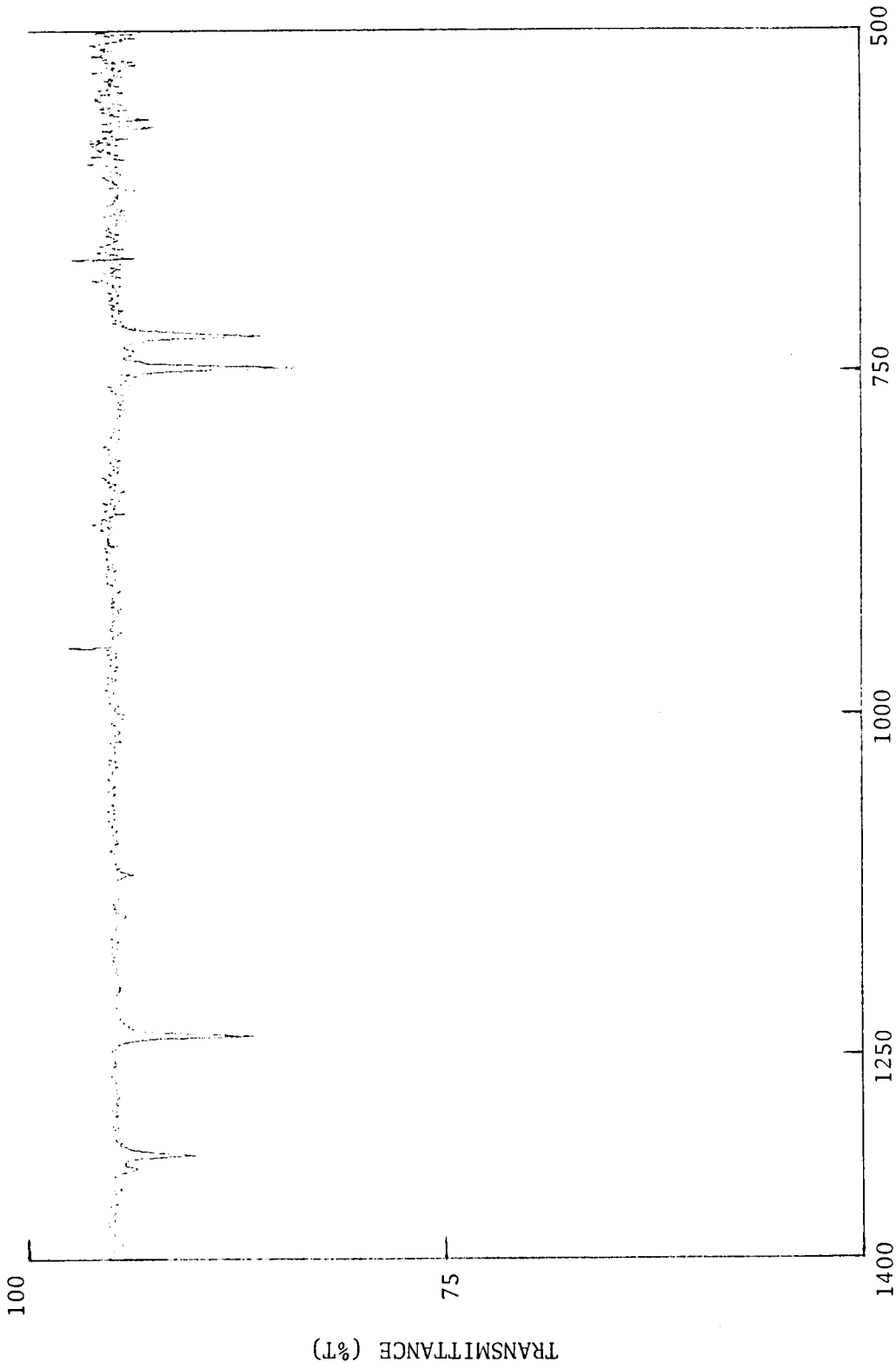


Figure 20. FT-IR spectrum of carbazole (5.7×10^{-3} M) in CS_2.

TABLE II

BANDS PRESENT BETWEEN 1400 AND 500 cm^{-1} FOR SIX PAH IN CS_2 LIQUID SOLUTION (5.7×10^{-3} M)

PAH	Band Positions (cm^{-1})				
Phenanthrene	734	811			
Anthracene	726	878			
Pyrene	711 744	841	1182		
Carbazole	725 747			1237	1324
Chrysene	758	811			
Benzo (a) Pyrene	688 741 747 759	822 837 880			

1 to 6 cm^{-1} with respect to the peak locations in the KBr spectra; shifts to both higher and lower frequencies (with respect to peak positions in KBr) are noted.

A spectrum of the same mixture of four PAH (anthracene, phenanthrene, pyrene, and carbazole), in equal amounts as used in the KBr studies, is shown in Figure 21, using 2.5×10^{-2} g of mixture dissolved in 5 ml CS_2 (7.0×10^{-3} M in anthracene and phenanthrene, 7.5×10^{-3} M in carbazole, and 6.2×10^{-3} M in pyrene). All bands in the spectrum can be assigned by matching peaks with the reference spectra, except the broad band at 725 cm^{-1}. The bands of anthracene and carbazole at 726 and 725 cm^{-1}, respectively, are again not resolved. The phenanthrene band at 734 cm^{-1} is easily resolved from the anthracene-carbazole band at 726 cm^{-1}, because the two weaker anthracene bands, observed in KBr, are absent and the phenanthrene band has shifted (2 cm^{-1}) to higher frequencies in the CS_2 solution.

Thus, all components of the mixture can be identified and only two bands could not be resolved. More complex mixtures, which add additional bands in the 760 to 725 cm^{-1} region, would make identification of individual components more difficult.

3. Attenuated Total Reflectance (ATR)

Spectra of anthracene and phenanthrene were recorded using an ATR apparatus; the spectra are shown in Figures 22 and 23. A deposit containing 2.3×10^{-7} moles of each PAH was used. The spectra are very similar to those obtained in a KBr matrix. The bandwidths at half

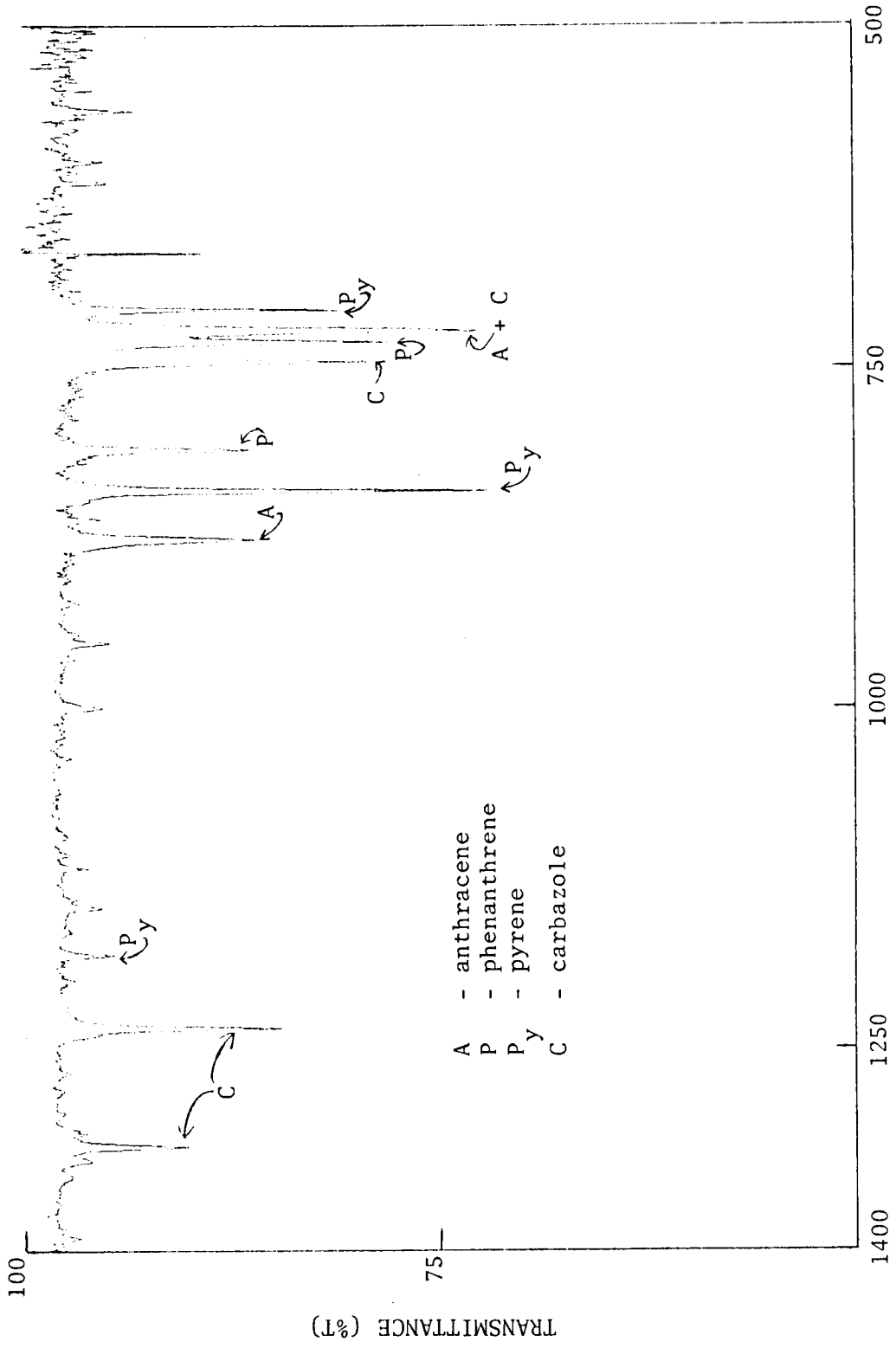


Figure 21. FT-IR spectrum of anthracene, phenanthrene, pyrene, and carbazole mixture in CS_2.

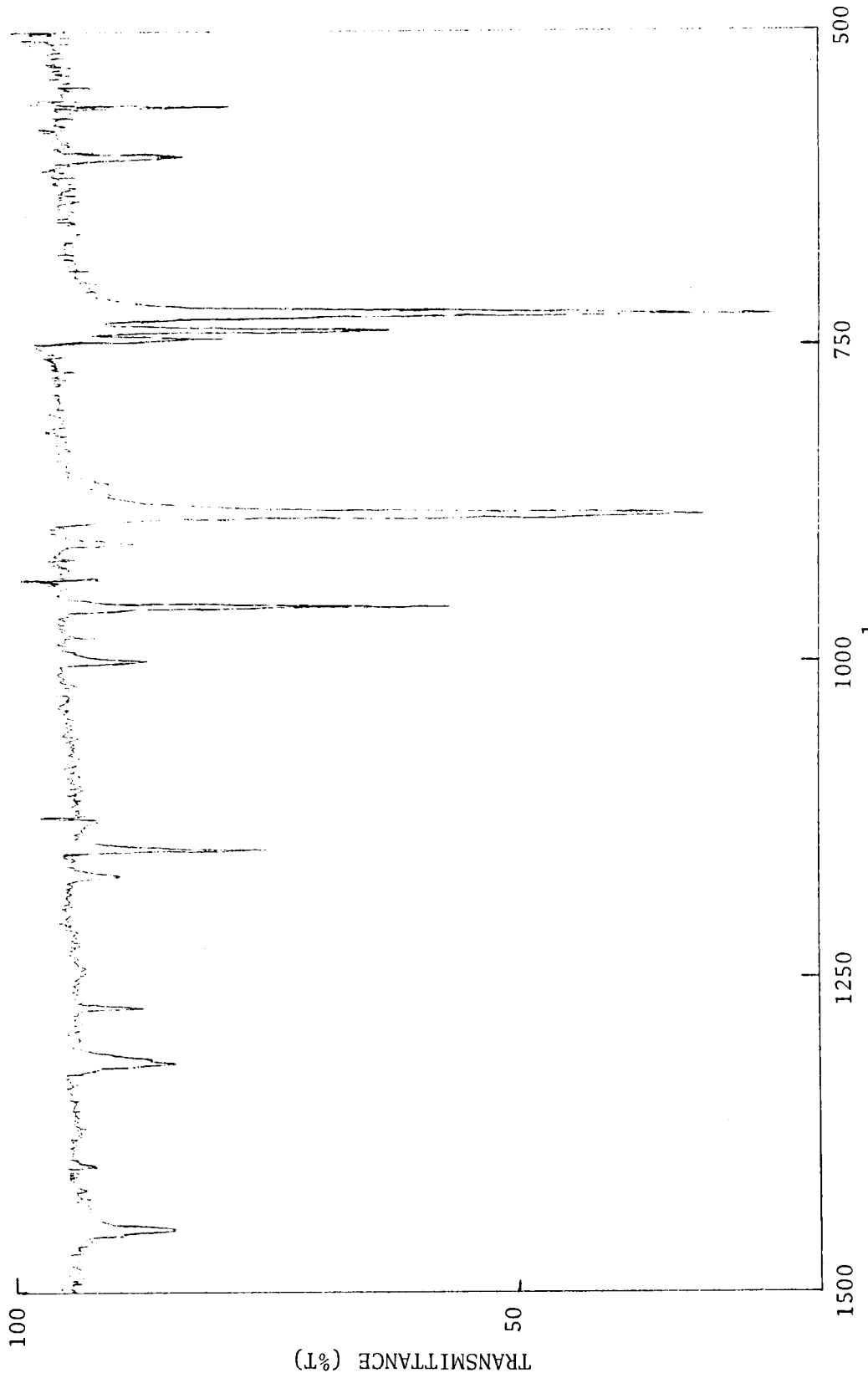


Figure 22. FT-IR spectrum of anthracene using ATR.

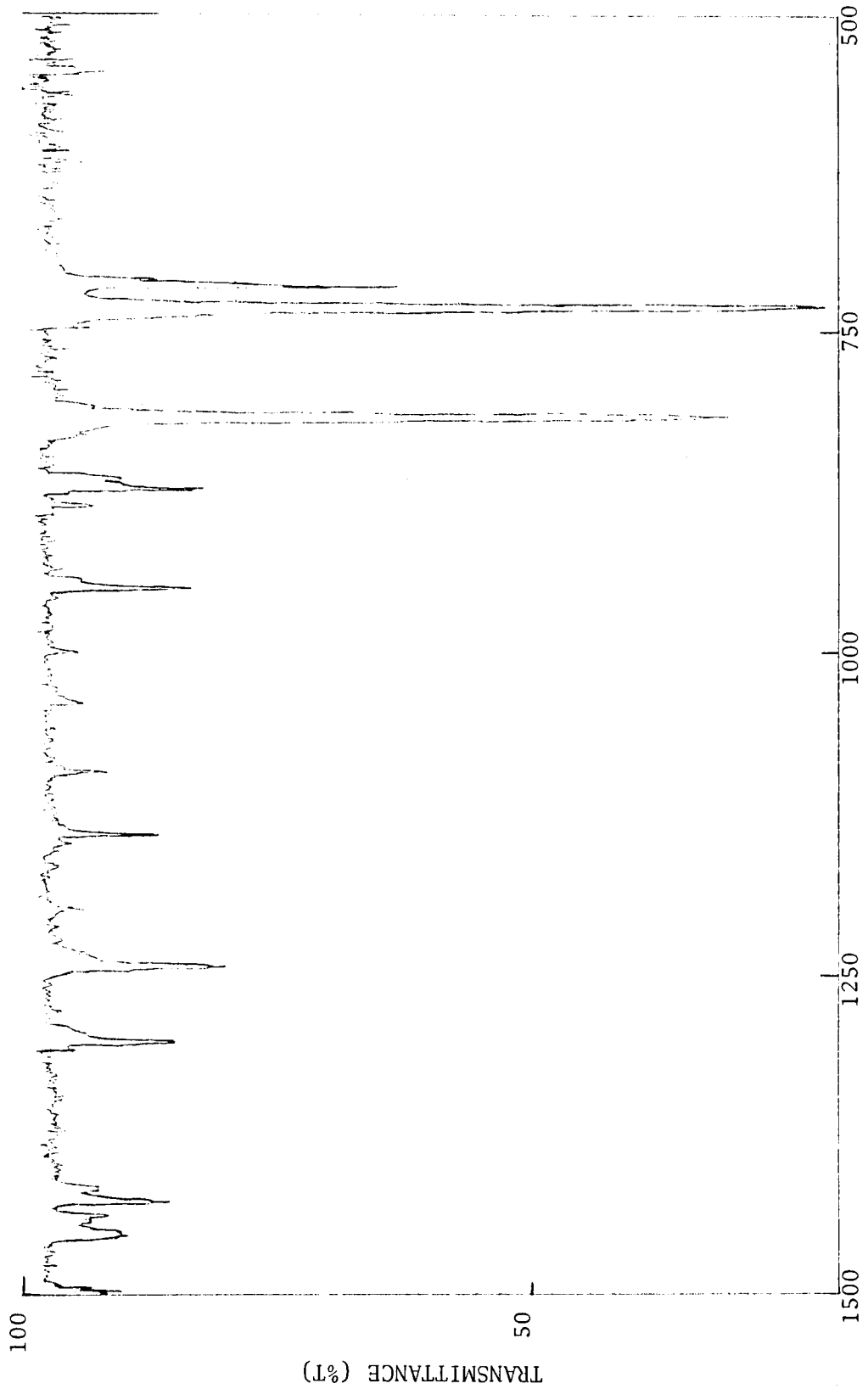


Figure 23. FT-IR spectrum of phenanthrene using ATR.

maximum are 3 to 4 cm^{-1} for anthracene; the two weaker bands at 738 and 744 cm^{-1} observed in KBr pellets but not in liquid solutions are present in the ATR spectra. The positions of the peaks are also the same as in the KBr spectra. It should be noted that, using ATR, the entire sample deposit is observed by the spectrometer; using KBr pellets, the amount of sample in the pellet actually observed is difficult to determine.

An ATR spectrum of a mixture of phenanthrene and anthracene (Figure 24), using a resolution of 2.0 cm^{-1}, shows that the three anthracene bands at 726, 738, and 744 cm^{-1} and the phenanthrene band at 734 cm^{-1} have coalesced to form one broad band, as was also observed in KBr.

4. Mulls

Spectra of anthracene and phenanthrene were recorded in a mineral-oil mull (Figures 25 and 26). The spectra are of poor quality and bands from the mineral-oil matrix (strong broad bands at 1440, 1375, and 723 cm^{-1}, and weaker broad bands at 1300, 1160, 1020, and 980 cm^{-1}) obscure some PAH bands. The intensities of the mineral-oil bands are so great as to make their subtraction from the spectrum difficult without simultaneously eliminating some of the bands of the PAH.

C. QUANTITATIVE STUDIES

1. Reproducibility

A set of ten spectra (each spectrum was an average of 100 spectra) at 2.0 cm^{-1} resolution, using the same KBr pellet (1:600 mole ratio of

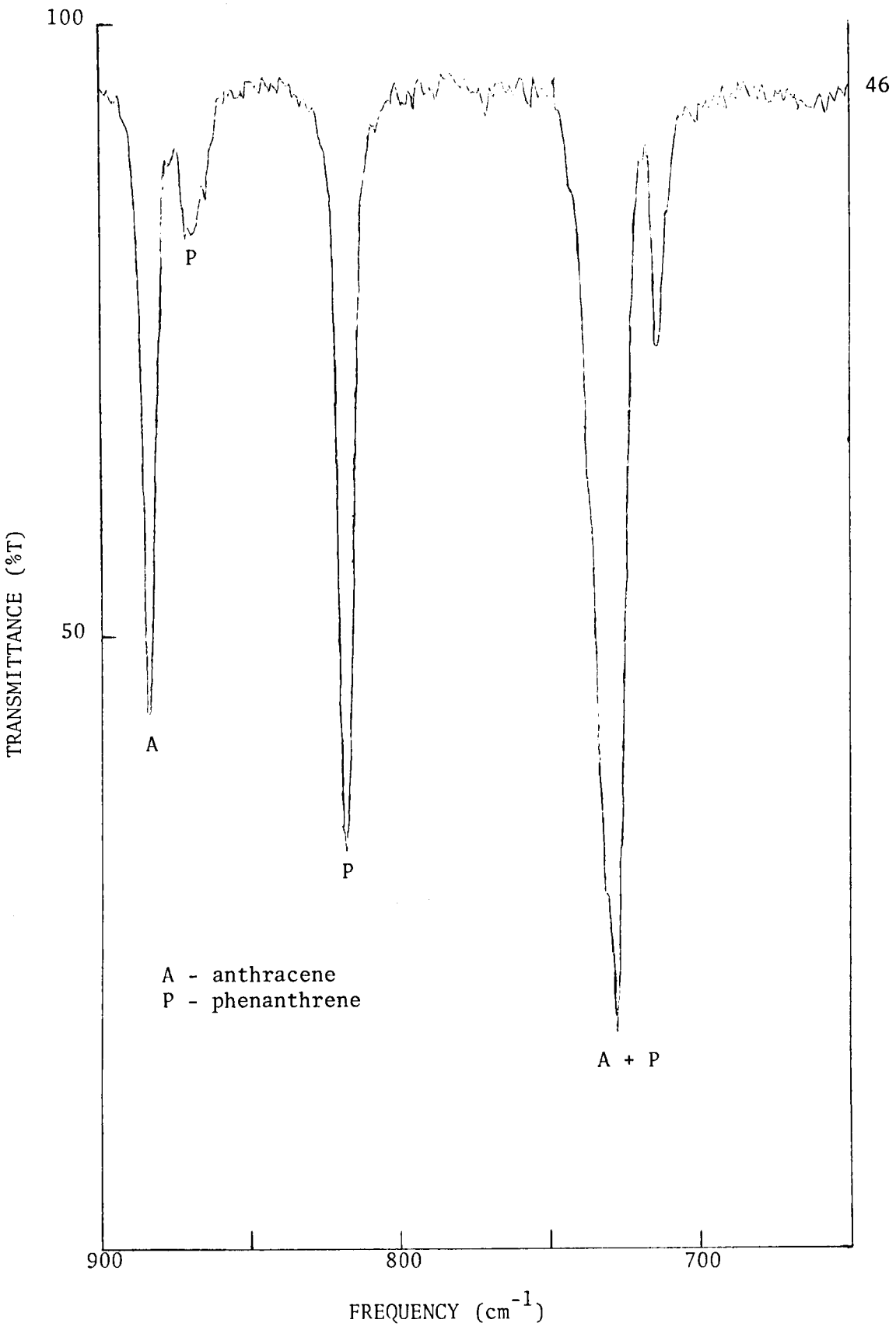


Figure 24. FT-IR spectrum of anthracene and phenanthrene mixture using ATR at 2.0 cm^{-1} resolution.

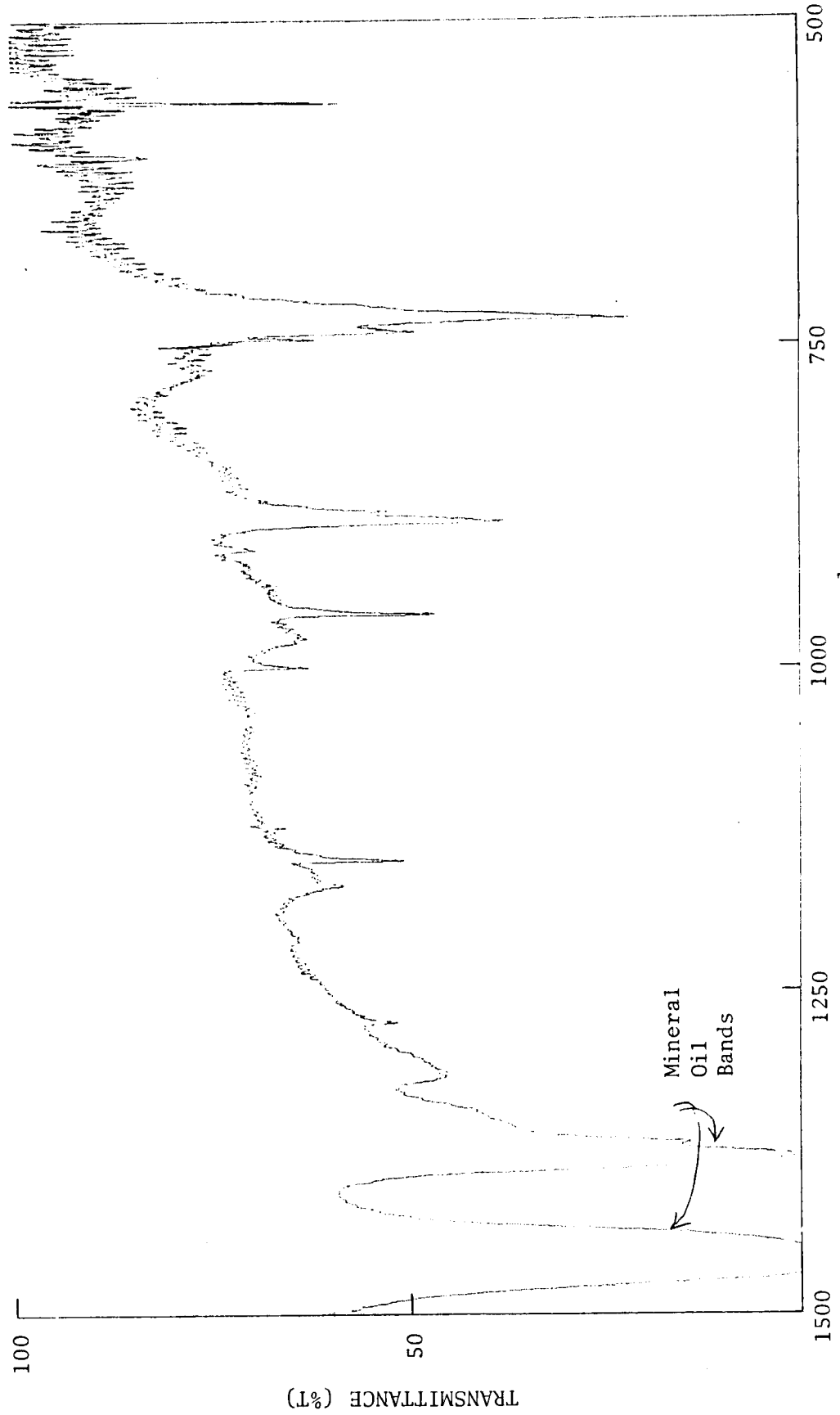


Figure 25. FT-IR spectrum of anthracene in mineral oil mull.

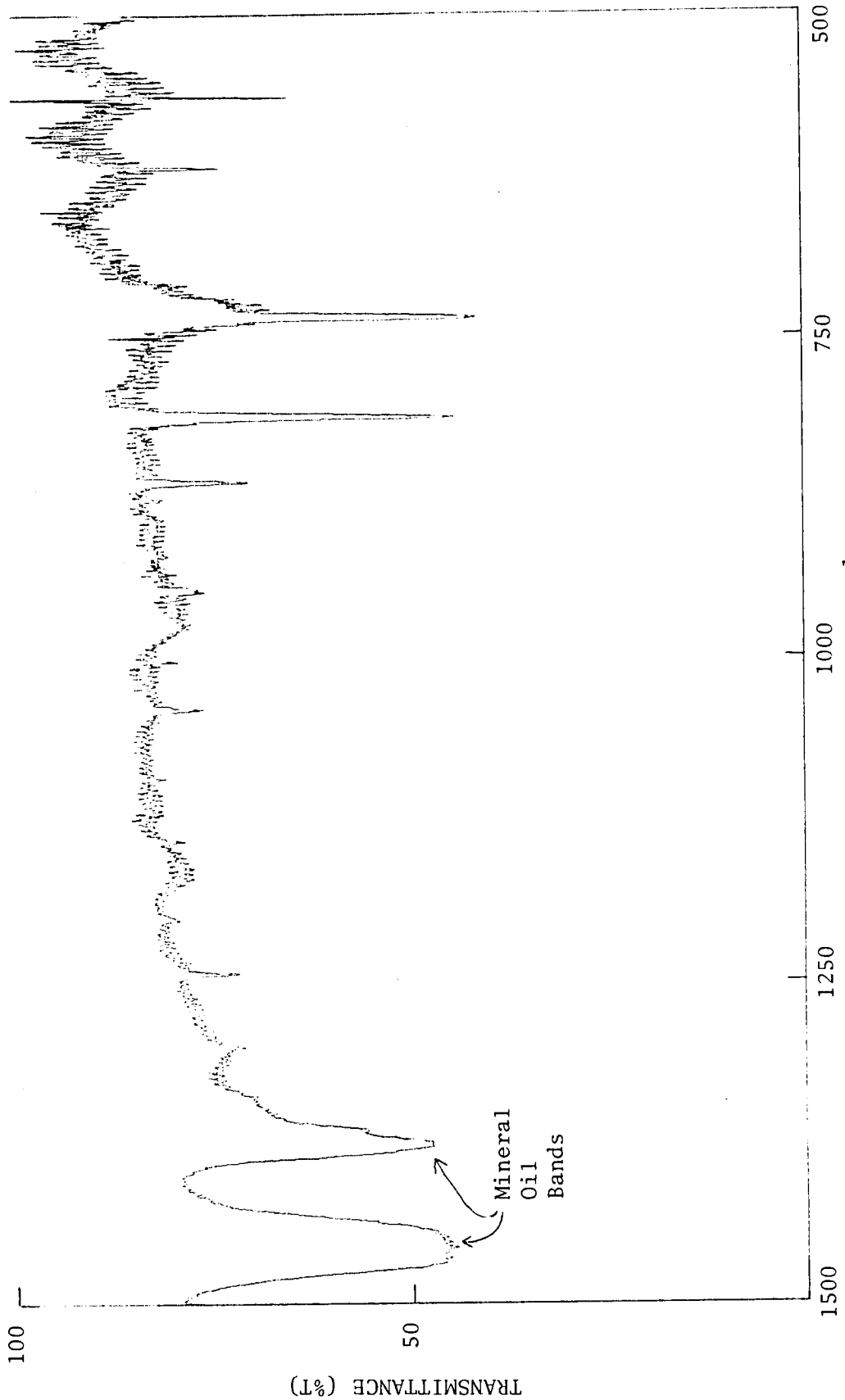


Figure 26. FT-IR spectrum of phenanthrene in mineral oil mull.

anthracene to KBr, about 1.4×10^{-6} moles of anthracene in 8.5×10^{-4} moles of KBr) to determine the reproducibility of spectra recorded using KBr pellets in the FT-IR spectrometer. Table III shows the average peak heights and standard deviations for each of five bands in the 1500 to 600 cm^{-1} region. The average relative standard deviation (the average value of the absolute standard deviation of the peak height divided by the peak height) for these bands is 0.42%. This result can presumably be taken as a measure of the reproducibility that can be obtained from the FT-IR spectrometer. It should be noted that the transforms were calculated in single precision; the use of new, double-precision, software may increase the quantitative precision of the spectrometer.

Spectra of four separate KBr samples, each containing a 1:560 mole ratio of anthracene to KBr, were recorded and the peak heights of the three major bands in each spectrum were compared with those in the other three spectra. The results are shown in Table IV. The average relative standard deviation for these data is 3.2%, almost seven times greater than that for an individual pellet.

Another set of ten spectra (each spectrum was an average of 100 spectra), using a single CS_2 solution, 6×10^{-3} M in phenanthrene, was recorded in sequence at 2.0 cm^{-1} resolution to determine the reproducibility of solution spectra recorded by the FT-IR spectrometer. Table V lists the average peak heights and standard deviations for the three bands in the 1500 to 600 cm^{-1} region. The average relative standard deviation of the peak heights is 0.46%. Note that the average relative standard deviation for ten spectra of the same KBr pellet was 0.42%, indicating that these

TABLE III

REPRODUCIBILITY OF SPECTRAL PEAK HEIGHTS FOR ANTHRACENE IN THE SAME KBr PELLET

$\lambda(cm^{-1})$	Absorbance	Average Peak Height (%T)	Standard Deviation (%T)	Relative Standard Deviation (%)
1449	0.089	18.52	0.169	0.91
1148	0.300	50.05	0.097	0.19
957	0.369	57.20	0.266	0.46
884	0.840	88.46	0.176	0.20
727	0.991	89.76	0.292	0.32

TABLE IV

REPRODUCIBILITY OF SPECTRAL PEAK HEIGHTS FOR ANTHRACENE IN DIFFERENT KBr PELLETS

$\lambda(cm^{-1})$	Pellet 1		Pellet 2		Pellet 3		Pellet 4		Standard Deviation (%T)	Relative Standard Deviation
	(%T)	(Abs.)	(%T)	(Abs.)	(%T)	(Abs.)	(%T)	(Abs.)		
957	4.57	0.266	47.6	0.281	44.9	0.258	46.8	0.274	1.2	2.6
884	71.2	0.541	74.2	0.588	70.5	0.530	76.0	0.620	2.6	3.5
727	72.2	0.556	75.3	0.607	71.2	0.541	71.2	0.638	2.7	3.6

TABLE V

REPRODUCIBILITY OF SPECTRAL PEAK HEIGHTS FOR PHENANTHRENE IN THE SAME CS_2 SOLUTION

$\lambda(cm^{-1})$	Absorbance	Average Peak Height (%T)	Standard Deviation (%T)	Relative Standard Deviation (%)
1242	0.038	8.40	0.072	0.86
812	0.439	63.60	0.221	0.35
735	0.735	81.60	0.135	0.16

figures do indeed appear to represent a measure of the precision of the FT-IR spectrometer.

Spectra of four different CS_2 solutions, each 3.7×10^{-3} M in anthracene, were recorded and the peak heights of the two major bands in each spectrum were compared with those in the other spectra. The results are shown in Table VI. The average relative standard deviation for these bands is 2.8%, again almost seven times that of a series recorded using a single solution.

A comparison of the ratios of the peak heights from Table IV, page 50 and Table VI was made to determine the reproducibility of the relative peak heights within each spectrum. An average variation of less than 1.0% (0.77% for Table IV and 0.55% for Table VI) was obtained between the four spectra from each Table, indicating that the peak heights within each spectrum, obtained using both KBr pellets and solutions, are reproducible.

A major source of imprecision in the peak height determination is proper definition of the baseline. For both KBr and CS_2 samples, the variation in peak height for a series of samples of the same concentration is approximately seven times larger than any deviation which can be attributed to the instrument. This result shows that the precision in quantitative studies is principally dependent on the reproducibility of sample preparation. It is somewhat surprising that KBr pellets yielded quantitative precision equal to that for liquid solutions, since the former are notoriously difficult to prepare reproducibly.

TABLE VI

REPRODUCIBILITY OF SPECTRAL PEAK HEIGHTS FOR ANTHRACENE IN DIFFERENT CS_2 SOLUTIONS

$\lambda(cm^{-1})$	Pellet 1		Pellet 2		Pellet 3		Pellet 4		Standard Deviation	Relative Standard Deviation
	(%T)	(Abs.)	(%T)	(Abs.)	(%T)	(Abs.)	(%T)	(Abs.)	(%T)	
878	7.0	0.029	7.1	0.029	7.0	0.029	7.4	0.034	0.19	2.7
727	13.8	0.065	13.8	0.065	13.8	0.065	14.6	0.069	0.40	2.8

2. Beer's Law

The spectra of a series of KBr pellets, containing varying amounts of anthracene, were recorded to determine the feasibility of using KBr pellets for quantitative studies. The results are shown in Figure 27. At low concentrations (less than 3.0×10^{-4} moles of anthracene per mole of KBr) the peak heights become almost random, dependent on the sampling and mixing of the sample. The peak intensities rapidly increase to a maximum at a mole ratio of about 3×10^{-3}:1. Above this mole ratio, the absorbance actually decreases as the concentration of anthracene increases. It is conceivable that, above a mole ratio of 3×10^{-3}:1, the concentration of anthracene becomes sufficiently large that the solute molecules are no longer "isolated" in the KBr matrix. The resulting interactions between the anthracene molecules cause peak broadening and severe deviations from Beer's law. Obviously, if quantitative studies were to be performed in KBr, all sample concentrations would be required to fall in the region from 3.0×10^{-4} to 3×10^{-3} moles of anthracene per mole of KBr. This limitation of the "linear dynamic range" severely limits use of KBr pellets for quantitative studies.

The spectra of a series of CS_2 solutions of varying anthracene concentration were recorded to determine the feasibility of employing CS_2 solutions in quantitative studies. The spectra were recorded using both 8 µl (0.1 mm pathlength) and 64 µl (1.0 mm pathlength) cells. The results are shown in Figures 28 and 29, respectively. The Beer's law plots of the results obtained from both cells exhibit a linear response

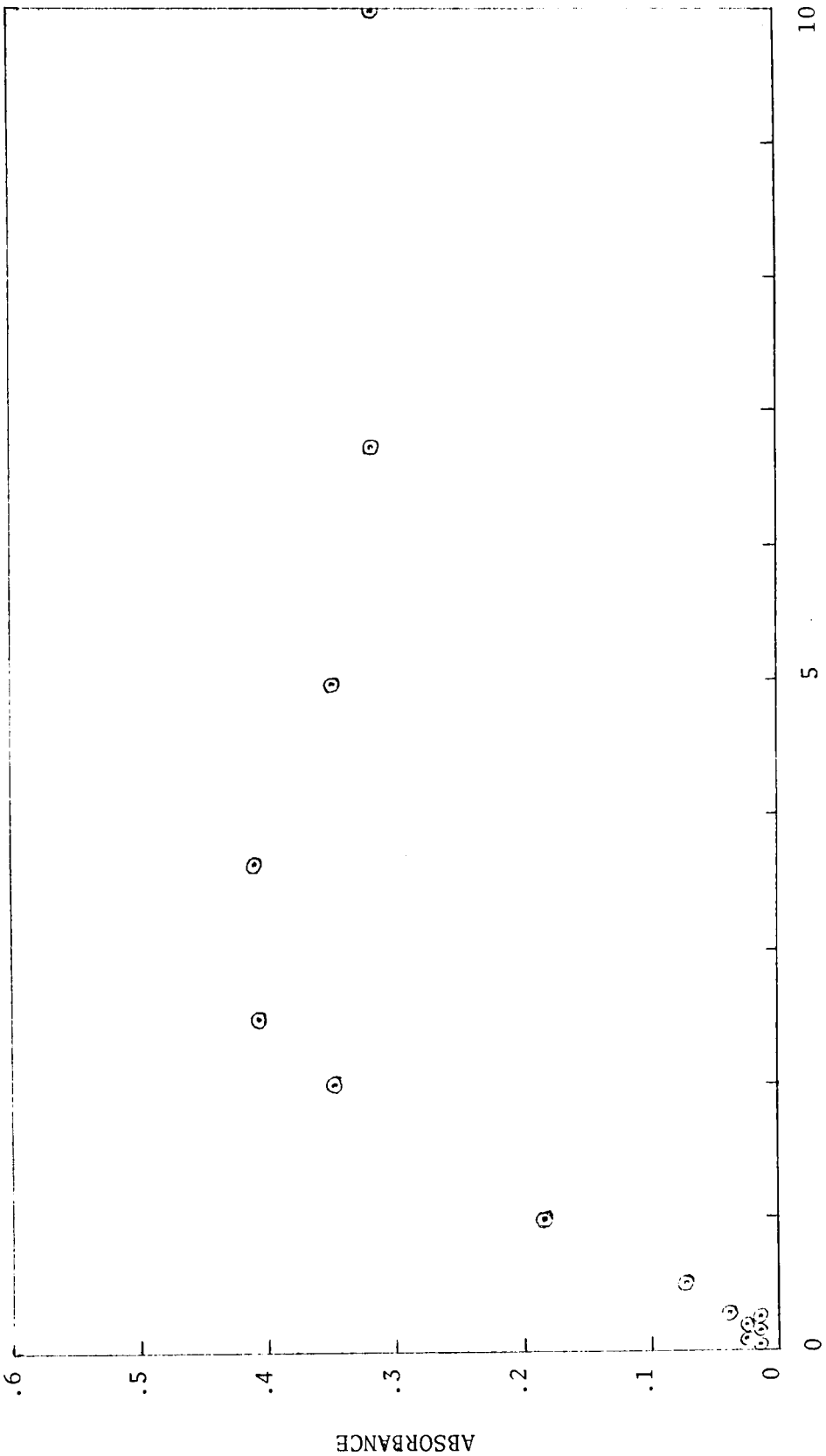


Figure 27. Beer's law plot for anthracene in KBr using the 727 cm^{-1} band.

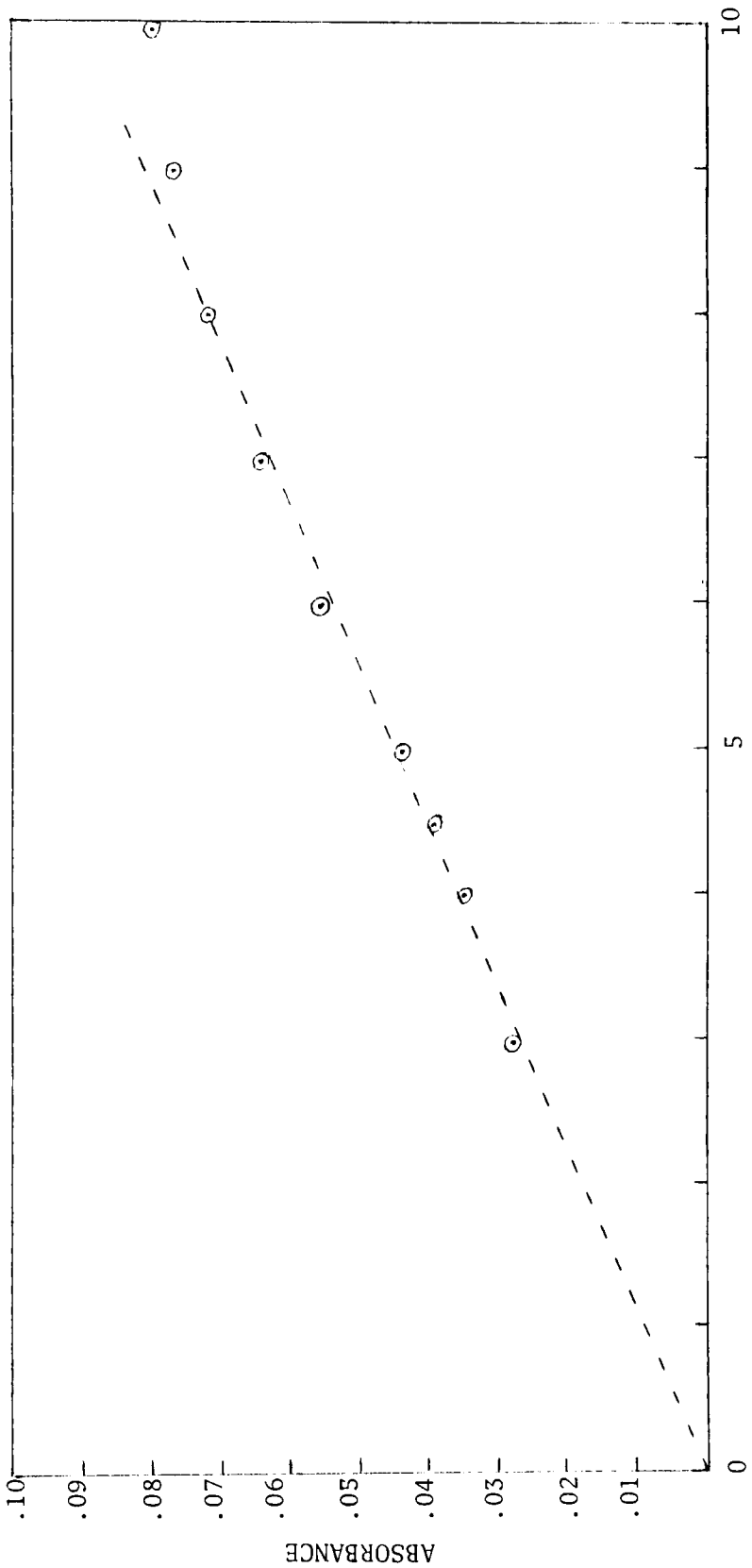


Figure 28. Beer's law plot for anthracene in CS_2 using a 8 µl cell and the 726 cm^{-1} band.

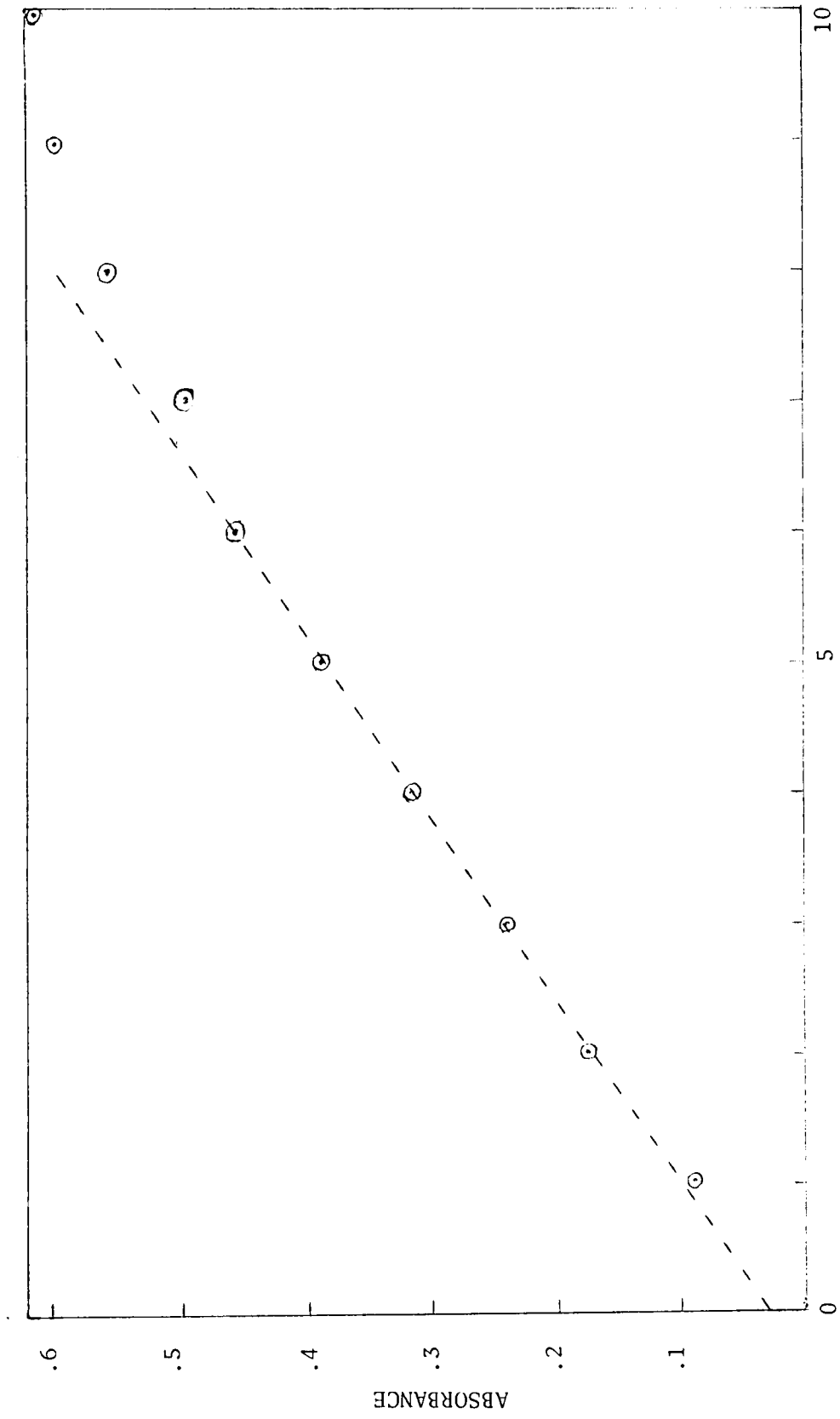


Figure 29. Beer's law plot for anthracene in CS_2 using a 64 µl cell and the 726 cm^{-1} band.

from the detection limit to 8.0×10^{-3} M (8 µl cell) or 6.5×10^{-3} M (64 µl cell). Thus, the use of CS_2 solution spectra for quantitative analysis of relatively low concentrations (to less than 5×10^{-4} M for anthracene) appears feasible.

Calculations were made to determine the molar absorptivity (ε) of anthracene in CS_2 solutions using the 726 cm^{-1} band. The average value calculated from the data in the linear region of Figure 28, page 56, is 900 liter $mole^{-1}$ cm^{-1}. The data from Figure 29, page 57, yielded an average value for ε of 820 liter $mole^{-1}$ cm^{-1}.

3. Detection Limits

The detection limits for pyrene (in KBr pellets, CS_2 solutions, and on ATR crystals) and carbazole (in KBr pellets and CS_2 solutions) were determined using the FT-IR spectrometer. That quantity of analyte which produces a signal-to-noise ratio of 2 to 1 is commonly employed as a definition of the "detection limit" for that substance. For all determinations, a series of five separate samples of the same concentration was prepared and the average signal-to-noise ratio was used. The detection limits obtained are listed in Table VII.

Very little work has been performed in the quantitative analysis of PAH by mid-IR spectroscopy. Boiteau et al. (32) performed some quantitative studies for PAH in micro-KBr discs and reported a "sensitivity threshold" of 1 µg for pyrene, coronene, and dibenzo [a, e] pyrene. The 1 µg "sensitivity threshold" for pyrene is a factor of seven lower than the detection limit determined in this study, though the

TABLE VII

DETECTION LIMITS OF PYRENE AND CARBAZOLE IN KBr, CS_2, AND USING ATR

Medium	Pyrene		Carbazole	
	Moles	Grams	Moles	Grams
KBr	3.8×10^{-8}	7.0×10^{-6}	2.4×10^{-8}	4.0×10^{-6}
CS_2	1.3×10^{-8}	2.6×10^{-6}	1.2×10^{-8}	2.0×10^{-6}
ATR	2.4×10^{-8}	4.8×10^{-6}		

definition of "sensitivity threshold" (29) is not clear. Nevertheless, on the basis of this admittedly imprecise comparison, it is not obvious that FT-IR provides any enhancement in detectability over conventional IR. It should, however, be noted that no attempt was made in this work to employ micro-KBr disc techniques (33, 34) or to employ the beam-condensing optics required for FT-IR microsampling. The use of a CsI beamsplitter, which produces a more intense signal between 900 and 500 cm^{-1} than the KBr beamsplitter employed in this work, should also improve the signal-to-noise ratio and the detection limits.

D. FT-IR ADVANTAGE

In order to determine what advantages, if any, were offered by the FT-IR system over a conventional dual-beam grating infrared spectrometer, a KBr pellet containing carbazole (1:10,000 mole ratio) was prepared. The spectrum of this pellet was recorded on the Digilab FTS-20 spectrometer (Figure 30, a) and on a Perkin-Elmer 257 spectrometer (Figure 30, b). The FTS-20 spectrum consisted of 100 spectra signal-averaged at a resolution of 1.0 cm^{-1}. The Perkin-Elmer 257 spectrum was collected at a slow scan rate (50 cm^{-1} per minute) with an exit slit setting which should yield a nominal resolution of 2.0 cm^{-1} at 1000 cm^{-1}. The times required to obtain the two spectra were 33 minutes and 48 minutes, respectively.

In Figure 30a, the signal-to-noise ratio at 1458 cm^{-1} is 12 while in Figure 30b, the band is difficult to detect at all, because of interference from atmospheric water and carbon dioxide bands. The

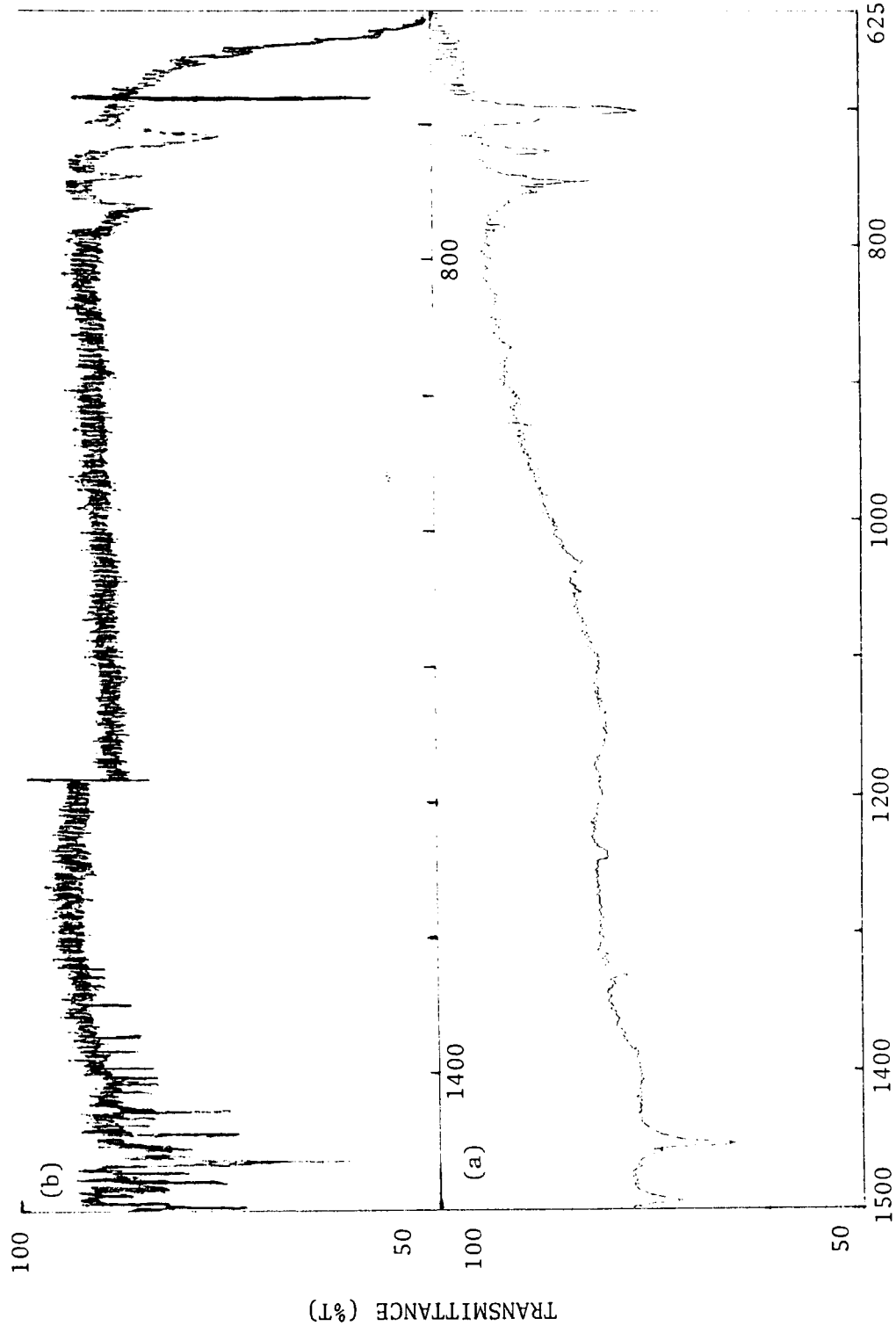


Figure 30. Spectrum of carbazole in the same KBr pellet, using (a) Digilab FTS-20 and (b) Perkin-Elmer 257 (note: filter change at 1170 cm^{-1} in b).

signal-to-noise ratio at 726 cm^{-1} in Figure 30a is slightly greater than four while, in Figure 30b, the corresponding band yields a signal-to-noise ratio of slightly greater than two.

The FT-IR spectrometer, therefore, provides more rapid collection and processing of data at high resolution as well as increasing the signal-to-noise ratio by a factor of about two, compared with the dispersive instrument for comparable data acquisition times. The use of a minicomputer in conjunction with the interferometer in the FT-IR spectrometer provides capability for a wide variety of data handling and storage capabilities. These advantages indicate that the use of the FT-IR spectrometer for high-resolution studies of a variety of compounds should be preferred over a conventional dual beam grating infrared spectrometer. To adequately exploit the advantages offered by FT-IR will, however, require increased attention to microsampling techniques (33, 34), which are not completely straightforward in FT-IR spectroscopy due to the very large exit aperture in the interferometric spectrometer. In general, the "state of the art" in mid-IR instrumentation has now developed to the point that sample preparation, rather than the instrumentation itself, often limits the detection limits and spectral resolution which can be obtained (34).

CHAPTER IV

CONCLUSIONS

1. Potassium bromide pellets, liquid solutions, and attenuated total reflectance sampling procedures for PAH all produced spectra of comparable quality (as defined by the half-widths of the individual spectral bands). Mulls produced spectra of poor quality by comparison with the other three sampling procedures.

2. Individual sample preparation of both KBr pellets and CS_2 liquid solutions yielded reproducible spectra with respect to relative peak heights and wavenumber positions. Thus, qualitative analysis of relatively simple mixtures (four to five components) appears feasible in these media.

3. In terms of detection limits, liquid solutions were slightly superior to ATR or KBr pellets, but the differences were not large (about a factor of three). Detection limits for PAH were of the order of 2 μg.

4. Of the four sample matrices studied in this work, liquid solutions appear to show the greatest promise for quantitative analyses. Linear Beer's law plots were obtained from 8×10^{-3} M to the detection limit (about 1.5 decades) in liquid solutions in CS_2. In contrast, KBr pellets produced nonlinear plots which could not be employed for quantitative work unless samples were restricted to a small concentration range (less than one decade).

5. Detection limits obtained in this FT-IR study were slightly less than those obtained in earlier studies by conventional IR spectroscopy using microsampling techniques. The use of true IR microsampling procedures (not attempted in this exploratory study) and a CsI beamsplitter in the FT-IR spectrometer (which should provide a significantly enhanced signal-to-noise ratio in the 900 to 500 cm^{-1} region) should result in significant improvement in the detection limits; such studies are strongly recommended for future investigation.

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VITA

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