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EVALUATING OPEN-PATH FTIR SPECTROMETER DATA  
USING DIFFERENT QUANTIFICATION METHODS, LIBRARIES,  
AND BACKGROUND SPECTRA OBTAINED UNDER VARYING  
ENVIRONMENTAL CONDITIONS

by

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A technical report submitted to the Faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in Public Health in the Department of Environmental Sciences and Engineering.

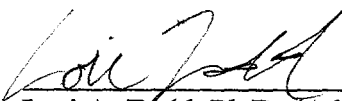
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**ABSTRACT**

Studies were performed to evaluate the accuracy of open-path Fourier Transform Infrared (OP-FTIR) spectrometers using a 35 foot outdoor exposure chamber in Pittsboro, North Carolina. Results obtained with the OP-FTIR spectrometer were compared to results obtained with a reference method ( a gas chromatograph equipped with a flame ionization detector, GC-FID). Concentration results were evaluated in terms of the mathematical methods and spectral libraries used for quantification. In addition, the research investigated the effect on quantification of using different backgrounds obtained at various times during the day. The chemicals used in this study were toluene, cyclohexane, and methanol; and these were evaluated over the concentration range of 5-30 ppm.

Two different quantification methods were used in the analyses to calculate concentrations and were performed manually using Grams 386 software (Galactic, Inc.): the traditional peak area method (which involved calculating the area of the peaks utilizing

the trapezoidal rule of integration) and an interactive subtraction method. The different spectral libraries used for quantification included: the Hanst library (137 ppm-m toluene, 388 ppm-m cyclohexane, and 27 ppm-m methanol ), and the EPA library (249 ppm-m toluene). An EPA library spectrum for cyclohexane and methanol was not available.

To investigate the effect on quantification of using different backgrounds, concentration data files were analyzed using the backgrounds taken at the start of the experiments, and subsequent backgrounds obtained later the same day. The backgrounds contained varying amounts of water vapor and other atmospheric constituents.

Using the Hanst library for quantifying toluene, there was no significant difference between open-path and GC-FID concentrations, regardless of the method of quantification, for concentrations of 10 ppm and below. However, for concentrations between 10 ppm and 30 ppm, there was a significant difference between open-path and GC-FID concentrations.

Using the EPA library for quantifying toluene, there was no significant difference between open-path and GC-FID measurements, regardless of the method of quantification, for concentrations of 15 ppm and below. However, for concentrations between 15 ppm and 30 ppm, there was a significant difference between open-path measurements analyzed by the subtraction method and GC-FID concentrations. There was no significant difference between GC-FID concentrations and open-path measurements quantified by the peak area method for all concentrations studied.

For cyclohexane, all concentrations were significantly higher than the reference method, regardless of the quantification method. There was no significant difference between concentrations obtained using the two quantification methods for concentrations

of 5 ppm and below. A regression through the origin was performed on the cyclohexane peak area and subtraction curves and each respective slope was compared to the slope of the GC-FID curve. When a ratio factor for the slope of the cyclohexane peak area and subtraction curves was applied to the open-path measurements, there was no significant difference between the GC-FID measurements and open-path FTIR concentrations.

Water vapor was used as a marker to characterize the backgrounds obtained each day. Each data file was analyzed with the original and subsequent backgrounds from the same day to study the effect on quantification. The magnitude of the effect varied among chemicals as follows: (1) In general, wetter and dryer surrogate toluene backgrounds significantly increased concentrations. (2) For cyclohexane and methanol, wetter surrogate backgrounds significantly increased concentrations and dryer surrogates significantly decreased concentrations. (3) Differences in water vapor partial pressures of less than 5 % resulted in quantification results being significantly different than the results obtained with the original background for all three chemicals.

## Introduction

Numerous integrated sampling methods are available to enable an industrial hygienist to identify and quantify gases and vapors in workplace air. These methods include: activated charcoal tubes and passive diffusion badges to detect hydrocarbons, silica gel tubes to detect inorganic and polar compounds, and liquid impingers for absorption of gaseous contaminants (2). The main disadvantages of these methods are: 1) that the sample concentrations represent averages over time and 2) that the samples need to be sent to an analytical laboratory for analyses which can take days to weeks to perform. This results in poor temporal resolution of chemical concentrations during a day, and a long lag time for receiving results.

To enable the industrial hygienist to obtain real-time identification and quantification of gases and vapors and, therefore, good temporal resolution, devices are available that include colorimetric detector tubes and direct reading instruments (such as the gas chromatograph equipped with a flame ionization detector, and infrared spectrometers). There are several disadvantages to using colorimetric detector tubes: some color stains fade or change with time, the chemical of interest must be identified ahead of time to select the appropriate tube, there are problems with cross-sensitivity, and the concentration estimate range and accuracy is limited ( $\pm 25\%$ ).

While GC-FIDs are both sensitive and selective, they can only be used to detect a limited number of compounds during any sampling session. Measurements for each

chemical are usually obtained within 10 minutes. They also require frequent calibration and cannot be used to identify multiple components simultaneously.

Infrared spectrometers, such as the MIRAN (miniature infrared analyzer, Foxboro, Inc.) can detect a wide range of chemicals, and measurements can be obtained quickly, in less than a minute. The major disadvantages of this method are low sensitivities ( ppm range), and inaccuracies in concentration measurements when interferences are present. While near-real time measurements can be obtained using both GC-FIDs and MIRANs, they are point samplers and can obtain concentrations only for the specific locations where they are placed. Therefore, there is poor spatial resolution of chemical concentrations.

Open path-fourier transform infrared (OP-FTIR) spectroscopy can potentially produce concentrations that have both good spatial and good temporal resolution. They are very sensitive and selective, and can provide near real-time quantification of gases and vapors in air that are of industrial hygiene concern at ppb-ppm concentrations over large areas (5). There are several advantages of using OP-FTIR spectrometers for industrial hygiene applications (8,24,25,27,38) which include the ability to: monitor multiple chemicals simultaneously in near real-time (within seconds), monitor non-invasively without human exposure, produce data very rapidly (within a matter of minutes) with very low limits of detection (ppb-ppm), avoid sample integrity concerns (arising from contamination, holding times, and chemical interactions), and obtain concentration measurements over large spatial areas. Because of the ability to collect many sequential short term measurements, good temporal resolution can be obtained; this is important for evaluating short term peak exposures and investigating the air flow of chemicals. These short term

sequential measurements can be integrated over time to obtain time weighted average concentrations which are important for chronic exposures.

OP-FTIR spectrometers consist of an optical source and a detector which may be placed up to several hundred meters apart. There are two possible open-path monitoring configurations, bistatic and monostatic. A bistatic configuration is one in which the infrared source is placed on one side of the contaminant plume and the detector is placed on the other side. In a monostatic configuration, the infrared source and detector are located on the same side of the contaminant plume. A retroreflector, consisting of an array of corner cube mirrors, is used to return the IR beam directly upon itself to the detector. The infrared beam from the optical source traverses the open path (optical path) to the detector, where the chemicals absorb light at characteristic wavelengths. A sample spectrum and clean background are ratioed to obtain a transmission spectrum. The negative log of this spectrum is taken to obtain an absorbance spectrum. The concentration analysis is based upon Beer's Law which states that the absorbance of a component is directly proportional to concentration ( $A = aCL$  where  $A$  is absorbance,  $a$  is the optical absorption coefficient,  $C$  is the concentration of the gas, and  $L$  is the path length). The concentration obtained for each chemical is integrated over the entire optical path, and is usually expressed as the concentration-pathlength product (such as ppm-meters).

Despite the enormous potential of the use of OP-FTIR spectrometers for industrial hygiene applications, there has been only a limited number of studies on instrument performance and accuracy (37, 38). In these indoor laboratory studies, good correlation

was found between the open-path measurements and point samples taken along the beam that were analyzed by GC-FID and GC-ECD. There are many factors that can affect the accuracy of OP-FTIRs. These include: the background used for quantification, instrument performance, and the method and spectral library used for quantification.

There are several known problems associated with obtaining adequate field background spectra using OP-FTIR spectrometers for the identification and quantification of compounds in air (15, 20). These problems include the difficulty in obtaining a clean background due to target gases always being present in the air, and changing environmental conditions (temperature, carbon monoxide, water vapor). There are no consistent guidelines to help investigators choose and understand the implications of collecting particular background spectra under given environmental conditions.

The purpose of this research was: 1) to track different quality control parameters; 2) evaluate quantification accuracy (relative to the reference method, GC-FID) using different methods of quantification and spectral libraries; and 3) to evaluate the effect on accuracy of using different background spectra (containing varying amounts of water vapor) obtained over the course of a single day.

A 35 foot Teflon-lined exposure chamber was used that enabled the entire OP-FTIR beam to be immersed in a homogeneous concentration. Chemicals were introduced into the chamber in vapor form and were mixed and equilibrated to ensure homogeneity. A range of 5-30 ppm was generated for each chemical. Homogeneous contaminant concentrations were generated in the exposure chamber and OP-FTIR measurements were compared to point sample measurements obtained in the chamber and analyzed by GC-

FID. For each experiment, quantification was performed using the clean background taken before the experiments and subsequent clean backgrounds taken during the course of the day. Backgrounds from the same day were evaluated to ensure that no bias was introduced due to day to day variations in instrument performance.

Open-path FTIR and GC-FID measurements were obtained simultaneously while documenting both temperature and relative humidity. After each concentration was generated in the chamber, the chamber was exhausted and a new background was obtained.

## Background

Outdoor field studies were performed to validate the accuracy of open-path FTIR spectrometers for 100-500 meter path lengths by releasing known gases in the air and comparing the open-path measurements with point sample measurements taken along the beam (15,17,31,32,34). A wide variability in accuracy was found among OP-FTIR systems that have been tested outdoors and compared with point samples taken along the beam. The variability could be due to point samples that are spread widely apart, changing environmental conditions (temperature, water, & carbon dioxide), and winds shifting the contaminant plume out of the infrared beam where there are no point samples. One study compared open-path FTIR measurements of xylene, benzene, and styrene with summa canister point samples analyzed by a gas chromatograph / mass spectrometer (GC/MS). The open-path FTIR spectrometer measurements of benzene and xylene were 22 % lower and 25 % higher respectively. The styrene measurements were not statistically different than the GC/MS results (32).

An outdoor field study was conducted in Kansas which documented the quantitative performance of three open-path FTIR systems using a pathlength of 100m (17). Quantitative accuracy, relative to summa canister samples, for non-halogenated volatile organic compounds varied depending on the open-path FTIR system used. The results for non-halogenated compounds, expressed as a percentage of the true concentration, ranged

from 73 % to 225 % with 115 % as the mean. The results for toluene ranged from 85.7% to 157 %.

Another study that was part of the Superfund Innovative Technology Evaluation program (SITE) compared open-path FTIR measurements, over a 250 meter pathlength, with time-integrated canister samples that were analyzed by GC/MS (26). Comparison of the chlorobenzene FTIR and canister data showed a high variability which was not correlated with concentration. At 110 ppb, open-path FTIR and summa canister results were not significantly different. For concentrations of 75 ppb and 125 ppm, the FTIR measurements were 50% - 100% higher than summa canister measurements. Over the range of 20 ppb - 200 ppb, p-dichlorobenzene measurements were not statistically different than summa canister results.

A limited number of indoor studies have been performed to analyze the performance of open-path FTIR systems using shorter pathlengths than outdoor studies. Indoor studies can be controlled more easily than outdoor studies.

Experiments were performed to compare open-path FTIR measurements with point samples taken along the beam (analyzed by GC-FID) in an indoor 140 cubic meter controlled ventilation chamber (38). Acetone was used as the tracer gas and open-path FTIR measurements consisted of 128 co-added scans at 2 cm<sup>-1</sup> wavenumber resolution. The open-path FTIR measurements agreed within 50% of the GC-FID readings with most of the readings agreeing within 15 %.

The importance of obtaining adequate background spectra is emphasized in the literature (10,12,33,38). It can be difficult or impossible to obtain a clean background spectrum from uncontaminated air during a work shift when chemical processes are occurring throughout the day. One study suggests storing a library of background readings that cover a range of humidity and other environmental conditions (38). Another recommended that background data collection should be carried out, as a minimum, every 2 hours during "quiet" (stable environmental conditions) days, every half hour during times when fronts are passing, and when the water vapor partial pressure changes by 5 % (33). These papers did not address the rationale for how often to take backgrounds, nor the effect on quantification of taking infrequent backgrounds.

## Materials and Methods

An outdoor exposure chamber located eighteen miles south of the University of North Carolina at Chapel Hill was used for the experiments, see Figure 1. The chamber has a wooden A-frame structure lined with 5 mil clear Teflon film. The interior dimensions of the chamber are 5.6 meters high, 5.2 meters wide, and 11.8 meters long. The side walls of the structure form right angles to the floor at a height of 0.6 meters. The volume of the chamber is 193.7 cubic meters. The chamber was operated so that its contents were exhausted at a rate of approximately 552 cubic feet/hour (8). The chamber was equipped with four, four-blade fans located 0.46 meters off the chamber floor to provide mixing of the chamber air. The optical path length used for the experiments was 10 meters. The chamber was equipped with sampling ports at the height of the open-path FTIR beam, and a Fisher Scientific brand hygrometer to provide temperature and relative humidity measurements. Homogeneity of the chamber was demonstrated in a previous paper (1).

A Midac (Midac Corporation; Irvine, California) open- path FTIR spectrometer was used in these experiments. The bistatic Midac open-path system used in these experiments consisted of an 8" IR source, Michelson-type interferometer, potassium bromide optics, and an In/Sb sandwich detector. This detector was most sensitive to the hydrocarbon region of 2800 - 3200  $\text{cm}^{-1}$ , which was the region used in all the analyses.

Before each set of experiments, a calibration curve for the GC-FID was obtained. A Shimadzu model 14A GC (located in a laboratory underneath the exposure chamber) equipped with a 10 meter DB-5 packed column was used. The concentrations were

obtained by diluting 30.7 ppm NIST certified toluene or cyclohexane gas mixtures with air in a Hamilton gas-tight syringe. The gases were obtained from Scott Specialty Gases in Durham, North Carolina. The analytical accuracy of both mixtures was plus or minus two percent. Calibration curves consisted of 3-5 points to span the concentrations generated in the chamber [ Figure 2 shows a typical calibration curve. The remainder of the calibration curves are located in Appendix C]. Three successive injections were made for each point on the calibration curve; two of the three injections had to agree within 5% in order to accept the two values for points on the calibration curve. A linear regression was performed on the calibration curves to check that the slope wasn't significantly different from one and that the correlation coefficient was a least 0.98. Finally, the calibration curve was compared to previous calibration curves to monitor instrument operation. When all three checks were completed, the calibration curve was accepted as valid.

At the beginning of each experiment, before chemicals were introduced into the chamber, two background spectra were acquired using 128 scans and 1.0 wavenumber resolution (0.5  $\text{cm}^{-1}$  for methanol). A known quantity of liquid chemical was then introduced via a "u-shaped" glass tube underneath the chamber, volatilized using a hot air gun, and the vapors were carried up into the chamber where they were mixed using the fans. After equilibration was reached, in about 10 minutes, the open-path FTIR spectrometer scanned the air. One hundred twenty-eight co-added scans and 1  $\text{cm}^{-1}$  wavenumber resolution was used for toluene and cyclohexane, and 0.5  $\text{cm}^{-1}$  wavenumbers was used for methanol. While the FTIR was scanning, point samples were

pulled using a metal bellows pump, through a insulated teflon line to the sampling manifold. Two 0.3 ml Tedlar bags were filled for each sample concentration, using the sampling manifold, and several injections of 500 uL were made into the GC-FID (housed in a laboratory underneath the exposure chamber) were made. Significant concentration changes (due to leakage and adsorption onto the bags) were only encountered when bags were left sitting for more than one hour. The bag samples were analyzed quickly, within 10 minutes, to negate these effects.

The following quality control parameters were used for each data run: single beam transmission spectra were checked for evidence of non-linearity, two successive backgrounds were obtained and noise was calculated using the Grams 386 RMS noise software package, and a NIST certified polystyrene film absorbance spectrum was obtained to check for peak wavenumber shifts and peak height and peak area variability. A noise value of less than or equal to  $1 \times 10^{-3}$  was considered acceptable. Two polystyrene peaks were tracked in the region of the analyses: 2922  $\text{cm}^{-1}$  and 3025  $\text{cm}^{-1}$ . The position, intensity, and area of these peaks was documented. Temperature and relative humidity was documented for all experiments. The percent water vapor was calculated from the temperature and humidity measurements.

### *Toluene experiments*

Liquid toluene was injected into the u-tube under the chamber, volatilized, and a sweep stream of clean outside air was used to carry the vapors up into the chamber where they were mixed and allowed to equilibrate for about 10 minutes (depending on the

concentration). A spectrum was acquired using the Midac open-path spectrometer using 128 co-added scans and 1 cm<sup>-1</sup> wavenumber resolution. While the features of the toluene can be resolved using a 4 cm<sup>-1</sup> resolution, a resolution of 1 cm<sup>-1</sup> wavenumber was chosen because no significant difference in quantification was observed between this resolution and 4 cm<sup>-1</sup>, and water vapor interference was better resolved, thus easier to separate out, at this higher resolution. Using a lower resolution can introduce quantification errors caused by sharp water vapor absorption bands being broadened and contributing to the absorption bands of the compounds of interest. Both the Hanst and EPA spectral libraries were used, see Figures 3 and 4.

After the chemical was allowed to equilibrate, open-path measurements were obtained and point samples were collected in Tedlar bags. For the point samples, two Tedlar sampling bags were collected at each concentration for comparison and to ensure homogeneity. Samples from the bags were injected into the GC-FID for comparison with the open-path FTIR measurement at each concentration point. Successive injections were made from each bag until three results were within 5 % of each other.

When this first concentration run was completed, the chamber was completely exhausted of the toluene. The chamber was exhausted between runs to ensure independence of each concentration and to enable background and sample spectra to be acquired under similar environmental conditions. After the chemical was exhausted from the chamber, a new background (128 scans and 1 cm<sup>-1</sup> resolution) was obtained. A total of four different backgrounds were obtained on each day.

A second concentration of toluene was generated in the chamber, allowed to equilibrate, and measured with the same instrument parameters as described above. This procedure was repeated with two more toluene concentrations resulting in a minimum of four injections each day. Five days of experiments were carried out to yield twenty-five concentration points for analysis. The order and amount of toluene injected each day was varied such that no two consecutive days had the same order of concentrations. The five concentrations injected into the chamber were, 5, 10, 15, 20, and 25 ml of toluene, generating concentrations of 6, 12, 17, 23, and 29 ppm respectively. [ Figure 5 is a representative toluene absorbance spectrum obtained by the Grams 386 software package from Galactic industries. Appendix D contains the remainder of the toluene spectra acquired] The absorbance spectrum for each concentration was analyzed quantitatively by the methods of interactive subtraction and integration of peak area as provided in Grams 386 software package by Galactic. The 2800-3100  $\text{cm}^{-1}$  wavenumber region was used for quantification, which corresponded to the most sensitive IR region for the detector used. The library spectra used for quantification were the Hanst library (137 ppm-m) and the EPA library (249 ppm-m).[See Figures 3 & 4]

To compare quantitative results, each of the spectra taken was first analyzed with the background taken at the beginning of the experiments, and with each of the three surrogate backgrounds obtained the same day. Only backgrounds from the same day were used to minimize the effect of instrument performance. Figure 6 demonstrates the interference (specifically, the more jagged appearance as compared to Figure 5) of water vapor in the toluene hydrocarbon absorbance peaks.

### *Cyclohexane experiments*

The five different cyclohexane concentrations generated were: 6, 11, 17, 23, and 29 ppm (5, 10, 15, 20, and 25 ml). Four injections of cyclohexane were performed each day to yield 20 concentration points for analysis. The order and amount of cyclohexane injected each day was varied such that no two consecutive days had the same order of concentration. The chamber was exhausted between injections and a new background was acquired. Each of the spectra taken was first analyzed with the clean background taken at the beginning of the experiment and with each of the three surrogate backgrounds obtained the same day to compare quantitative results. The open-path FTIR parameters used were 128 co-added scans and 1 cm<sup>-1</sup> wavenumber resolution. A one wavenumber resolution was chosen to retain peak shape and to better resolve water vapor lines. The region for analysis used was 2900-2950 cm<sup>-1</sup> wavenumbers. The Hanst reference spectra for cyclohexane is located in Figure 7. [An example of a cyclohexane absorbance spectrum acquired in this region is shown in Figure 8. The remaining spectra are contained in Appendix E]

### *Methanol Experiments*

Difficulty was encountered when trying to obtain a GC-FID calibration curve with methanol; the methanol randomly absorbed onto the column and desorbed later which invalidated results. Therefore, open-path FTIR accuracy experiments were not performed. The estimated concentrations of methanol generated in the chamber were: 3,

6, 12, 15, and 30 ppm (5,10,15,20, and 25 ml). Four injections of methanol were performed each day to yield 20 concentration points for analysis. The order and amount of methanol injected each day was varied such that no two consecutive days had the same order of concentrations. The chamber was exhausted between injections before a new background was acquired. Each of the spectra taken was first analyzed with the clean background taken at the beginning of the experiment and then with each of the three surrogate backgrounds obtained the same day to compare quantitative results.

The region for analysis was 2800-2900  $\text{cm}^{-1}$  wavenumbers using 128 co-added interferograms and 0.5  $\text{cm}^{-1}$  resolution. This resolution was chosen in order to resolve the fine peak structure in this region and to match the Hanst library spectrum. The Hanst library spectrum is pictured in Figure 9. [Figure 10 illustrates a representative methanol absorbance spectrum. The remaining methanol spectra obtained are contained in Appendix F]

## Results and Discussion

The results of the FTIR quality control parameters were as follows. The intensity of the polystyrene peaks at 3025 cm<sup>-1</sup> and 2922 cm<sup>-1</sup> averaged 1.33 and 1.78 with a standard deviation of 0.0031 and 0.0029, respectively. The area of these peak averaged 17.63 and 59.24 with a standard deviation of 0.2804 and 0.3613 respectively (See Table 1). [A representative polystyrene film absorbance spectrum is located in Figure 11 and the remainder of the spectra can be found in Appendix G]

The peak to peak noise was calculated using a RMS noise package obtained from Galactic Corporation. The RMS noise calculated in the region 2820-2850 cm<sup>-1</sup> averaged 2.83 E-04 with a standard deviation of 2.4 E-05. (See Table 1).

Although the quality control parameter results indicate reliable instrument performance, getting the instrument to that point on a day to day basis was difficult. In the course of this study, the liquid nitrogen dewar lost its vacuum three times and the detector had to be sent back to the manufacturer. In addition, the laser (which guides the scanning of the mirror) went out of alignment twice and had to be shipped back to the manufacturer for realignment. Because the manufacturer considers the instrument a field instrument, it should perform in the field and these events should not have occurred. In addition, whenever the instrument power was turned on, there was an electrical communication problem between the detector and the software on the computer (most likely due to a glitch in the software) and the mirror wouldn't scan unless the computer was de-bugged and the system was repowered in a specific order.

Another quality control check involved comparing the GC responses for toluene and cyclohexane. The GC-FID response should be proportional to the number of carbons present. Toluene has 7 carbons and cyclohexane has 6 carbons. Therefore, the response for toluene (for the same concentration) should be approximately 1.2 times the cyclohexane response. For all concentrations, the toluene response was 1.1 times the cyclohexane response which indicates that the GC is functioning properly.

### *Error Analysis*

The sources of error that effect quantification accuracy include the injection error for the GC calibration curves, injection error of the bag samples, the analytical accuracy of the calibration gases, and the precision of the quantification results. The largest of these was the precision of the FTIR quantification results with an associated error of 2.5% RSD. This error was negligible compared to the differences in quantification results observed.

### *Accuracy*

Toluene was quantified, using both subtraction and peak area methods, with the Hanst and EPA libraries. The peak area method involved integrating (using the trapezoidal rule of integration) the area under the sample peak and comparing it to the area under the same reference peak. With interactive subtraction, the sample and reference absorbance files were manually ratioed out until there appeared to be only noise left along the baseline. The ratio factor obtained represented the percent concentration of the data file, relative to

the reference file. Both quantification methods were performed using Grams 386 software from Galactic Corporation.

Using the Hanst library, there was no significant difference between toluene concentrations and the reference method (matched-pair t-test;  $\alpha = 0.05$ ,  $p = 0.88$ ) for concentrations of 10 ppm and below. However, for concentrations greater than 10 ppm, there was a significant difference between the two methods ( $p = 0.02$ ), see Figure 12.

Using the EPA library, there was no significant difference between toluene concentrations obtained using the peak area and subtraction methods for concentrations of 10 ppm and below (matched pair t-test;  $\alpha = 0.05$ ,  $p = 0.037$ ). For concentrations of 15 ppm and above, there was a significant difference between the two methods ( $p = 0.0004$ ) and the subtraction method relative to the reference method ( $p = 0.0002$ ). There was no significant difference between the peak area and reference method for all concentrations studied ( $p = 0.912$ ), see Figure 13.

In the Kansas field study (17), toluene concentrations obtained, expressed as a percentage of true concentration, ranged from 85.7% to 157%. The range of toluene concentrations obtained in this study was 44% to 126%.

For the path length used, the toluene EPA library represented 28 ppm and the Hanst 15 ppm. The results for toluene in this research were closer to the reference method for the EPA library. This could be due to the fact that the EPA library bracketed the concentration range studied better than the Hanst library.

All concentrations of cyclohexane, obtained using peak area and subtraction methods, yielded concentrations of cyclohexane that were significantly different from the reference

method ( $p = 0.0000314$  and  $0.0000681$  respectively). There was no significant difference between cyclohexane concentrations obtained using the peak area and subtraction methods for cyclohexane concentrations of 5 ppm and below ( $p = 0.10$ ). However, for concentrations greater than 5 ppm, there was a significant difference between the two methods ( $p = 0.000022$ ). Both methods overestimated the true concentration with the subtraction method overestimating as much as 50%, see Figure 14.

A regression through the origin was performed on the cyclohexane peak area and subtraction curves and each respective slope was compared with the slope of the GC-FID curve. A ratio factor was obtained and applied to open-path measurements such that the difference between GC-FID measurements and FTIR concentrations wasn't significant.

The regression line for cyclohexane peak area concentration vs. GC-FID concentration was  $y = 1.37x$ . This gave a slope ratio factor of 1.37. This indicates that when the concentrations obtained using the peak area method are lowered by 13.7 %, they will be the same, statistically ( $\alpha = 0.05$ ), as the reference method.

The subtraction regression equation was  $y = 2.30x$ . This gave a slope ratio factor of 2.3. This indicates that when concentrations obtained using the subtraction method are reduced by 23 %, they will be the same, statistically ( $\alpha = 0.05$ ), as the reference method.

The agreement between the cyclohexane subtraction and peak area methods deteriorated as concentration increased. This is most likely because at higher concentrations, the noise is easier to recognize, relative to the peak heights, and therefore wouldn't be included in the analysis.

As a quality control check for quantification, the concentrations that were expected in the chamber based on volume injected and chamber volume were calculated. For each injection, the concentration calculated was not significantly different from the concentration obtained by the GC-FID. This verifies the accuracy of the calibration gases obtained from NIST used to get the GC calibration curves.

### *Surrogate Backgrounds*

Using different backgrounds drastically impacted quantification results. The magnitude of the effect varied between chemicals. Tables 2-4 illustrate the impact on quantification of using different backgrounds for toluene, cyclohexane, and methanol, respectively.

Water vapor was used as a marker to track surrogate backgrounds. Water vapor content was calculated from temperature and relative humidity measurements obtained with the hygrometer. The hygrometer used was a Fisher Scientific brand hygrometer. Measurements from the hygrometer were compared to an independent resistance thermometer setup which recorded temperature. The difference between temperature readings from the thermometer setup and the temperature readings from the hygrometer was not significantly different.

When assuming no wavenumber shifts between sample and background files and a wetter surrogate background is used, concentration would be expected to decrease from truth. Likewise, if a dryer surrogate background is used, concentrations would be

expected to increase from truth. The FTIR Open-Path Guidance Document (33) recommends that a new background be taken whenever the partial pressure of water vapor changes by 5 % or greater. The results obtained in this study will be compared to this value.

When toluene backgrounds had a higher water vapor content than the original background, 70 % of concentration results increased and 30 % decreased. When toluene backgrounds had a lower water vapor content than the original, 57 % of concentration results increased and 43 % decreased. Even when two different backgrounds (containing the same amount of water vapor) from the same day were used, the concentration differences were significant and as great as 38 %. For water vapor partial pressure changes of 5 % and less, 83 % of the quantification results obtained were statistically different from those obtained with the original background. These results contradict the 5 % guideline stated in the FTIR Open-path Guidance Document. For water vapor partial pressure changes greater than 5 %, 76 % of the quantification results obtained were statistically different from those obtained with the original background, see Figure 15.

When the cyclohexane backgrounds had a higher water vapor content than the original, 63 % of quantification results increased, 25 % decreased, and 12.5 % remained the same. When a dryer surrogate background was used, 6 % of quantification results increased, 88 % decreased, and 6 % remained the same. For water vapor partial pressure changes of 5 % and greater, 44 % of quantification results were statistically different than results obtained using the original background. There was no data obtained for partial pressure changes of less than 5 %, see Figure 16.

When methanol backgrounds had a higher water vapor content than the original background, 67 % of the concentrations increased and 33 % decreased. When a background with a lower water vapor content than the original was used, 75 % of concentrations decreased, 25 % stayed the same and none increased. When two different backgrounds with the same water vapor content were used, the concentration differences were significant and as high as 20 %. For water vapor partial pressure changes of 5 % and less, 92 % of quantification results were significantly different than the results obtained with the original background. These results also contradict the 5 % guideline given in the FTIR Open-path Guidance Document. For water vapor partial pressure changes greater than 5 %, 60 % of the quantification results were significantly different than the results obtained with the original background, see Figure 17. For a summary of the surrogate

background results obtained with all three chemicals, see Table 5.

Significant differences in quantification results were encountered when two different backgrounds with the same water vapor content were used and surrogate results were always higher. This may be due to the fact that the noise level of the absorbance file obtained with the original background, was lower than the noise level of the absorbance background obtained with the surrogate background.

Changes in water vapor content of the backgrounds impacted toluene more than the other chemicals. This may be due to the fact that there are more water vapor peaks in the toluene absorbance region used for quantification in this study than for the other two chemicals.

None of the chemicals followed the expected trend of : dryer surrogate yields higher quantification results and wetter surrogate yields lower quantification results. In fact, any trends seen were in the reverse direction. This indicates that there are other factors present affecting quantification other than partial pressure of water vapor.

## Conclusions

Results of the quality control parameter studies are encouraging in terms of day to day instrument performance. However, other difficulties were encountered with instrument performance, such as the liquid nitrogen dewar (which cools the detector) losing vacuum and the laser (which guides the scanning mirror) losing alignment, thus stopping the mirror from scanning.

Before definite results can be given for accuracy, the effects of using different libraries and methods of quantification must be fully evaluated. However, two major findings are: 1) For toluene, the ideal combination for quantification in this research was the peak area method and the EPA library. For both methods, results obtained with the EPA library were closer to reference method than results obtained with the Hanst library. 2) For cyclohexane, both peak area and subtraction methods overestimated the concentration present when the Hanst library was used. However, when a ratio factor obtained from linear regression was applied, the concentrations obtained from both methods could be statistically corrected such that they were not significantly different than the GC-FID reference method results.

These studies have demonstrated that varying environmental conditions drastically affect quantification when backgrounds are not obtained frequently. Deviations from expected concentrations presented in this paper were as high as 102 % for toluene, 25 % for cyclohexane, and 39 % for methanol. Changes in water vapor partial pressure of less than 5 % resulted in quantification differences of up to 51 % for toluene and 39 % for methanol. These results indicate a problem with the 5 % guideline given in the FTIR Open-path Guidance Document. Toluene quantification was affected most by changing environmental conditions followed by

cyclohexane and methanol respectively. No significant trend was noted and results varied among the three chemicals used.

Water vapor was not an ideal marker to indicate when a new background should be taken. This was because for differences in water vapor as small as 2%, quantification results were significantly different. In addition, for water vapor differences as great as 36%, some differences in quantification results were found to be insignificant. More studies need to be done to thoroughly evaluate the relationship between effect on quantification and percent water vapor change. One possible solution would be to subtract out a water vapor spectrum (at appropriate concentration) from background and sample spectra.

TABLE 1

## QUALITY CONTROL

<u>TEST</u>	<u>VALUE</u>	<u>N</u>	<u>STD. DEVIATION</u>
Polystyrene Peak (3025 cm-1)			
height	1.33	16	0.0031
area	17.63	16	0.2804
Polystyrene Peak (2922 cm-1)			
height	1.78	16	0.0029
area	59.2	16	0.3613
Peak to Peak Noise (2820-2850 cm-1)	2.83 X 10 <sup>-4</sup>	46	2.4 X 10 <sup>-5</sup>

\* N = number of data files used

TABLE TWO

FILE	PW	BCKGD	PW	W/D	CHANGE	NOISE	H or L	% DIFF
T10-17-1	8.4	B10-17-3	8.2	ORIGINAL	X	0.000296	X	X
T10-17-1	8.4	B10-17-5	7.1	D	13%	0.000395	H	30
T10-17-1	8.4	B10-17-6	6.5	D	21%	0.000382	L	51
T10-17-4	7.2	B10-17-5	7.1	ORIGINAL	X	0.000244	X	X
T10-17-4	7.2	B10-17-6	6.5	D	8.50%	0.000389	L	36
T10-17-4	7.2	B10-17-3	8.2	W	15.50%	0.000315	H	64
T10-19-1	11.1	B10-19-3	11	ORIGINAL	X	0.00033	X	X
T10-19-1	11.1	B10-19-5	10.9	D	0.90%	0.00037	H	24
T10-19-1	11.1	B10-10-7	11	SAME	0%	0.00039	H	38
T10-19-3	11	B10-19-5	10.9	ORIGINAL	X	0.0003	X	X
T10-19-3	11	B10-19-3	11	W	0.90%	0.00058	H	51
T10-19-3	11	B10-19-7	11	W	0.90%	0.00045	H	5.3
T10-19-5	10.9	B10-19-7	11	ORIGINAL	X	0.00041	X	X
T10-19-5	10.9	B10-19-3	11	SAME	0%	0.000624	H	5.7
T10-19-5	10.9	B10-19-5	10.9	D	0.90%	0.000563	L	15.9
T10-22-1	12.2	B10-22-3	12.4	ORIGINAL	X	0.000275	X	X
T10-22-1	12.2	B10-22-5	12.5	W	0.80%	0.000439	L	2.4
T10-25-1	12.6	B10-25-3	12.8	ORIGINAL	X	0.000644	X	X
T10-25-1	12.6	B10-25-5	9.1	D	28.90%	0.000845	H	1.6
T10-25-1	12.6	B10-25-7	8.1	D	36.70%	0.000109	H	18.8
T10-25-4	9.2	B10-25-5	9.1	ORIGINAL	X	0.000587	X	X
T10-25-4	9.2	B10-25-3	12.8	W	40.70%	0.000635	H	9.1
T10-25-4	9.2	B10-25-7	8.1	D	11%	0.000658	H	9.1
T10-25-6	8.2	B10-25-3	12.8	W	58%	0.000431	L	12.2
T10-25-6	8.2	B10-25-5	9.1	W	12.30%	0.000535	L	37.4
T10-25-6	8.2	B10-25-7	8.1	ORIGINAL	X	0.00028	X	X
T10-17-3	8.5	B10-17-3	8.2	ORIGINAL	X	0.000379	X	X
T10-17-3	8.5	B10-17-5	7.1	D	16.55	0.000496	L	0.9
T10-17-3	8.5	B10-17-6	6.5	D	23.50%	0.000498	L	36.2
T10-23-1	15	B10-23-3	15.6	ORIGINAL	X	0.000174	X	X
T10-23-1	15.6	B10-23-5	13.5	D	13.50%	0.0003	H	2
T10-23-1	15.6	B10-23-7	12.8	D	12.80%	0.000394	H	20
T10-23-3	13.4	B10-23-3	15.6	W	16.40%	0.000276	H	218
T10-23-3	13.4	B10-23-5	13.5	ORIGINAL	X	0.000198	X	X
T10-23-3	13.4	B10-23-7	13.6	W	0.74%	0.000359	H	45
T10-23-5	13.4	B10-23-3	15.6	W	14.70%	0.000448	H	88

TABLE TWO

T10-23-5	13.4	B10-23-5	13.5	D	0.74%	0.000485	H	102
T10-23-5	13.4	B10-23-7	13.6	ORIGINAL	X	0.000368	X	X
T10-24-1	7.4	B10-24-3	7.6	ORIGINAL	X	0.000625	X	X
T10-24-1	7.4	B10-24-5	7.6	SAME	0	0.000451	H	12
T10-24-3	7.8	B10-24-5	7.6	SAME	0	0.000546	X	X
T10-24-3	7.8	B10-24-3	7.6	ORIGINAL	X	0.000821	L	2.9
T12-16-1	6	B12-16-2	6.1	ORIGINAL	X	0.000758	X	X
T12-16-1	6	B12-16-3	5.7	D	6.6	0.000842	L	4.5
T12-16-1	6	B12-16-4	5.8	D	4.9	0.0001	H	18.2

Pw = partial pressure of water vapor

W/D = wetter or dryer surrogate

Change = difference between two backgrounds

H or L = quantification result higher or lower

% Diff = percent difference from value obtained using original background

TABLE THREE

FILE	Pw	BCKGD	Pw	WD	CHANGE	H or L	% DIFF
C12-6-1	15.1	B12-16-2	15.1	ORIGINAL	X	X	X
C12-6-1	15.1	B12-16-3	11.1	D	26.50%	L	10.9
C12-6-2	14.5	B12-16-2	15.1	ORIGINAL	X	X	X
C12-6-2	14.5	B12-16-3	11.1	D	26.50%	L	1.6
C12-6-3	10.5	B12-16-2	15.1	W	36%	H	3.4
C12-6-3	10.5	B12-16-3	11.1	ORIGINAL	X	X	X
C12-6-4	10.6	B12-16-2	15.1	W	36%	H	2
C12-6-4	10.6	B12-16-3	11.1	ORIGINAL	X	X	X
C12-7-1	14.3	B12-7-2	14.1	ORIGINAL	X	X	X
C12-7-1	14.3	B12-7-3	10.5	D	25.50%	L	11.8
C12-7-1	14.3	B12-7-4	9.3	D	34%	L	4.4
C12-7-2	13.7	B12-7-2	14.1	ORIGINAL	X	X	X
C12-7-2	13.7	B12-7-3	10.5	D	25.50%	L	8.5
C12-7-2	13.7	B12-7-4	9.3	D	34%	L	2.3
C12-7-3	10	B12-7-2	14.1	W	34.30%	H	4.5
C12-7-3	10	B12-7-3	10.5	ORIGINAL	X	X	X
C12-7-3	10	B12-7-4	9.3	D	11.40%	H	1.5
C12-7-4	10.1	B12-7-2	14.1	W	34.30%	H	1.5
C12-7-4	10.1	B12-7-3	10.5	ORIGINAL	X	X	X
C12-7-4	10.1	B12-7-4	9.3	D	11.40%	L	1.5
C12-7-5	9.3	B12-7-2	14.1	W	52	SAME	0%
C12-7-5	9.3	B12-7-3	10.5	W	12.9	L	1.2
C12-7-5	9.3	B12-7-4	9.3	ORIGINAL	X	X	X
C12-7-6	9.5	B12-7-2	14.1	W	52	H	1.6
C12-7-6	9.5	B12-7-3	10.5	W	12.9	SAME	0
C12-7-6	9.5	B12-7-4	9.3	ORIGINAL	X	X	X
C12-8-1	5.8	B12-8-2	5.9	ORIGINAL	X	X	X
C12-8-1	5.8	B12-8-3	5.4	D	8.50%	L	9.2
C12-8-1	5.8	B12-8-4	4.7	D	20%	L	10.7
C12-8-2	6.1	B12-8-2	5.9	ORIGINAL	X	X	X
C12-8-2	6.1	B12-8-3	5.4	D	8.50%	L	5.4
C12-8-2	6.1	B12-8-4	4.7	D	20%	L	6.2
C12-8-3	5.3	B12-8-2	5.9	W	9.30%	H	5.7
C12-8-3	5.3	B12-8-3	5.4	ORIGINAL	X	X	X
C12-8-3	5.3	B12-8-4	4.7	D	13%	L	5.7
C12-8-4	5.2	B12-8-2	5.9	W	9.30%	H	2.8

TABLE THREE

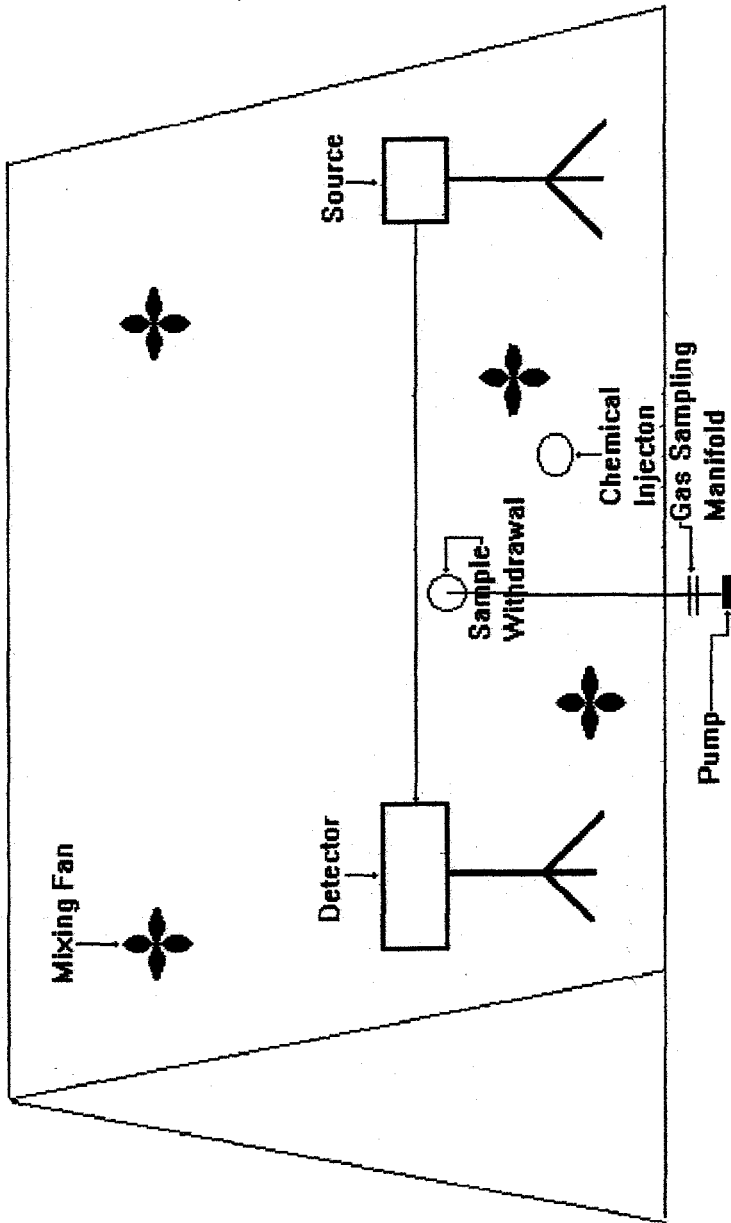
C12-8-4	5.2	B12-8-3	5.4	ORIGINAL	X	X	X
C12-8-4	5.2	B12-8-4	4.7	D	13%	L	2.8
C12-8-5	4.7	B12-8-2	5.9	W	25.50%	H	4.4
C12-8-5	4.7	B12-8-3	5.4	W	14.90%	H	2.
C12-8-5	4.7	B12-8-4	4.7	ORIGINAL	X	X	X
C12-8-6	4.6	B12-8-2	5.9	W	25.50%	H	0.6
C12-8-6	4.6	B12-8-3	5.4	W	14.90%	L	0.3
C12-8-6	4.6	B12-8-4	4.7	ORIGINAL	X	X	X
C12-9-1	4.9	B12-9-2	4.9	ORIGINAL	X	X	X
C12-9-1	4.9	B12-9-3	5.8	W	18.40%	L	3.3
C12-9-2	4.8	B12-9-2	4.9	ORIGINAL	X	X	X
C12-9-2	4.8	B12-9-3	5.8	W	18.40%	L	1.9
C12-9-3	5.8	B12-9-2	4.9	D	16%	L	1
C12-9-3	5.8	B12-9-3	5.8	ORIGINAL	X	X	X
C12-9-4	5.9	B12-9-2	4.9	D	16.00%	SAME	0
C12-9-4	5.9	B12-9-3	5.8	ORIGINAL	X	X	X

TABLE FOUR

<u>FILE</u>	<u>PW</u>	<u>BCKGD</u>	<u>PW</u>	<u>W/D</u>	<u>CHANGE</u>	<u>H or L</u>	<u>% DIFF</u>
M11-20-1	6.6	B11-20-2	7.3	ORIGINAL	X	X	X
M11-20-1	6.6	B11-20-3	7.3	SAME	0.00%	L	19.9
M11-20-1	6.6	B11-20-4	8.8	W	20.50%	L	15.8
M11-20-2	7.3	B11-20-2	7.3	SAME	0%	H	5.4
M11-20-2	7.3	B11-20-3	7.3	ORIGINAL	X	X	X
M11-20-2	7.3	B11-20-4	8.8	W	20.50%	H	7.3
M11-20-3	7.4	B11-20-2	7.3	D	17%	L	7.2
M11-20-3	7.4	B11-20-3	7.3	D	17%	SAME	0
M11-20-3	7.4	B11-20-4	8.8	ORIGINAL	X	X	X
M12-12-1	3.6	B12-12-2	3.5	ORIGINAL	X	X	X
M12-12-1	3.6	B12-12-3	3.5	SAME	0%	L	18.1
M12-12-1	3.6	B12-12-4	3.4	D	2.90%	L	39.4
M12-12-2	3.5	B12-12-2	3.5	ORIGINAL	X	X	X
M12-12-2	3.5	B12-12-3	3.5	SAME	0%	L	11.3
M12-12-2	3.5	B12-12-4	3.4	D	2.90%	L	24.2
M12-12-3	3.5	B12-12-2	3.5	SAME	0%	H	6.4
M12-12-3	3.5	B12-12-3	3.5	ORIGINAL	X	X	X
M12-12-3	3.5	B12-12-4	3.4	D	2.90%	L	25.1
M12-12-5	3.4	B12-12-2	3.5	W	2.90%	H	15.4
M12-12-5	3.4	B12-12-3	3.5	W	2.90%	H	10.1
M12-12-5	3.4	B12-12-4	3.4	ORIGINAL	X	X	X
M12-12-7	3.4	B12-12-2	3.5	W	2.90%	H	6.7
M12-12-7	3.4	B12-12-3	3.5	W	2.90%	H	0.6
M12-12-7	3.4	B12-12-4	3.4	ORIGINAL	X	X	X
M12-15-2	6.9	B12-15-2	7.1	ORIGINAL	X	X	X
M12-15-2	6.9	B12-15-3	6.1	D	14.10%	L	10.5
M12-15-2	6.9	B12-15-4	5.4	D	23.90%	L	12.4
M12-15-4	6.1	B12-15-2	7.1	W	16.40%	L	4.1
M12-15-4	6.1	B12-15-3	6.1	ORIGINAL	X	X	X
M12-15-4	6.1	B12-15-4	5.4	D	11.50%	SAME	0
M12-15-6	5.9	B12-15-2	7.1	W	31.50%	H	2.8
M12-15-6	5.9	B12-15-3	6.1	W	13%	L	2.3
M12-15-6	5.9	B12-15-4	5.4	ORIGINAL	X	X	X

FIGURE 1: TEFLON EXPOSURE CHAMBER

\*\*\* not to scale



all Figures need captions

FIGURE 2

CYCLOHEXANE GC CALIBRATION-- 12/9/94

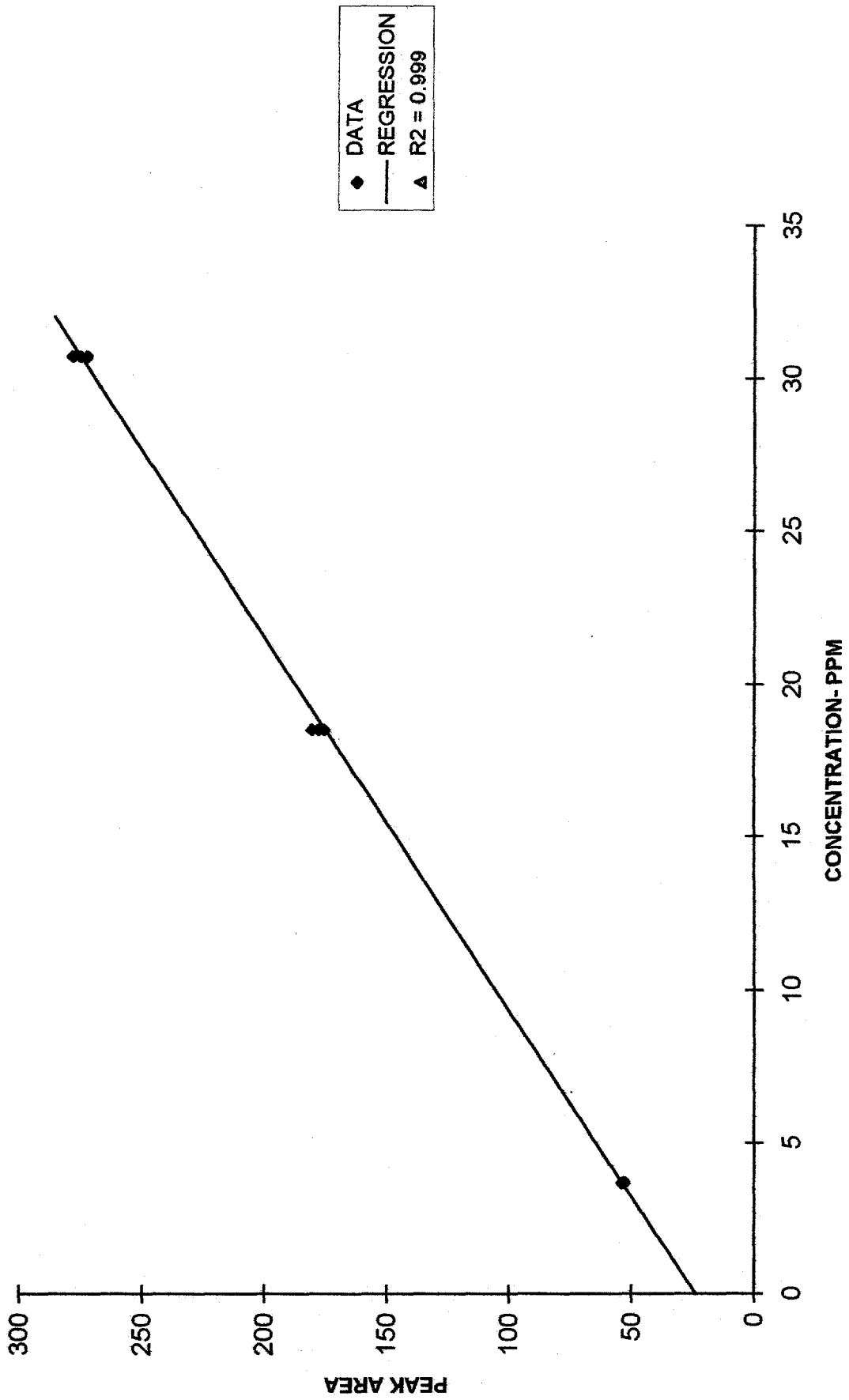
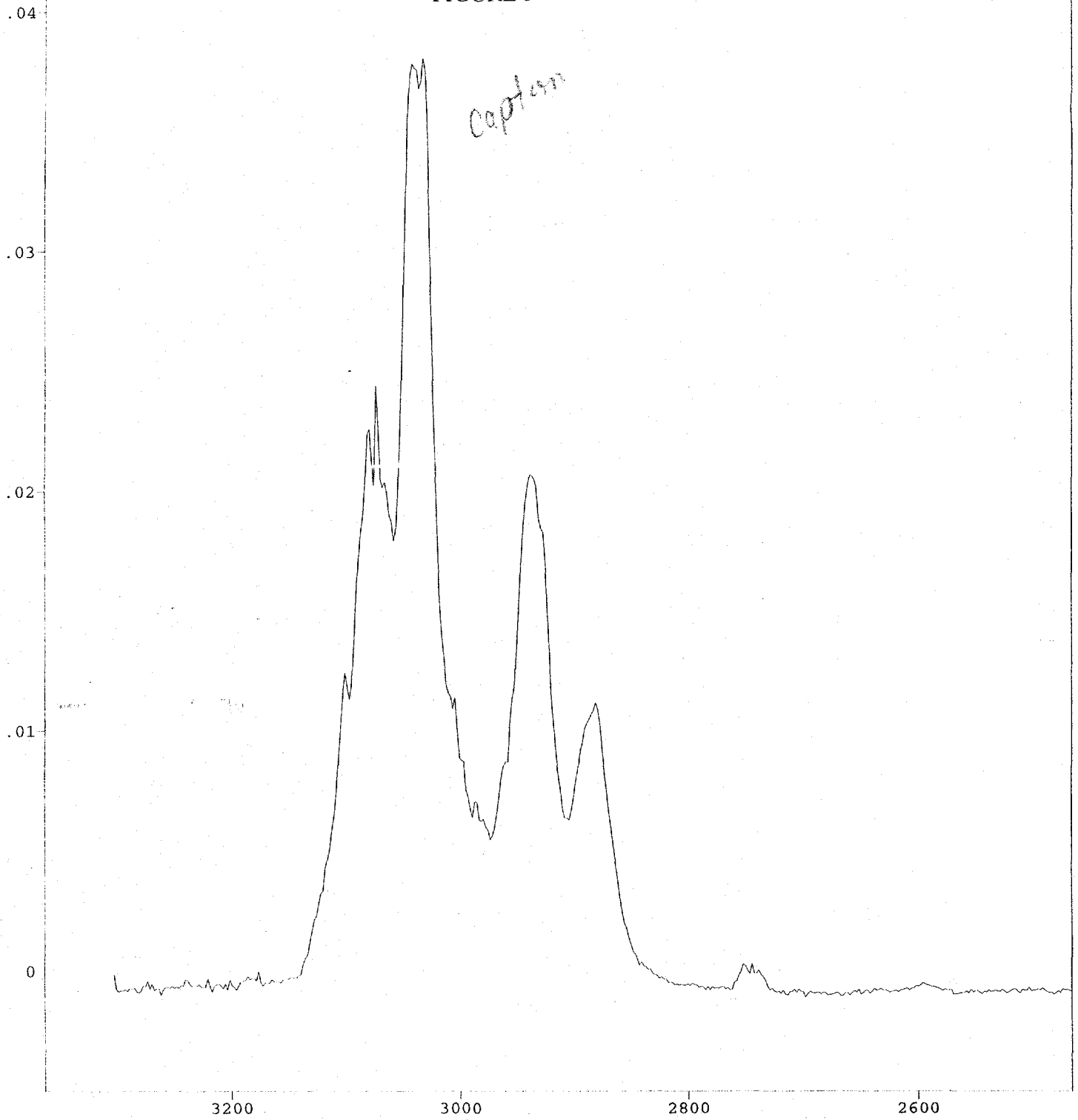


FIGURE 3



Absorbance / Wavenumber (cm-1)

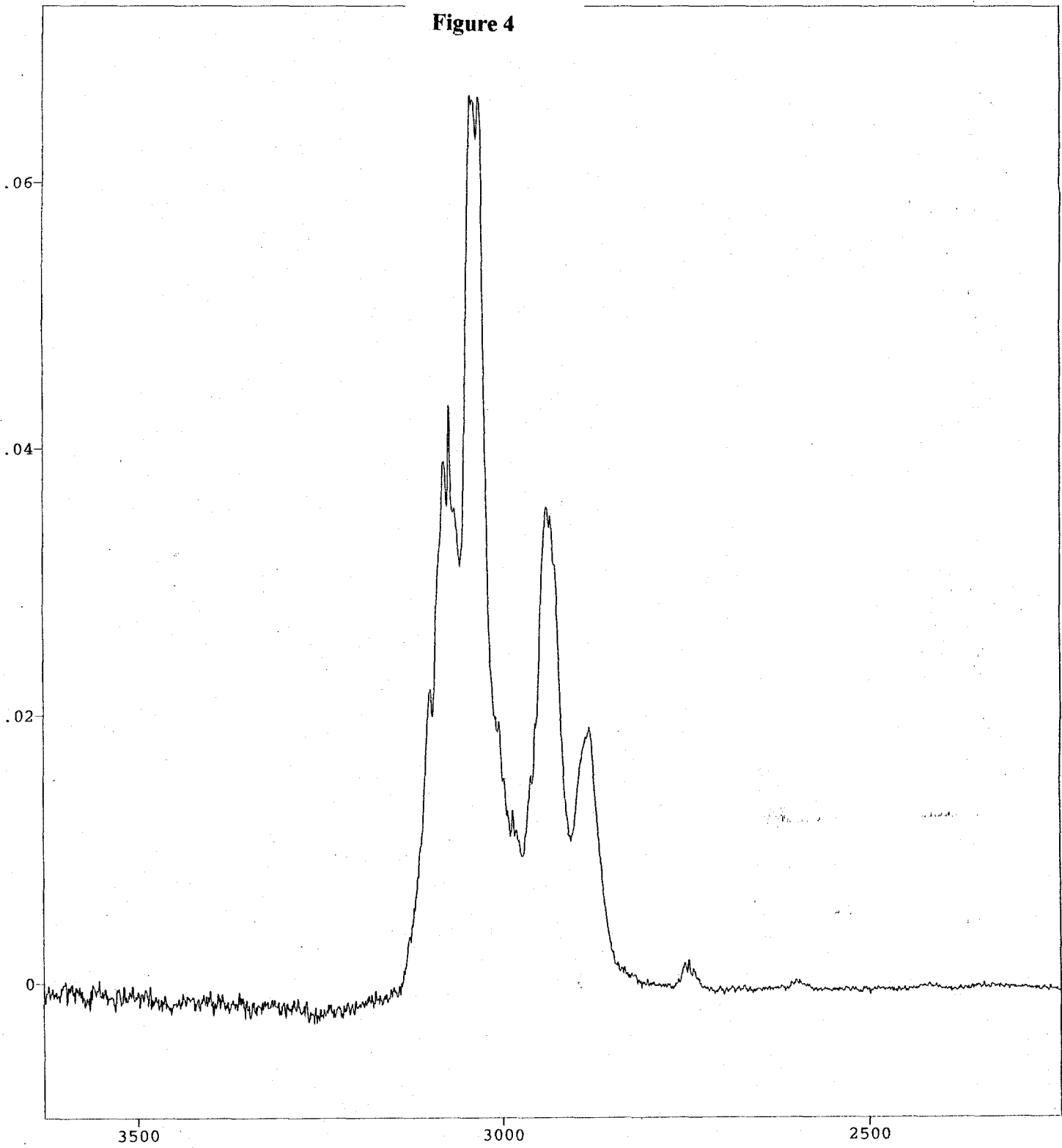
Paged Y-Zoom CURSOR

File #21: TOL-DR

8/11/92 1:18 PM Res=.5cm-1

Toluene, 137 ppm-meters in 1 atm. N2.

Figure 4



Absorbance / Wavenumber (cm-1)

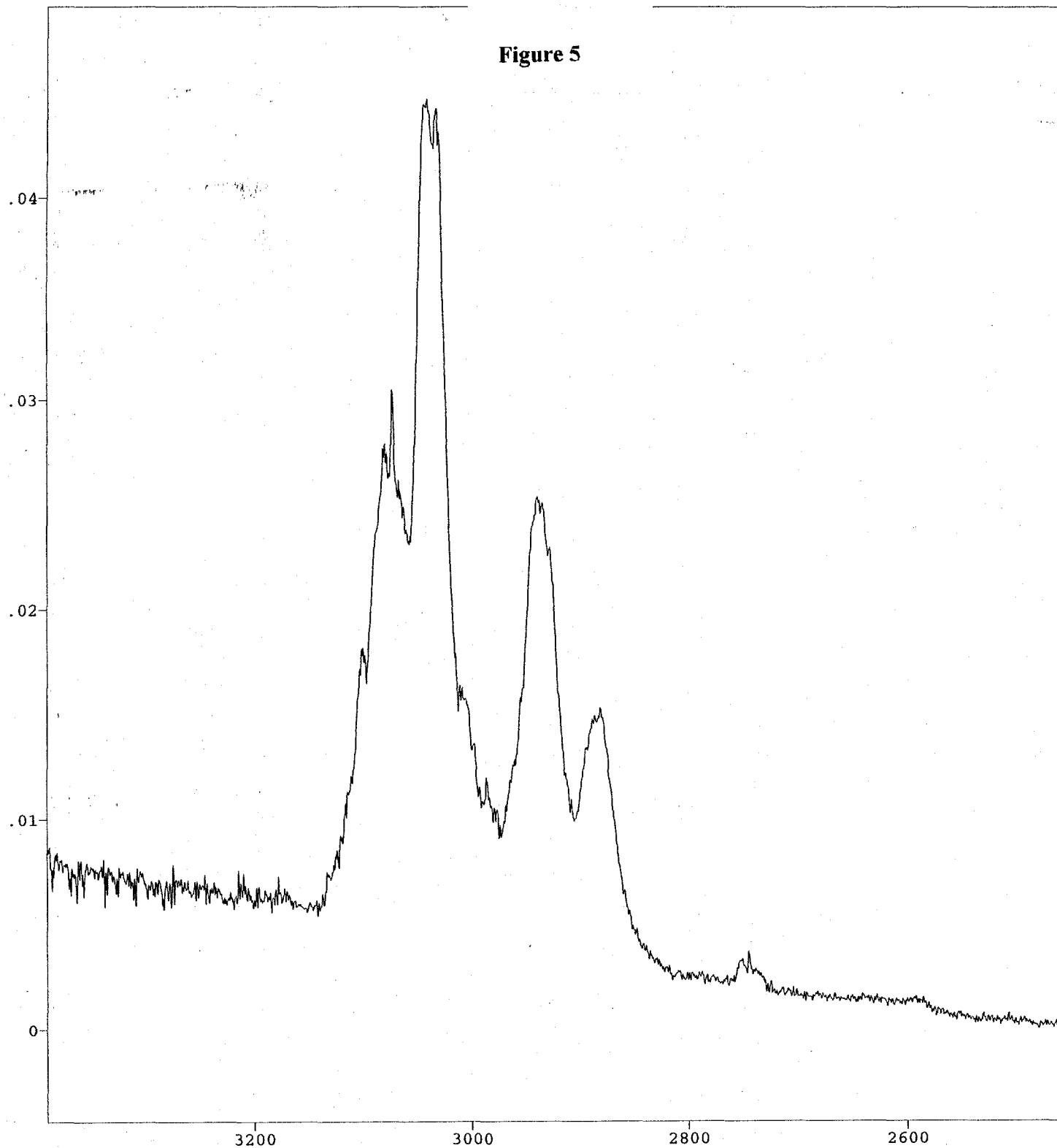
Paged Y-Zoom CURSOR

File #19 : ZTOLU249

3/8/93 11:52 AM Res=1 cm-1

Toluene, 249 ppm-m, in 1 atm dry N<sub>2</sub>. (728.82 cm-1)

Figure 5



Absorbance / Wavenumber (cm-1)

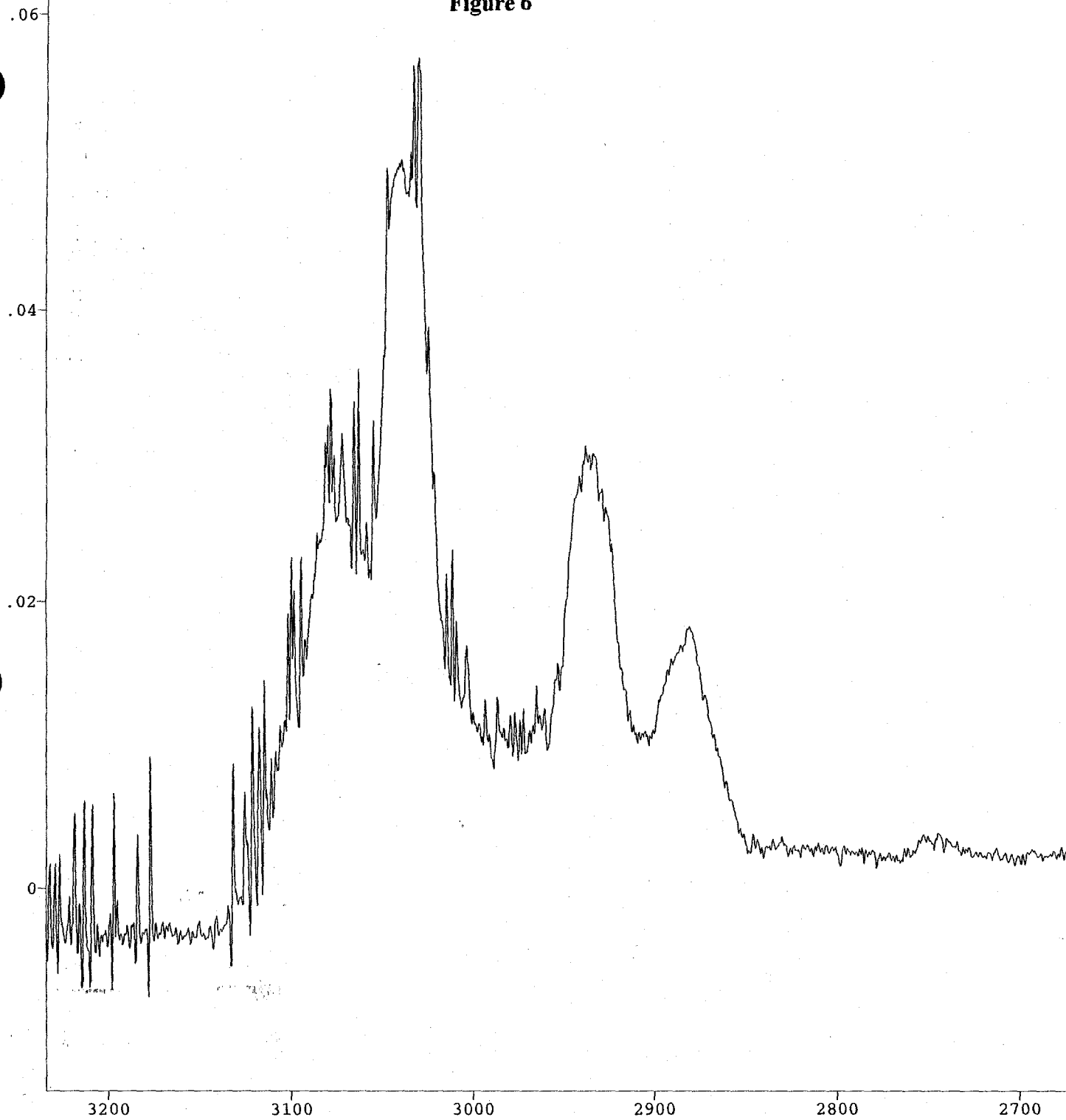
Paged Y-Zoom CURSOR

File # 8 : T10-23-5

10/23/94 7:43 PM Res=1cm-1

20 ml toluene 1 cm-1

Figure 6



Absorbance / Wavenumber (cm-1)

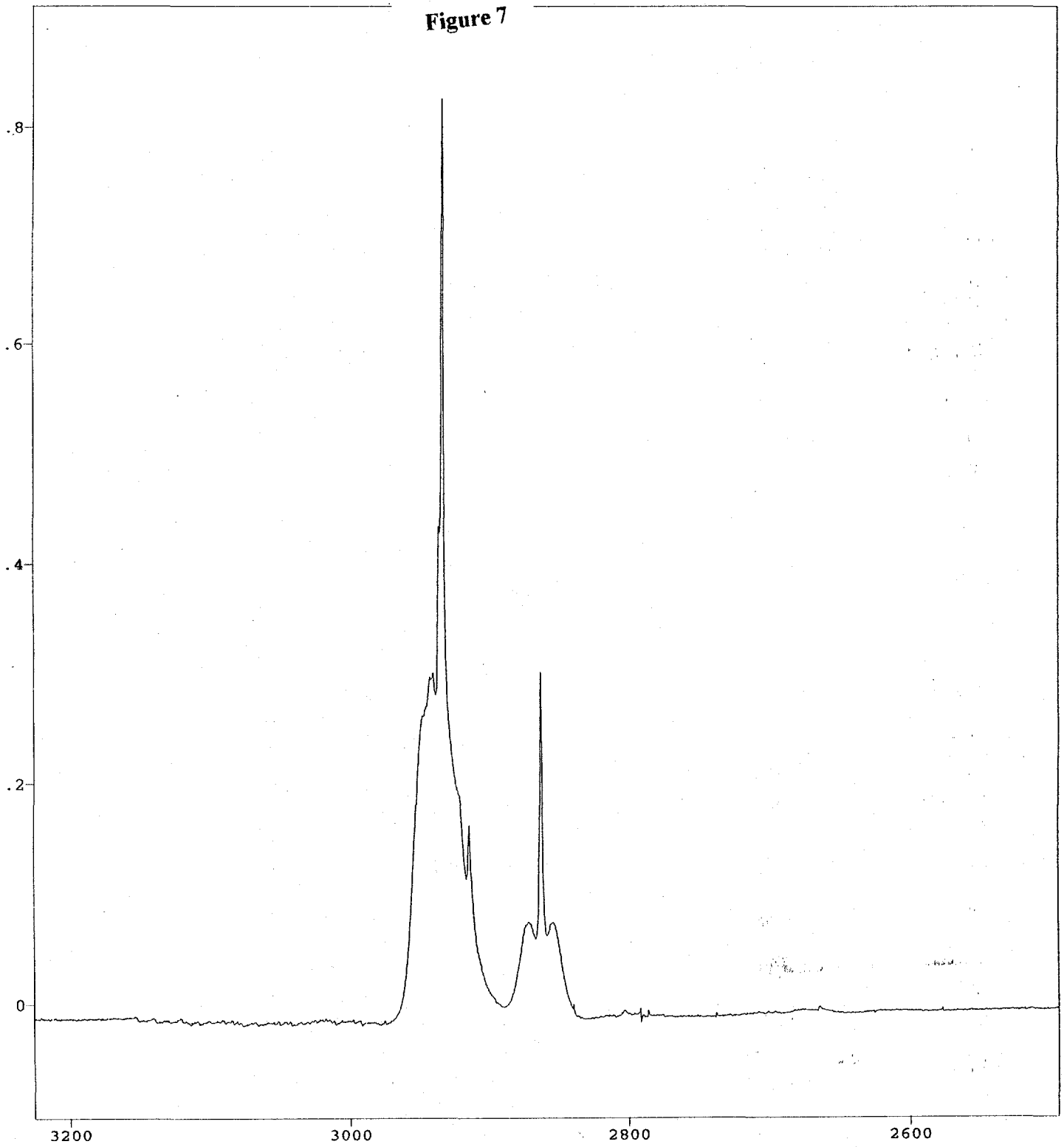
Paged Y-Zoom CURSOR

File 26 : T10-17-1

10/17/94 1:00 PM Res=1cm-1

25 ml toluene

Figure 7



Absorbance / Wavenumber (cm-1)

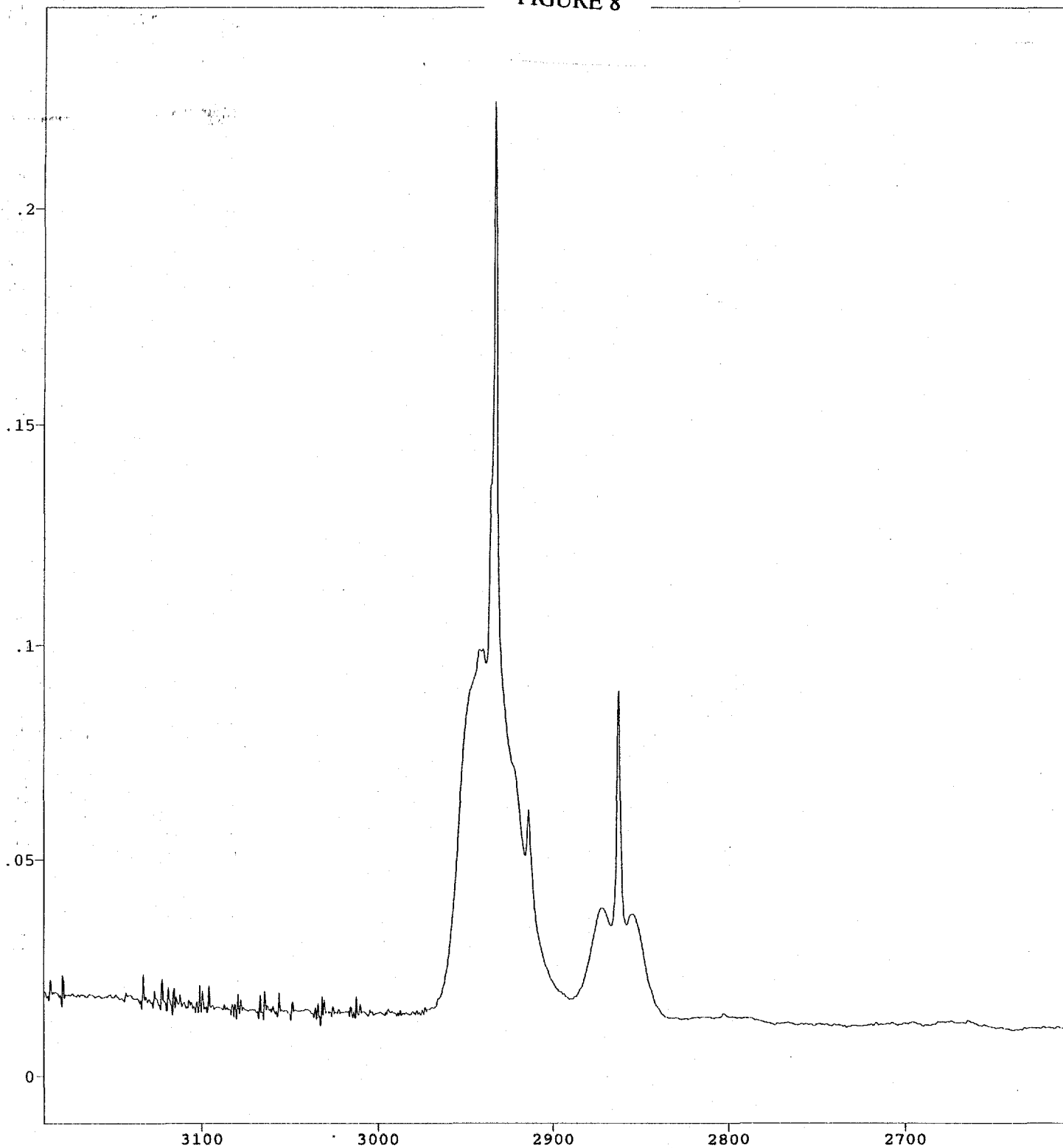
Paged Y-Zoom CURSOR

#18 = CYHA221

2/27/88 2:04 PM Res=0.5 cm-1

Cyclohexane, 221 micro-atm. meters, in 1 atm. N2.

FIGURE 8



Absorbance / Wavenumber (cm-1)

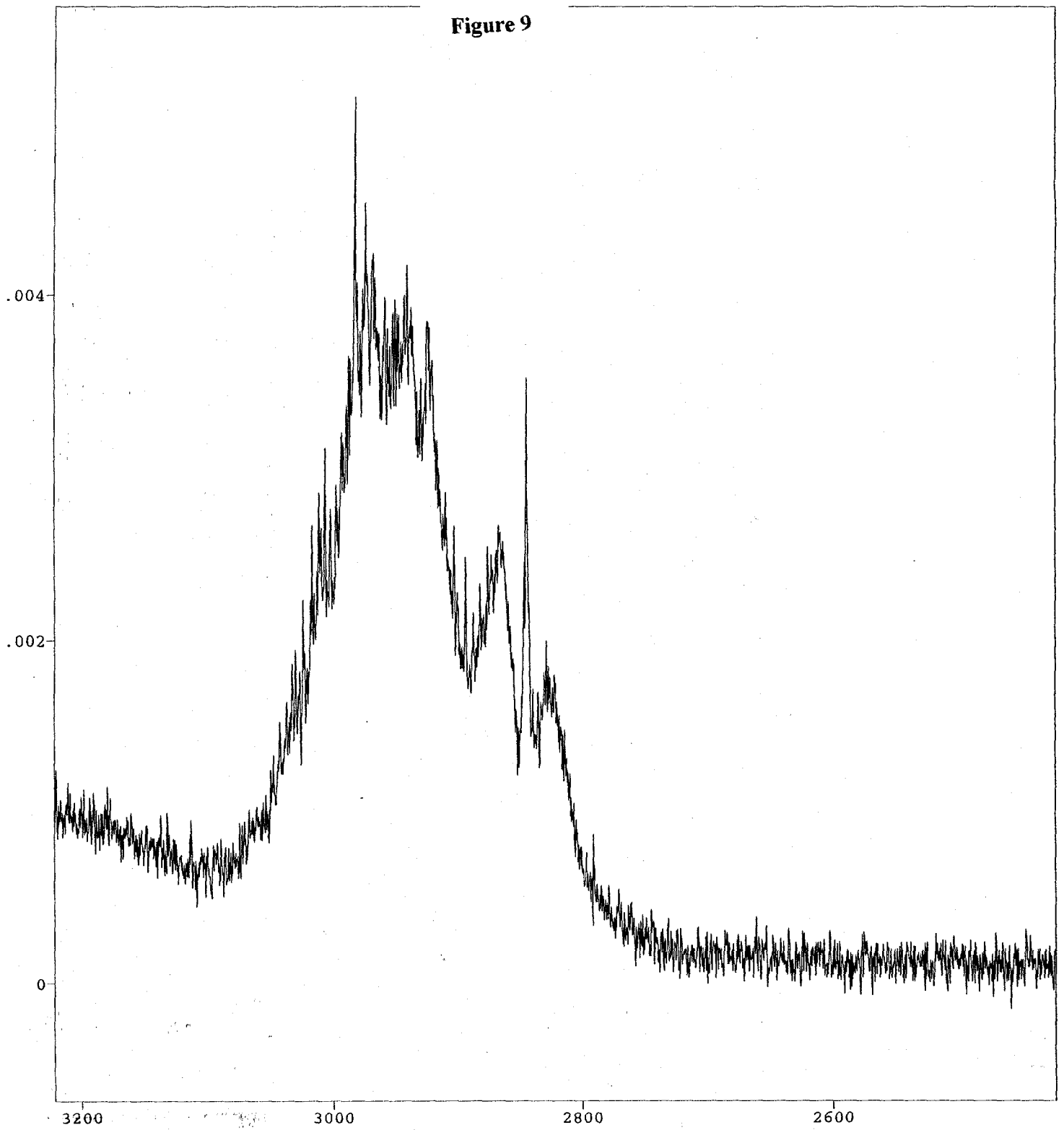
Paged Y-Zoom CURSOR

#10 : C12-7-1

12/7/94 1:12 PM Res=1cm-1

5 ml cyclohexane

Figure 9



Absorbance / Wavenumber (cm-1)

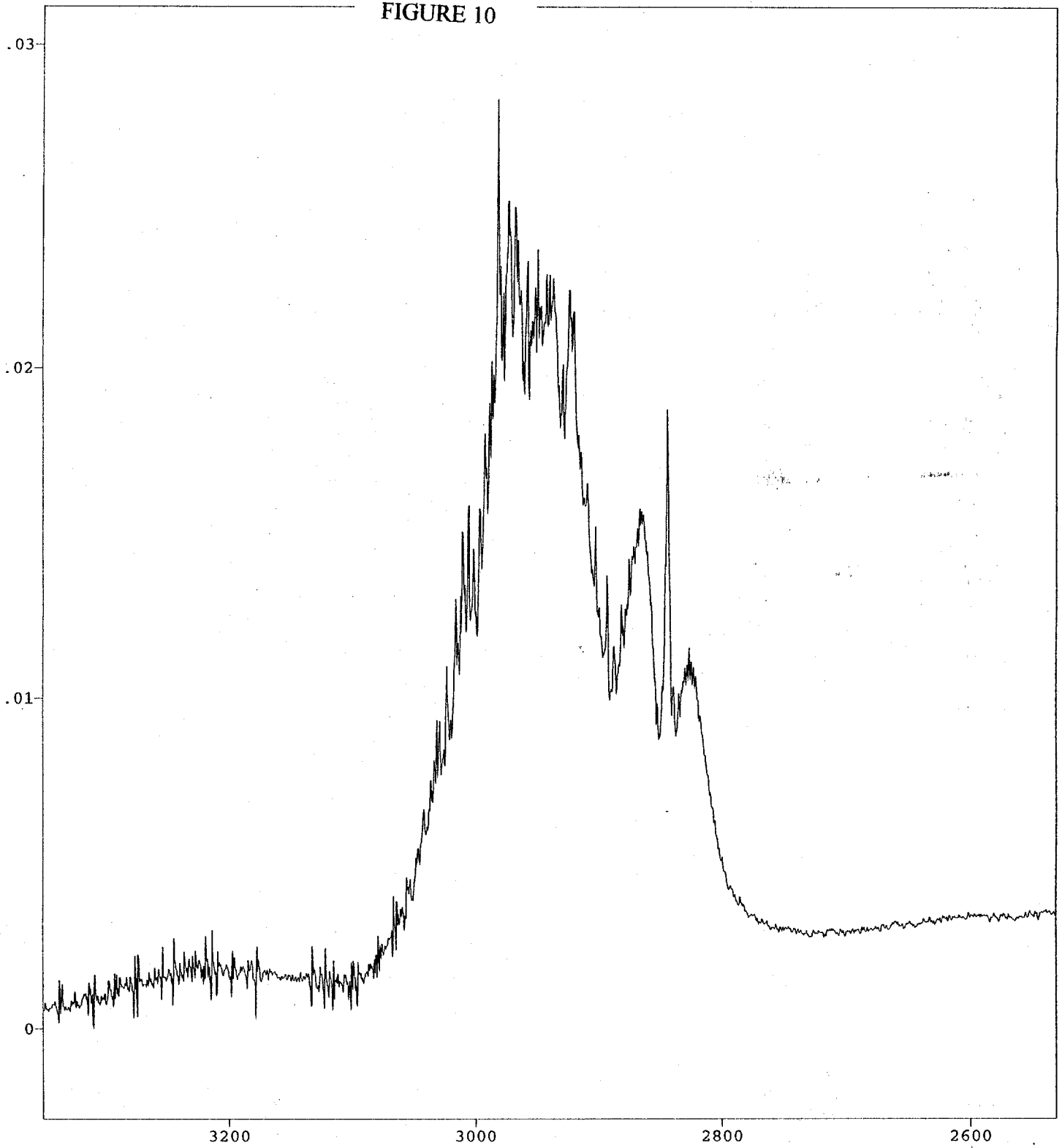
Paged Y-Zoom CURSOR

#20 = MEOH27

11/7/87 10:56 AM Res=0.5 cm-1

Methanol, 27 micro-atm. meters, in 1 atm. N2.

FIGURE 10



Absorbance / Wavenumber (cm-1)

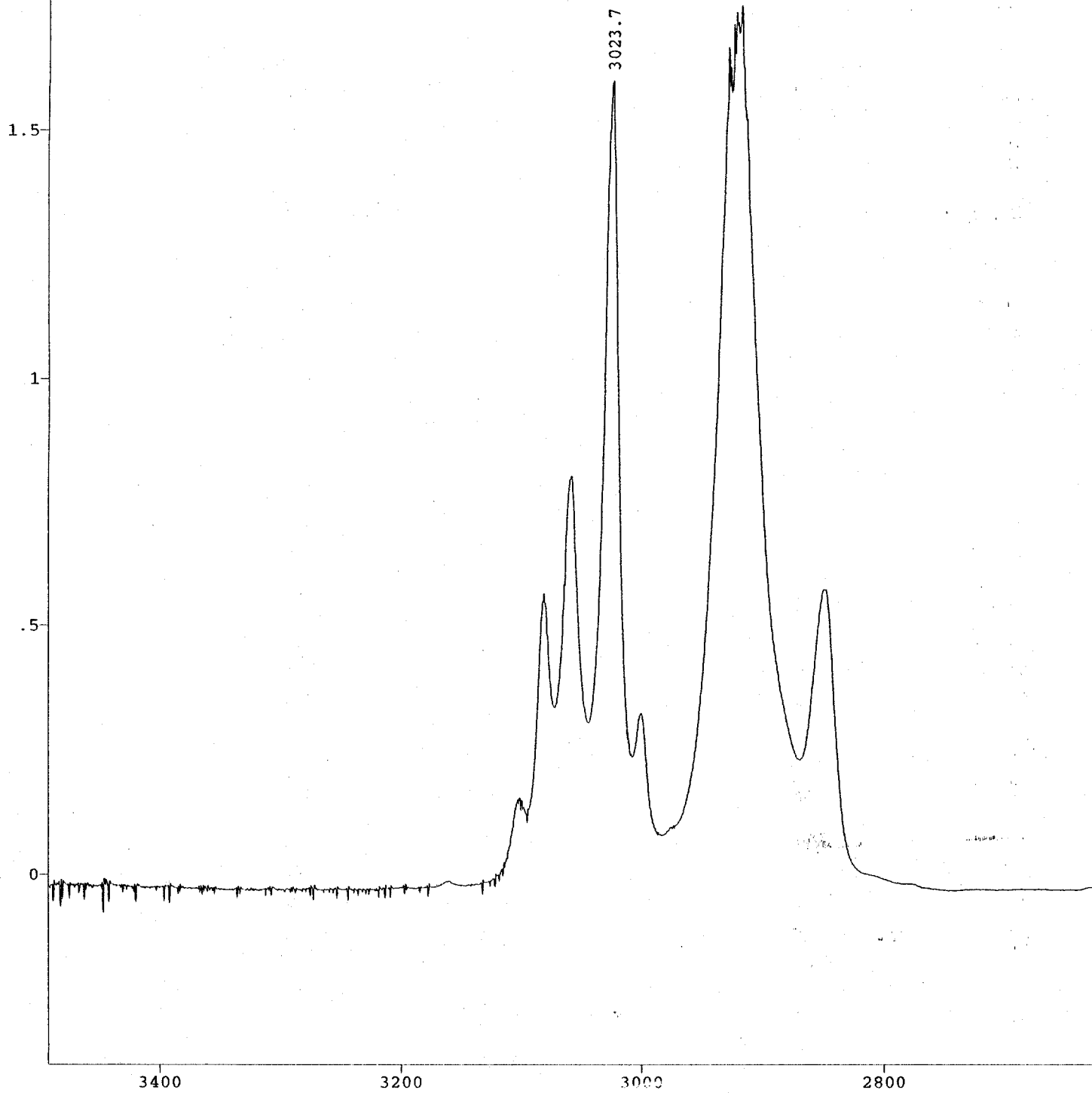
Paged Y-Zoom CURSOR

#16 : M12-12-1

12/12/94 1:05 PM Res=1cm-1

5 ml methanol

Figure 11



Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

#26 : P10-17-A

10/17/94 12:10 PM Res=1cm-1

poly film

FIGURE 12

TOLUENE- PEAK AREA VS. SUBTRACTION-HANST

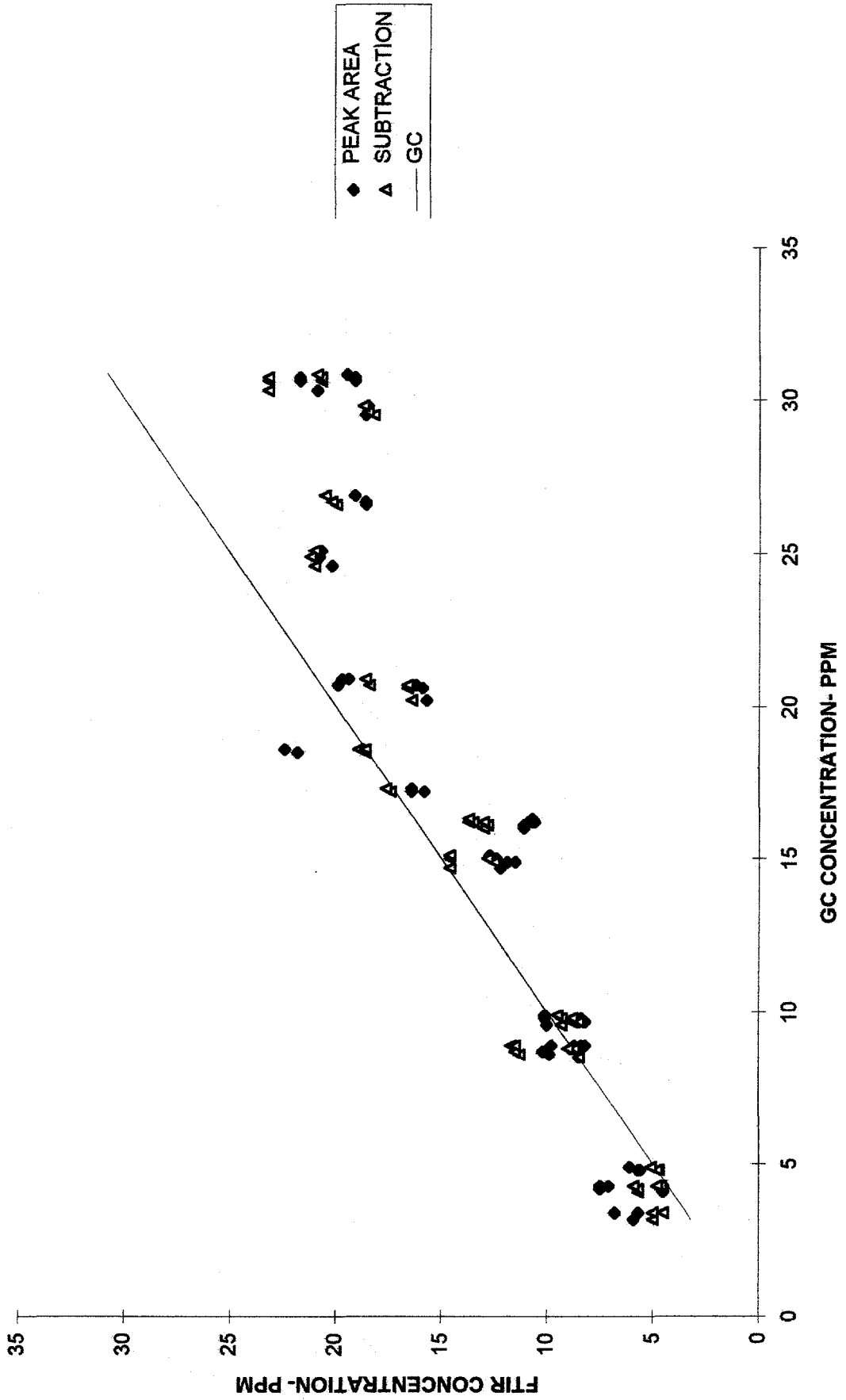


FIGURE 13

TOLUENE- PEAK AREA VS. SUBTRACTION- EPA

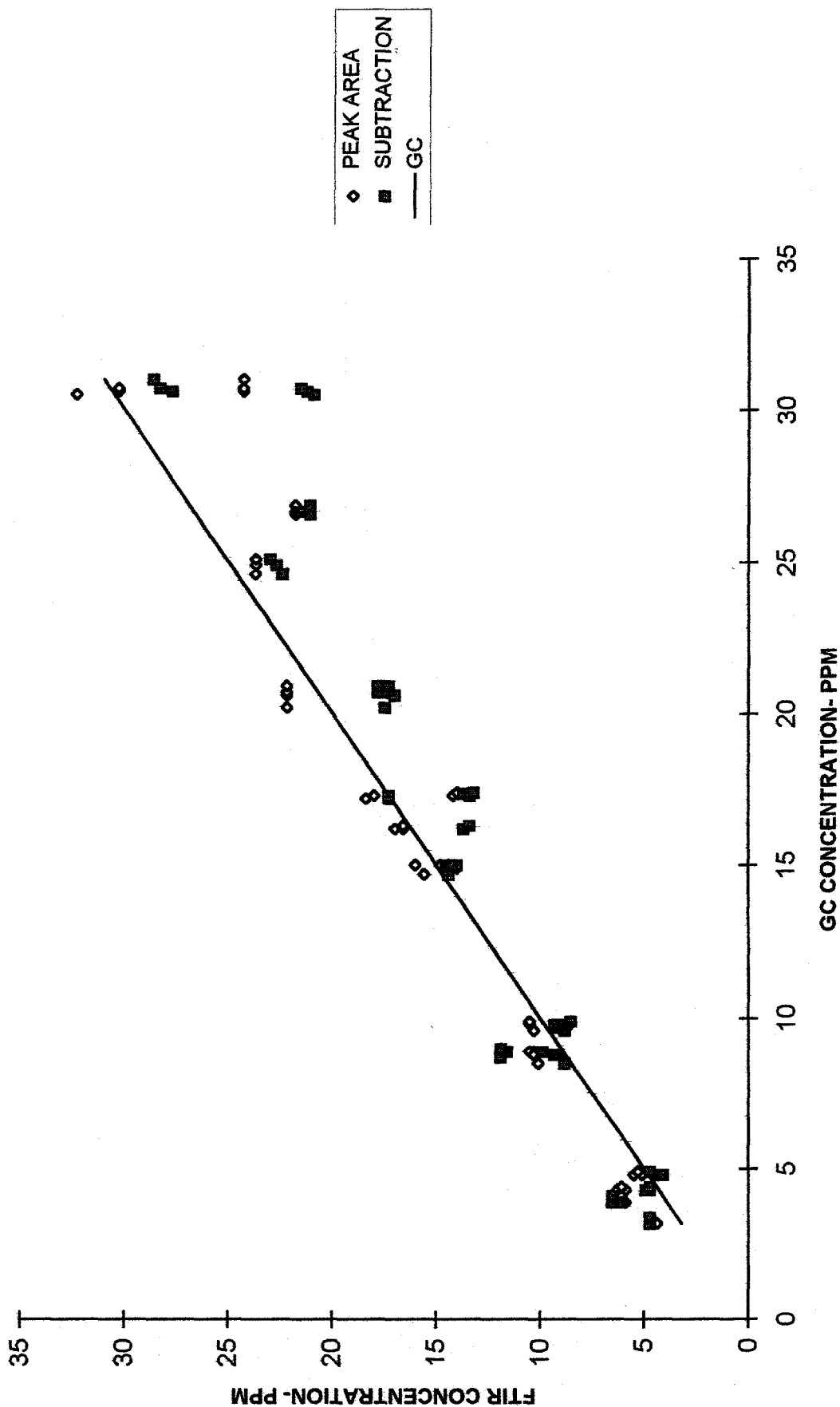
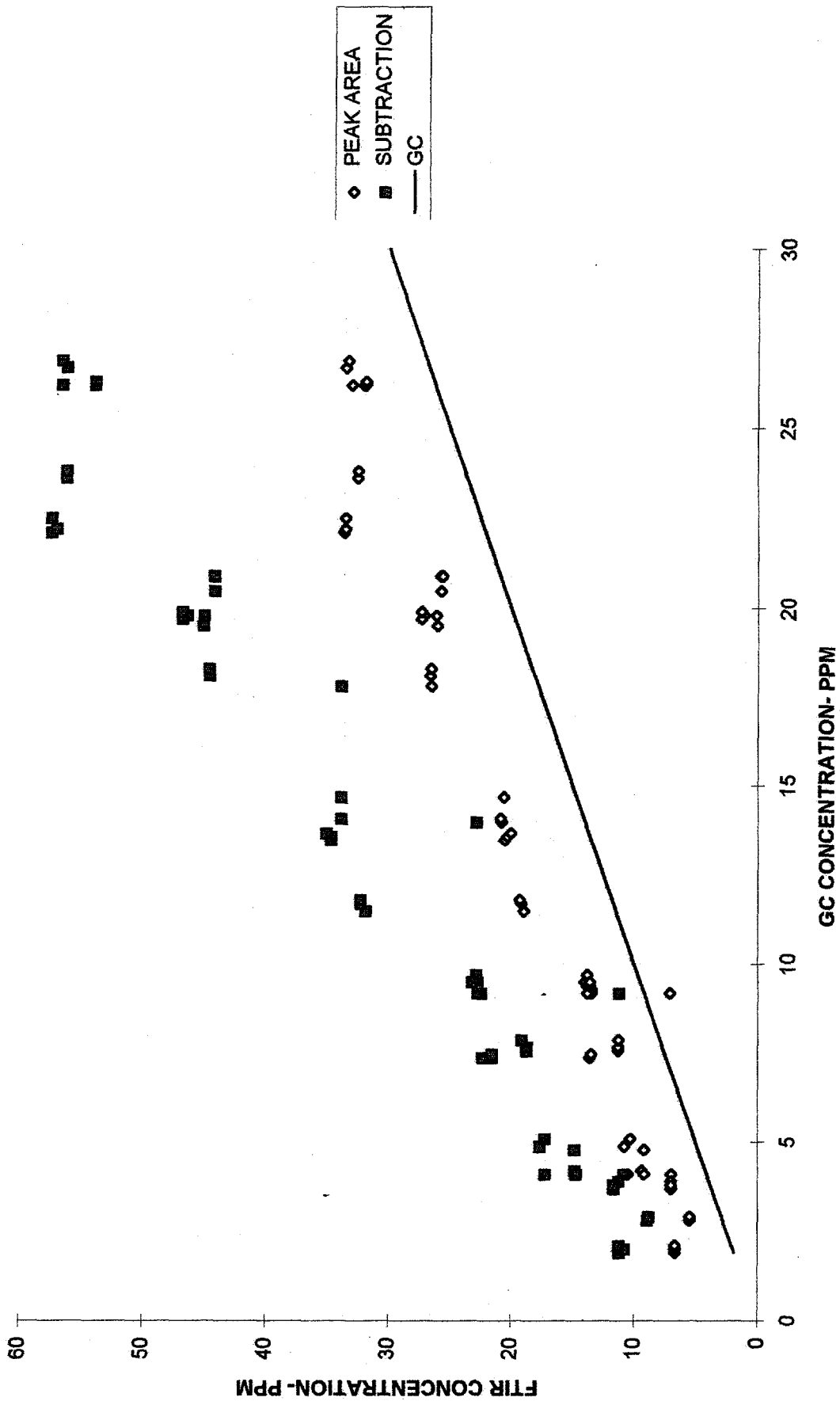


FIGURE 14

CYCLOHEXANE- PEAK AREA VS. SUBTRACTION



## APPENDIX A : QUALITY ASSURANCE

### FTIR quality assurance

- 1) Check for detector saturation- background will be analyzed for negative transmittance of the CO<sub>2</sub> band and false energy at the low wavenumber region where the detector response should be zero. Both these checks are indicative of detector saturation.
- 2) Polystyrene film (SRM 1921)- NIST certified polystyrene film spectra will be taken each experimental day and peak location will be matched with this NIST specifications.
- 3) All data stored as interferograms for future manipulation if necessary- if reanalysis needs to be done with different apodization or quantification parameters for comparison, this will be possible if have the original interferogram instead of just a single beam spectra.
- 4) Data review after each day and during the course of a day's experiments- this will enable another look at FTIR response and ensure quality data.

### GC-FID quality assurance

- 1) Calibration curves using NIST- traceable certified gases and precision of injections- precision of injections must be within 5 % of each other and calibration curves must be fairly linear with a correlation coefficient of at least 0.9.
- 2) Baseline drift and other instrument anomalies will be checked to ensure data quality.
- 3) Reviewing data as it is obtained- the calibration curve obtained will be compared to previous calibration curves to check for similar instrument response

## APPENDIX B: REFERENCES

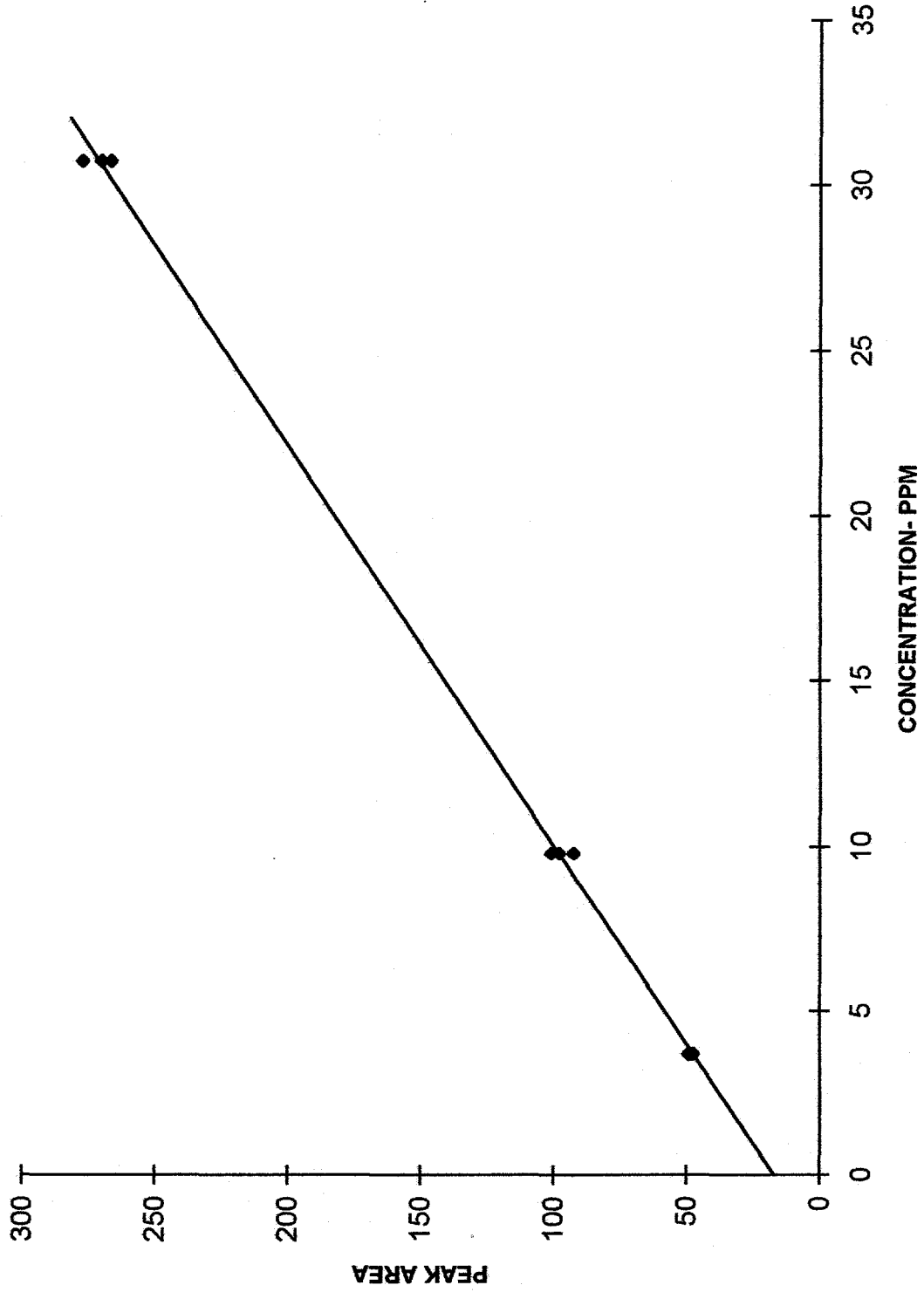
1. Hunt, Robert N.: Continuous Monitoring of Atmospheric Pollutants by Remote Sensing FTIR, Miles Inc. Publication P.O. Box 500, New Martinsville, WV 26155.
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3. Michigan University, Ann Arbor: Self-Training, Self-Optimizing Infrared Expert System. Prepared for National Institute for Occupational Safety and Health, Cincinnati, October 1990.
4. Demirigan, Jack C: The Potential of Passive-Remote Fourier Transform Infrared Spectroscopy to Detect Organic Emissions Under the Clean Air Act. U.S. Army, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.
5. Levine et al: Advantages and Disadvantages in the Use of FTIR and FIR Spectrometers for Monitoring Airborne Gases and Vapors of Industrial Hygiene Concern. Appl. Ind. Hyg. Vol.4, No.7, July 1989.
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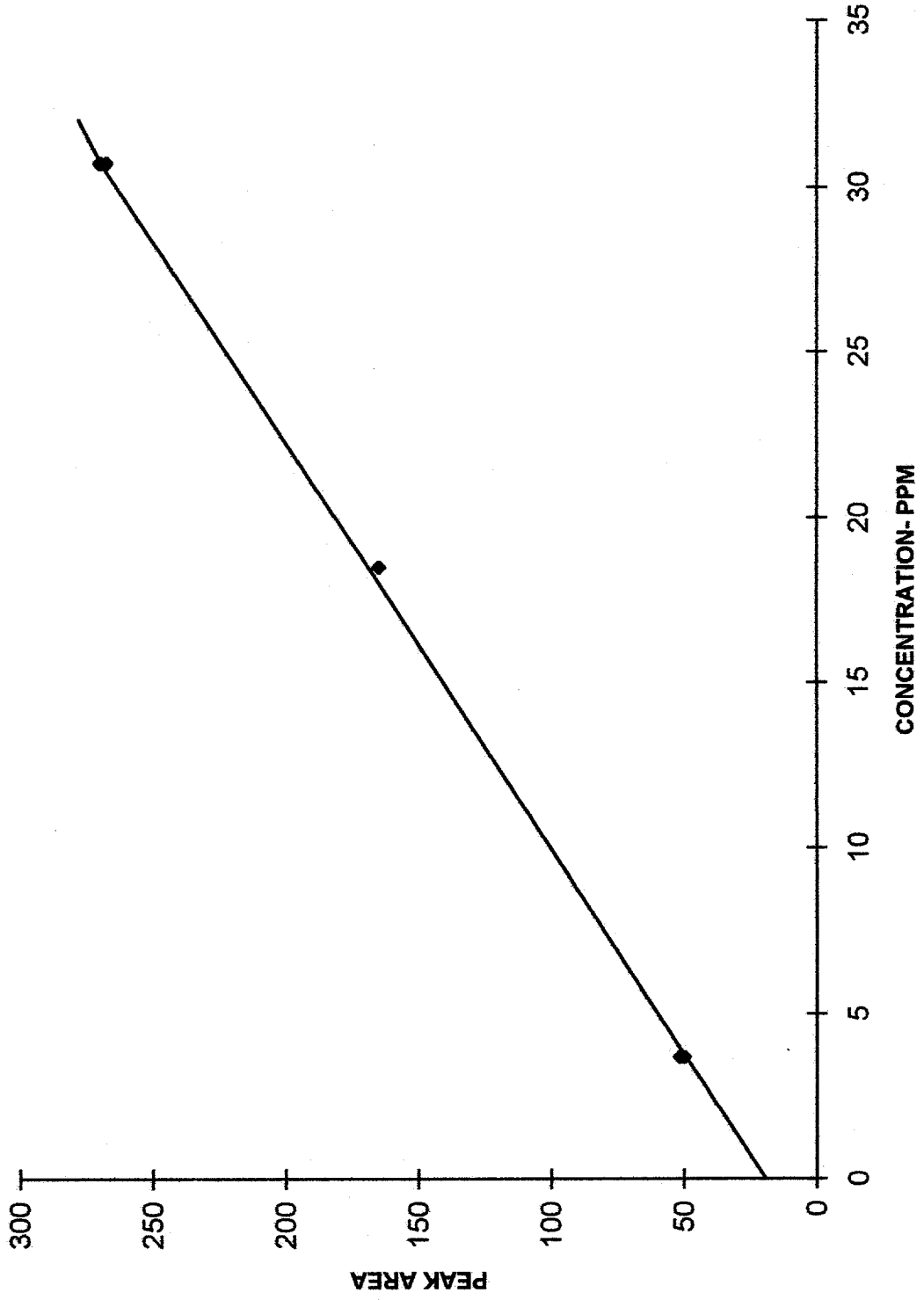
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**APPENDIX C: GC CALIBRATION CURVES**

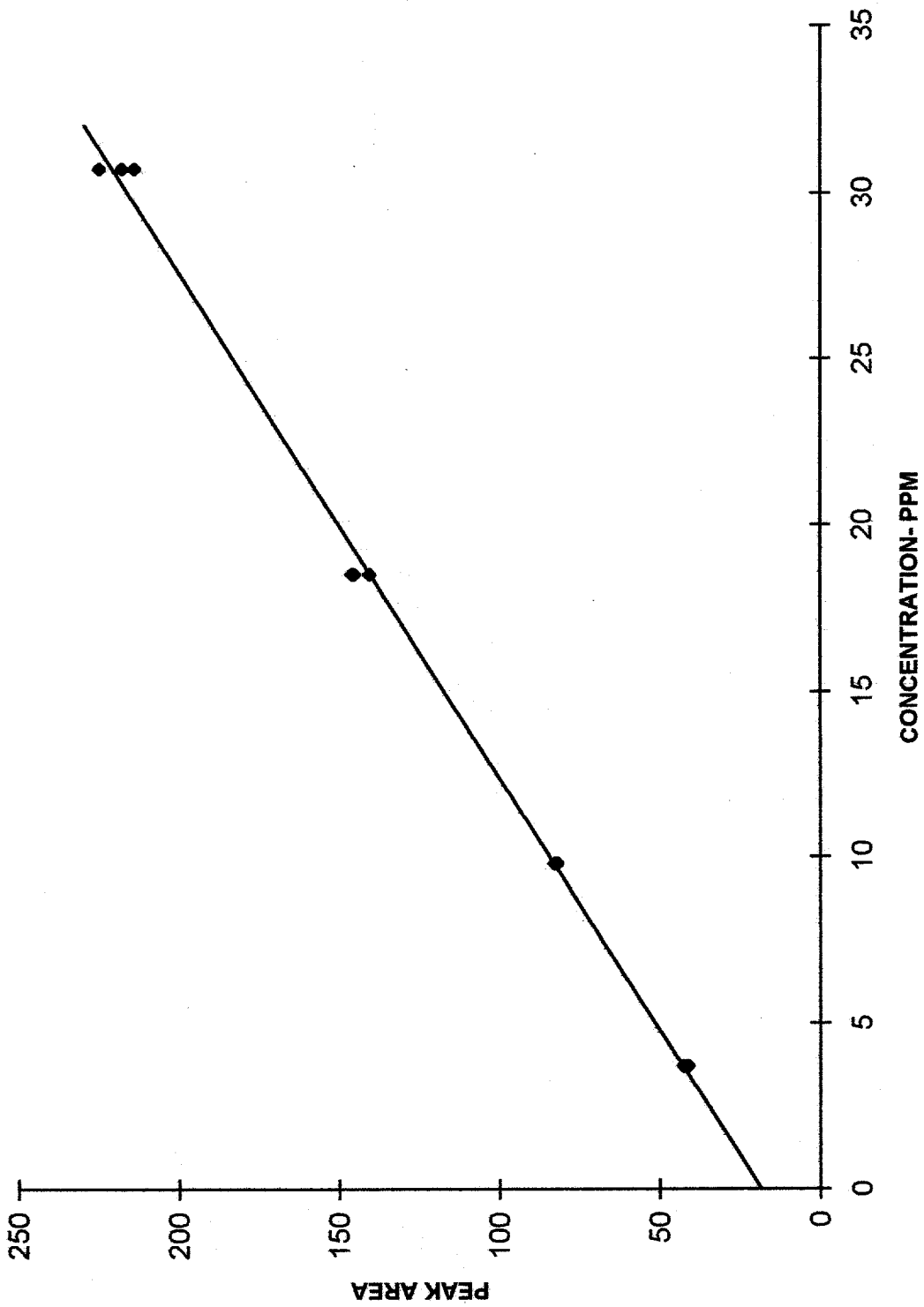
CYCLOHEXANE GC CALIBRATION CURVE-- 12/6/94



CYCLOHEXANE CALIBRATION CURVE-- 12/7/94

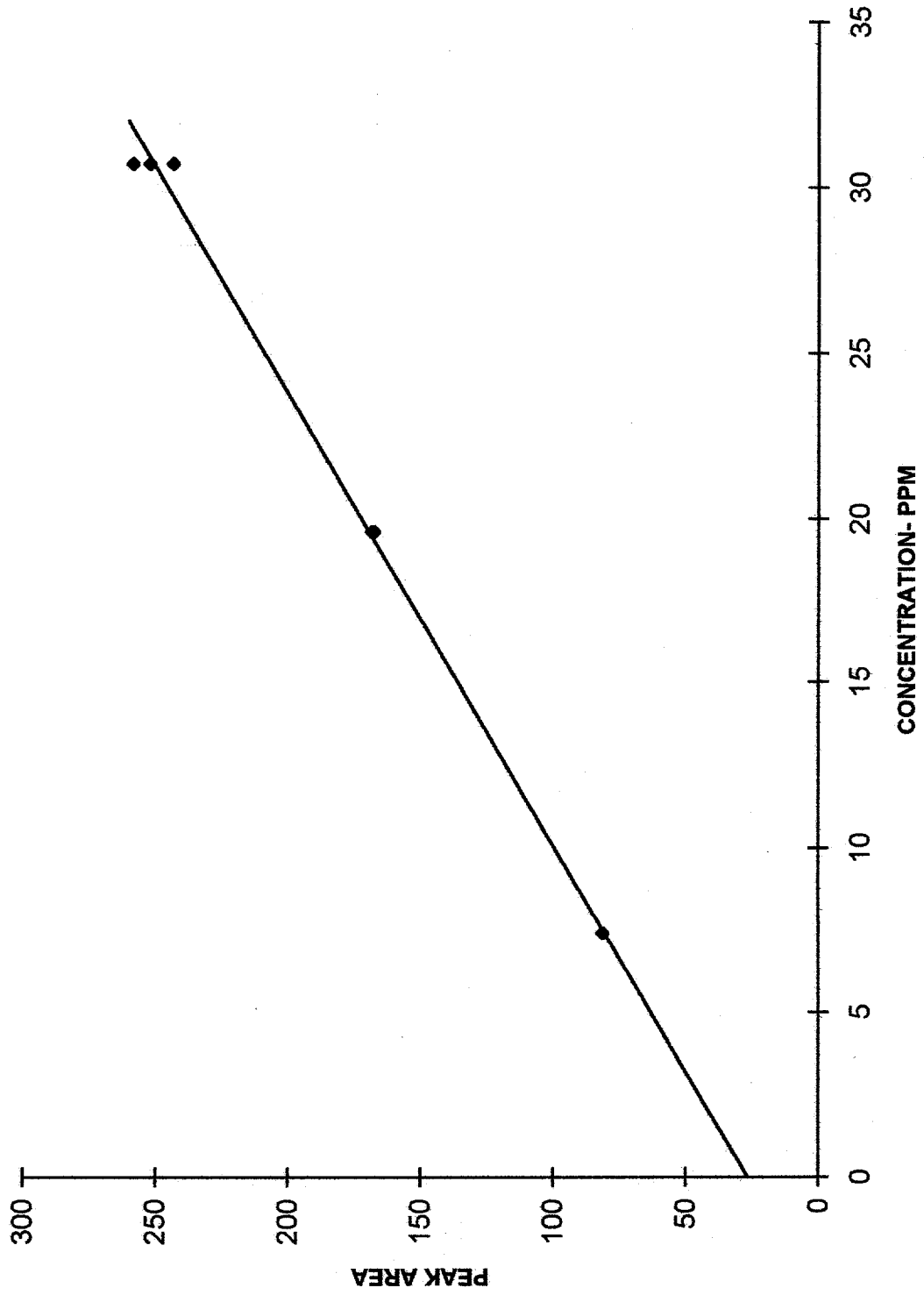


CYCLOHEXANE GC CALIBRATION CURVE-- 12/16/94

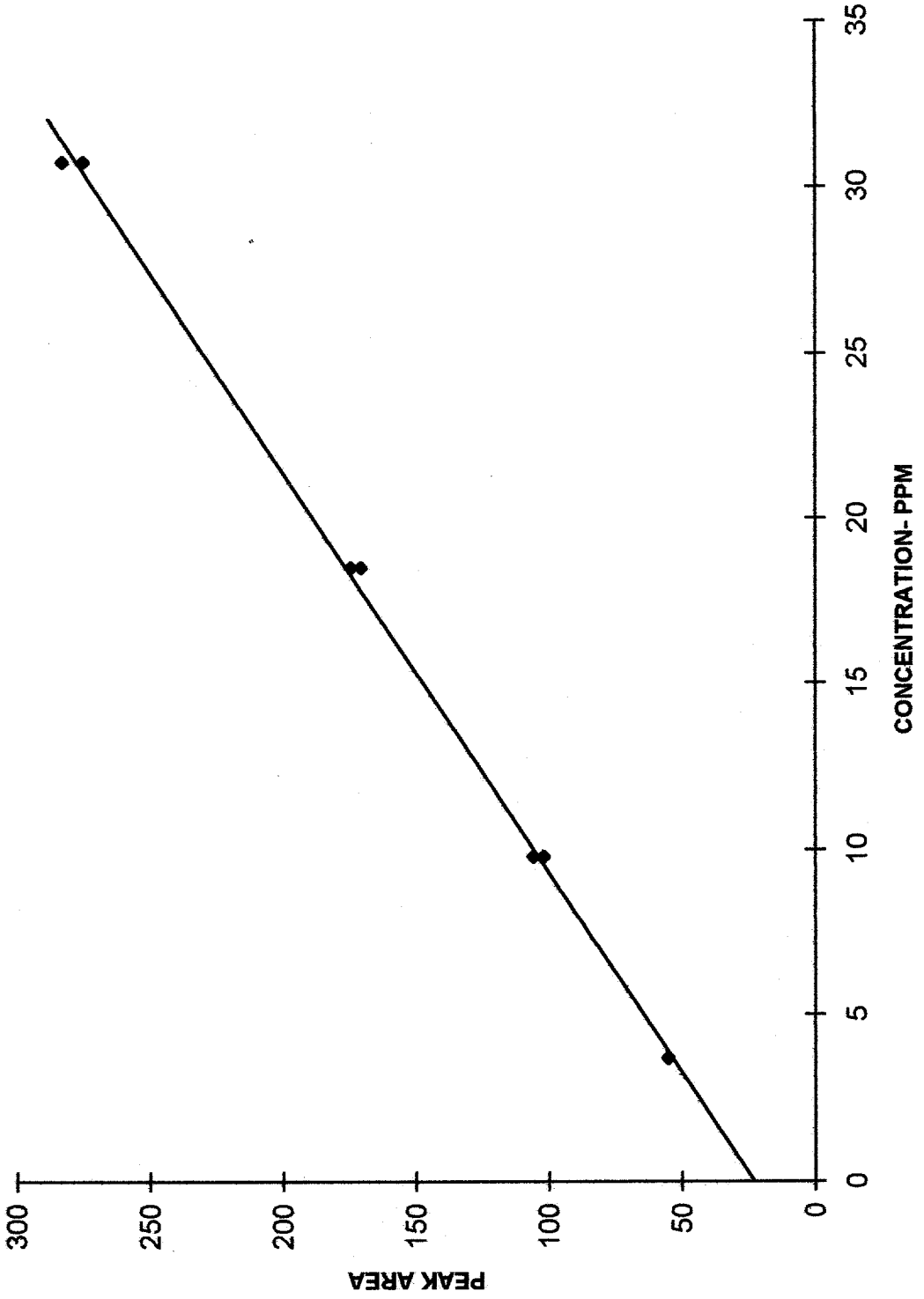


◆ DATA  
— REGRESSION  
▲ R2 = 0.997

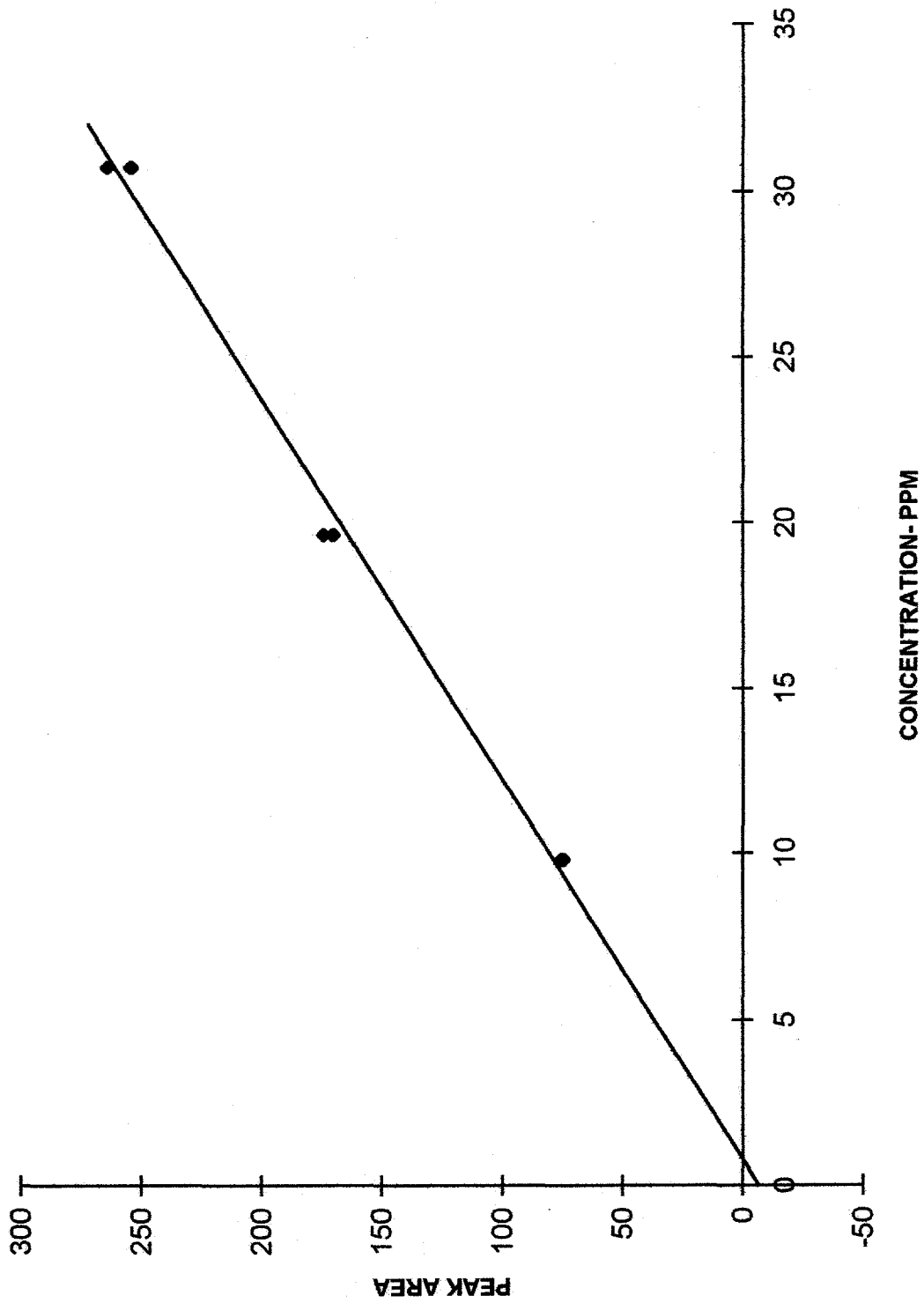
CYCLOHEXANE GC CALIBRATION CURVE-- 12/10/94



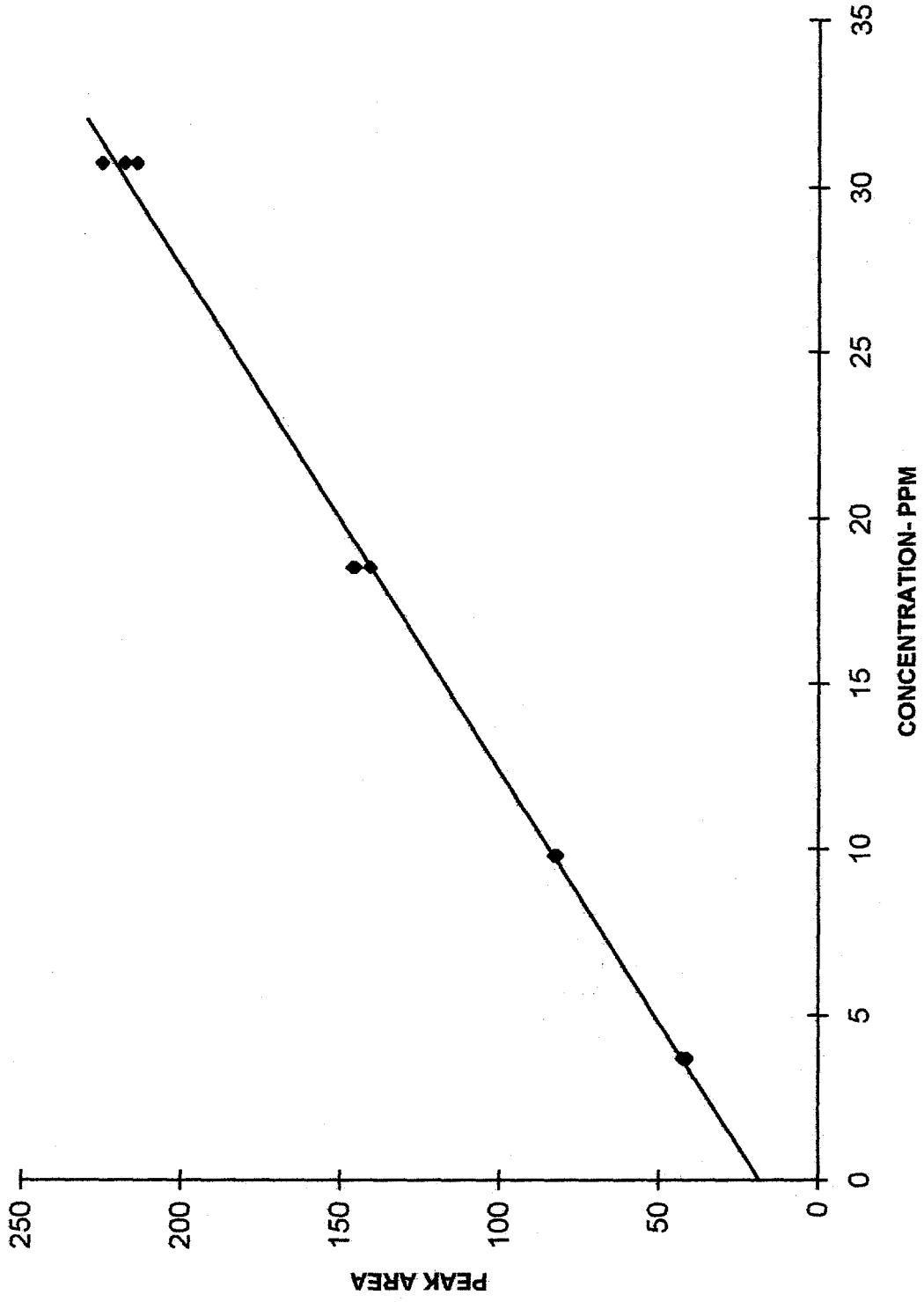
CYCLOHEXANE GC CALIBRATION CURVE-- 12/8/94



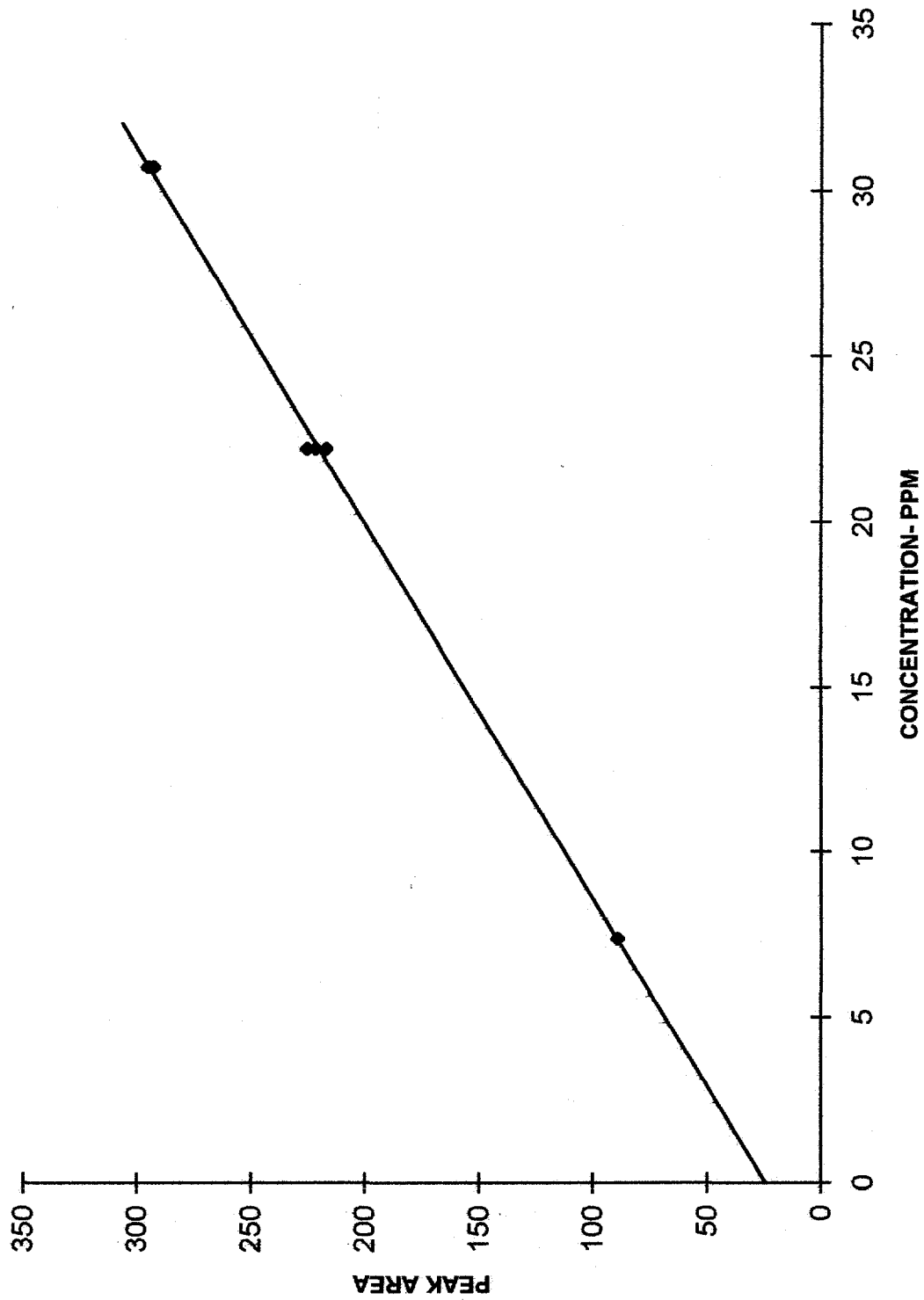
TOLUENE CALIBRATION CURVE-- 10/17/94



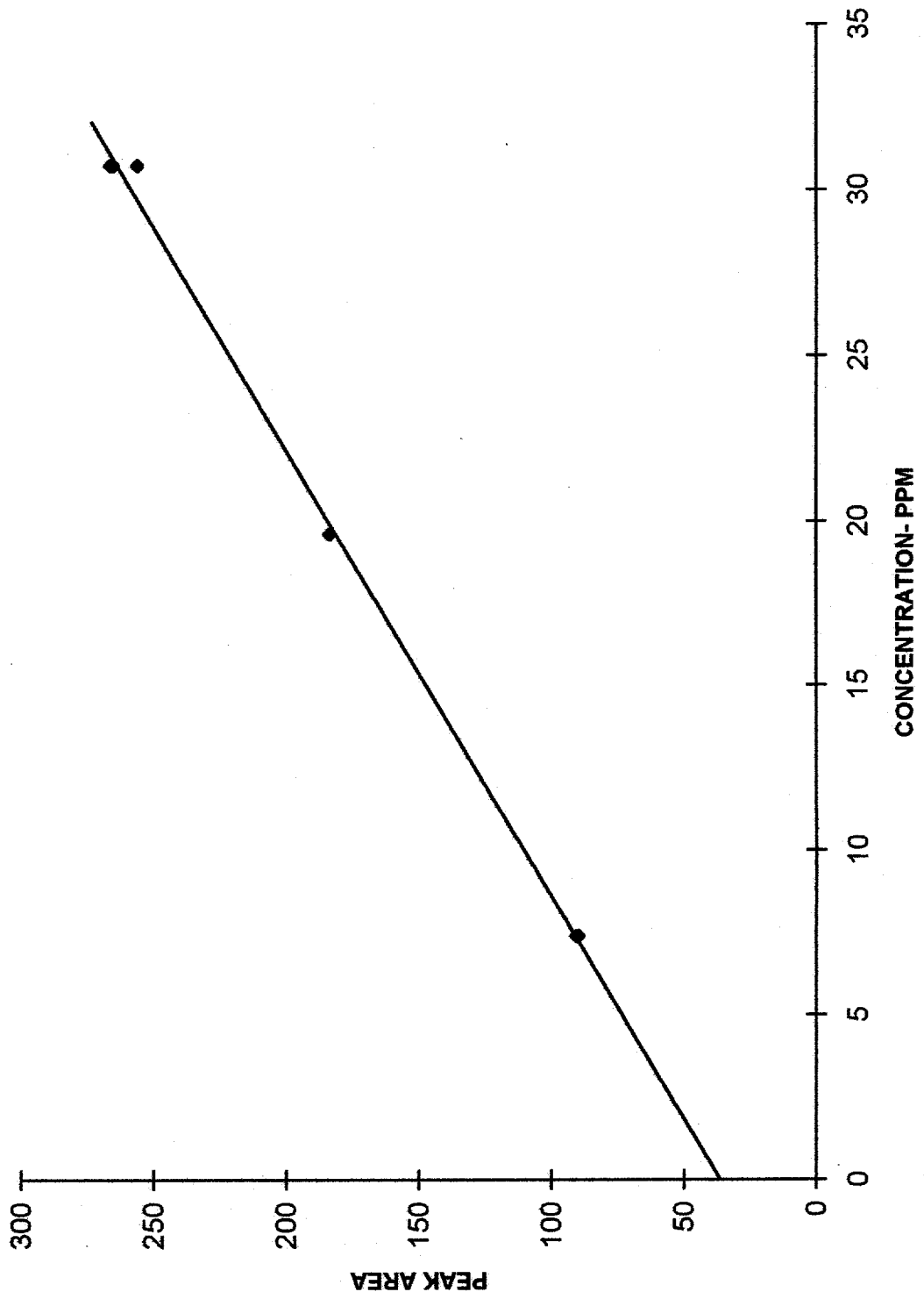
CYCLOHEXANE GC CALIBRATION CURVE-- 12/16/94



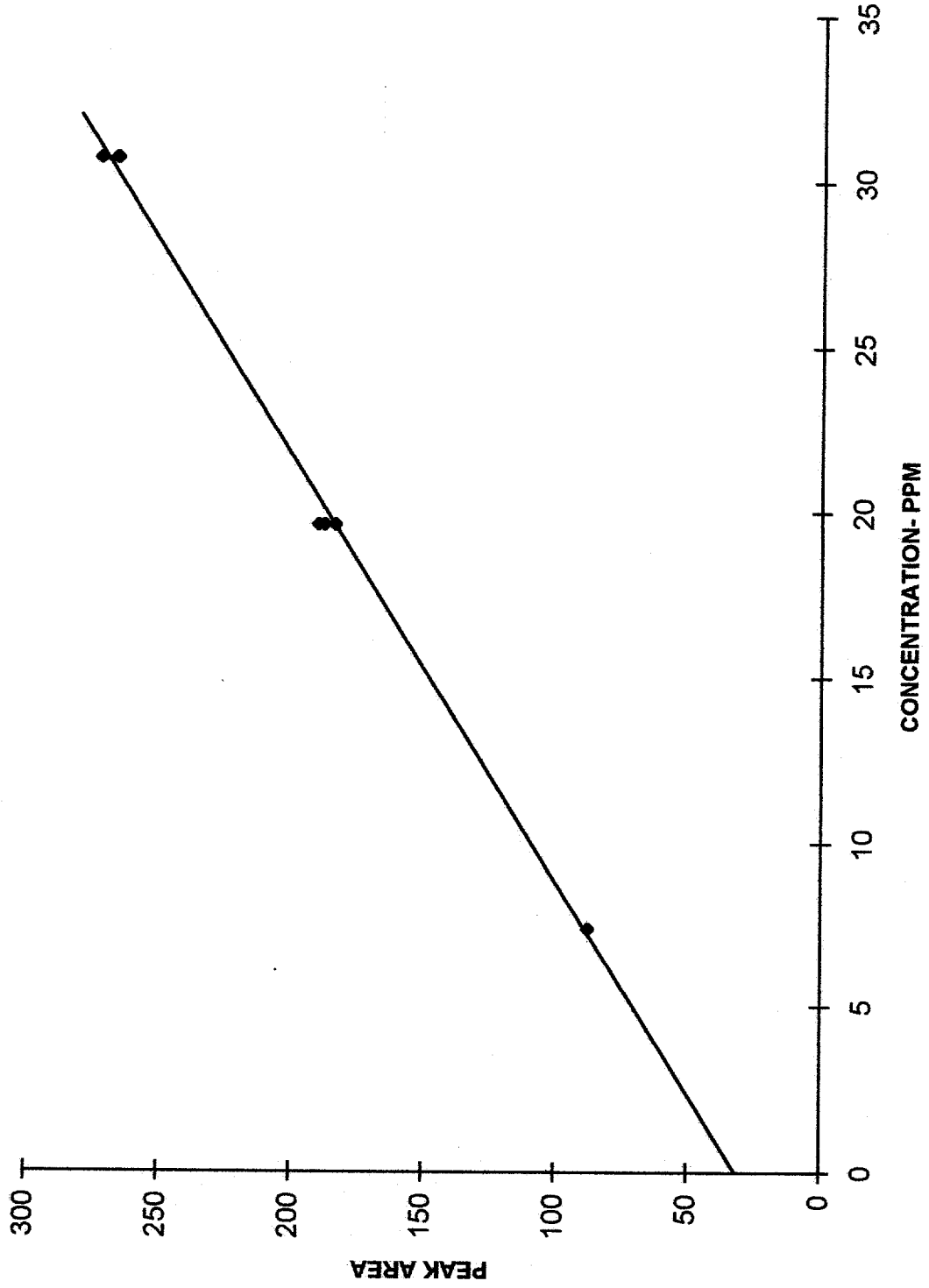
TOLUENE GC CALIBRATION CURVE-- 10/25/94



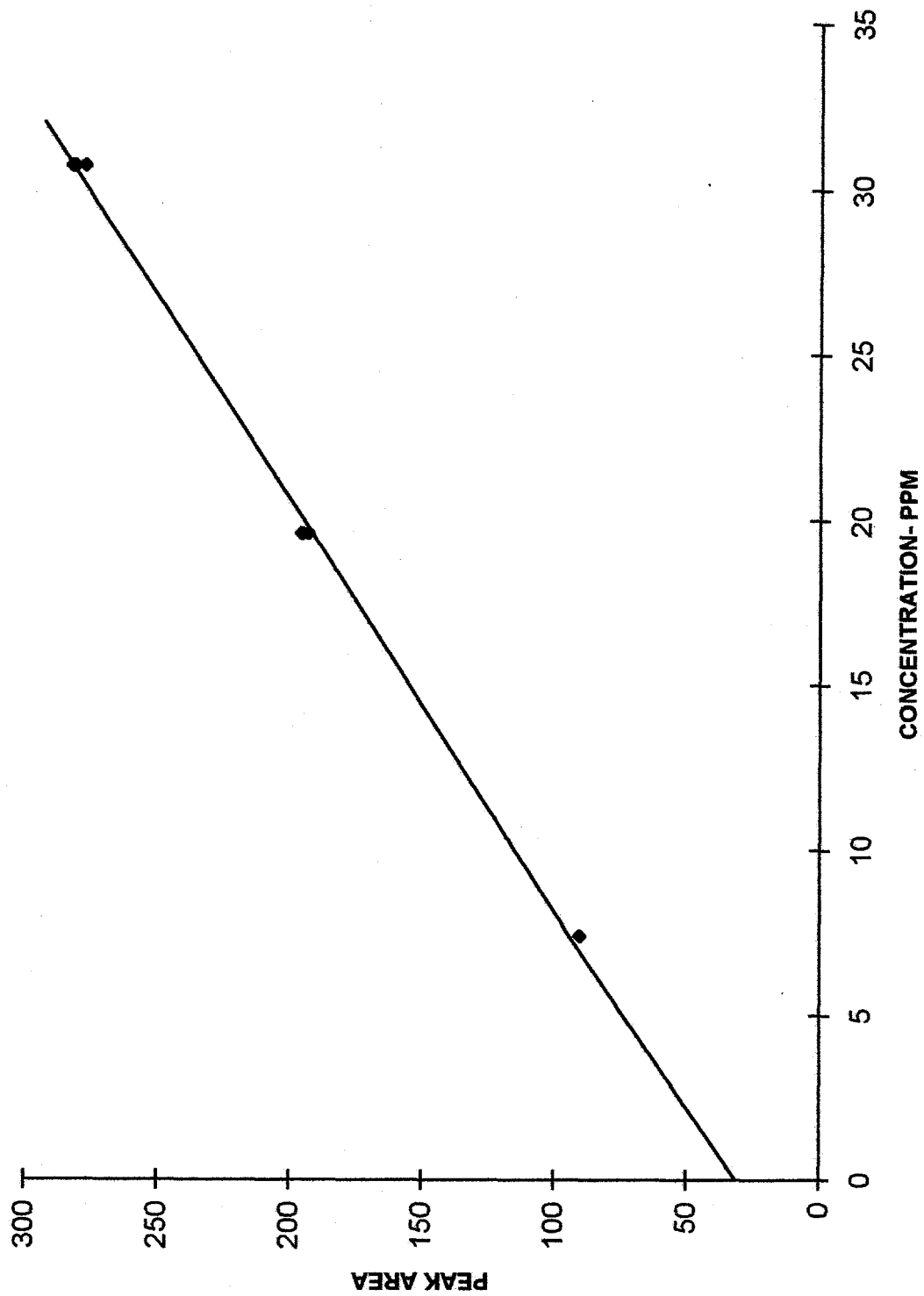
TOLUENE CALIBRATION CURVE-- 10/24/94



TOLUENE CALIBRATION CURVE-- 10/23/94

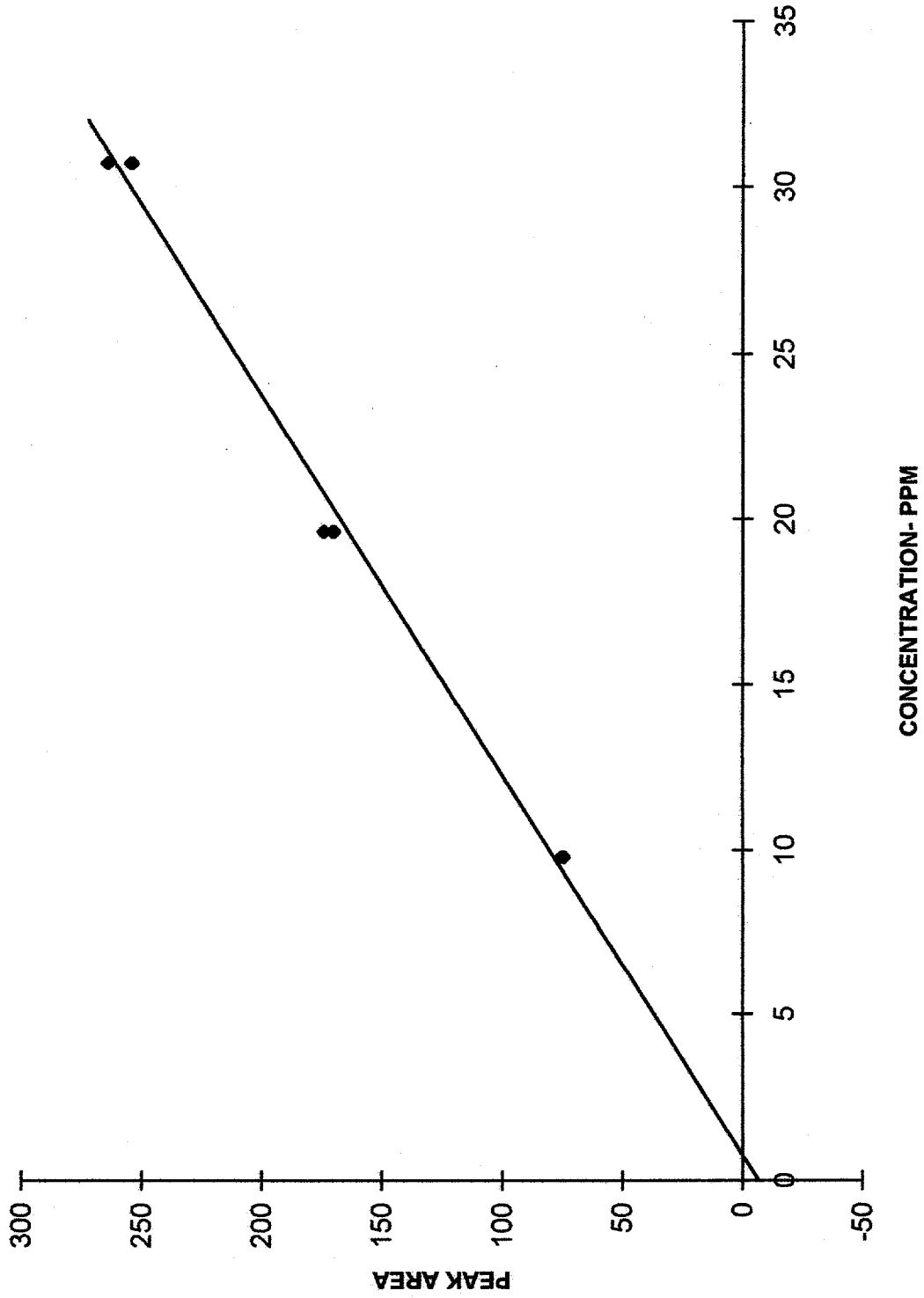


TOLUENE CALIBRATION CURVE-- 10/22/94

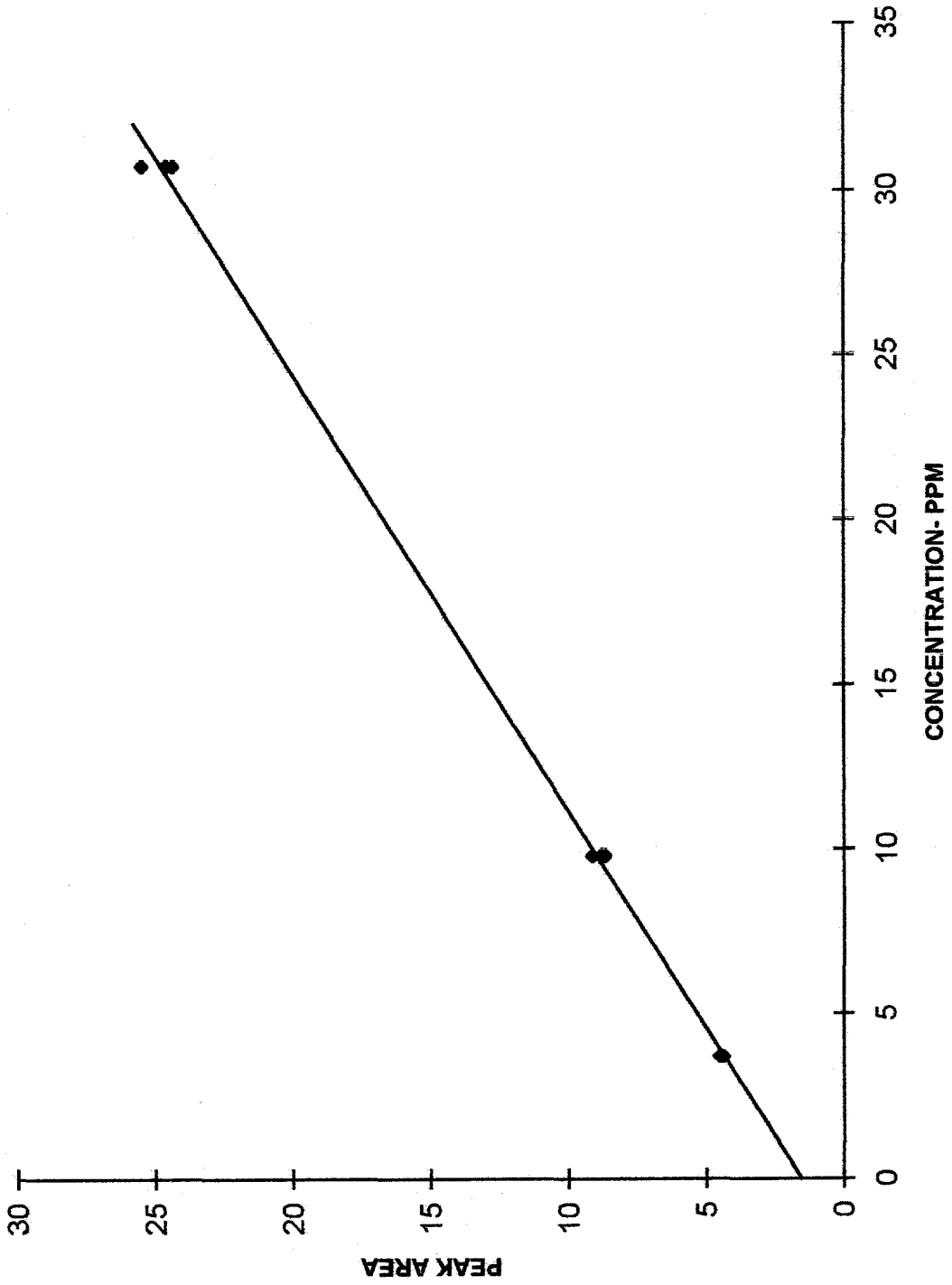


● DATA  
— REGRESSION  
▲ R<sup>2</sup> = 0.999

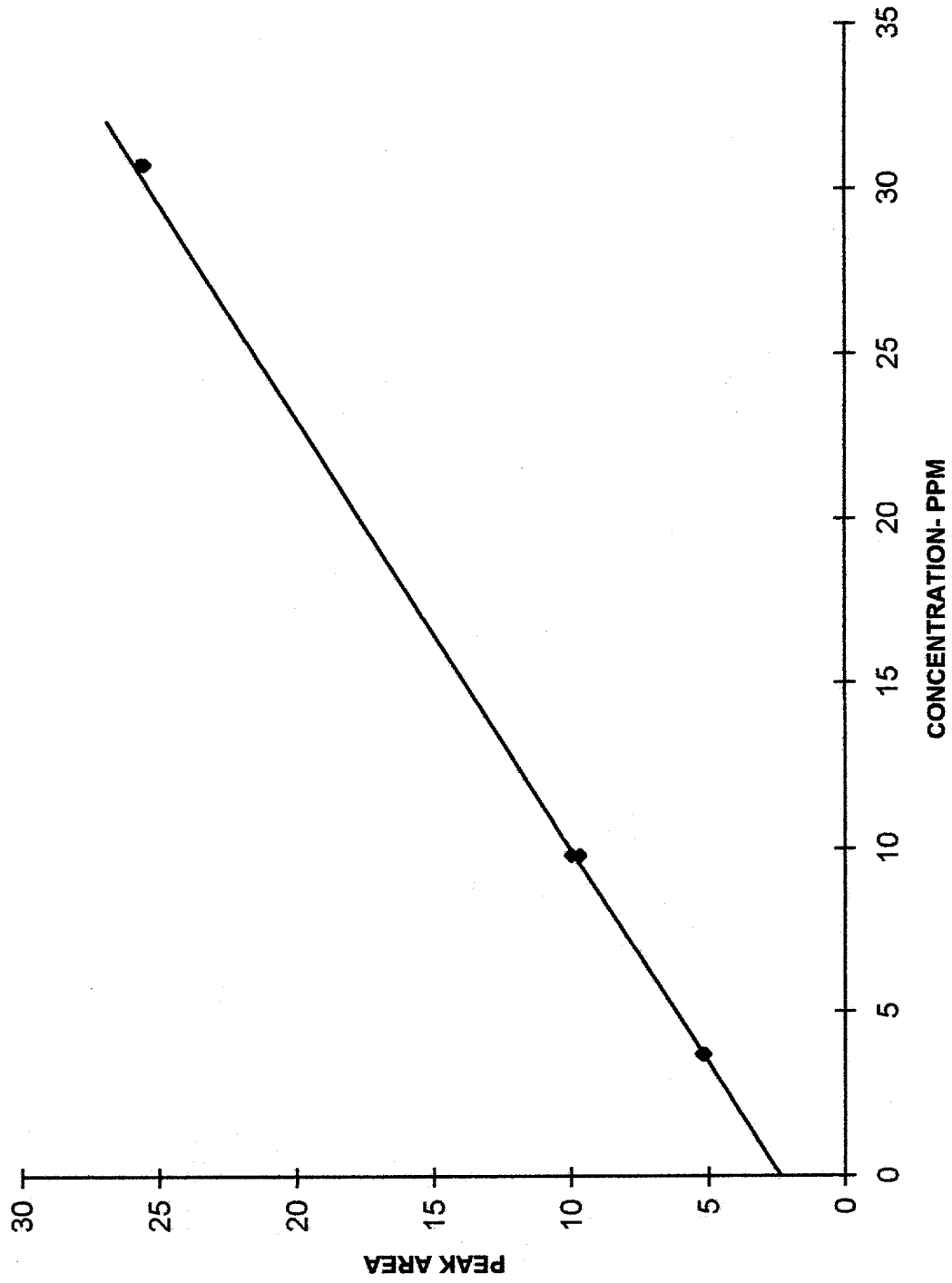
TOLUENE CALIBRATION CURVE-- 10/17/94



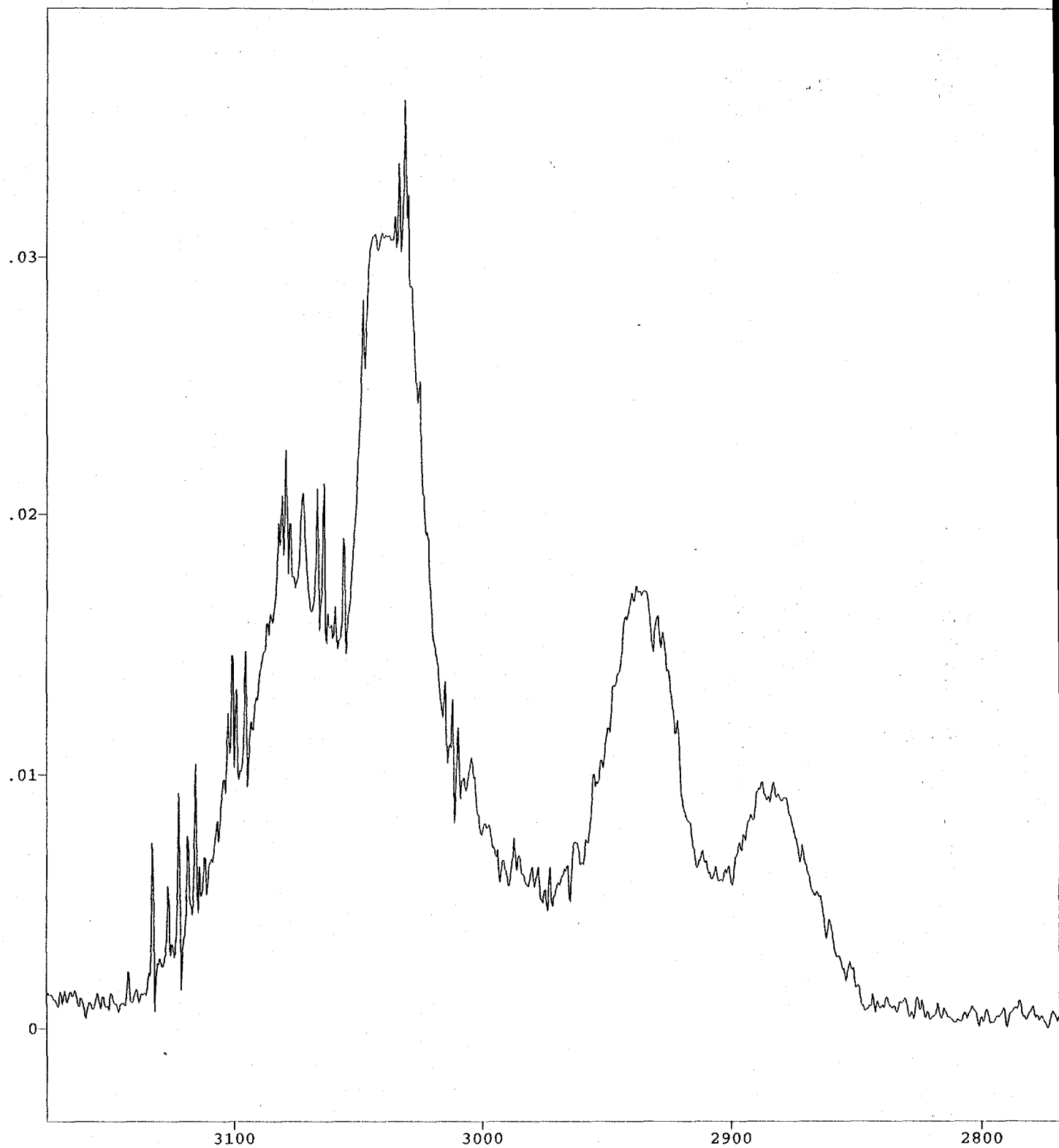
TOLUENE GC CALIBRATION CURVE-- 9/27/94



TOLUENE GC CALIBRATION CURVE-- 9/26/94



**APPENDIX D: TOLUENE ABSORBANCE SPECTRA**



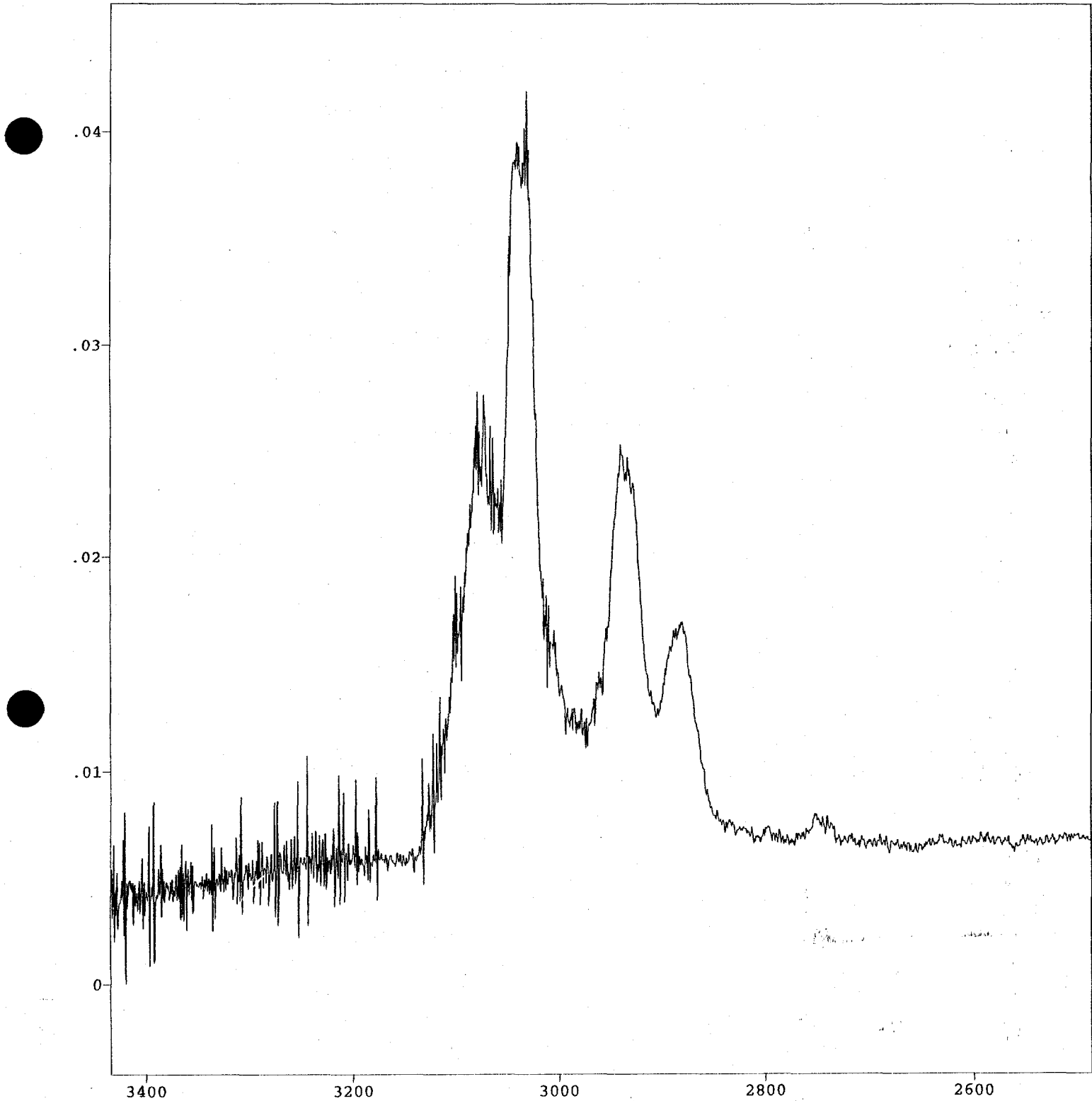
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #28 : T10-17-4

10/17/94 3:57 PM Res=1cm

15 ml toluene



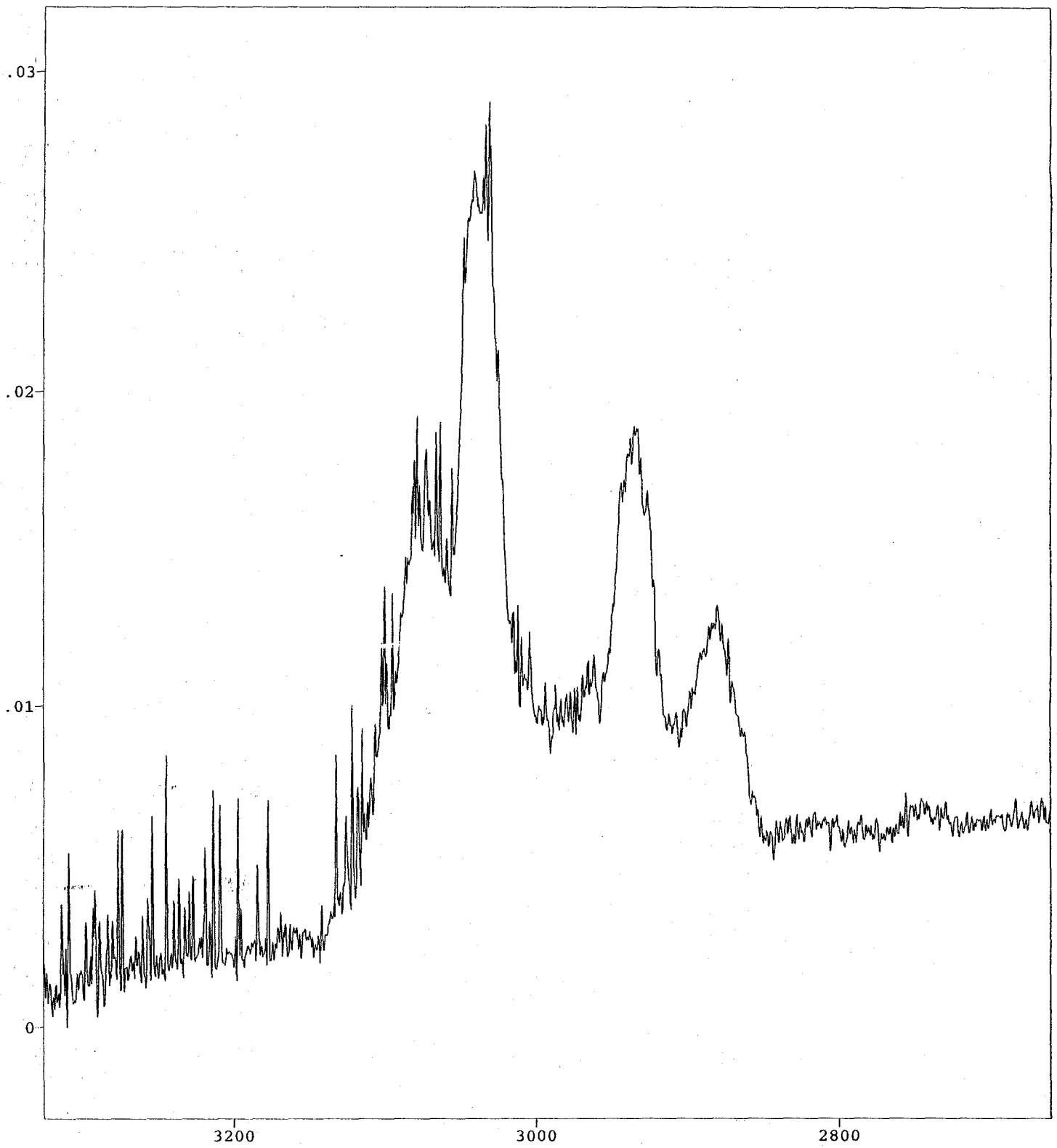
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

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10/19/94 1:38 PM Res=1cm-1

15 ml toluene 1 cm-1 10-19-94



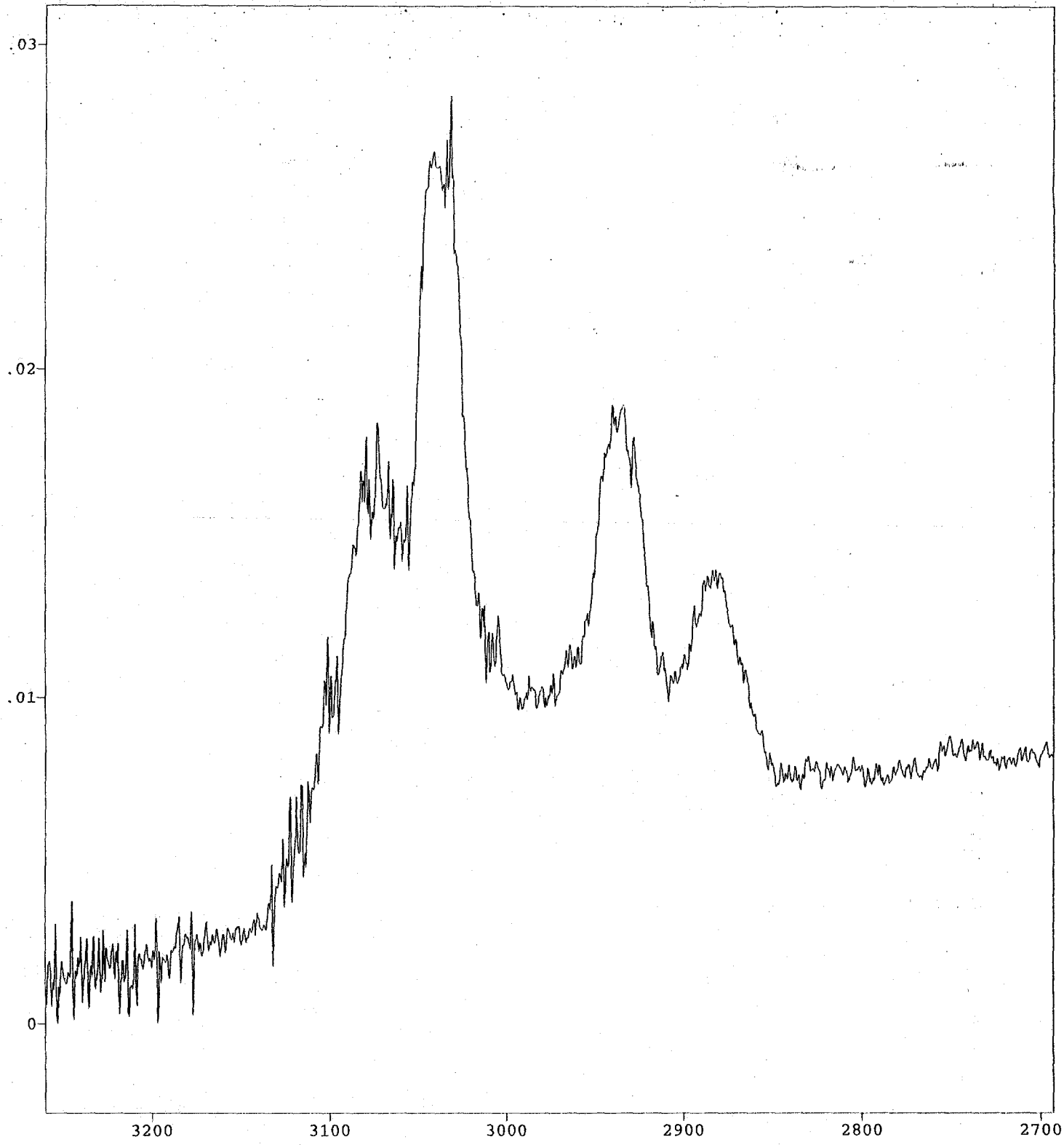
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File # 1: T10-19-1

10/19/94 12:17 PM Res=1cm-1

10 ml toluene- 1cm-1 10-19-94



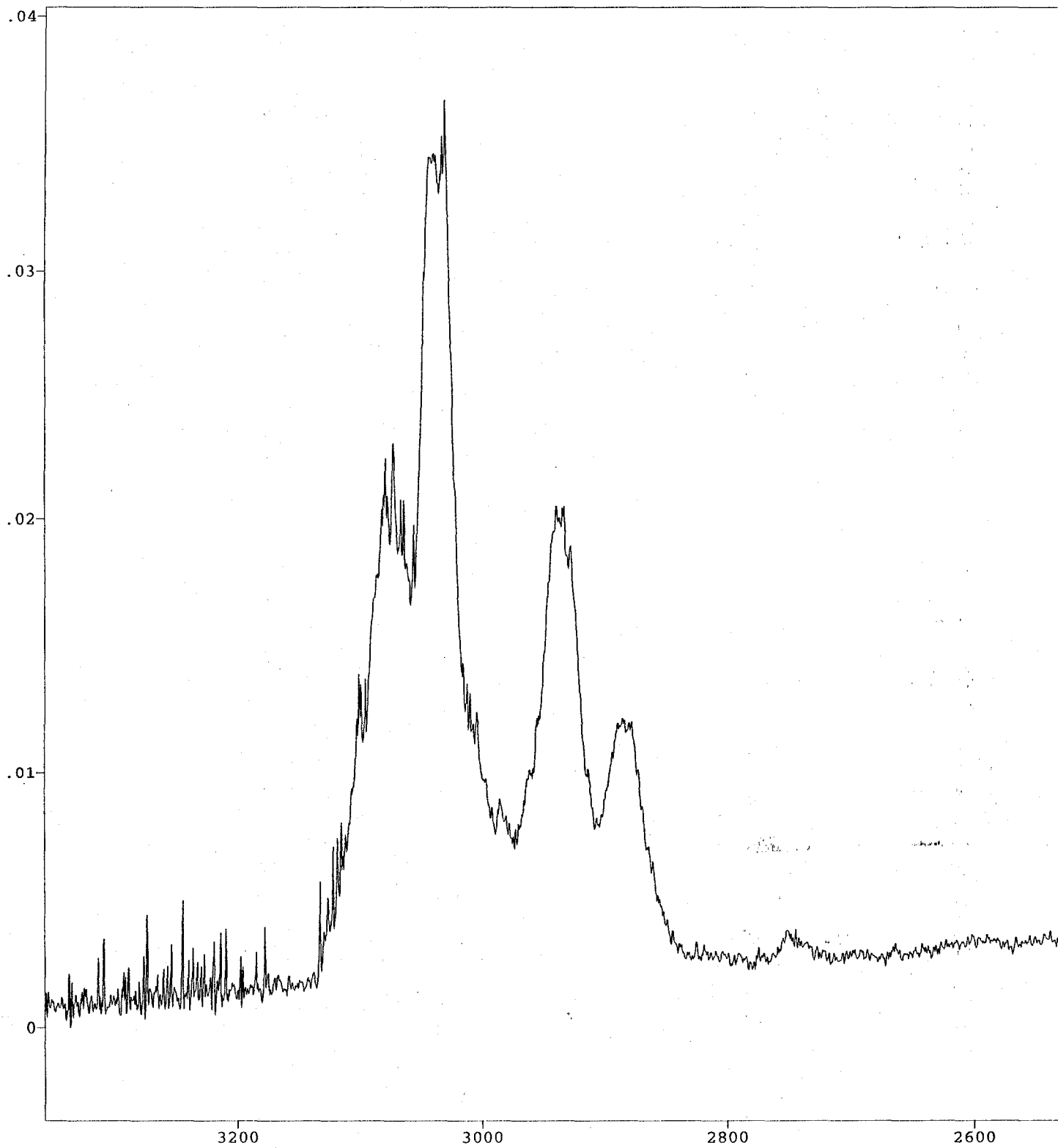
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

# 3 : T10-22-1

10/22/94 3:51 PM Res=1cm-1

10 ml toluene 1 cm-1



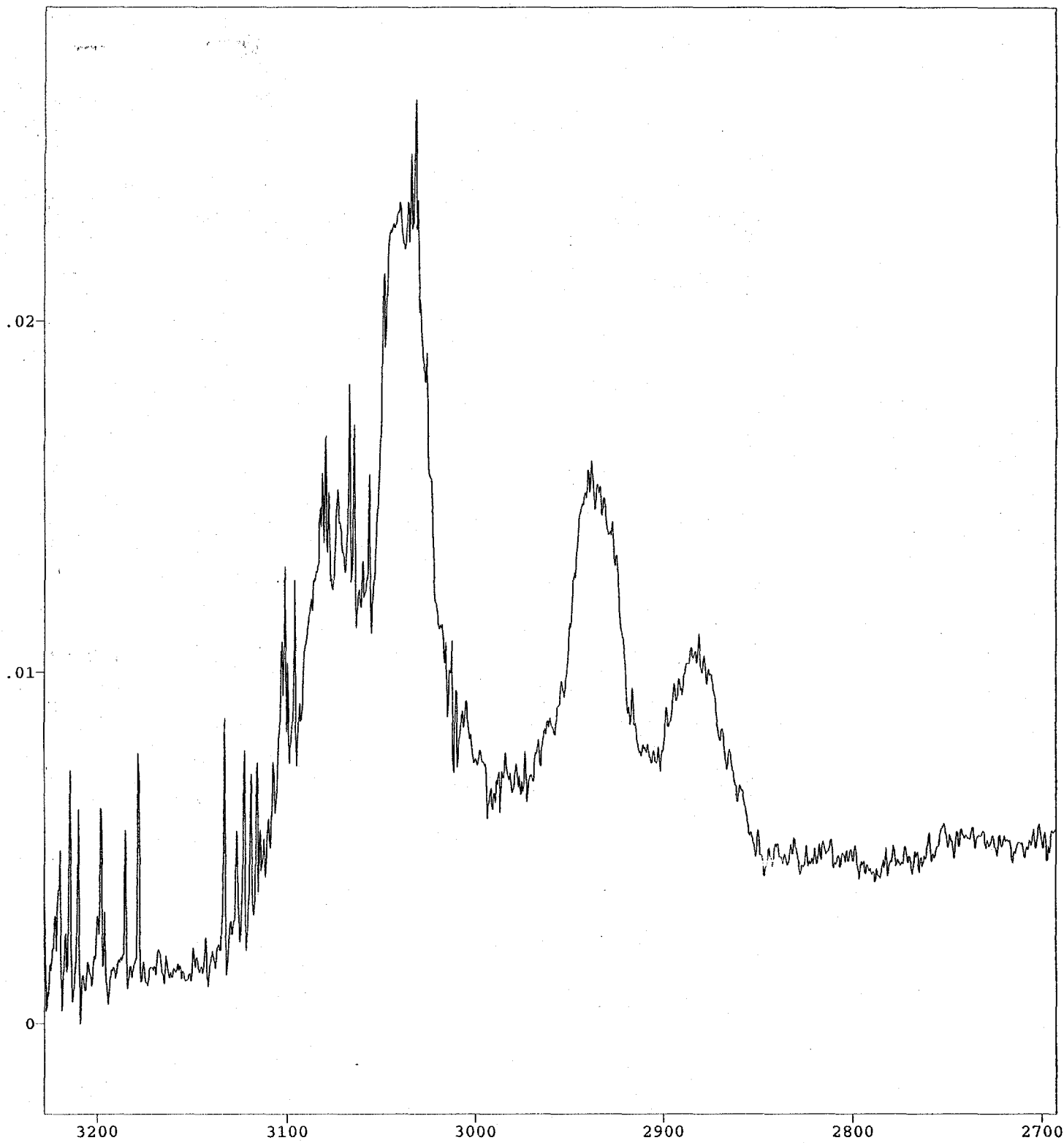
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

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15 ml toluene 1 cm-1



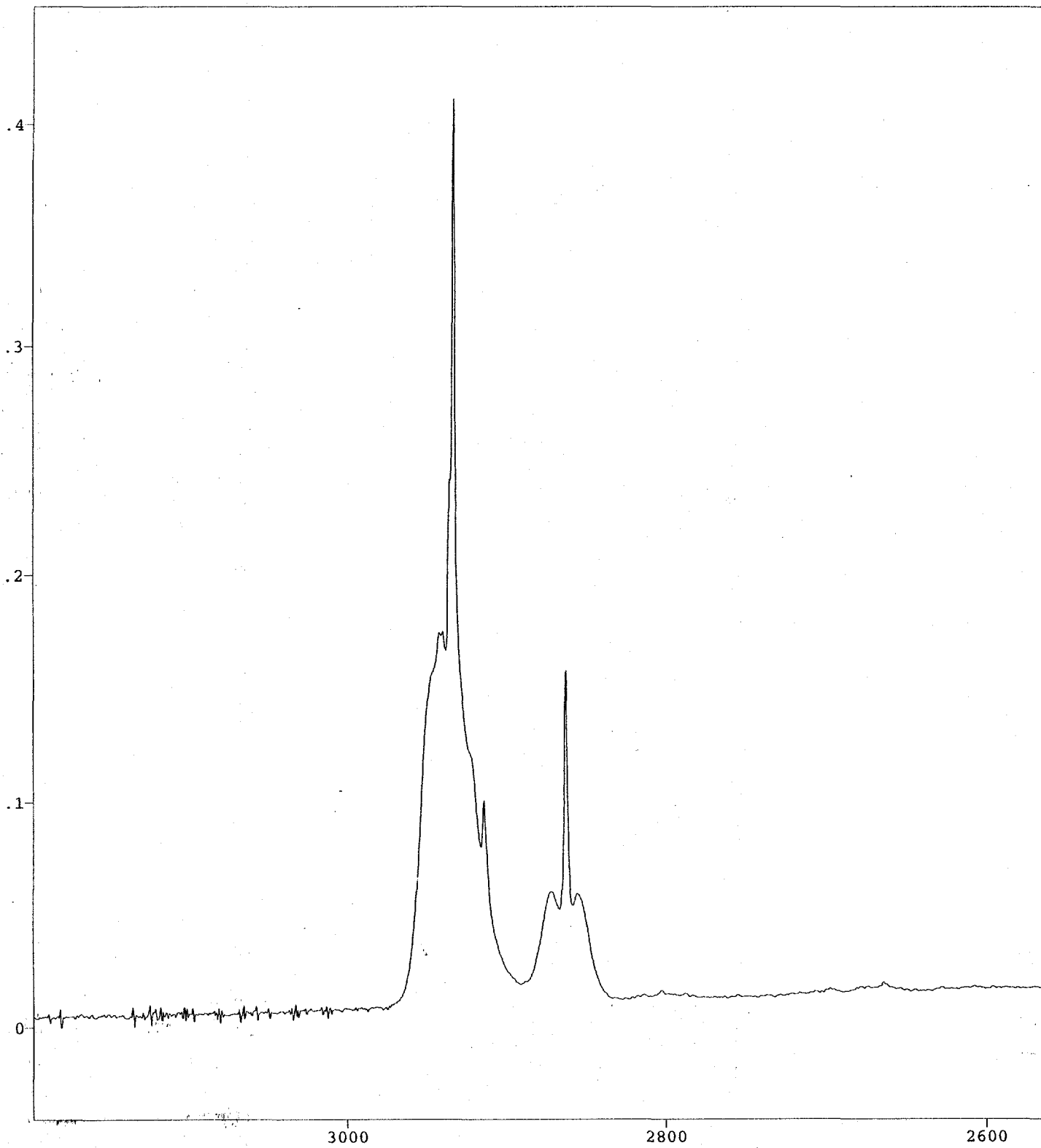
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

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10 ml toluene 1 cm-1



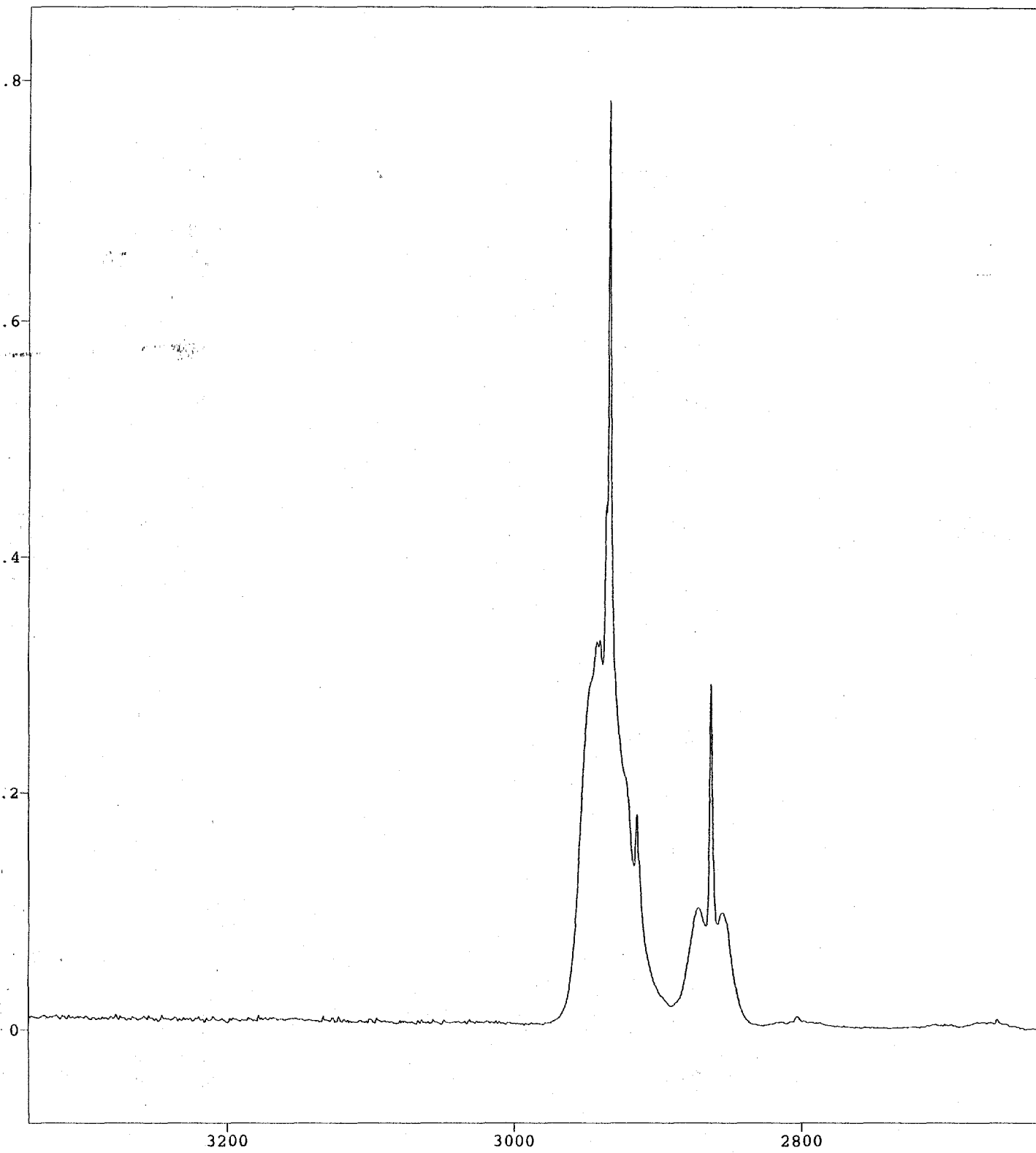
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

F#11: C12-7-3

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10 ml cyclohexane



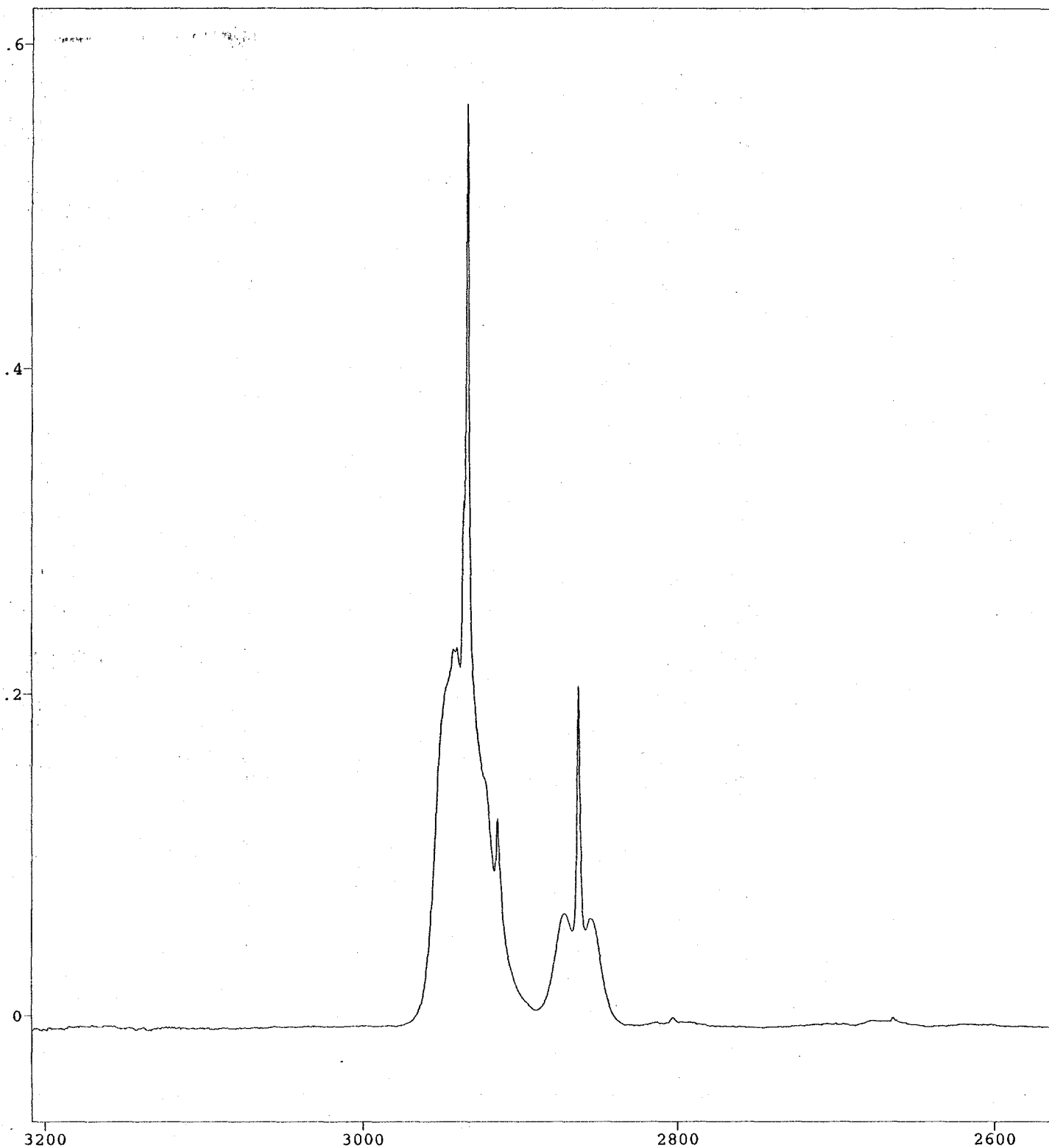
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #12 : C12-8-5

12/8/94 3:54 PM Res=1cm

20 ml cyclo



Absorbance / Wavenumber (cm-1)

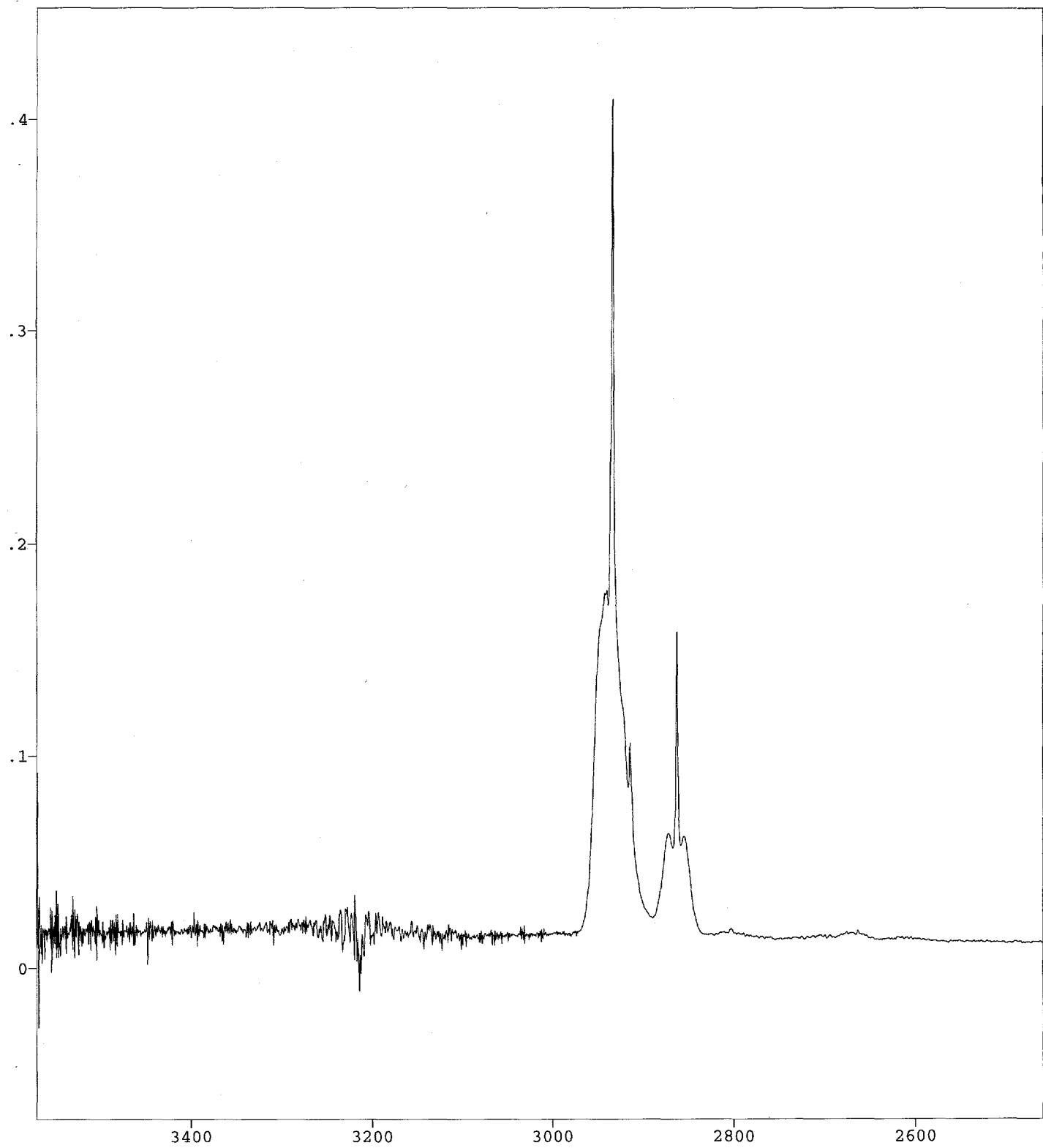
Paged Y-Zoom CURSOR

F13 : C12-9-1

12/9/94 12:28 PM Res=1cm-1

15 ml cyclohexane

**APPENDIX E: CYCLOHEXANE ABSORBANCE SPECTRA**



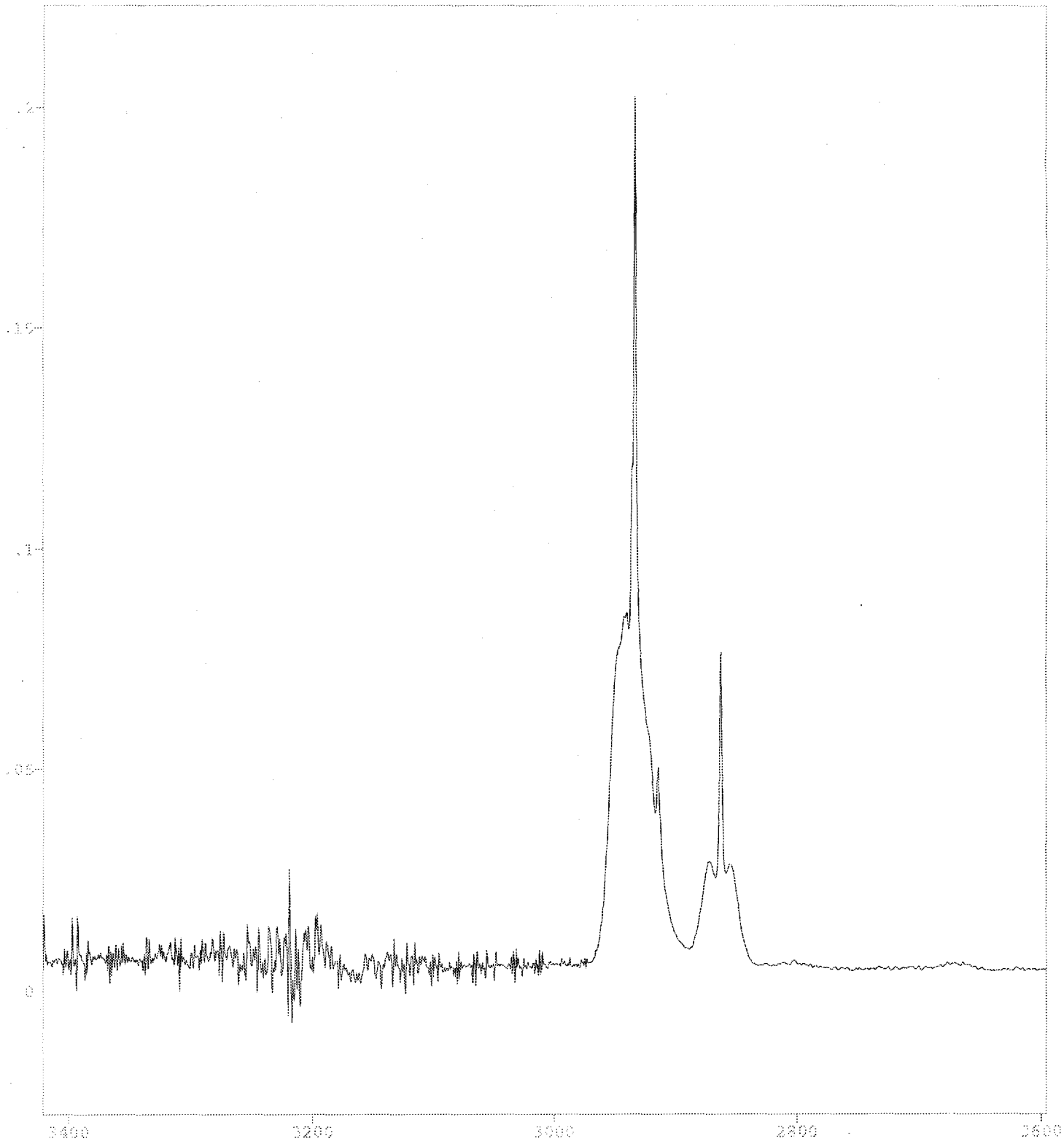
-1)

Paged Y-Zoom CURSOR

#14 : C12-6-2

12/6/94 12:04 PM Res=1cm-1

10 ml cyclohexane



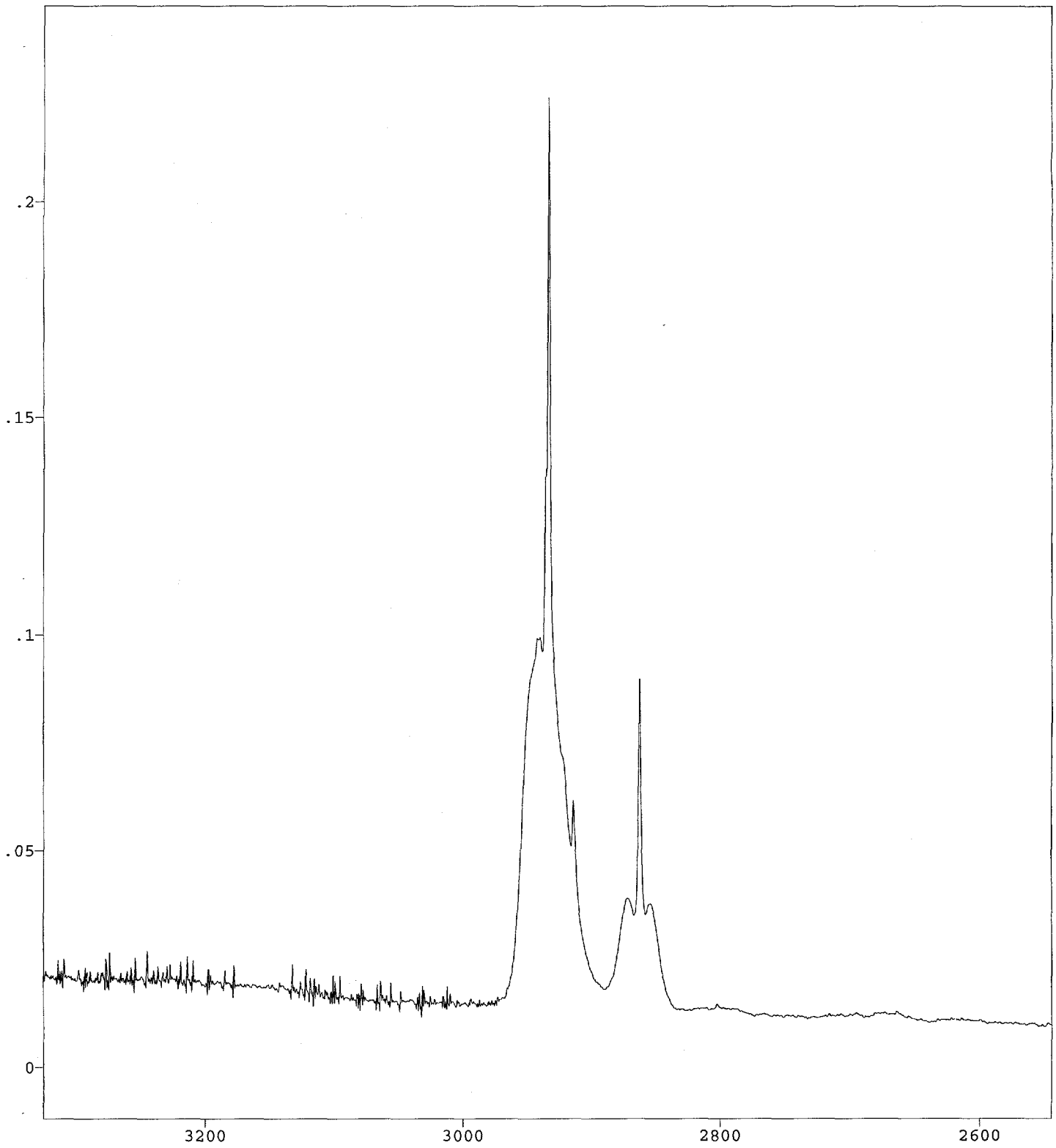
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Paged Y-Zoom CURSOR

#13 : C12-6-1

12/6/94 11:54 AM Res=1cm-1

5 ml cyclohexane



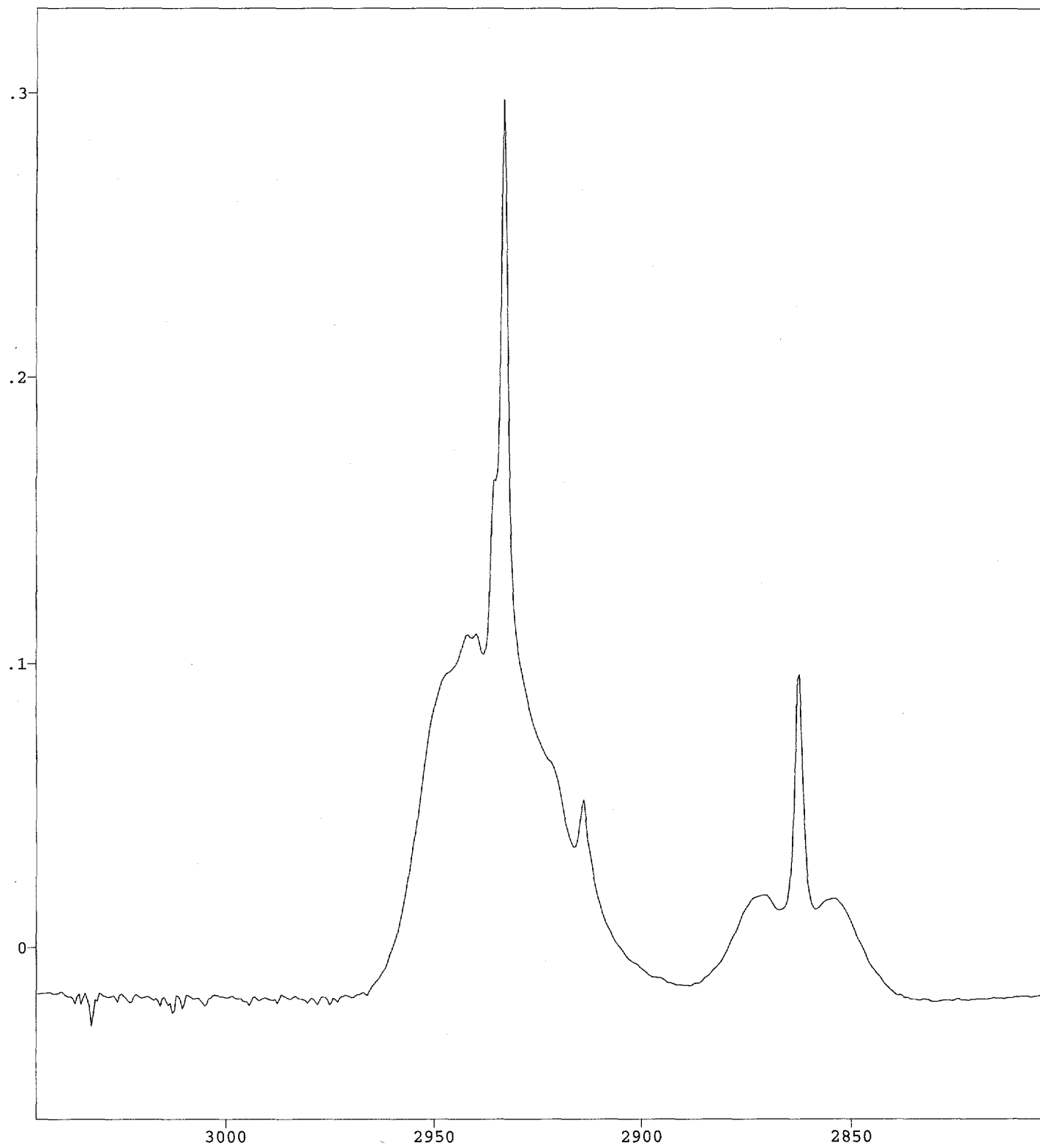
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Paged Y-Zoom CURSOR

#18 : C12-7-1

12/7/94 1:12 PM Res=1cm-1

5 ml cyclohexane



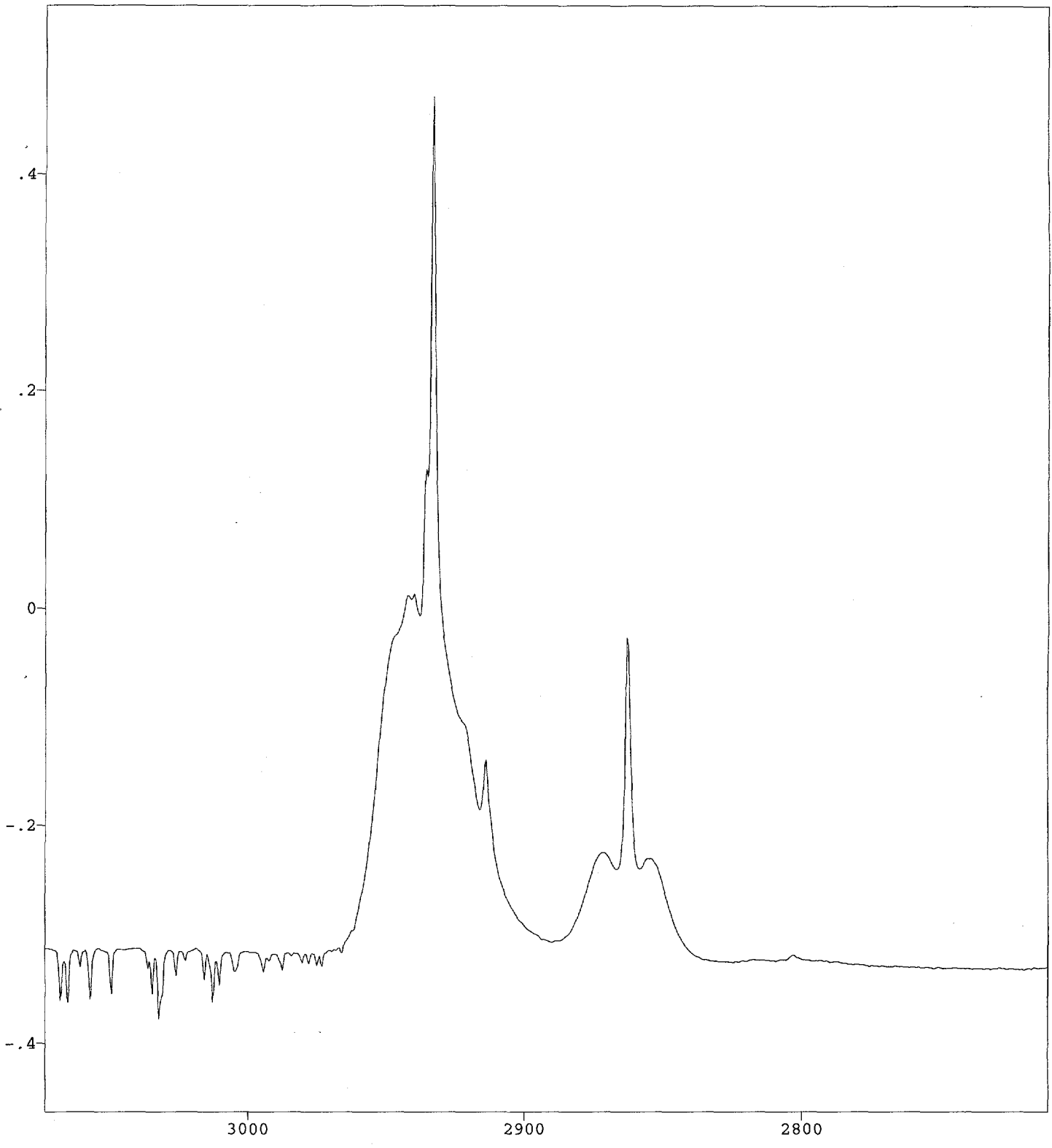
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Paged Y-Zoom CURSOR

#16: C12-6-4

12/6/94 2:25 PM Res=1cm-1

15 ml cyclohexane



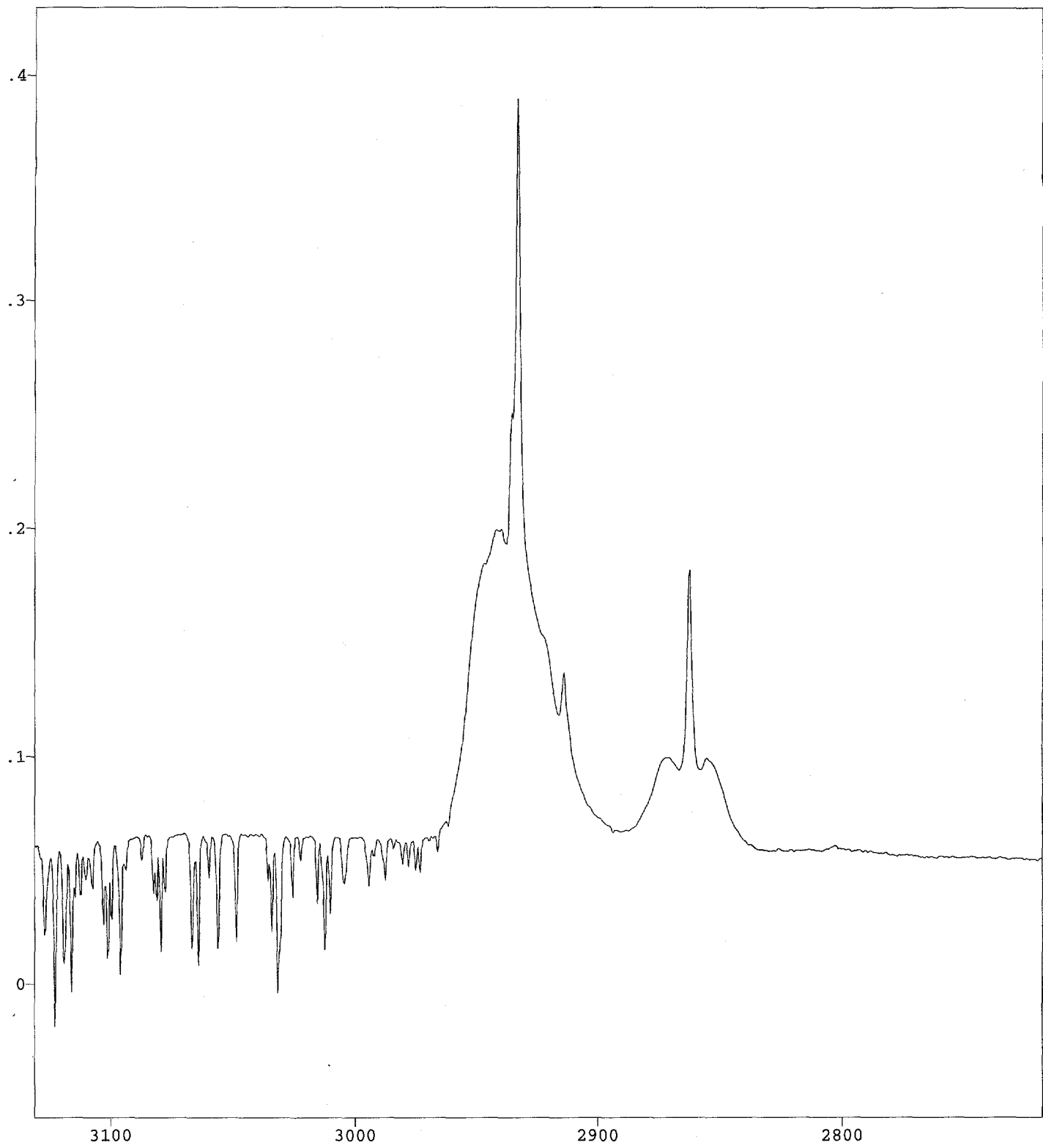
-1)

Paged Y-Zoom CURSOR

#28 : C12-8-5

12/8/94 3:54 PM Res=1cm-1

20 ml cyclo



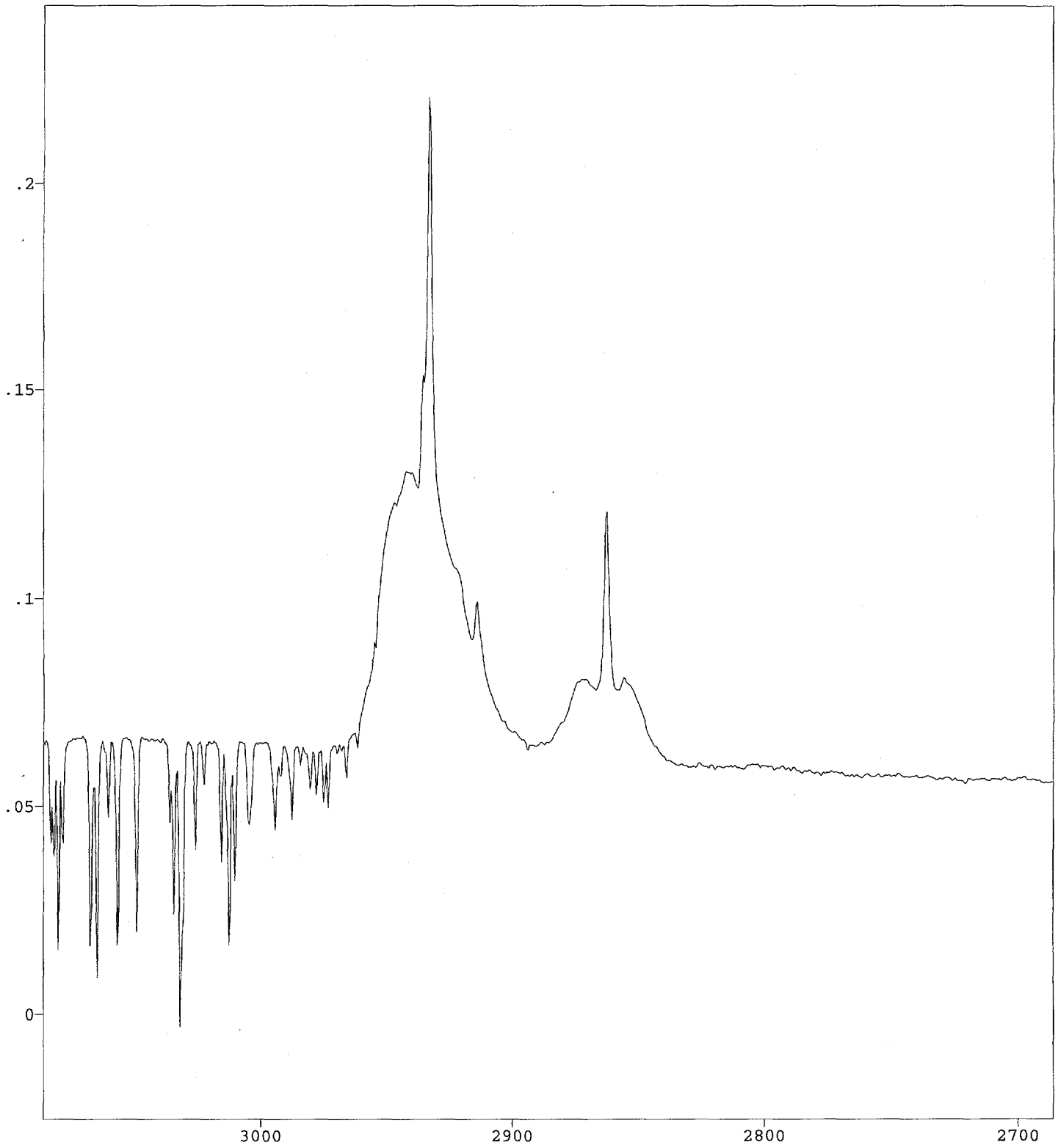
-1)

Paged Y-Zoom CURSOR

#27: C12-8-4

12/8/94 2:04 PM Res=1cm-1

10 ml cyclohexane



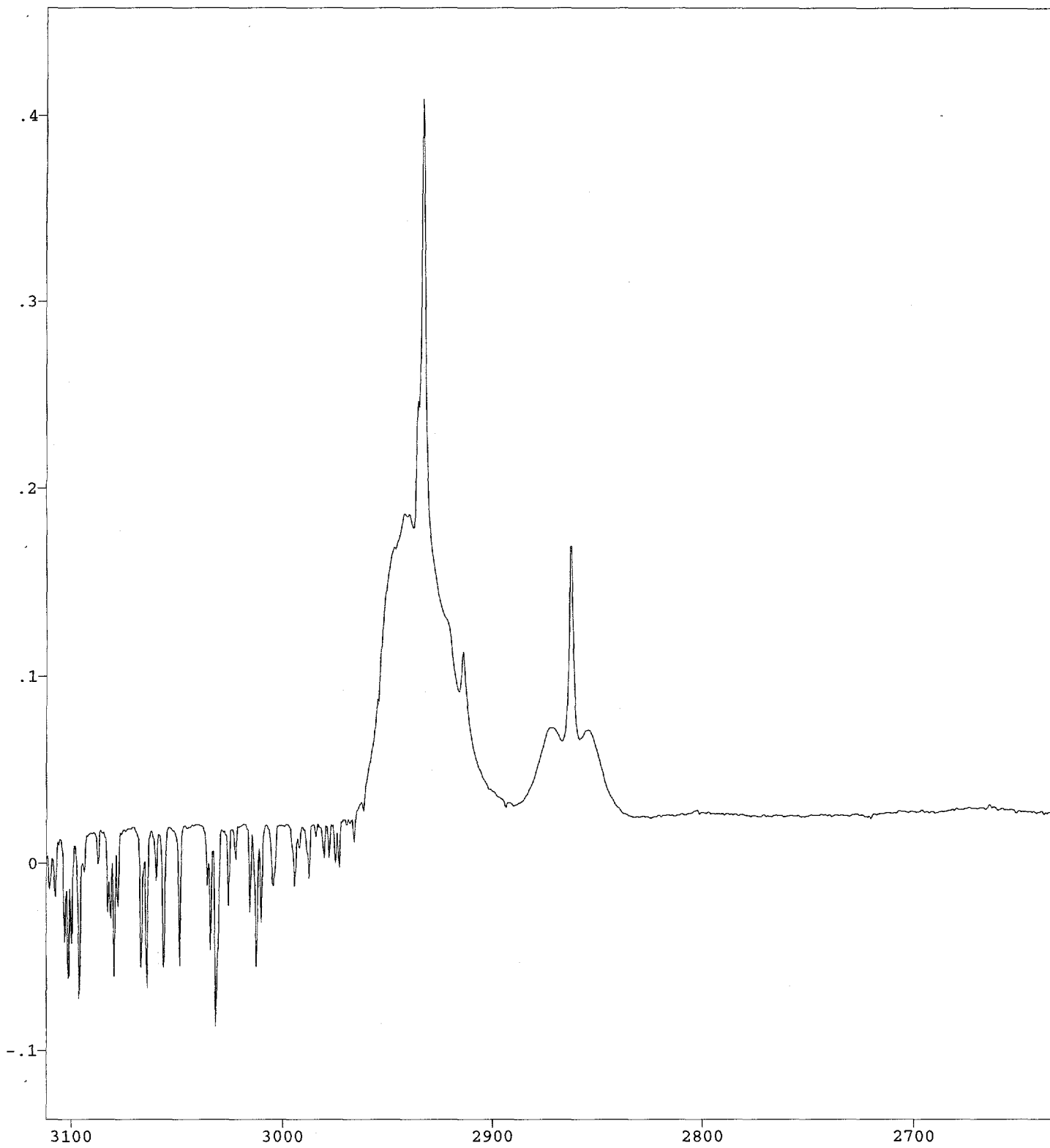
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Paged Y-Zoom CURSOR

#26: C12-8-3

12/8/94 1:56 PM Res=1cm-1

5 ml cyclohexane



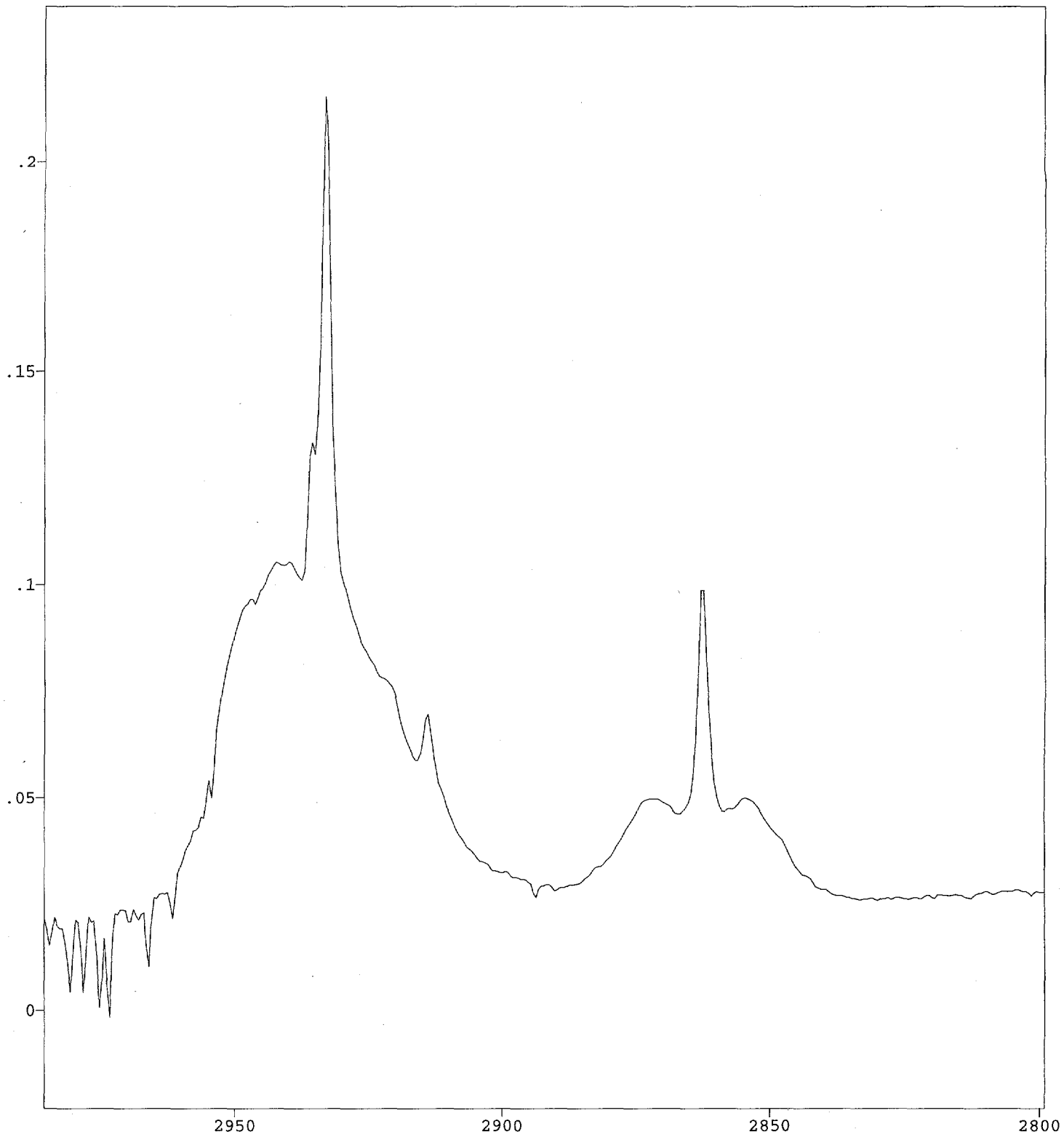
-1)

Paged Y-Zoom CURSOR

#25 : C12-8-2

12/8/94 12:28 PM Res=1cm-1

10 ml cyclohexane



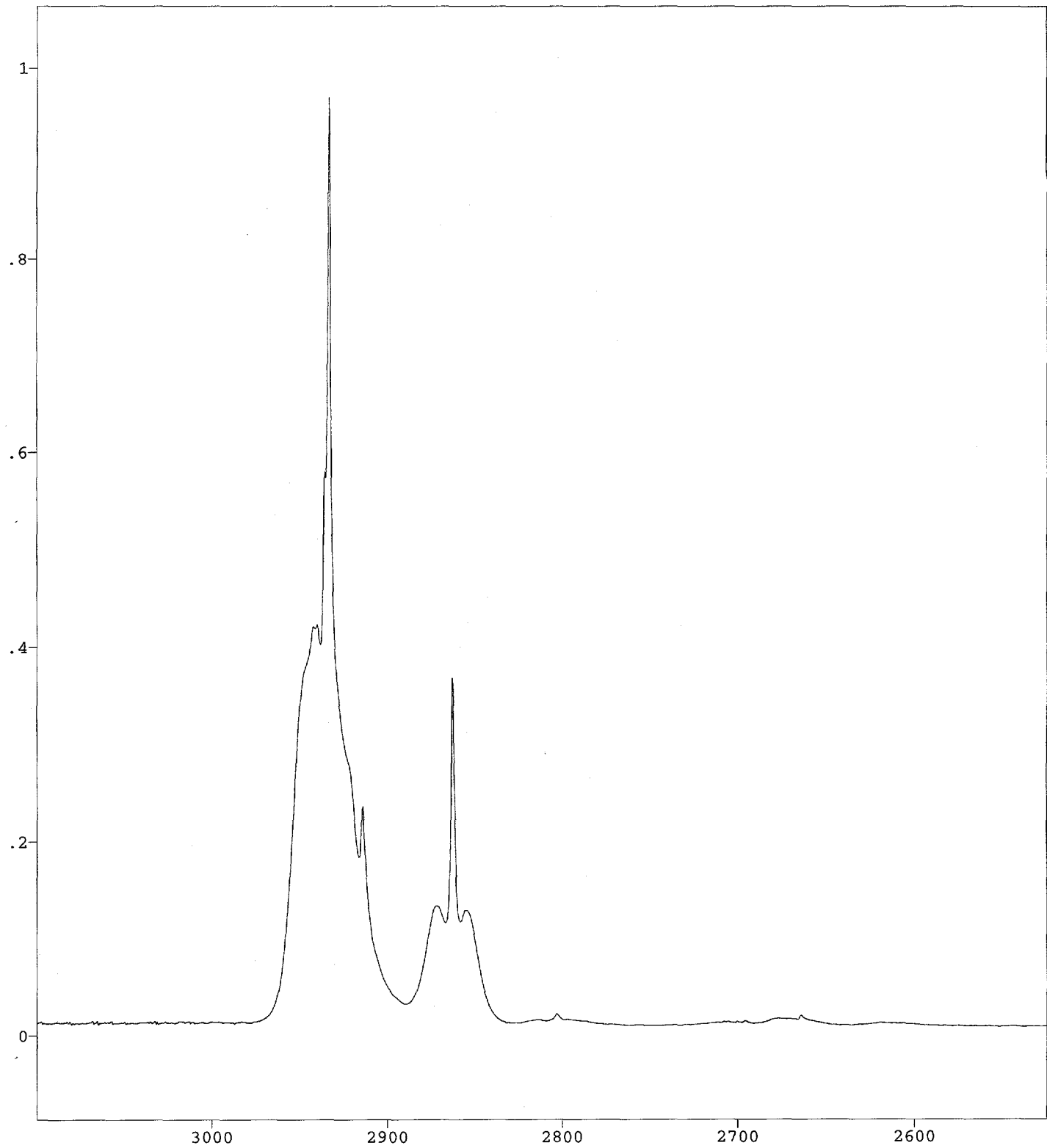
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Paged Y-Zoom CURSOR

#24: C12-8-1

12/8/94 12:17 PM Res=1cm-1

5 ml cyclohexane



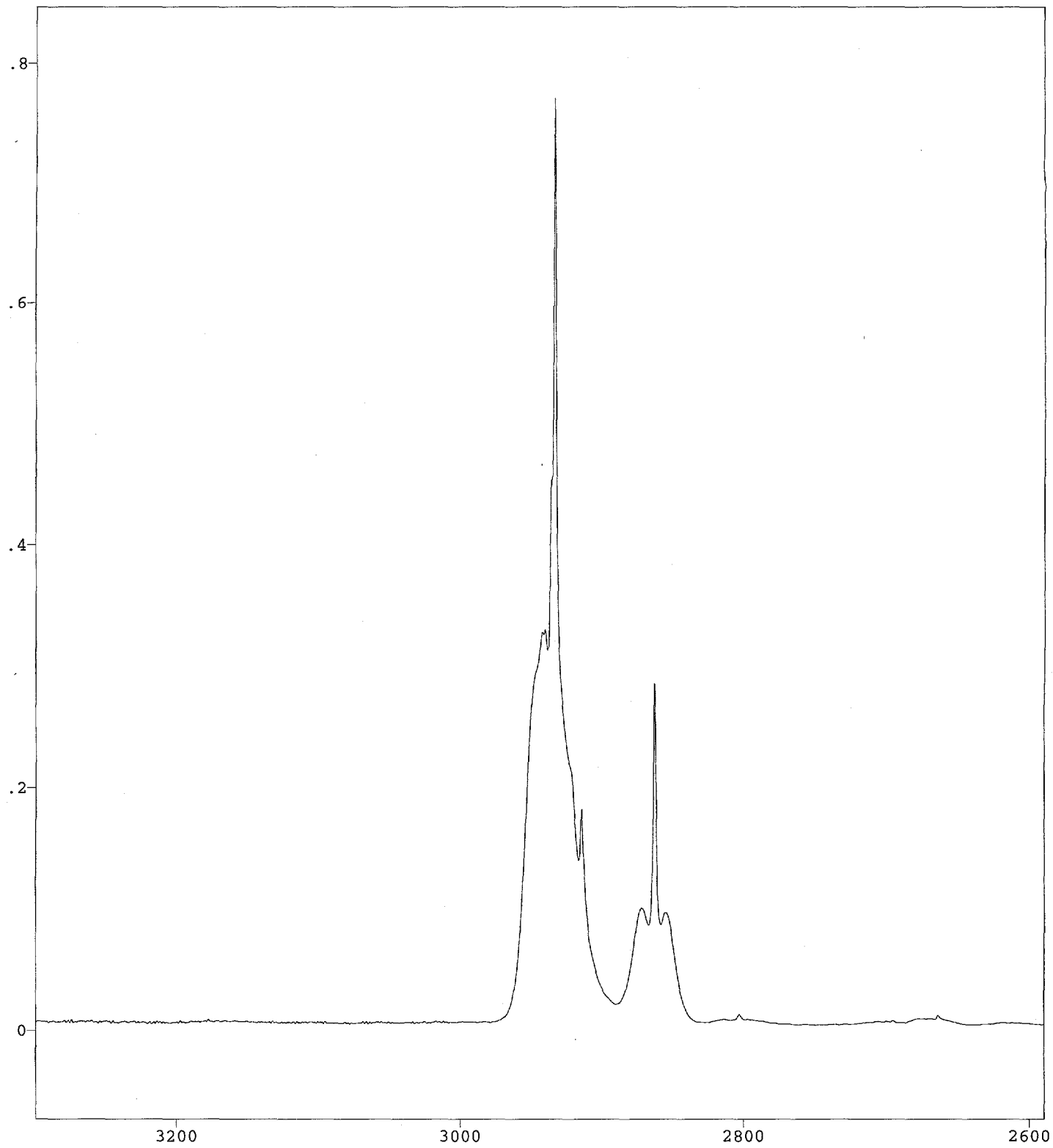
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Paged Y-Zoom CURSOR

#23 : C12-7-6

12/7/94 5:47 PM Res=1cm-1

25 real ml cyclo



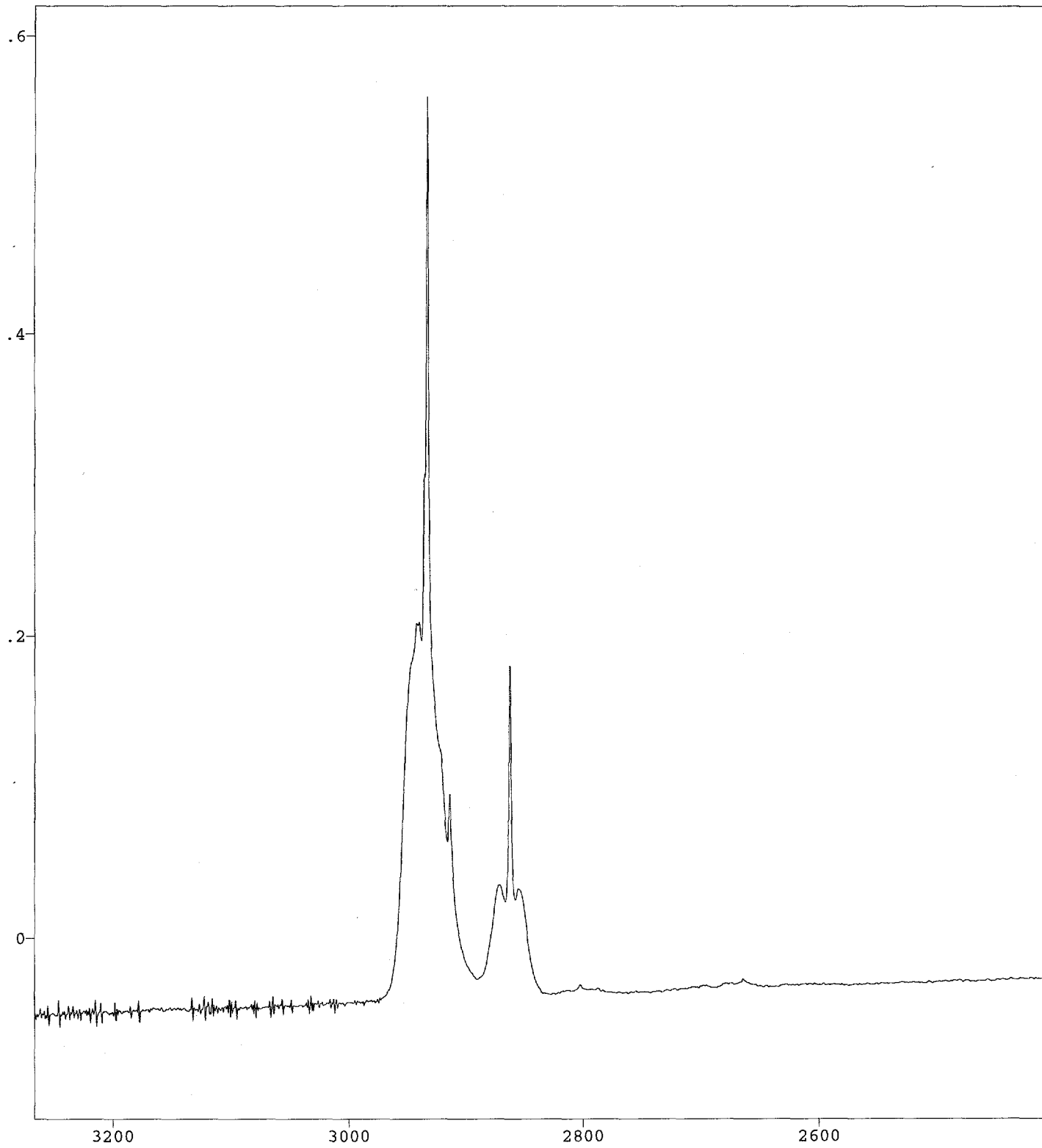
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Paged Y-Zoom CURSOR

#22 : C12-7-5

12/7/94 5:37 PM Res=1cm-1

25 ml cyclo



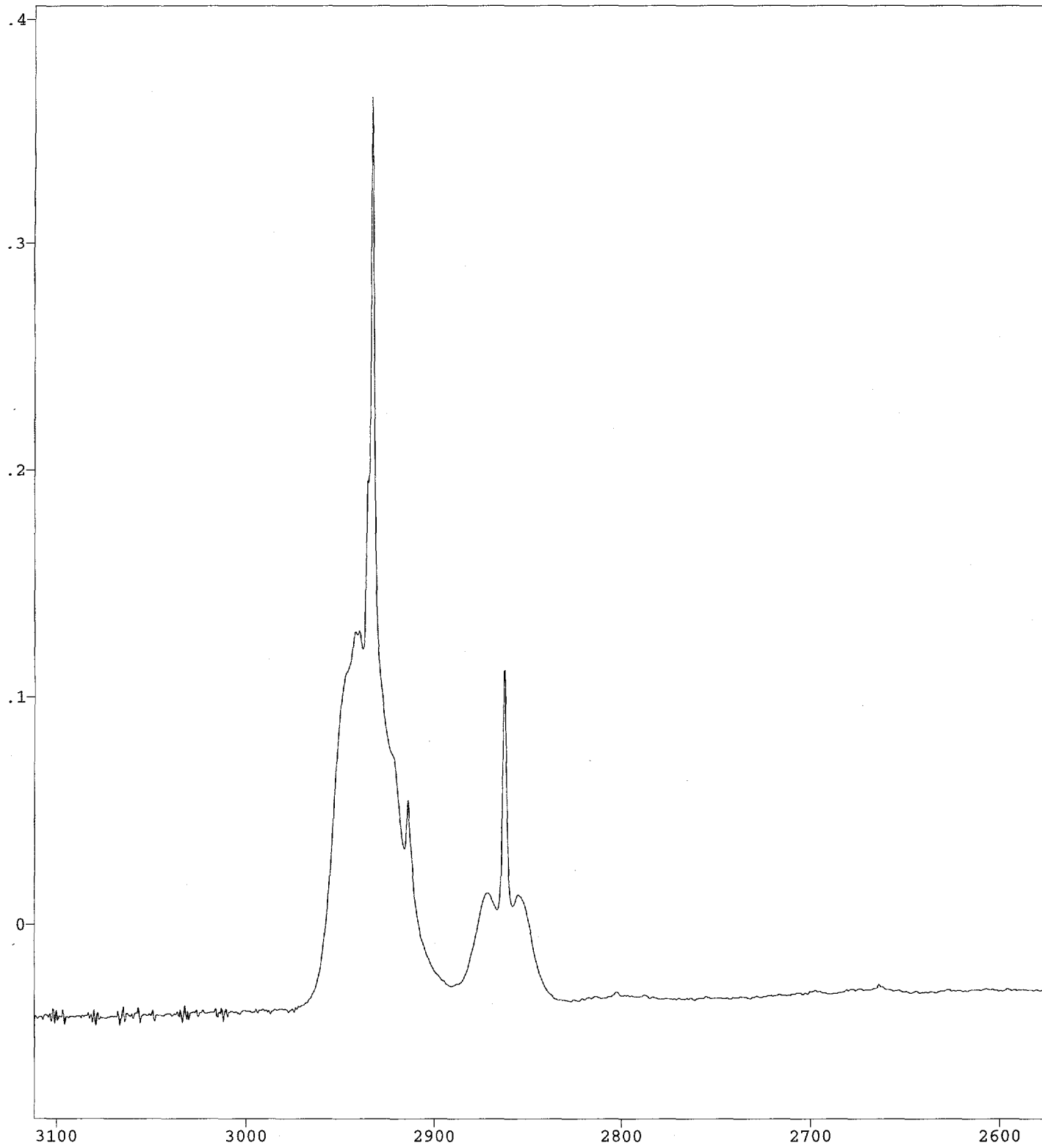
-1)

Paged Y-Zoom CURSOR

#21 : C12-7-4

12/7/94 3:09 PM Res=1cm-1

15 ml cyclohexane



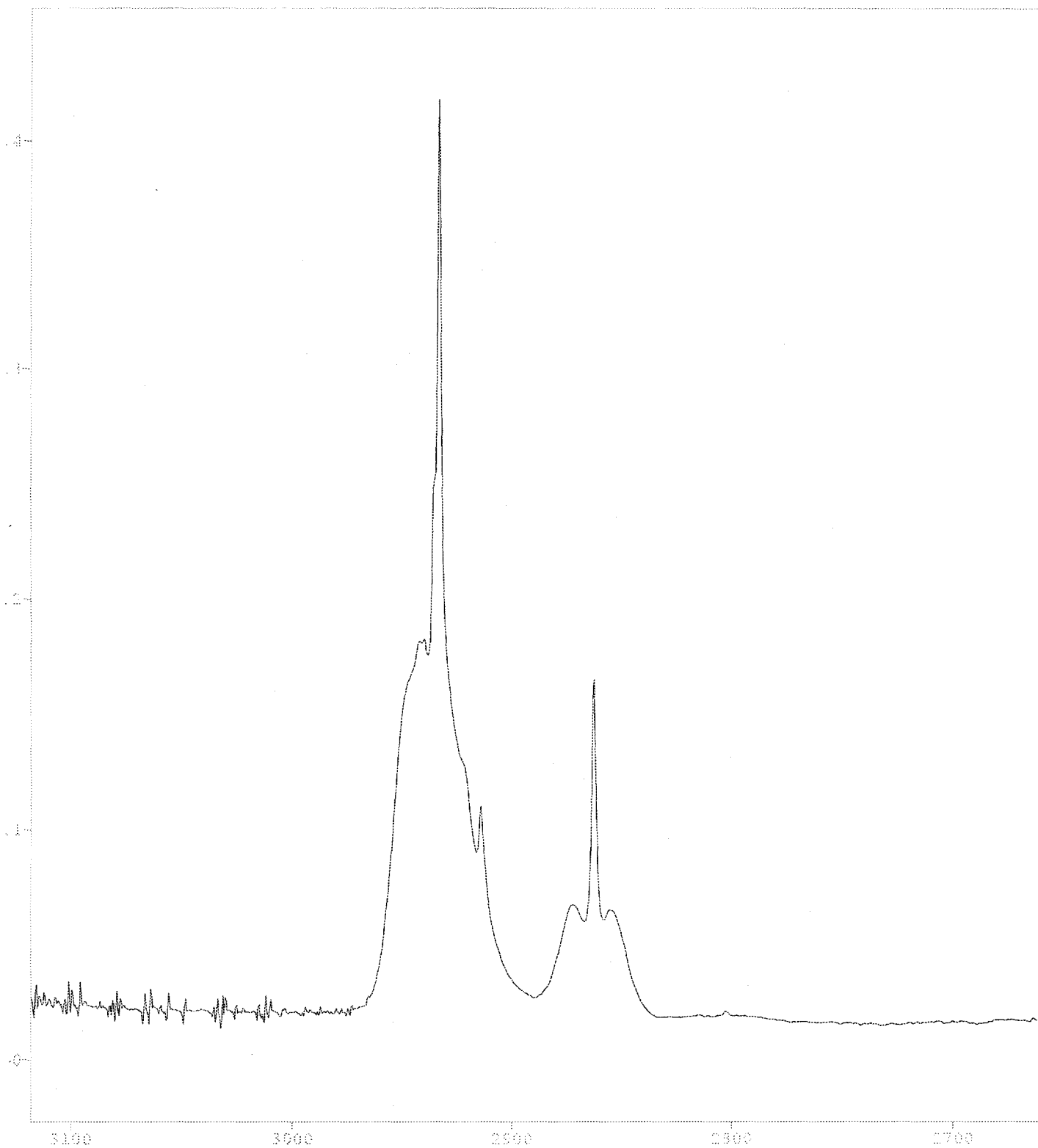
-1)

Paged Y-Zoom CURSOR

#20 : C12-7-3

12/7/94 3:01 PM Res=1cm-1

10 ml cyclohexane



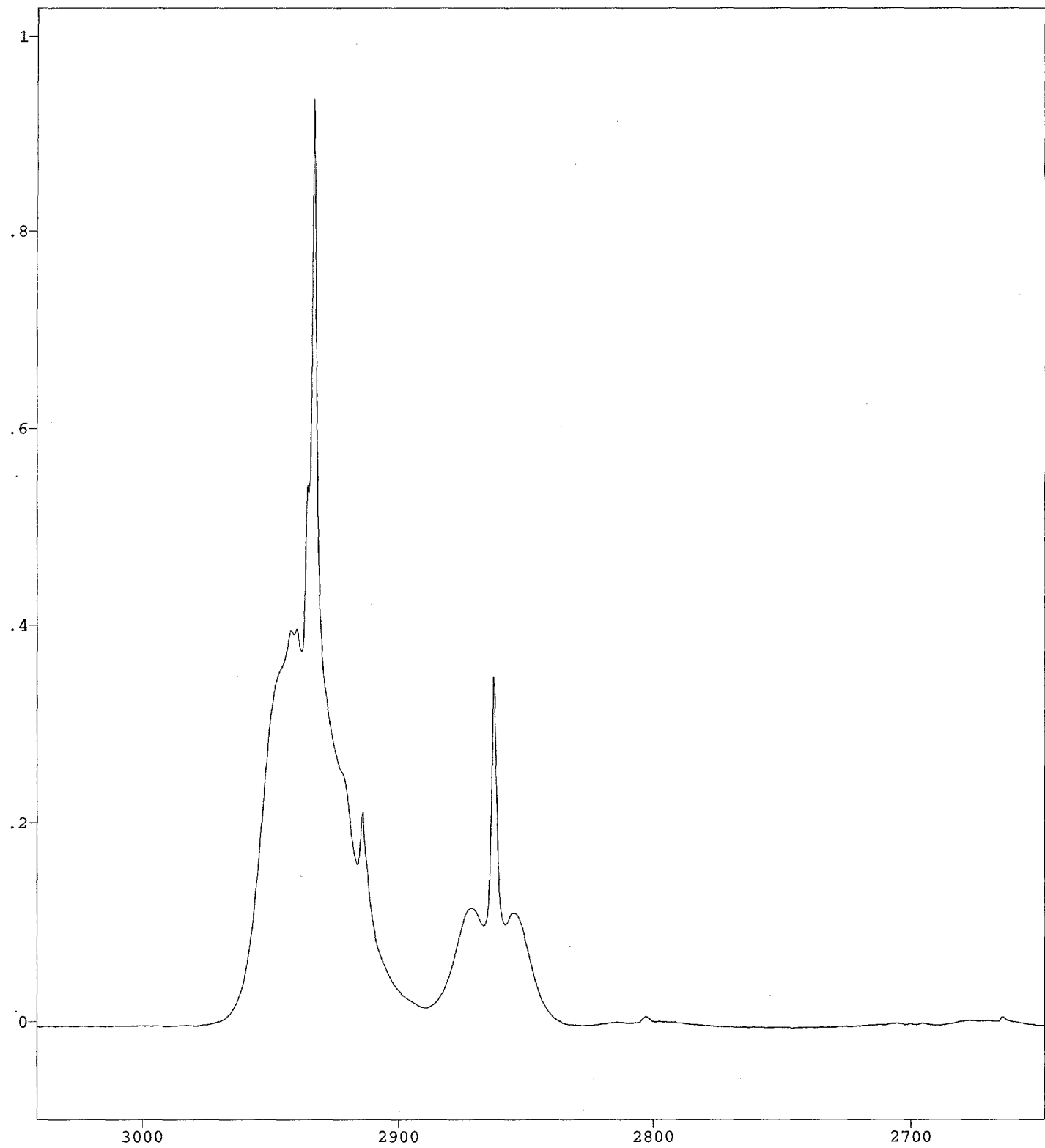
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Paged Y-Zoom CURSOR

#19 : C12-7-2

12/7/94 1:20 PM Res=1cm-1

10 ml cyclohexane



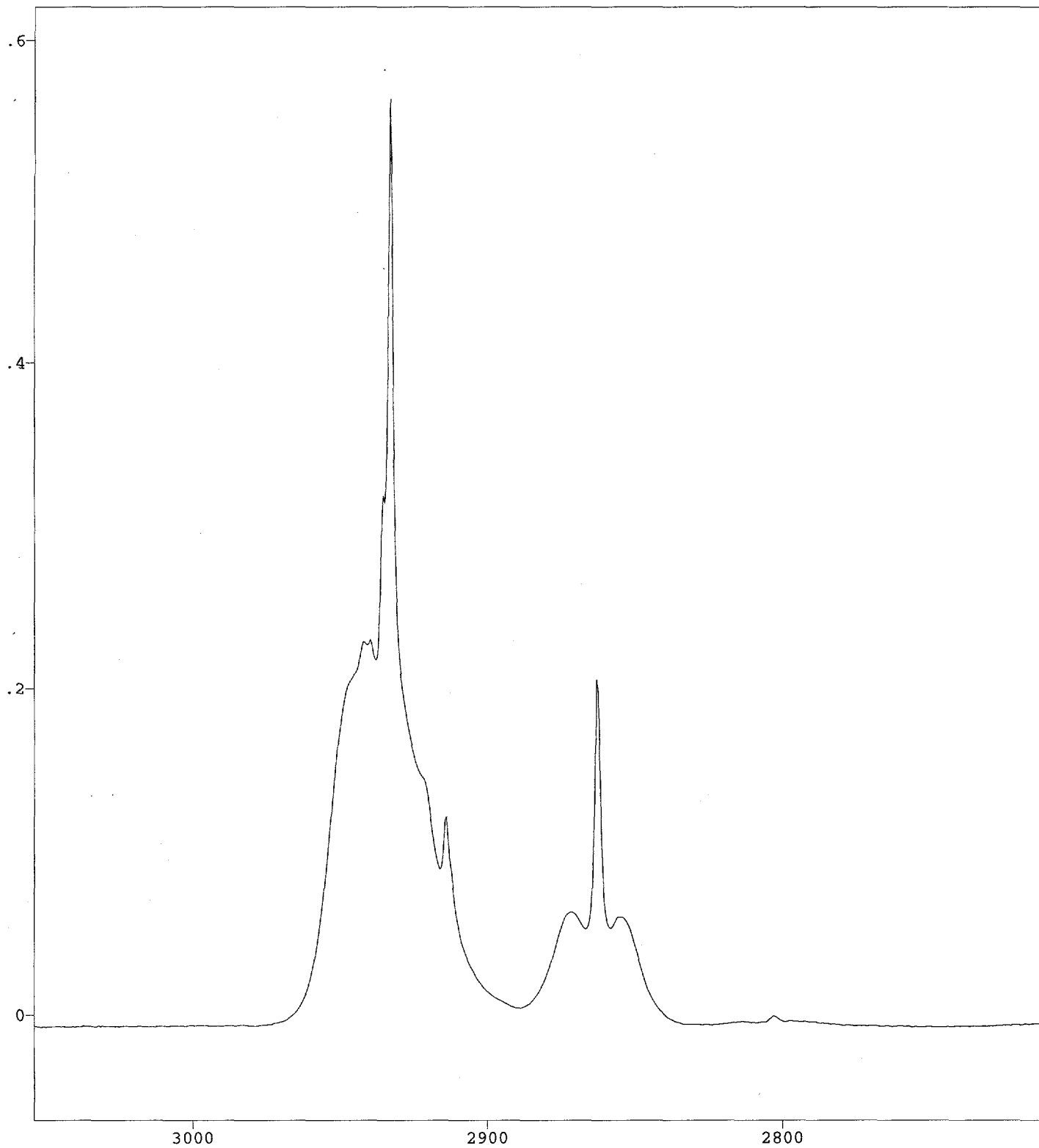
-1)

Paged Y-Zoom CURSOR

# 2 : C12-9-2

12/9/94 12:39 PM Res=1cm-1

20 ml cyclohexane



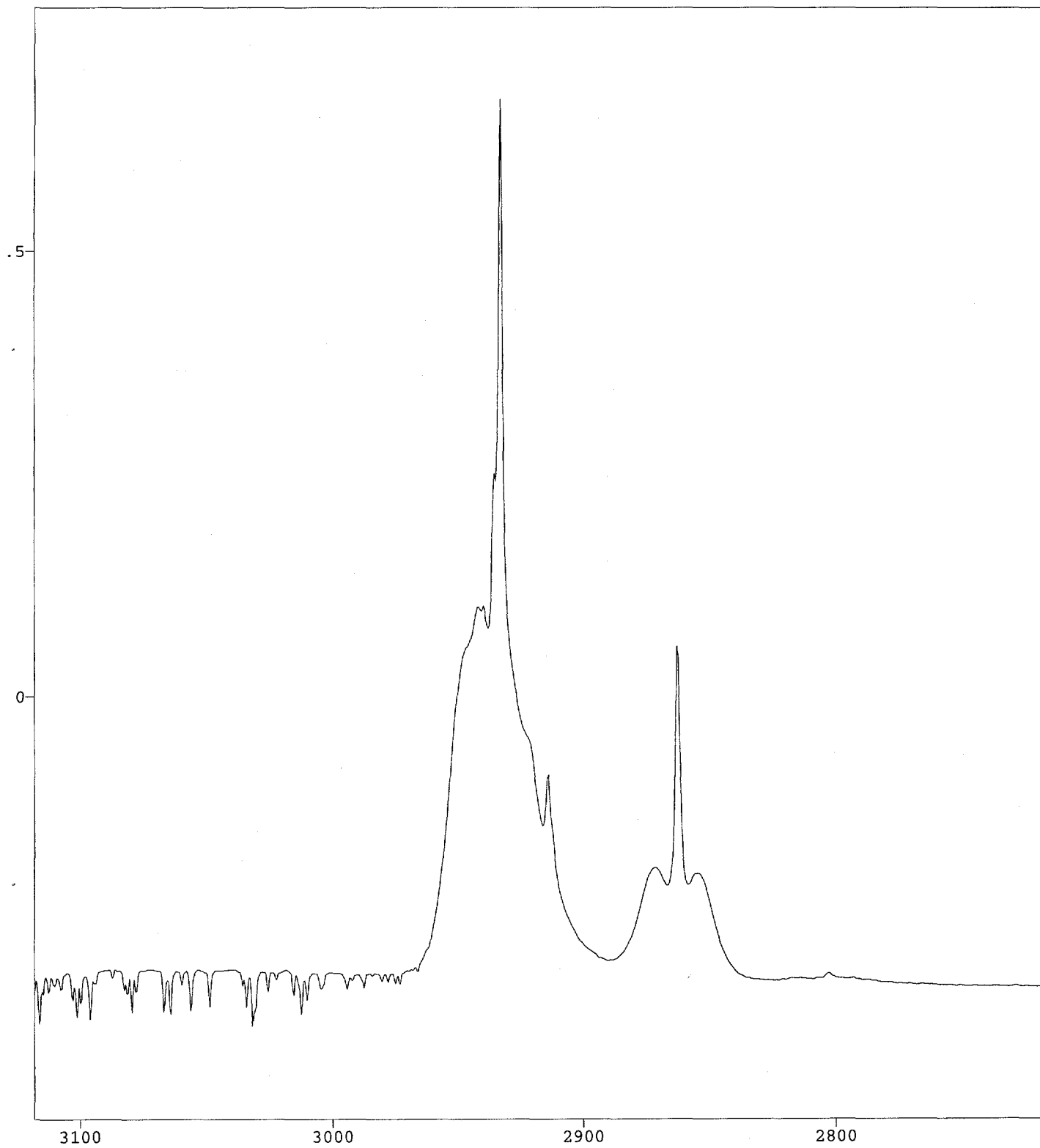
-1)

Paged Y-Zoom CURSOR

# 1: C12-9-1

12/9/94 12:28 PM Res=1cm-1

15 ml cyclohexane



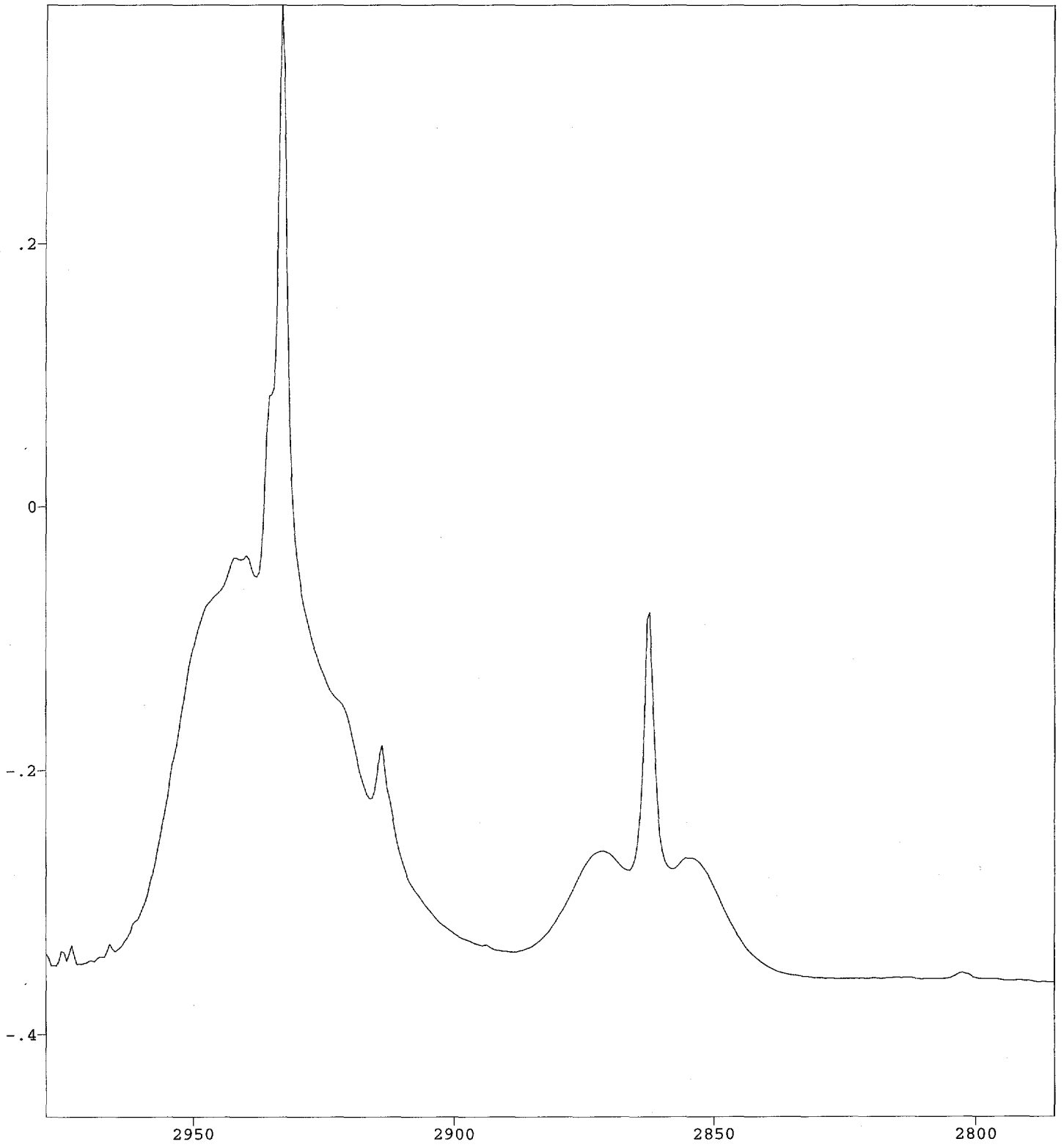
-1)

Paged Y-Zoom CURSOR

#29 : C12-8-6

12/8/94 4:02 PM Res=1cm-1

25 ml cyclo



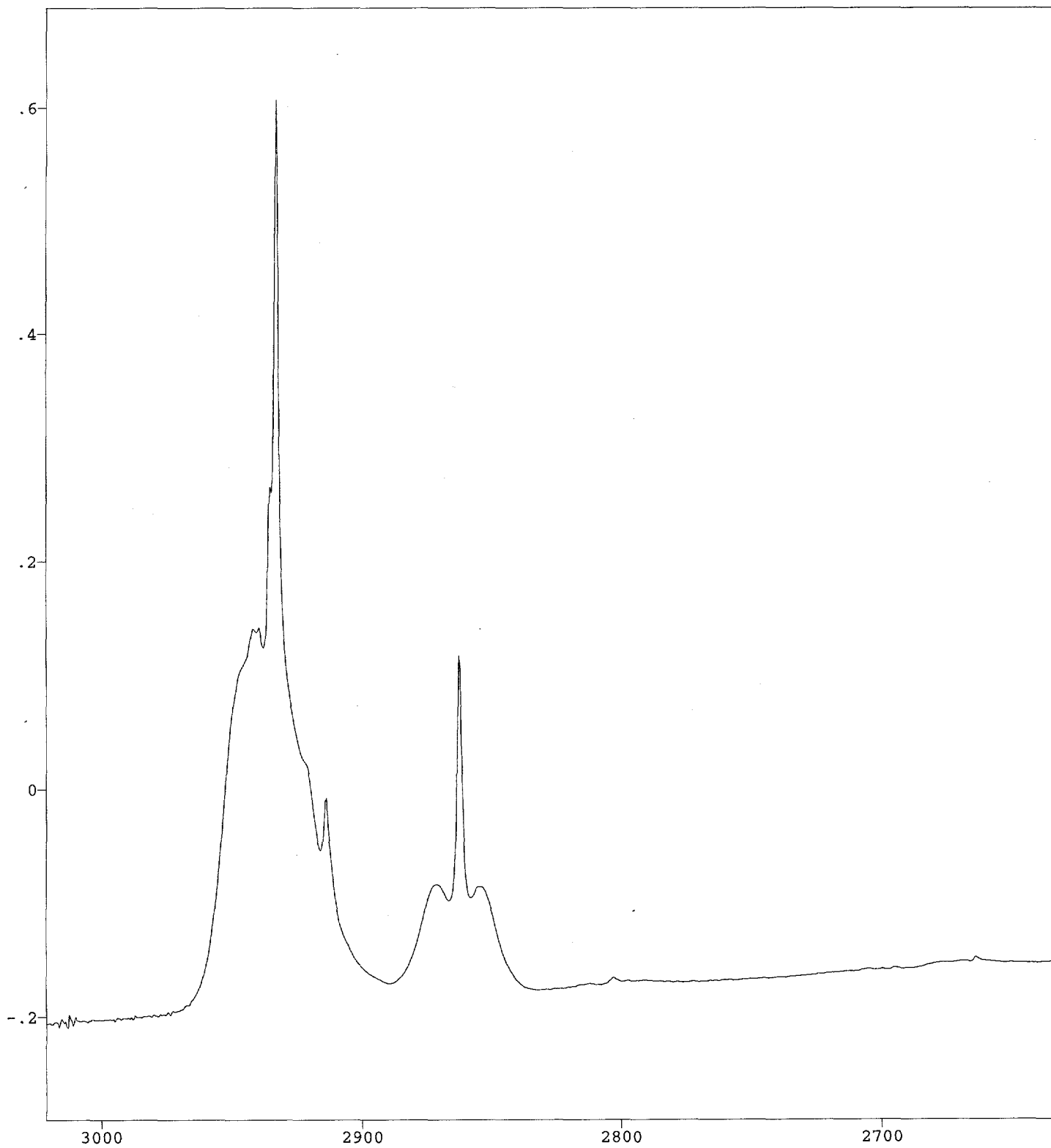
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Paged Y-Zoom CURSOR

File # 6: C12-10-1

12/10/94 1:48 PM Res=1cm-1

20 ml cyclohexane



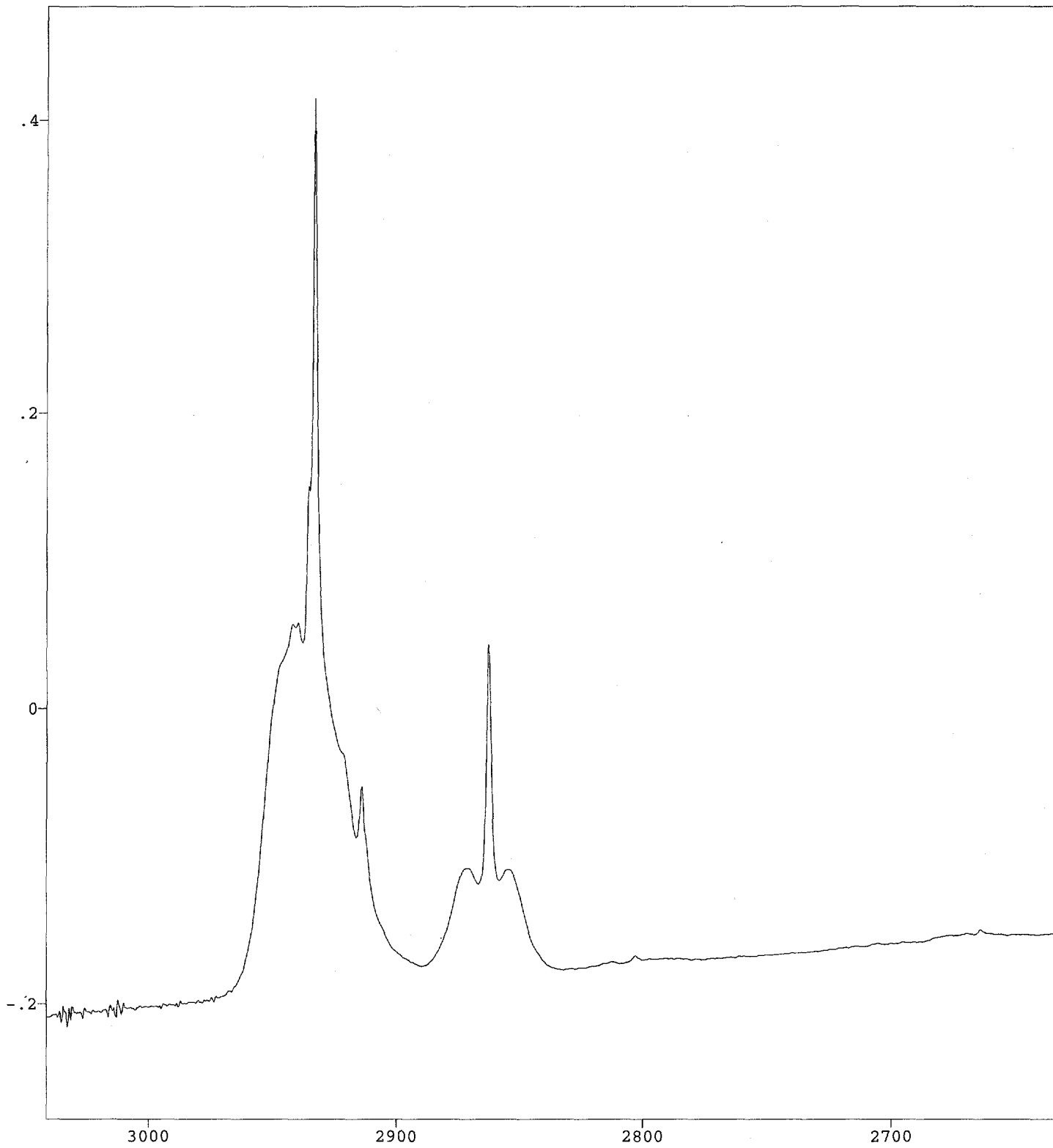
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Paged Y-Zoom CURSOR

File # 4 : C12-9-4

12/9/94 3:06 PM Res=1cm-1

20 ml cyclohexane

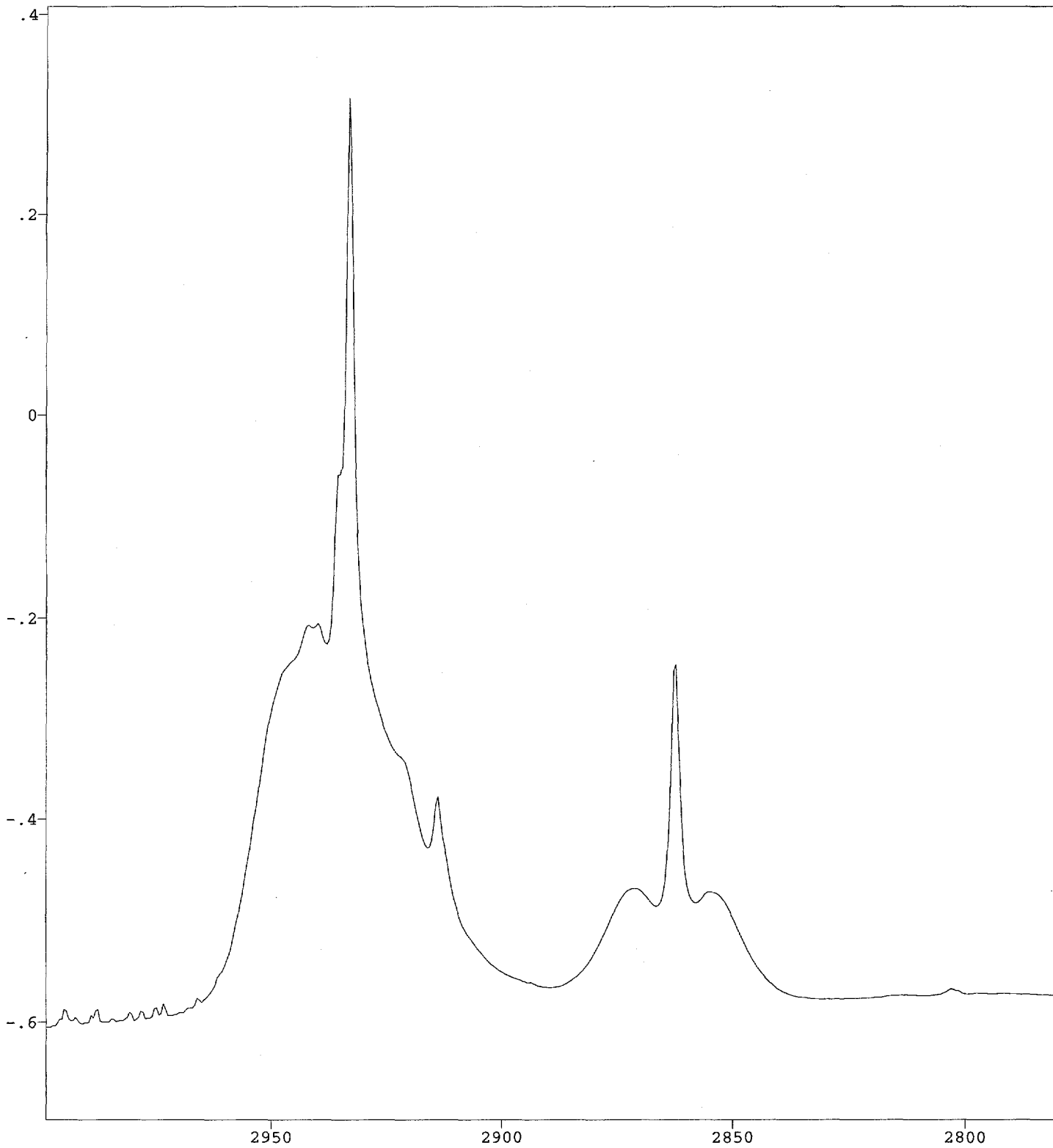


-1)

Sample # 3 : C12-9-3  
15 ml cyclohexane

Paged Y-Zoom CURSOR

12/9/94 2:53 PM Res=1cm-1



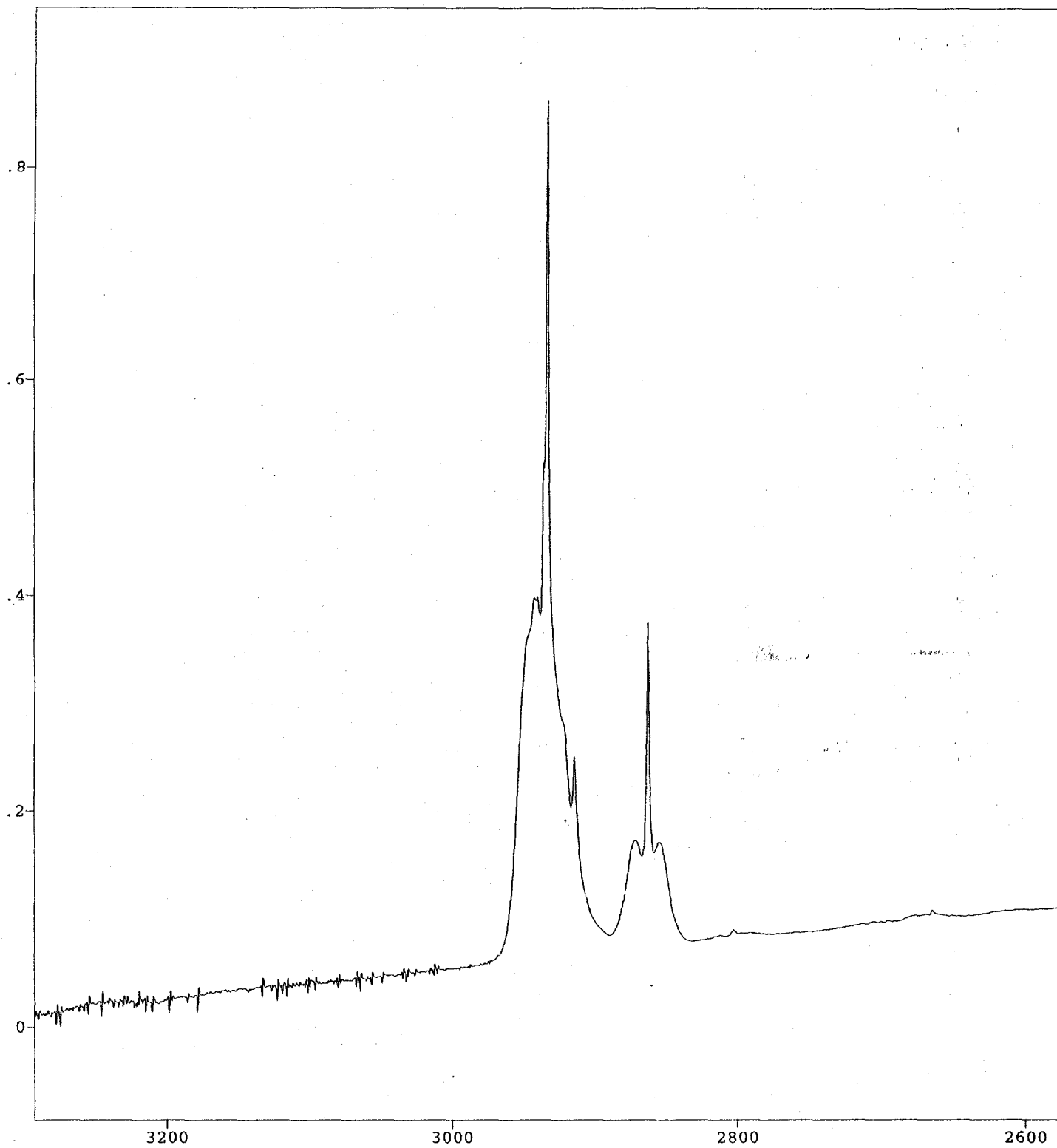
-1)

Paged Y-Zoom CURSOR

File # 7: C12-10-2

12/10/94 2:02 PM Res=1cm-1

25 ml cyclohexane



Absorbance / Wavenumber (cm-1)

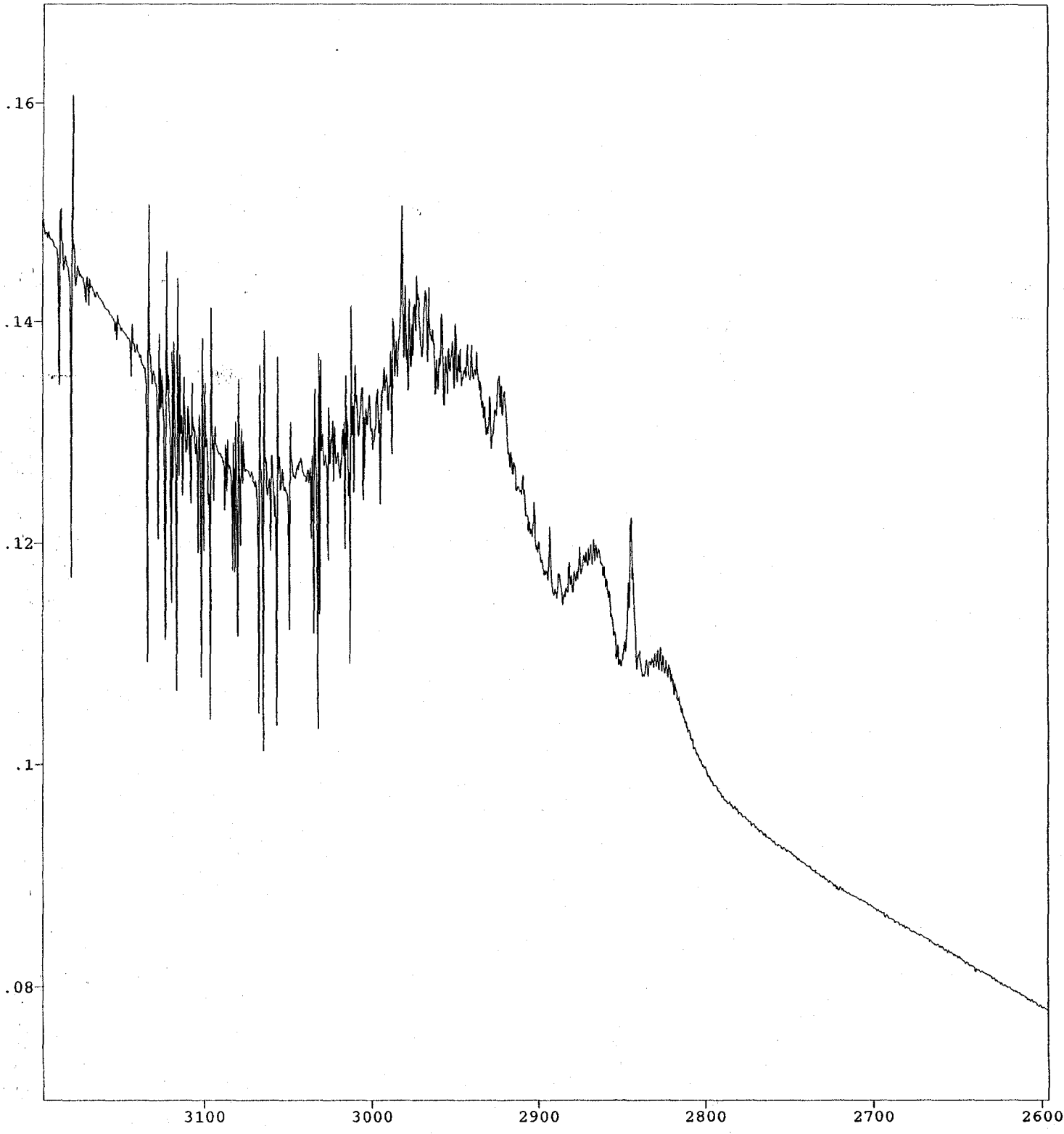
Paged Y-Zoom CURSOR

File #14 : C12-9-4

12/9/94 3:06 PM Res=1cm-

20 ml cyclohexane

**APPENDIX F: METHANOL ABSORBANCE SPECTRA**



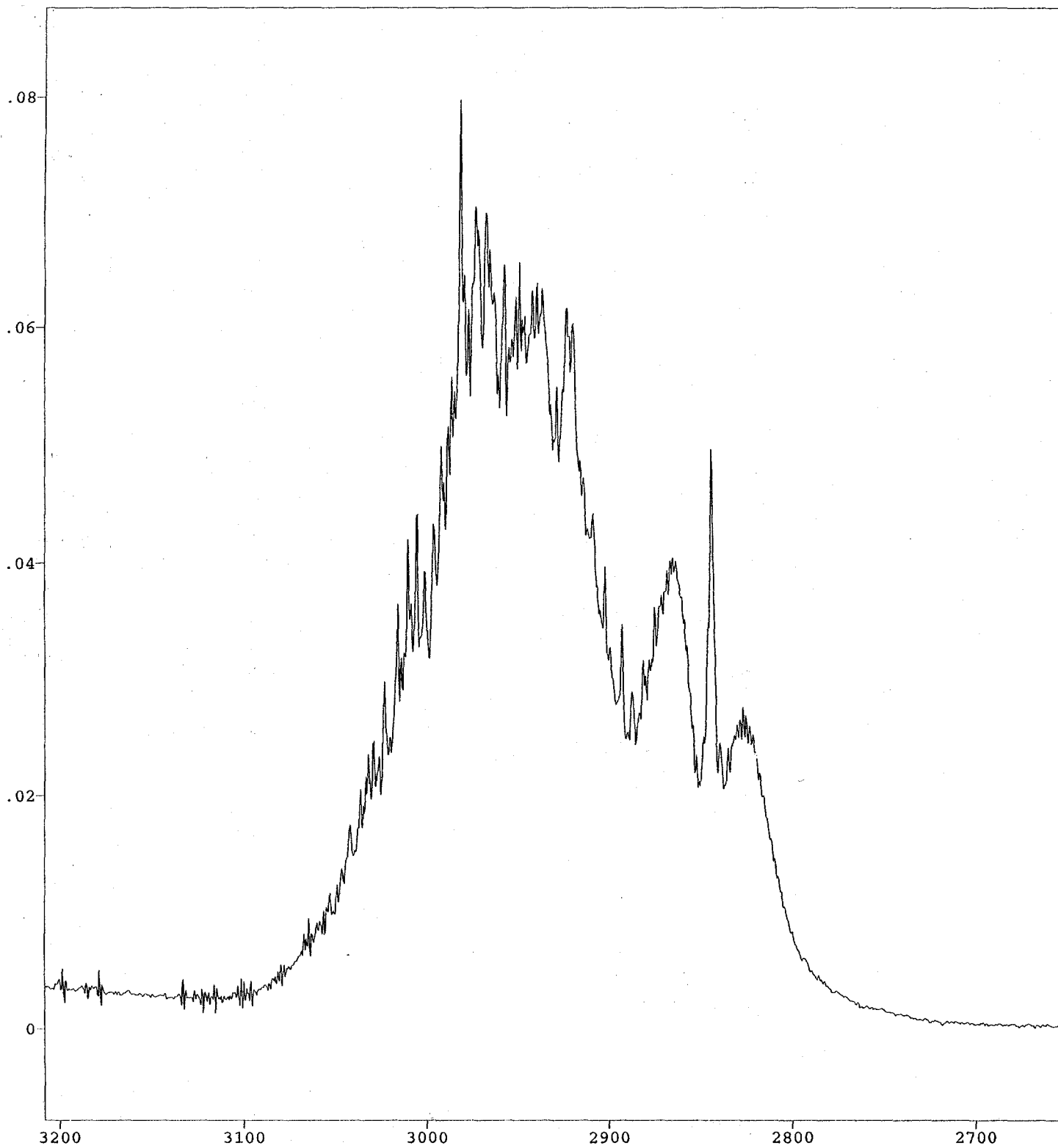
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #20 : M12-15-6

12/15/94 2:16 PM Res=0.5cm-1

6 ml methanol



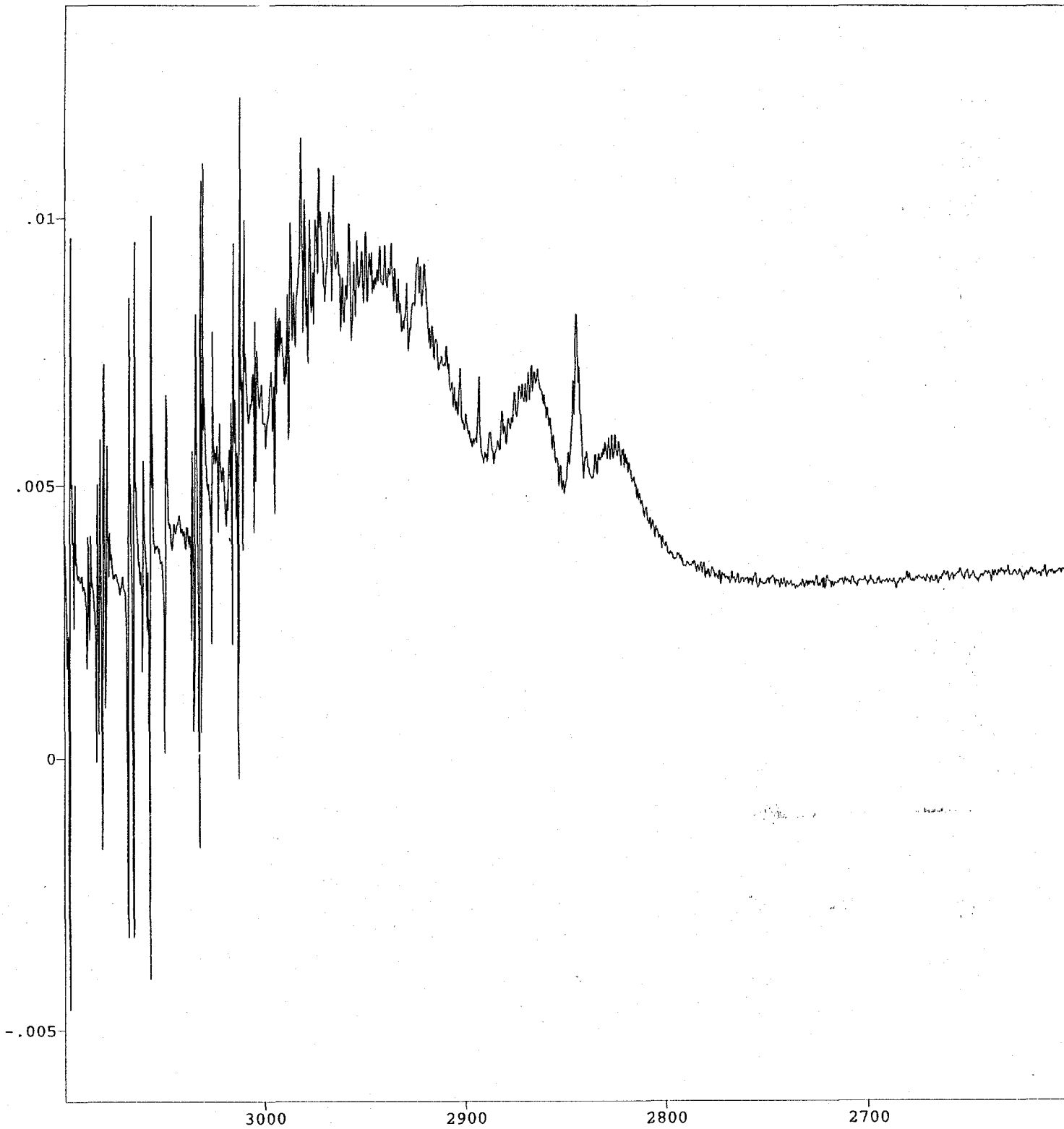
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

#17 : M12-12-4

12/12/94 2:55 PM Res=1cm-1

1]5 ml methanol



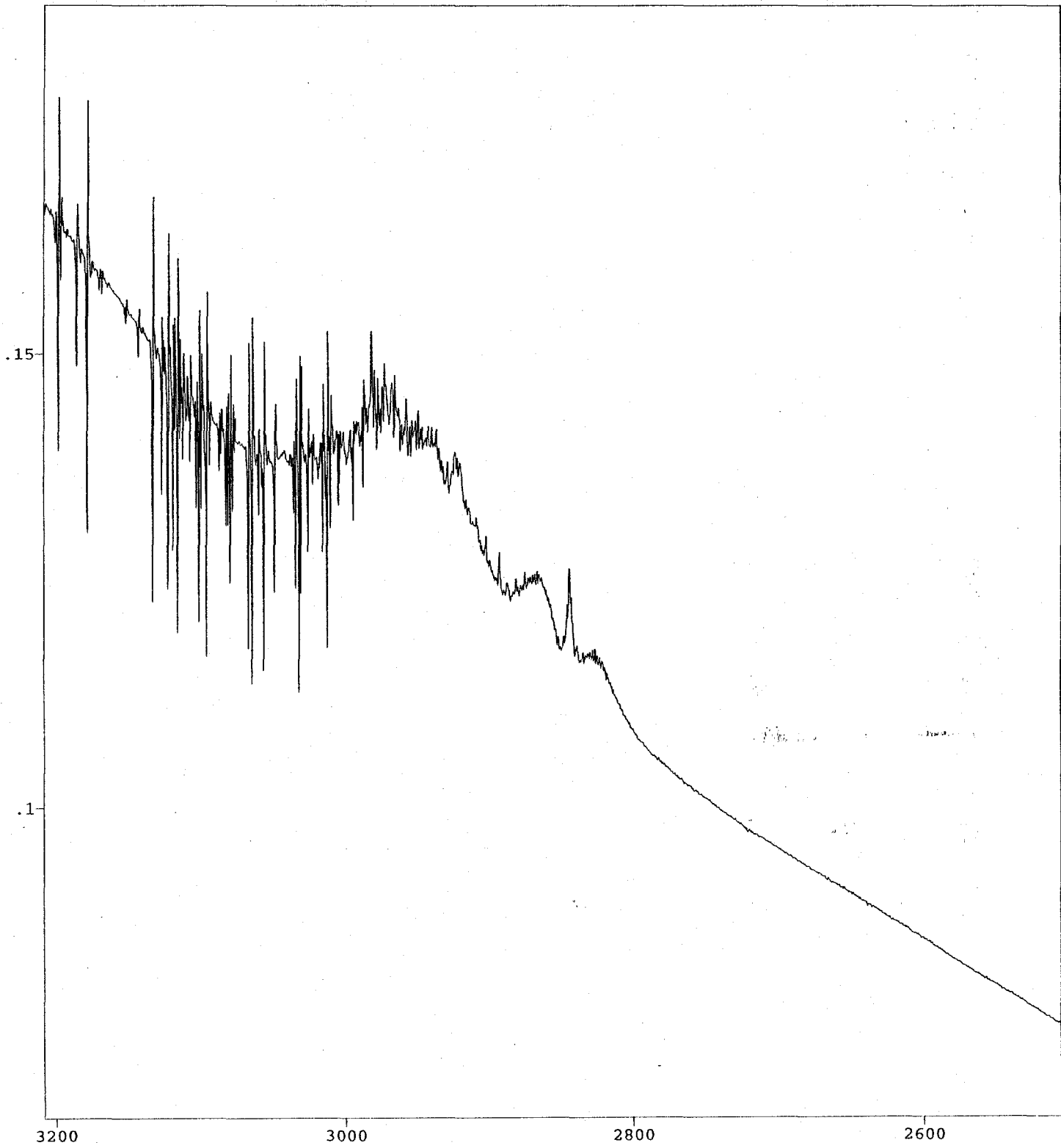
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #18 : M12-15-1

12/15/94 12:30 PM Res=0.5cm-

1.5 ml Imethanol



Absorbance / Wavenumber (cm-1)

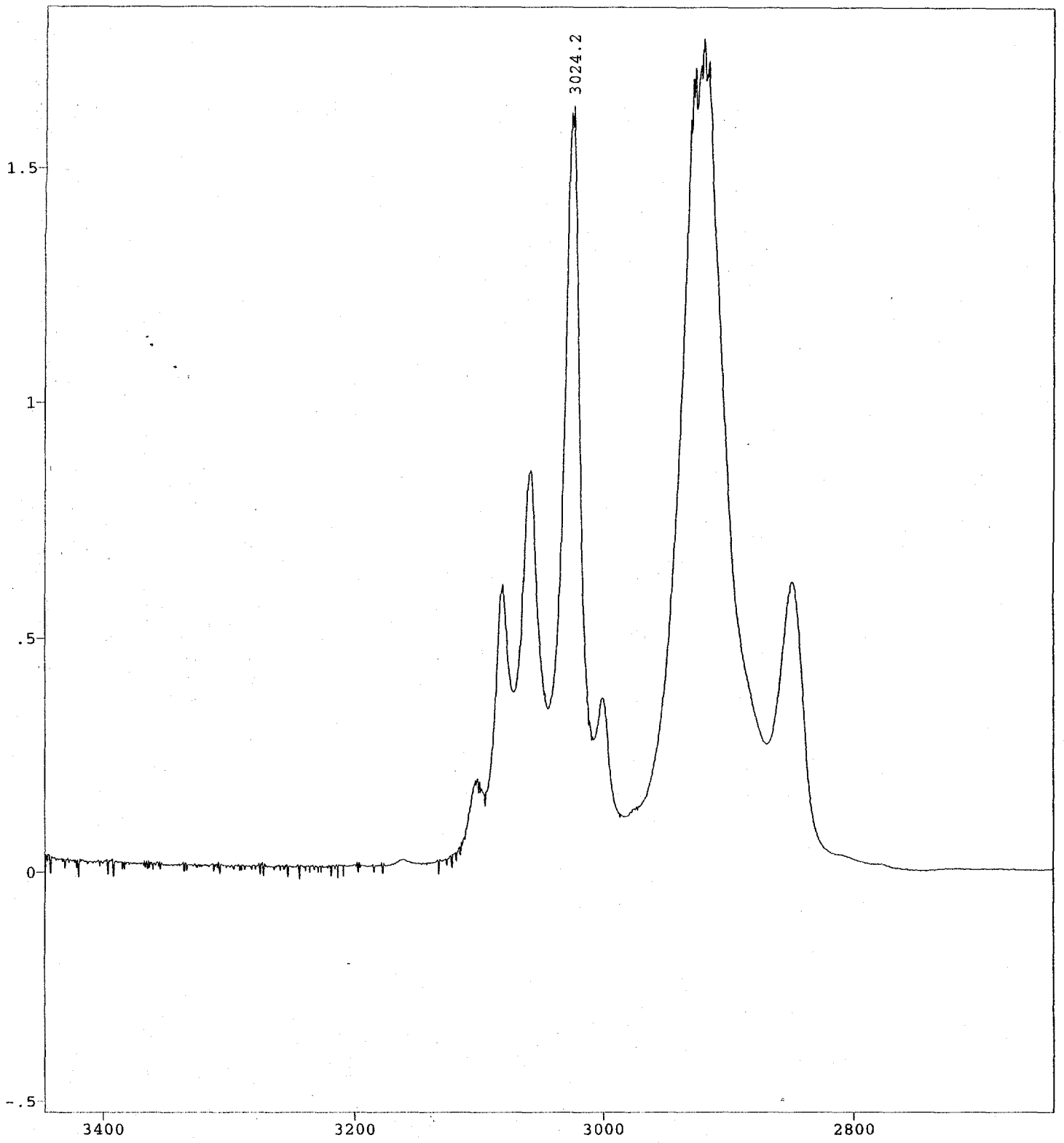
Paged Y-Zoom CURSOR

File #19 : M12-15-4

12/15/94 2:02 PM Res=0.5cm-1

4 ml methanol

**APPENDIX G: POLYSTYRENE FILM ABSORBANCE SPECTRA**



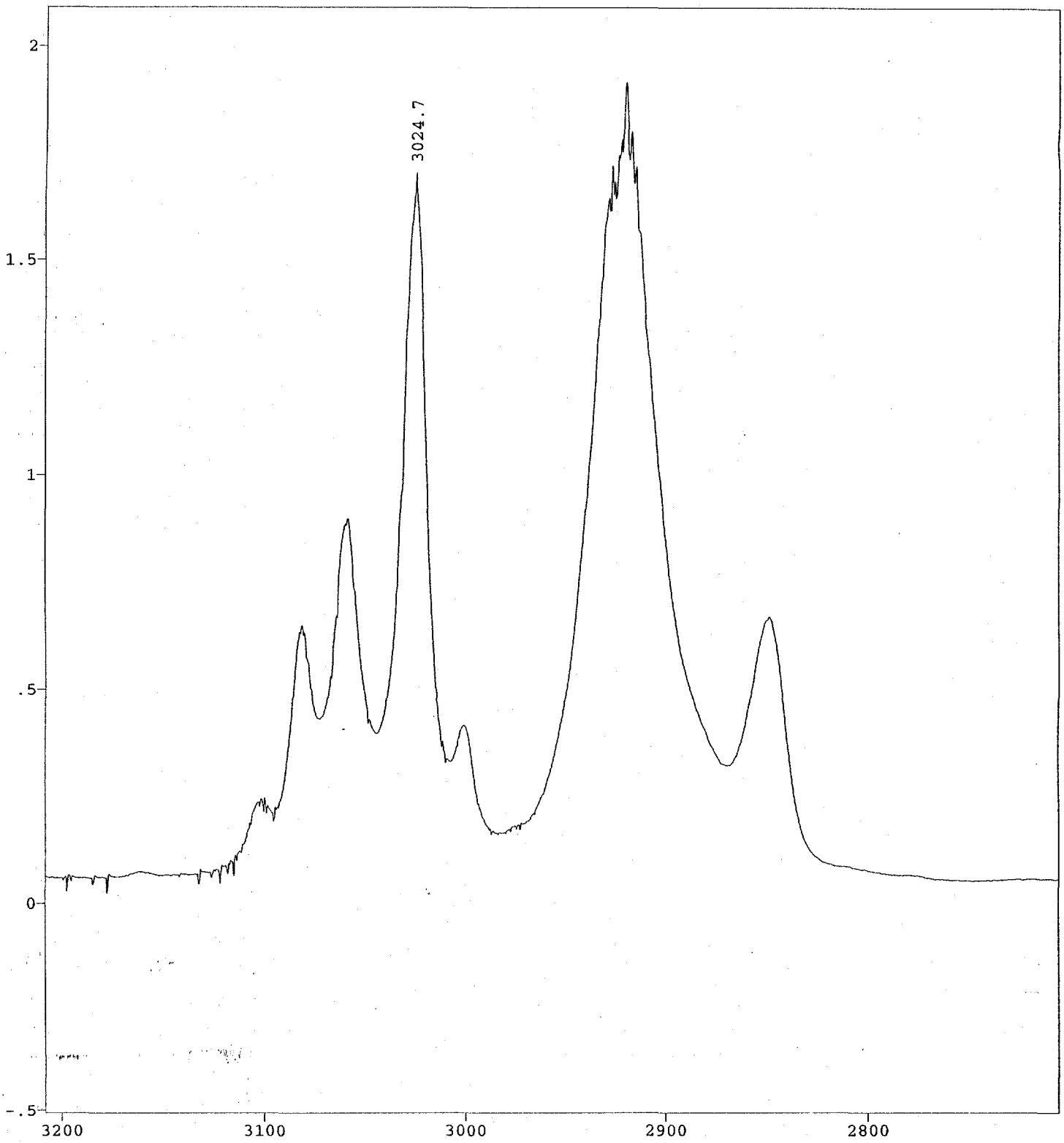
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

#27 : P10-19-A

10/19/94 11:42 AM Res=1cm-1

poly film



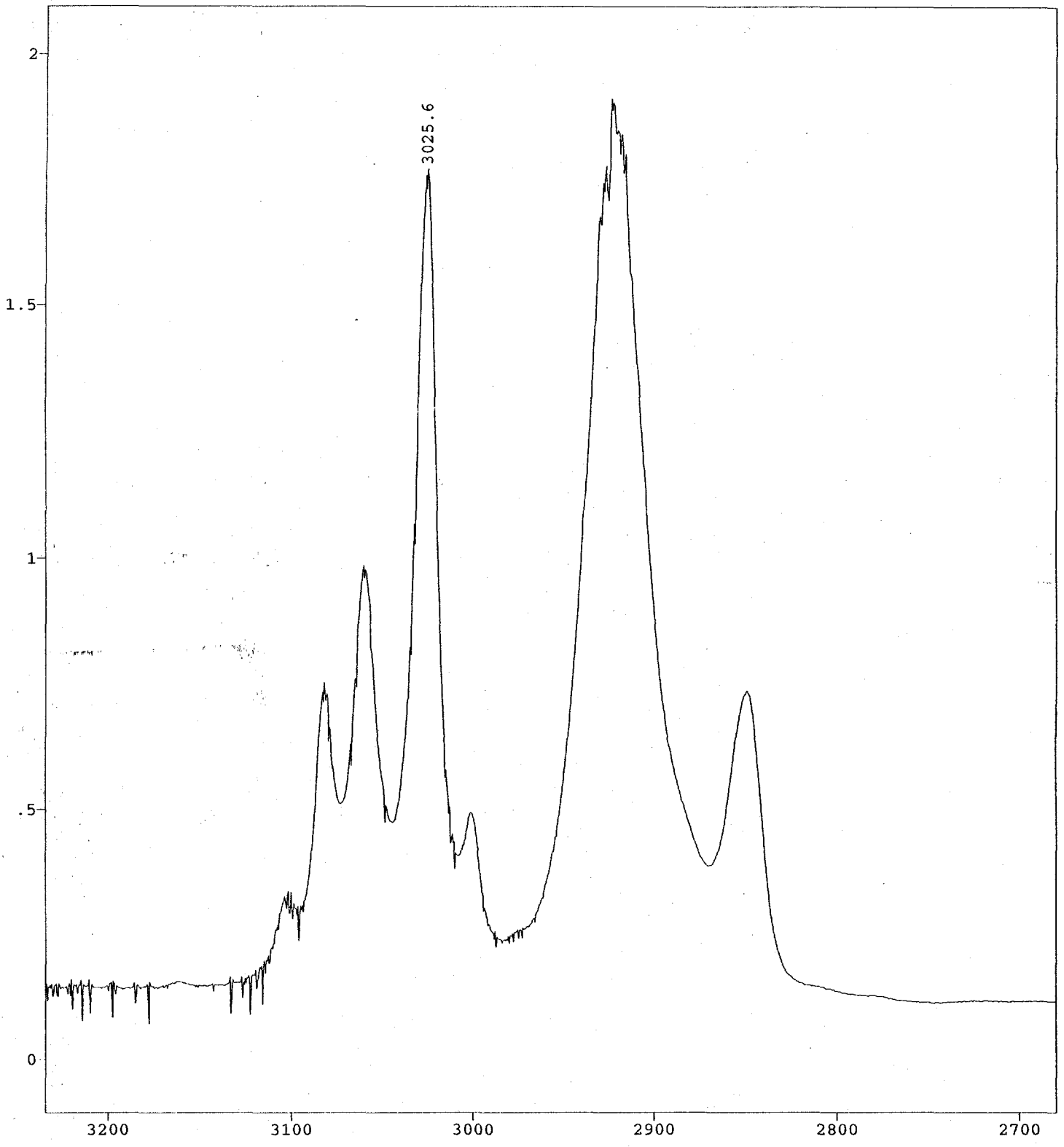
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

#26 : P10-22-A

10/22/94 3:07 PM Res=1cm-1

poly film 1 cm-1



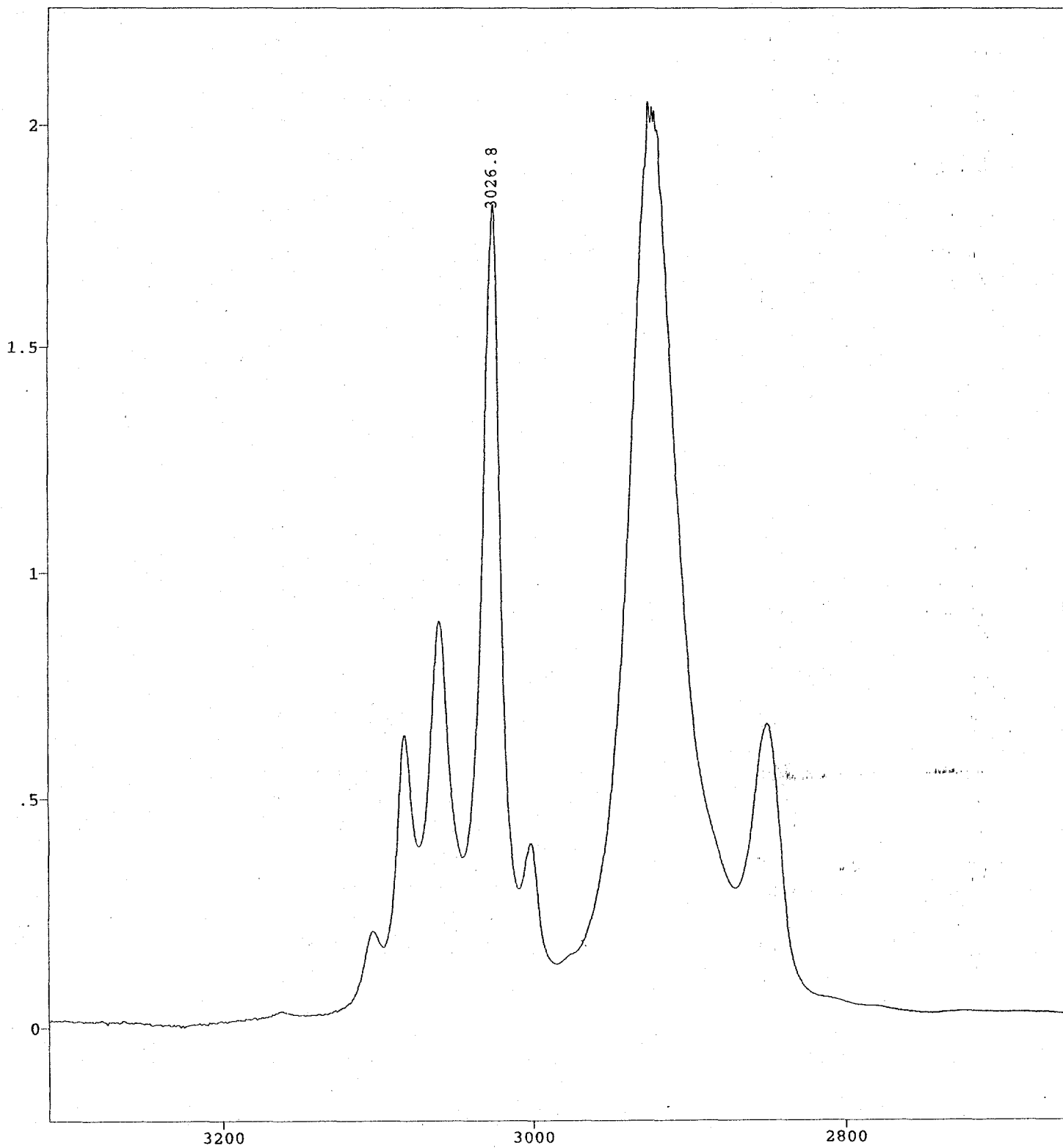
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #27 : P10-23-A

10/23/94 2:51 PM Res=1cm-1

poly film 1 cm-1



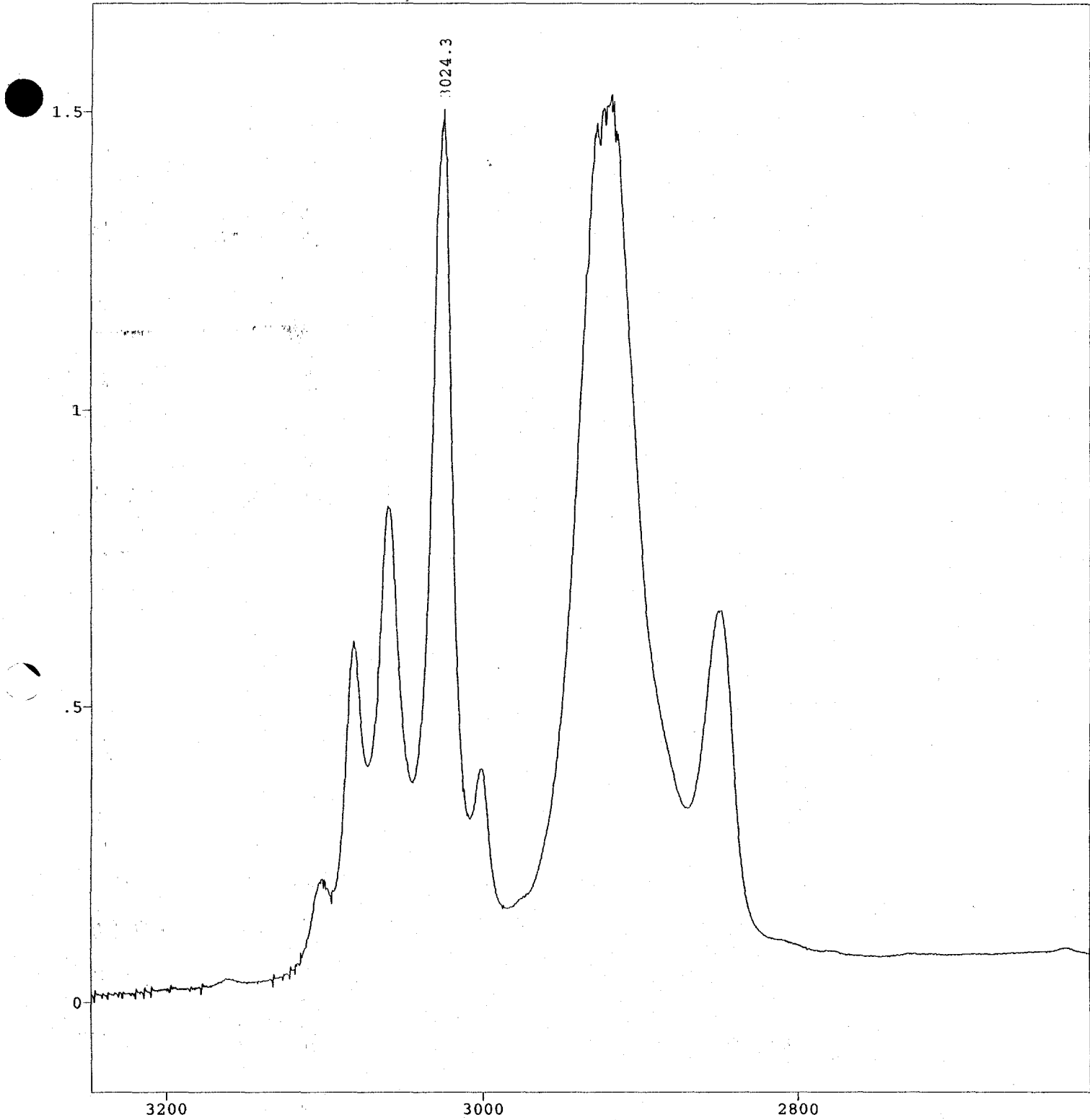
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #15 : P12-9-A

12/9/94 11:52 AM Res=1cm-1

poly film



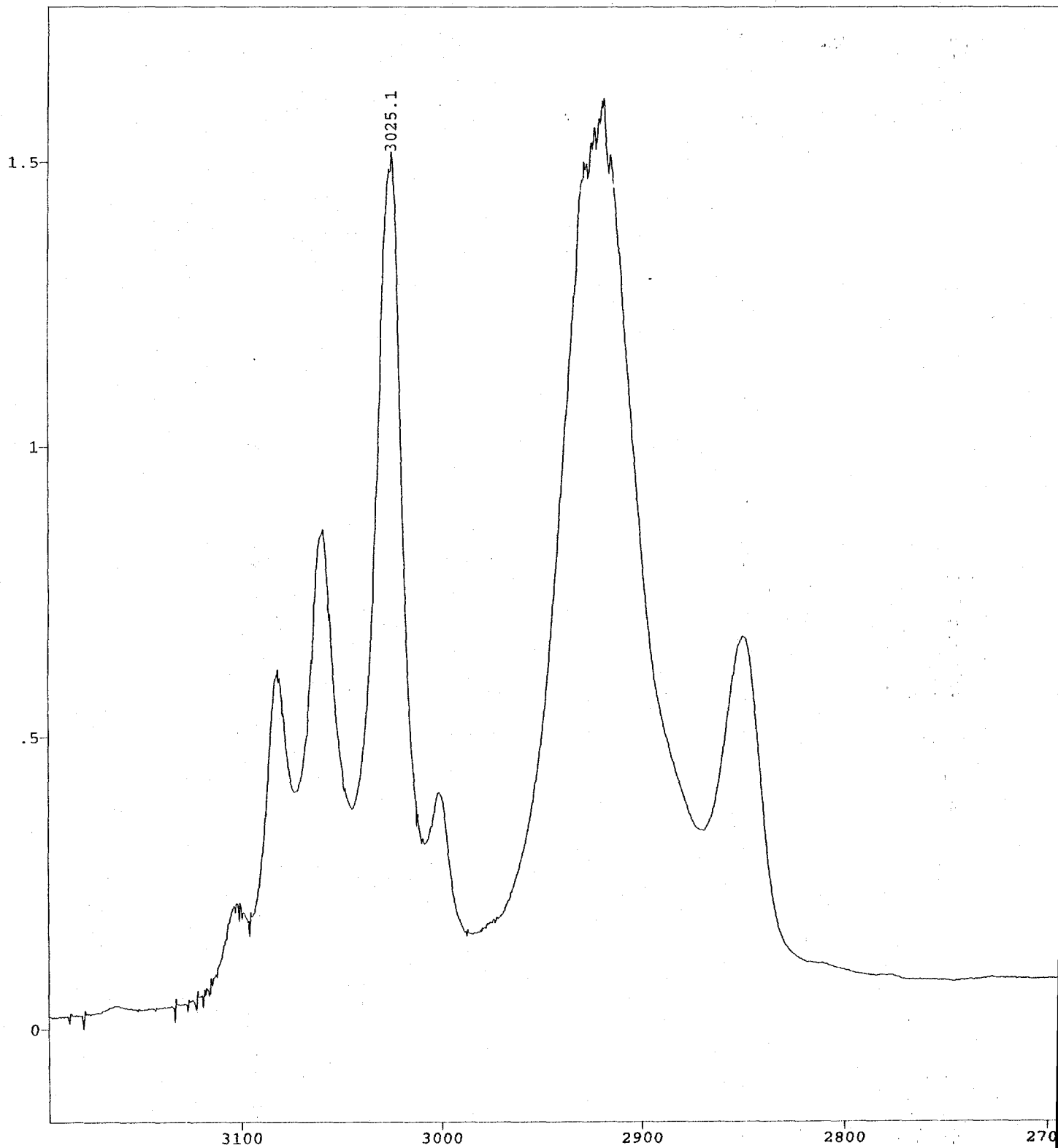
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #28 : P10-24-A

10/24/94 3:00 PM Res=1cm-1

poly film



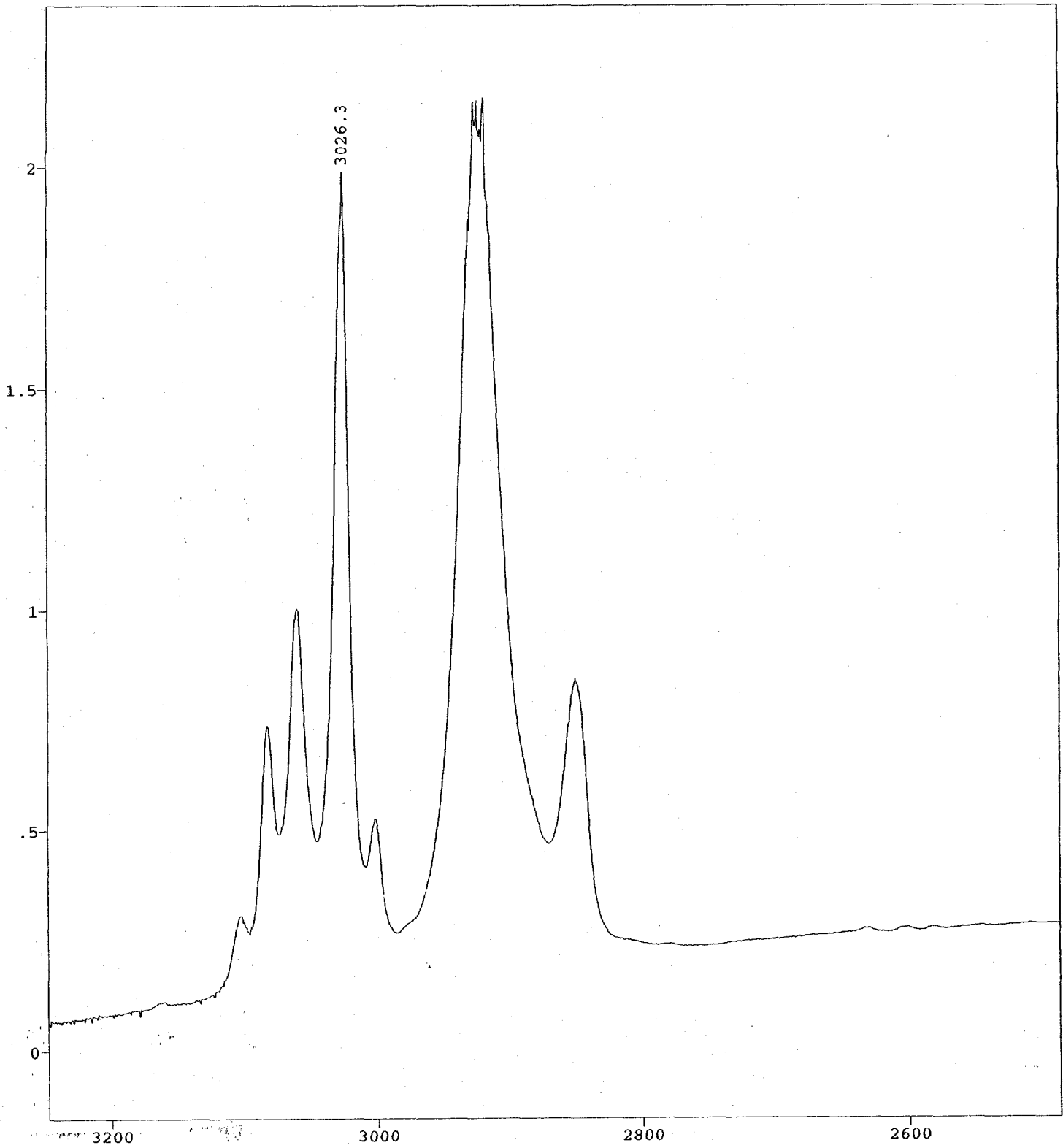
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURS

File # 2 : P10-25-A

10/25/94 12:10 PM Res=1cr

poly film 1 cm-1



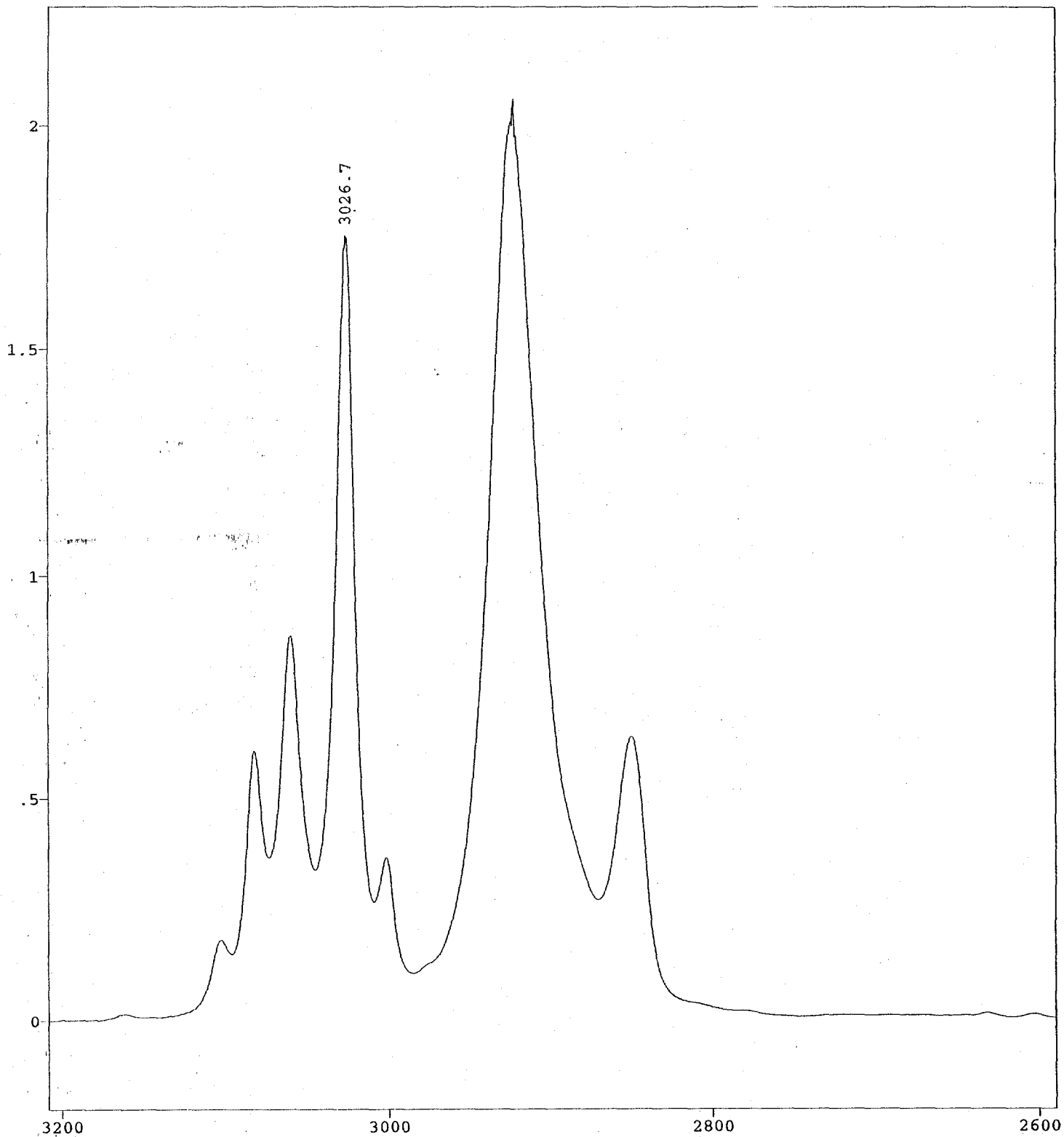
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File # 3: P11-23-A

11/23/94 8:57 AM Res=1cm-1

poly film



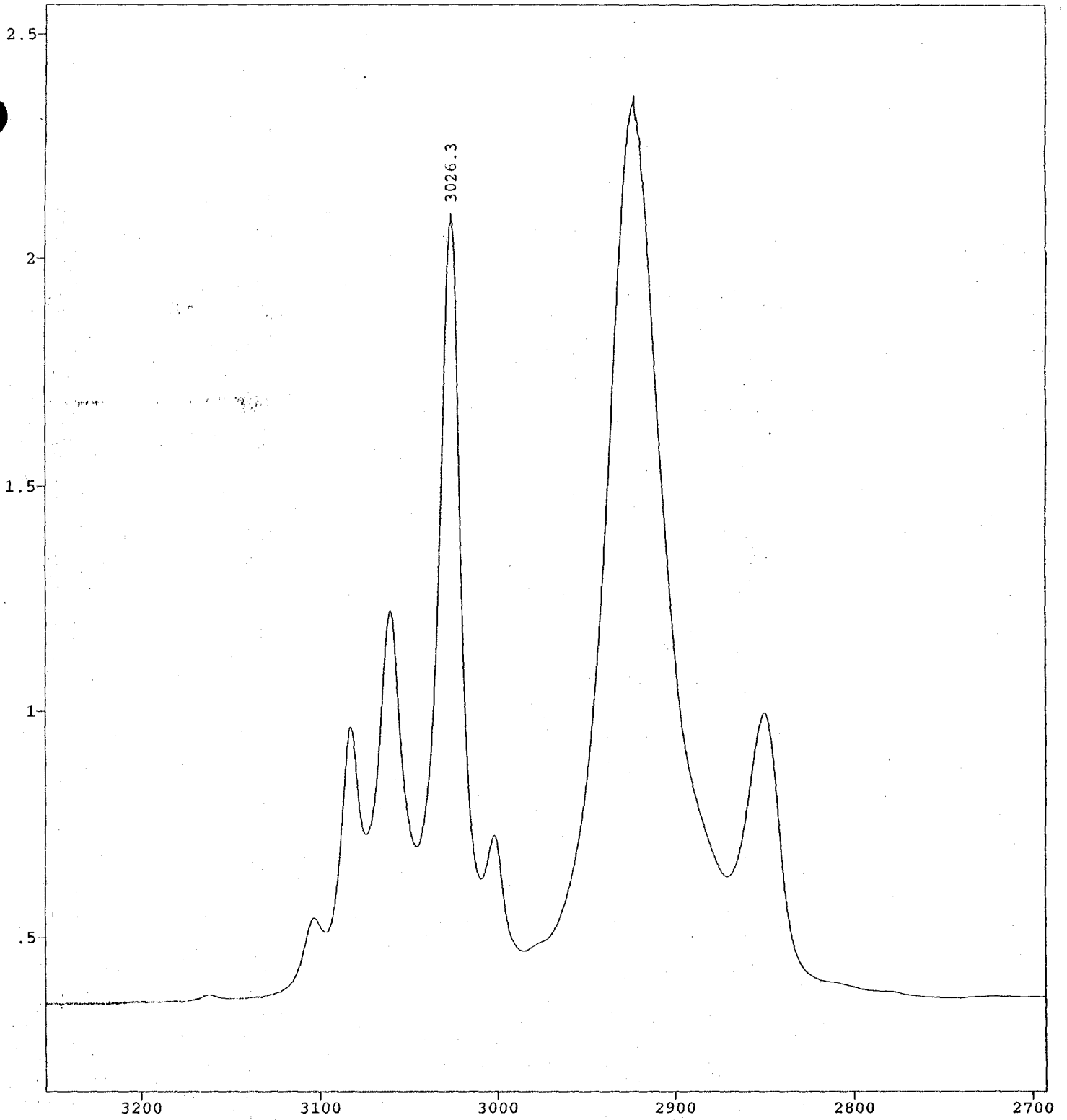
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

# 4 : P12-10-A

12/10/94 1:12 PM Res=1cm-1

poly film



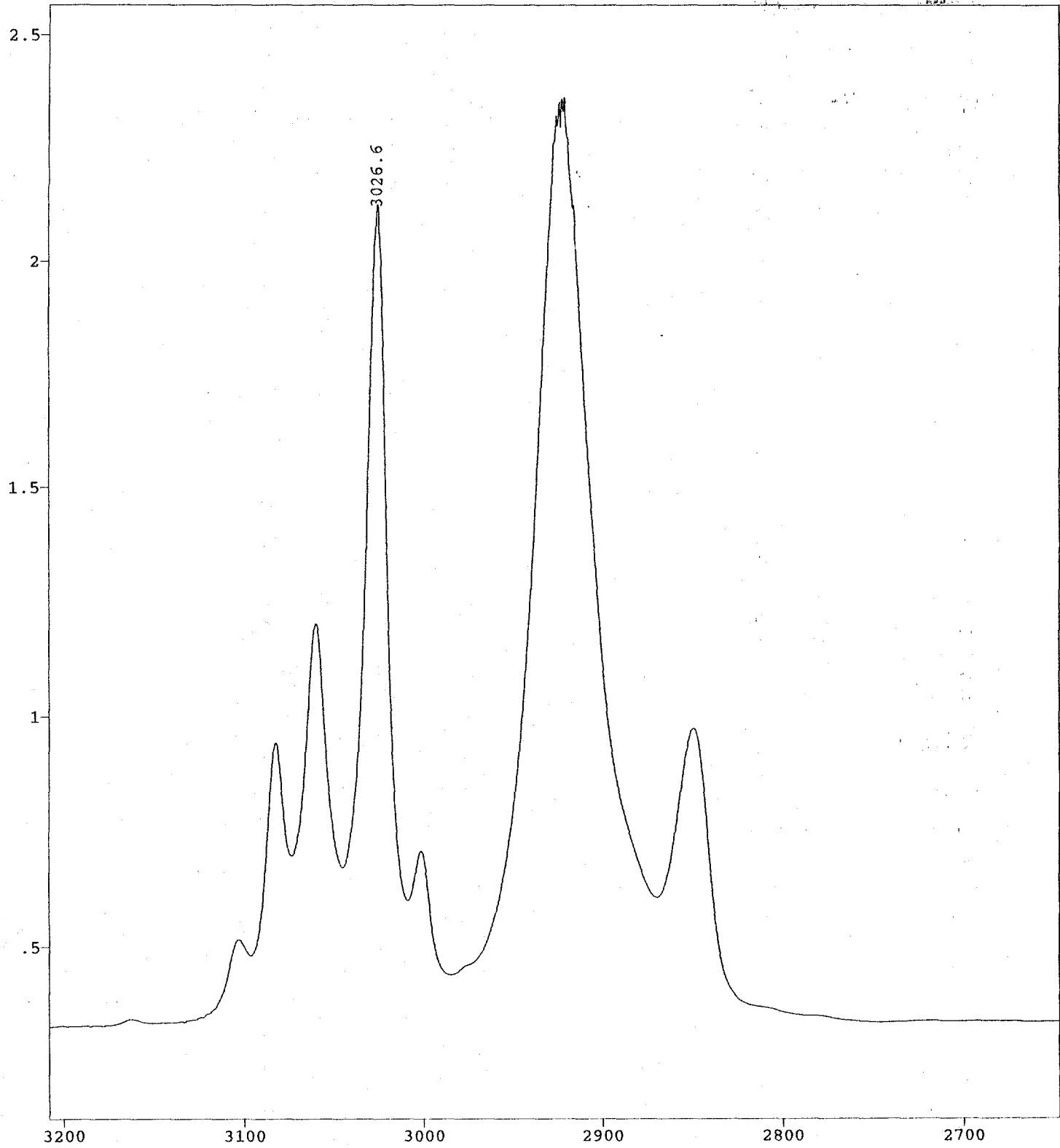
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

# 6 : P12-12-A

12/12/94 12:49 PM Res=1cm-1

poly film



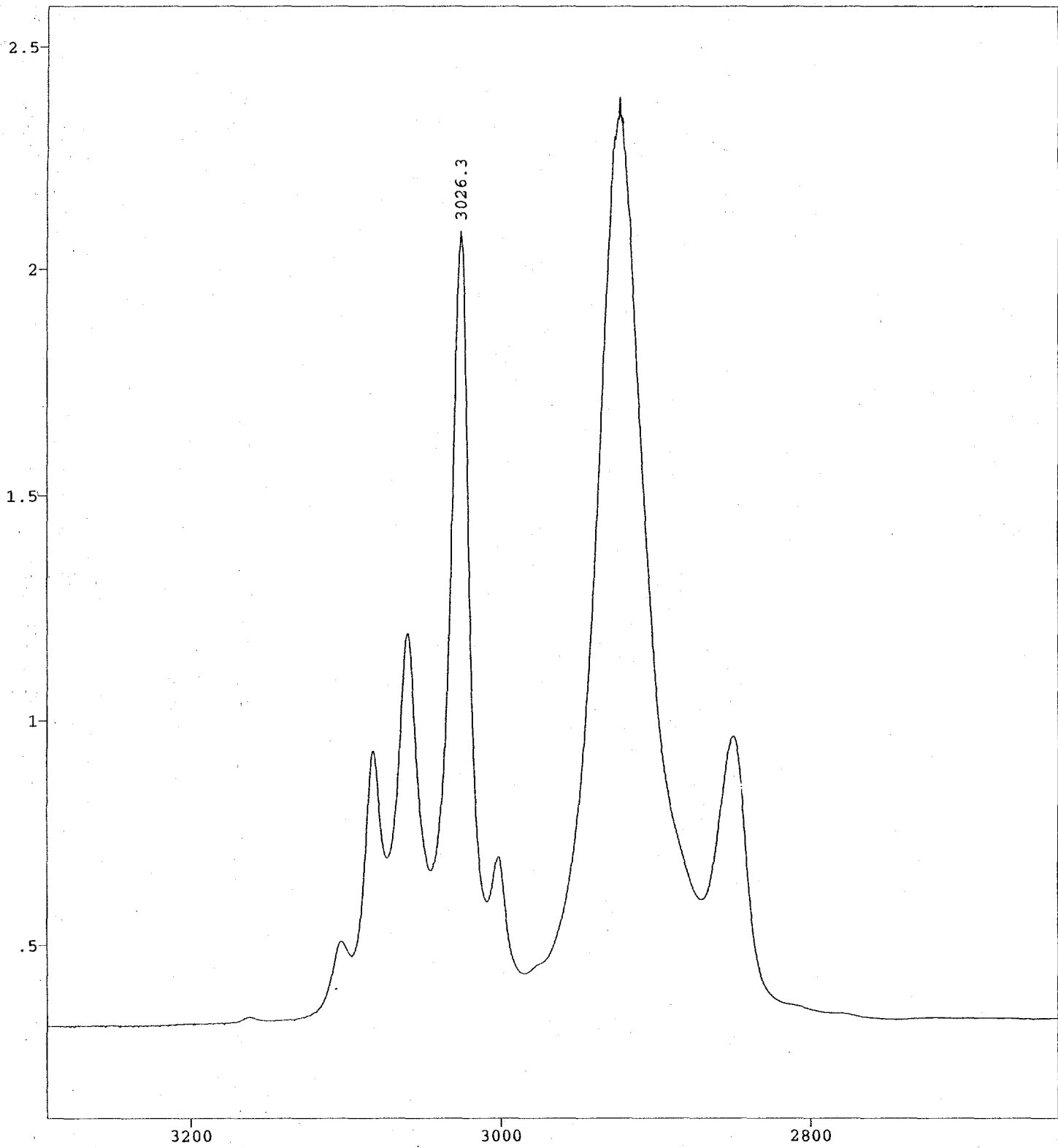
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File # 7: P12-13-A

12/14/94 1:54 PM Res=0.5cm-

poly film



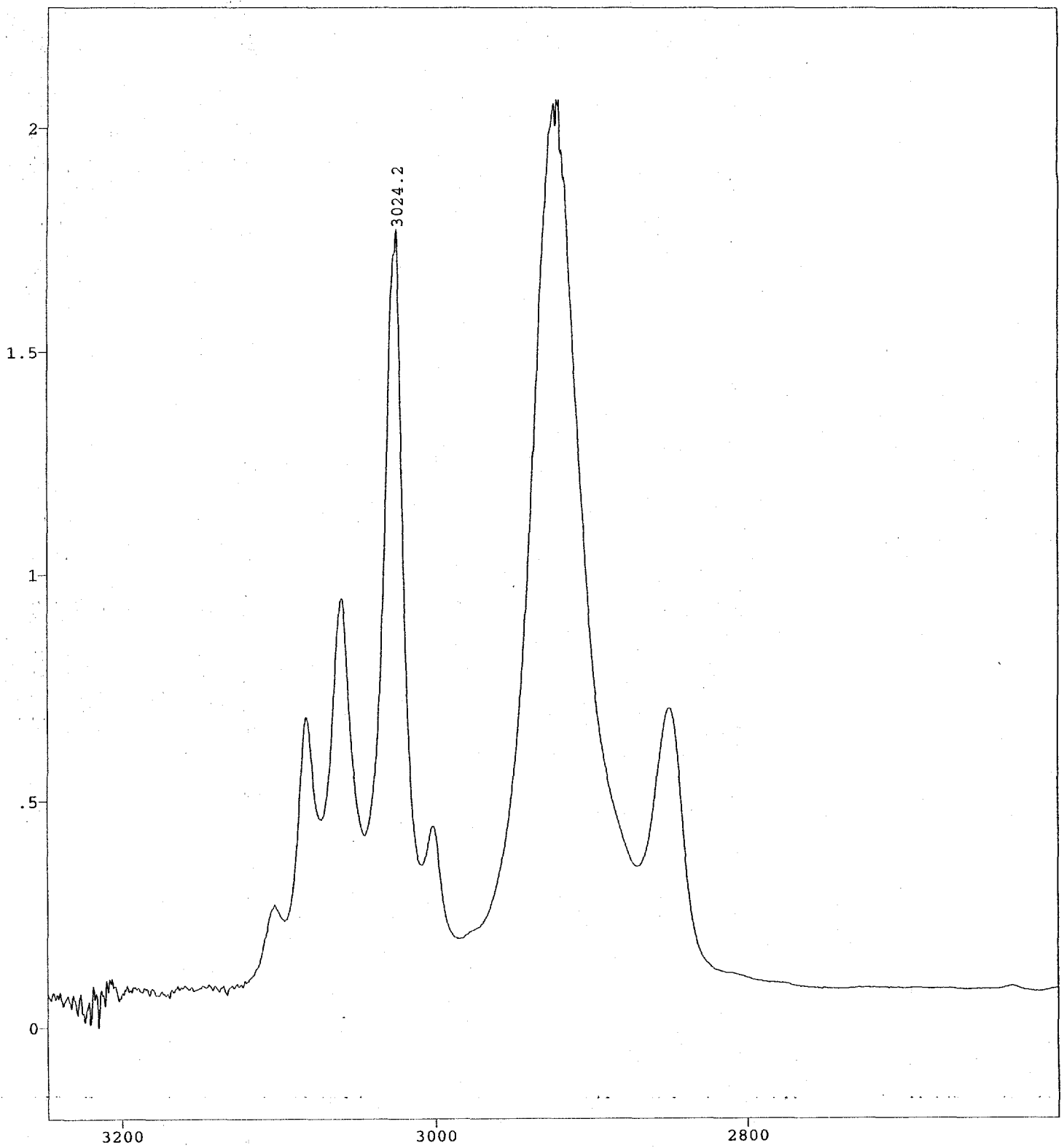
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

# 8: P12-15-A

12/15/94 12:12 PM Res=0.5cm-1

poly film



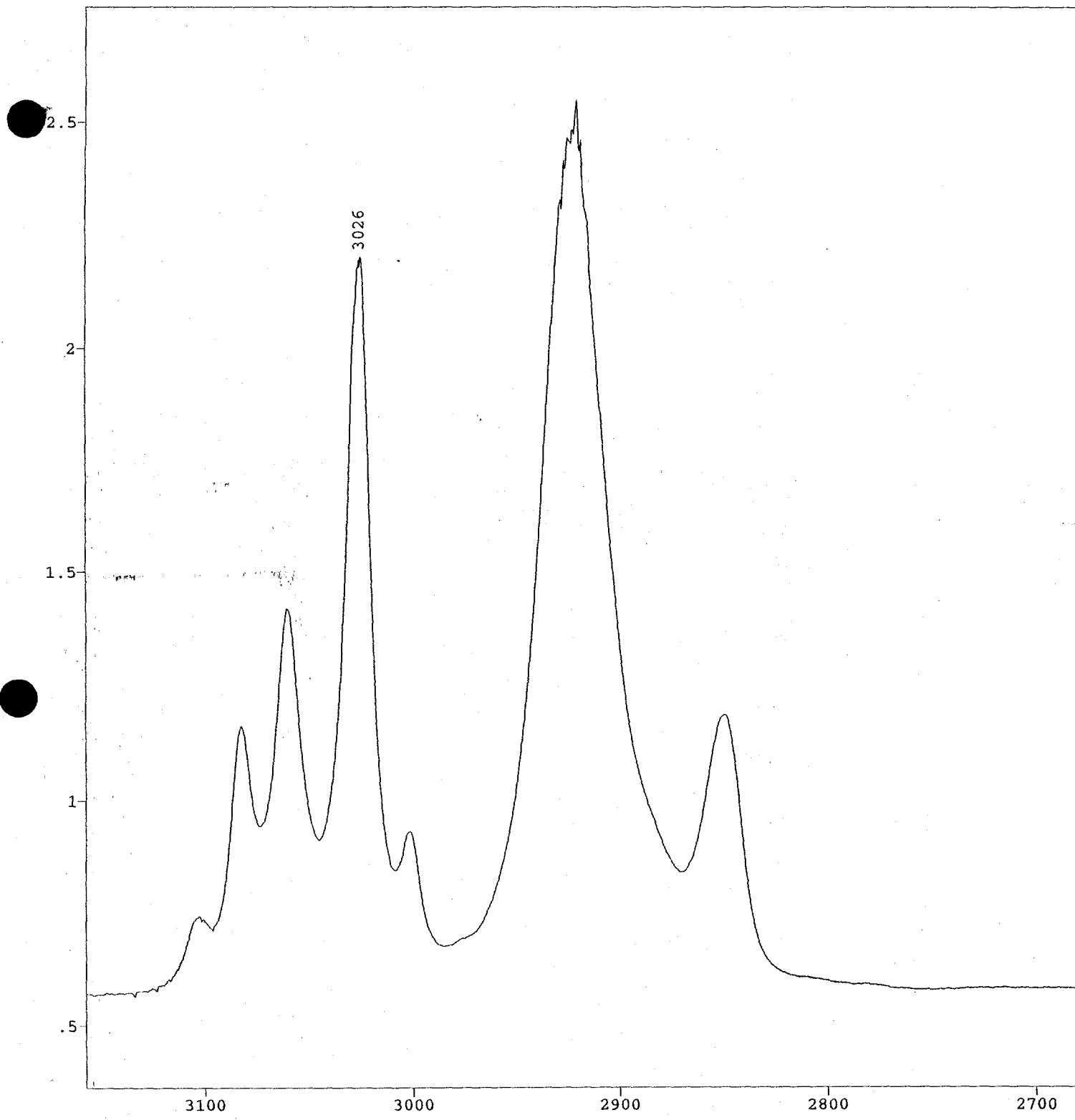
Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

File #12: P12-6-A

12/6/94 11:36 AM Res=1cm-1

poly film



Absorbance / Wavenumber (cm-1)

Paged Y-Zoom CURSOR

P13: P12-7-A

12/7/94 12:57 PM Res=1cm-1

poly film