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FTIR QUANTIFICATION OF INDUSTRIAL HYDRAULIC FLUIDS IN PERCHLOROETHYLENE

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DEDICATION

In loving and living memory of my late
dear mother Joginder Vati,
whom I never knew.

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ABSTRACT

The purpose of this summer research project was to investigate whether perchloroethylene can be used as a solvent for the quantitative analysis of industrial hydraulic fluids by infrared spectroscopy employing Beer's law. Standard calibration curves using carbon-hydrogen stretching (generic) and ester absorption peaks were prepared for a series of standard dilutions at low ppm levels of concentration of seven hydraulic fluids in perchloroethylene. The absorbance spectras were recorded with 1.5-10 mm fixed and variable path length sample cells made of potassium bromide. The results indicate that using ester infrared spectral peak, it is possible to detect about 20 ppm of the hydraulic fluid in perchloroethylene.

SUMMARY

1,1,2 trichloro-1,2,2 trifluoro ethane (CFC-113) commercially known as Freon-113 is the primary test solvent used for validating the cleaned hardware at the Kennedy Space Center (KSC). It is also used as a general laboratory solvent for analytical work in a variety of sample matrices at KSC. Due to the ozone depletion problem, the current United States policy calls for the phase out of Freons by 1995. A 1993 (May) preliminary report by Environmental Protection Agency (EPA) on the efforts to replace Freon-113 for the determination of oils and greases suggests the evaluation of the feasibility of utilizing infrared-based methods, and perchloroethylene (PCE) as an alternate validation and extraction solvent.

NASA's chlorofluorocarbon (CFC) replacement group at KSC has opted to persue the recommendations made in the EPA's report to investigate infrared method and PCE since PCE has high solvation compatibility with organics and generally considered non-toxic (OSHA's LD50). Infrared method of analysis with dispersive infrared spectrometers has been used extensively for qualitative identification, and for quantification at high parts per million (ppm) level or at percent level concentration of the analyte. However, with the advent of the Fourier transform method, state-of-the-art spectrometers have become available for quantification at low ppm level concentration of the analyte. In this project, experimental data was obtained to assess the applicability of the infrared method to the detection of industrial hydraulic fluids in PCE at low ppm levels of concentration.

Standard calibration curves were prepared for a series of standard dilutions of hydraulic fluids in PCE. The infrared absorbance spectras were recorded with an FTIR instrument operated from a computer-based data collection and spectral analysis system, and using fixed and variable path length potassium bromide sample cells.

The results indicate that it is possible to detect about 20 ppm of the hydraulic fluid in PCE using a generic or any other absorbance spectral peak of the analyte. By optimizing certain variables which may affect the interpretability of the results obtained, the method may equally be applicable to the detection of hydraulic fluids below 20 ppm.

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I-INTRODUCTION

1.1 Objective:

A feasibility study to investigate whether perchloroethylene can be used as a solvent for the quantitative analysis of industrial hydraulic fluids by Infrared Spectroscopy (FTIR).

1.2 Background:

1,1,2 trichloro-1,2,2 trifluoro ethane (CFC-113) known as Freon-113 is the primary test solvent used for validating the cleaned aerospace hardware at the Kennedy Space Center (KSC). For a safe space shuttle launch, it is of utmost importance that the hardware be verified clean of organic materials before use in an oxygen rich environment as that of the Orbiter.

Freon-113 is also used as a general laboratory solvent for analytical work in a variety of sample matrices at KSC. Material Science Laboratory's (MSL) standard procedure calls for the extraction of organic materials with Freon-113, and subsequent determination of the non-volatile residue (NVR) by gravimetric method.

Freons including CFC-113 are known to remain in the atmosphere long enough to migrate to altitudes due to their high volatility, and are known to be a threat to the earth's protective ozone layer. The Montreal protocol and the 1990 Clean Air Act calls for the accelerated reduction of the substances directly responsible for ozone depletion of the Antarctic ozone hole. The current United States Government policy calls for ending the production of these compounds, and phase out by 1995.

United States Environmental Protection Agency's (EPA) Clean Water Act (CWA), and Resource Conservation and Recovery Act (RCRA) requires an effluent discharge permit for all the industries connected to the wastewater treatment facilities. One of the parameters required for the permit is the analytical determination of oils and greases in the effluents. EPA's standard methodology calls for the utilization of Freon-113 as the extraction solvent for the determination of oils and greases in the effluents.

A 1993 (May) preliminary report by EPA on the efforts to replace Freon-113 for the determination of oils and greases suggests the evaluation of infrared-based methods, and perchloroethylene (PCE, also known as tetrachloroethylene) as an alternate extraction solvent. This report also acknowledges that a lot of efforts are going on at the national and international level to find a substitute for Freon-113.

Chlorofluorocarbon (CFC) replacement group at KSC in collaboration with NASA's and other independent research centers is also working on to find a substitute for CFC-113 for the validation process of cleaned parts. Among the options, the MSL group decided to pursue the recommendations of the EPA's preliminary report of investigating the infrared method using PCE as a replacement solvent since PCE has high solvation compatibility with organics, generally considered non-toxic (OSHAs LD50), and has a high B.P. (121 oC) compared to 48 oC for Freon-113.

Infrared methods of analysis with dispersive infrared spectrometers have been used extensively as a general analytical technique for identifying materials or "fingerprinting", and for quantification of analytes at high parts per million (ppm) or at percent concentration levels.

Infrared detectors in dispersive spectrometers are not frequency sensitive. With the advent of the Fourier tranform method, more sensitive, accurate, reliable and state-of-the-art Fourier transform infrared spectrometers (FTIR) have become available for the quantification work at low ppm levels since in FTIR, infrared frequencies are converted into audio frequencies, and the available detectors and electronics have the ability to track both frequency and intensity at the same time. This research project will focus basically to investigate the feasibility of extending the FTIR method for detecting low ppm concentration levels of industrial hydraulic fluids in PCE.

II-MATERIALS AND METHODS

2.1 Istrumentation:

2.1.1 FTIR Spectrometer:

The spectrometer used for this study was a Galaxy series 300 FTIR spectrometer manufactured by Mattson Instruments. The instrument employs a deuterium triglycine sulfate (DTGS) detector, a Michelson interferometer, and a standard high-intensity infrared source to cover the mid infrared range from 500 - 5,000 wavenumber (cm-1). The Michelson interferometer, which consists of a cesium iodide beam splitter, a fixed mirror and a moving mirror, preserves both the intensity and frequency information at the same time. An internal He-Ne monochromatic laser monitors the position of the moving mirror within the scan. The spectrometer was operated from a computer-based data-collection and spectral analysis analytical package called FIRST (Fourier Infrared Software Tools). The FIRST analytical package automatically collects the indicated number of interferogram scans, coadds the scans, performs the fast Fourier transform, processes the data, and plots the resulting sample spectrum. The block diagram of the system is presented in Figure 2-1.

The results presented in this report are obtained using the setting of 120 interferogram scans* at 4cm-1 resolution with detector gain setting of 4. A background spectrum of the solvent (PCE) was always obtained before the start of collecting the sample spectras since with an appropriate background spectrum in memory, the spectrometer coupled with FIRST automatically calculates the absorbance spectrum as a ratio of the sample spectrum to the background spectrum.

2.1.2 Sample Cells

The most common method of sample preparation for infrared examination of liquid samples involves placing an undiluted sample (0.01-0.1 mm thickness) between a pair of transparent crystal windows. The recorded spectrum will be

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*In FTIR, the scan is the mechanical displacement of the moving mirror assembly and their total reflects the sensitivity of the instrument (S/N ratio).

the most characteristic of the whole composition of the sample since no solvent or matrix interferences, and inter- and intra-molecular interactions will be present to contribute to the difficulties of band shifts and their identifications. However, in dilute solutions (less than 100 ppm range) one experiences all sorts of difficulties since spectras are recorded on thicker samples for obtaining useful analytical information. The greater the number of solvent molecules along the radiation path, the greater will be the interferences and absorption by solvent molecules. Therefore it is of utmost importance to optimize the sample thickness for obtaining useful spectral information.

Sealed- and variable path length liquid infrared cells (1.5-10 mm) having potassium bromide (KBr) and thallium bromide iodine (KRS-5) transparent windows were used for recording the absorbance spectras of the standard solutions of industrial hydraulic fluids in PCE at low ppm range of the analyte.

2.2 Industrial Hydraulic Fluids:

About 20 types of industrial hydraulic fluids and greases are commonly used at KSC. Eight of the industrial hydraulic fluids listed below were obtained from various sources at KSC, and were utilized for the preparation of the calibration curves. Most of them are ester-based hydrocarbon type fluids. During the course of this study, it was observed that one of the silicon-based fluid was not compatible with PCE. For this reason, this study is focussed on the preparation of standard curves for quantification for the seven hydraulic fluids.

Sample I.D.	**Name**
b	Red-Mil-H-5606
c	Rapid Tap Cutting Fluid
d	Dow Corning FS 1265 Fluid (this sample was found not to be compatible (Solubility) with PCE.
e	Mobile Jet II
f	Yellow Mil-H-83282
g	Green # 1530 (Houghto) Fluid
h	Brown (ASTM #3) 3 1537 Fluid
i	PL-S Lube Oil (General Purpose) # 1542

2.3 Perohloroethylene (solvent):

Perchloroethylene used for the preparation of all dilutions in this study was a Fisher brand reagent grade solvent having 0.5 percent of ethyl alcohol as a stabilizer. In the early part of the study, about 3/4 gallon of a bottle of the solvent was provided by a contractor group at KSC. Once the borrowed stock was consumed in the preparation of the dilutions, a newly purchased stock was used until the end of the study.

2.4 Test procedure:

2.4.1 Preparation of Standards:

Several series of standard dilutions of hydraulic fluids in PCE were prepared for recording the absorbance spectras. Dilutions lower than 100 ppm were prepared from a stock solution of each fluid in PCE. Since the objective of the project was to investigate the detection of the analyte in PCE, extreme care was taken not to cross-contaminate the standard dilutions. Auto pipettes of different sizes and brands available in the laboratory were used for dispensing small volumes of the solutions into the volumetric flasks for the preparation of standard dilutions. Tips for the pipettes were only used once for the transfer of solutions, and were disposed off properly. Dilutions of less than 100 ppm were prepared before the start of recording the absorbance spectrum, and were never stored for over 24 hours.

2.4.2 Cleaning Process:

The detection of an analyte at low ppm level of concentration requires that the whole solution handling process be standardized to avoid cross-contamination. It is not cost effective to use glassware and syringes in quantities for the preparation and transfer of large number of solutions. A simple and practical procedure was used for cleaning and filling of the sample cell with the prepared standard solutions.

2.4.2.1 Volumetric Flasks Cleaning:

25 ml volumetric flasks were used for the preparation of most of the standard dilutions. After each use, the flasks were washed with warm 0.5 percent Liquinox solution according

to the normal procedure used in the laboratory. After rinsing with deionized water, the flasks were dried in an oven maintained at 103 degrees Celcius. All the volumetric flasks were rinsed twice with PCE before the preparation of the standard dilutions.

2.4.2.2 Syringe Cleaning:

PCE for cleaning was transferred from a gallon bottle into two cleaned 50 ml beakers. The syringe used for filling the sample cell was cleaned twice with a 2 ml portion of the pure solvent from the first beaker. Both the times, the syringe was inverted and plunger moved to the outer-most end of the barrel for rinsing of the whole barrel with the solvent. It is not necessary to remove the barrel from the plunger. The plunger was moved up and down 3-5 times with paper tissue wipes at the tip of the syringe to soak the maximum amount of solvent on to the tissue wipes.

2.4.2.3 Cell Cleaning:

A cleaned syringe was filled with 1-2 ml of the solvent from the other beaker, and the solvent transferred gently into the sample cell. Depending on the size of the cell, the amount of the solvent to be transferred may vary. The teflon plugs were replaced and the cell was given a gentle swirling motion horizontally. The plugs were removed and the solvent was allowed to drain from the lower orifice (right orifice for circular adjustable cell) into a waste-beaker assigned for proper disposal. Paper tissue wipes were placed on top of the lower orifice of the cell to soak the maximum amount of the solvent onto the wipes without giving a drastic motion to the cell. The procedure was repeated with another portion of the solvent. It is probable that a trace amount of solvent may remain in the cell. It is assumed that this trace quantity of the solvent remained in the cell will be constant for all the standards in a series, and will have insignificant effect on the slope of the standard calibration curve.

2.4.3 Sample Cell Filling:

An appropriate amount of the standard solution was transferred into an aluminum dish from the 25 ml volumetric flask. 2-3 ml of this solution was drawn into a cleaned 5 ml Lauer syringe. This volume may vary depending on the thickness of the sample cell. Using a very light hand pressure, the solution was injected into the lower orifice of the metal plate of the cell. It is important that the cell should never be filled from the upper orifice at the top of the front plate of the cell. After the cell was filled, teflon plugs were replaced with a twisting motion to ensure a good seal. All the times paper tissue wipes were used to avoid the contact of the transferring solution with the cell windows. The filled cell was physically observed for any entraped bubbles of air before placing it in the cell holder of the instrument for recording the absorbance spectras.

III-RESULTS AND DISCUSSIONS

3.1 Infrared Absorbance Spectrum:

When radiation at a particular frequency strikes a molecule which has a vibrational frequency identical to the incident radiation, the molecule will absorb the radiant energy, and thus increasing the total energy of the molecule. If a pair or group of atoms is to absorb infrared radiation, it must undergo a change in dipole moment during the vibration. The changing dipole couples the vibration of the molecule with that of the incident radiation, and causes infrared absorption.

Identification of a certain principal spectral peak(s) of an analyte is necessary to be identified before calibration curves can be plotted for quantification. Special efforts were focussed to identify a particular generic peak in all the fluids which can be used for the preparation of a single calibration curve for detecting the total concentration of hydraulic fluids in a mixture. One percent dilutions of the hydraulic fluids were prepared in PCE, and their absorbance spectras were recorded for the identification of the most intense absorption peak(s). For quantitative work, the absorbance spectras were recorded at a sensitivity of 120 interferogram scans at 4 cm-**1** resolution. Triplicate spectras were recorded for each of the standard dilution, and the average of the three absorbance values obtained for a particular spectral peak was used for the preparation of the standard curves.

Ester-based hydrocarbon type fluids used in this project have spectral bands around 2700 to 3000 cm-**1**, and near 1700 and 1100 cm-**1**. Because hydrogen is a light element, spectral bands due to stretching of C-H bonds occur at a fairly high frequency. The large broad band from 2700-3000 cm-**1** (generic peak) is due to the stretching vibrations of the carbon-hydrogen bonds in the hydrocarbon chain backbone structure, and is very typical of organic compounds. Since it requires less energy to bend a bond than to stretch it, bands due to bond bending occur at low frequency. The peak near 1700 cm-**1** is typical of an ester group, and also C=C stretch peaks appear in this area. A typical absorbance spectra of a hydraulic fluid is presented in Figure 3-1.

3.2 Calibration Curves:

The absorbance data is useful for quantitative analysis of analytes in dilute solutions where Beer's law is applicable, and is that a linear relationship exists between the measured net absorbance and the concentration of an analyte in a solution. The net absorbance of the spectral peaks obtained for seven hydraulic fluids at various levels of concentration and sample thicknesses are presented in Figures 3-2 to 3-22 in the form of calibration curves. The net absorbance data was obtained using the analytical software package called FIRST. Regression analysis was done on each set of standards using analyte concentration as an independent variable and absorbance units as a dependent variable. The validation of the model is presented in the form of R Squared. It ranges up to one with one being optimal.

3.2.1 Mobile Jet II:

Figure 3-2 is a calibration curve for Mobile Jet II Fluid in PCE using 1743 cm-1 ester peak of the spectras recorded with a 1.5 mm KBr variable cell. The graph demonstrates a linear relationship between absorbance and concentration of the analyte in the range of 50-500 ppm with R2 of 0.99. The absorbance data of this series of standards (10-300 ppm only) along with the data obtained on standards prepared on a different date is presented in Figure 3-3. R2 of the two sets of data was found to be optimal (0.98). Although variation in the absorbance units of the two series of standards were observed, the two curves were found to have similar slopes.

Figure 3-4 demonstrates the erratic scattering in the absorbance data obtained on the generic C-H stretching peak as compared to the ester peak of the recorded spectras with a 1.5 mm KBr cell. During the course of the work, it was observed that too much background noise was resulting in the area of the generic peaks of the spectras, and it was impossible for the detector to distinguish between small variations in the absorbance units in solutions with analyte concentration at low ppm levels. The presence of several peaks/bands around 3000 wavenumber in the absorbance spectrum obtained on a pure solvent reflected the presence of some contaminant in the solvent. As a check, a similar observation was made on a newly opened solvent bottle at a later stage. This observation suggests that the presence of the unwanted organic compound(s) may be a part of this particular batch of solvent after all, and causing the background noise in the generic peak(s) area of the infrared spectra.

The absorbance data for the ester peak in Figure 3-4 reflect that it is possible to detect about 20 ppm of Mobile Jet II fluid in PCE R2 equal to 0.98. It was reasoned that the detection of the analyte may be improved by increasing the absorbance units with a larger sample size. The only cell of higher path length available in the laboratory was a KRS-5 cell having a variable path length of 2.5 mm. A calibration curve (Figure 3-5) in the range of 1-10 ppm of the analyte for the generic peak was prepared using the spectras recorded with the KRS-5 cell. The graph demonstrates highly scattered data obtained using the longer path length KRS-5 cell. 5 mm and 10 mm KBr fixed cells were purchased from Perkin Elmer Corporation, and absorbance data was obtained on the ester peak (1743 cm-1) using a 5 mm fixed path length sample cell. Figure 3-6 is a calibration curve of the net absorbance data obtained on an ester peak of the spectras recorded with 1.5 and 5 mm KBr cells. The slopes of the two lines were found to be reasonably similar with R2 values of about 0.98. Efforts were also made to use the absorbance data of the generic peak (2930 cm-1) for the preparation of the calibration curve. This resulted in failure due to the presence of several unresolved peaks in the generic peak area. The calibration curves (Figures 3-4 and 3-6) demonstrate that ester peak is stable and can be used for the quantification of Mobile Jet II in PCE. These graphs also demonstrate that about 20 ppm of the analyte in PCE can be detected under the experimental conditions.

3.2.2 Rapid Tap Cutting Fluid:

Figure 3-7 is a calibration curve for the Rapid Tap Cutting fluid in PCE using an infrared spectral peak of around 1086 cm-1. This particular spectral peak was found to be more intense compared to the ester peak (1720 cm-1) at high ppm levels of concentration of the analyte. Figure 3-7 demonstrates a linear relationship between the net absorbance units and the analyte concentration (R2 = 0.99) in the range of 50-500 ppm with the spectras recorded using a 1.5 mm KBr cell.

The ester and the generic peak was investigated for the preparation of the calibration curves below 100 ppm of the analyte in PCE since the area around 1,100 wavenumber was found to be full of scattered noise at low concentration levels. A series of standard dilutions of the analyte in PCE was made in the range of 20-100 ppm to investigate the possibility of detecting the analyte concentration below 50 ppm. The absorbance spectras were recorded with a 1.5 mm KBr cell. The net absorbance was calculated for the generic as well as for the ester peak, and was plotted as a function of the analyte concentration. Figure 3-8 demonstrates that we can detect about 20 ppm of the Rapid Tap Cutting fluid in PCE using the ester peak. R2 value of the absorbance data for the ester peak was found to be about 0.54. The lower R2 value may be attributed to a bad standard of 80 ppm of the analyte in PCE. The generic peak (2930 cm-1) in the concentration range of 20-100 ppm with a 1.5 mm KBr cell (Figure 9) as well as in the concentration range of 1-10 ppm with a 2.5 mm KRS-5 cell (Figure 3-9) gave scattered absorbance data similar to the Mobile Jet II sample. This reflects that the generic peak is not recommendable to be used with this solvent for quantification work due to the presence of other organics in the solvent which produces background noise bands in the generic peak area.

A series of standards (20-100 ppm) used for the preparation of the calibration curve with a 1.5 mm KBr cell was also used for the 5 mm KBr cell study. Figure 3-10 is a calibration curve of the net absorbance data of the ester peak of the spectras recorded with 1.5 mm and 5 mm KBr cells. The absorbance data of the two graphs follows a similar pattern. This reflects that 80 ppm standard is indeed a bad standard causing R2 value to go down drastically. The data also suggest that the optimum sample path length is somewhere between 1.5-5 mm.

3.2.3 Red Mil-H-5606 Fluid:

A series of standard solutions of Red Mil-H-5606 in the range of 10-1,000 ppm in PCE was prepared to verify Beer's law. Figure 3-11 is a calibration curve of the analyte using the generic peak (2928 cm-1) of the spectras recorded with a 1.5 mm KBr cell. The graph is found to be linear in the range tested except for some scattering of the data observed below 50 ppm level of the analyte. R2 was found to be equal to 0.99, and the graph suggests that it is possible to detect below 50 ppm of the analyte in PCE.

A new series of standards in the range of 20-100 ppm of the analyte was prepared in PCE for improving the detection of the analyte in PCE. The infrared absorbance spectras were recorded using 1.5 mm KBr cell. The absorbance data obtained on the generic peak (2928 cm-1) for this series is plotted in Figure 3-12 together with the generic peak absorbance data of Figure 3-11 between 20-100 ppm range (4 points) of the analyte. Scattering of the data for both the series was observed and R2 was found to be 0.72 and 0.90 respectively. The graph suggests that it is possible to detect as low as 20 ppm of the analyte without difficulty.

Figures 3-13 is a calibration graph for the generic (2928 cm-1) and the ester (1738 cm-1) peak of the spectras recorded with a 1.5 mm KBr cell. R2 for the ester peak was found to be 0.35 as compared to 0.72 for the generic peak. It reflects that there might be some other variables affecting the ester peak of Red Mil-H-5606 fluid in PCE at low ppm levels of concentration. In the range of 1-10 ppm concentration levels, scattering of the absorbance data was found to be similar to the Mobile Jet II and Rapid Tap Cutting fluid with the KRS-5 cell (Figure 3-14). Figure 3-15 is a calibration curve of the net absorbance data of the spectras recorded with a 5 mm KBr cell on two consecutive days on a series of standards with concentration of the analyte in the range of 20-100 ppm. The graph reflects that the absorbance data obtained on the ester peak with a larger sample size did not improve the detection limit of the Red Mil-H-5606 fluid in PCE. The absorbance data also reflect the instrumental drift on a low absorbance level (0.02 range) on a day to day basis.

3.2.4 Green # 1530 (Houghto) Fluid:

Figure 3-16 is a calibration graph for the Green #1530 Fluid in PCE in the concentration range of 20-1,000 ppm using a 1.5 mm KBr cell. The absorbance data of a more intense absorbance peak at 1157 wavenumber was used for the preparation of the calibration curve. The graph demonstrates a linear relationship for Beer's law with R2 equal to 0.97. It also demonstrates that it is possible to detect about 20 ppm of the analyte in PCE.

10 mm KBr sealed cell was also used for recording the absorbance spectras for improving the detection of the analyte in PCE. It was tried to use the intense peak at 1157 wavenumber for measuring the absorbance units of the recorded spectras. However, the efforts were met with little success due to high background noise in the region of 1157 wavenumber peak. Figure 3-17 is a calibration curve of the net absorbance data obtained for the ester peak (1738 cm-1) with 1.5 mm and 10 mm KBr cells. The absorbance data obtained for

the 10 mm KBr cell reflect that it is possible to detect about 20 ppm of the analyte in PCE, however scattering of the data was observed with the 10 mm KBr cell. With a 1.5 mm KBr cell, it was not possible to obtain a defined slope of the calibration graph using the ester absorbance spectral peak.

3.2.5. Brown (ASTM #3) # 1537:

Figure 3-18 is a calibration graph for the Brown # 1537 fluid using the generic peak (2854 cm-1) net absorbance data of the recorded spectras obtained with a 1.5 mm KBr cell, and also the absorbance data of the ester peak (1739 cm-1) of the spectras recorded with a 10 mm KBr cell. As expected, the absorbance units increased with the sample size. It is interesting to observe that the slope is identical for the graphs using two different absorption peaks. R2 for the absorbance data for all points obtained on the generic peak was found to be 0.97. The graph also reflects that about 20 ppm of the analyte can be detected in PCE.

3.2.6 Yellow Mil-H-83282:

The absorbance data obtained on the spectras recorded for a series of dilutions of Yellow Mil-H-83282 fluid in PCE with 1.5 mm and 10 mm KBr cells is presented in Figure 3-19. The slopes of the two graphs using the net absorbance data of the ester peak (1737 cm-1) are similar with R2 values equal to 0.94 to 0.99 for 1.5 mm and 10 mm KBr cells respectively. The calibration curve demonstrates that it is possible to detect about 20 ppm of the analyte in PCE.

3.2.7 PL-S Lube Oil # 1542:

The absorbance data obtained on the standard dilutions for PL-S Lube Oil # 1542 in PCE using different sample sizes for recording the spectras are presented in Figures 3-20 and 3-21 in the form of the standard curves. The scattering of the absorbance data is observed for the generic and also for the ester peak using a 10 mm KBr cell. The slopes of the graphs using the generic and ester peaks with a 1.5 mm cell is found to be similar (Figures 3-20 and 3-21). The absorbance data obtained on the ester peak (Figure 3-21) reflect that it is possible to detect about 20 ppm of the analyte in PCE.

3.2.8 Mixture of Hydraulic Fluids:

All the calibration curves prepared above for the detection of the hydraulic fluids were of the solutions of the pure fluids in PCE. Most of the absorbance data obtained on individual fluids has demonstrated that it is appropriate to use the ester peak (1739 cm-1) for the quantitative analysis of hydraulic fluids.

A series of dilutions of a mixture of five hydraulic fluids, Red Mil-H-5606, Rapid Tap Cutting fluid, Mobile Jet II, Yellow Mil-H-83282 and Brown ASTM # 3, was prepared in PCE to study the behavior of the ester absorbance peak in a mixture. The absorbance spectras were recorded with 1.5 mm and 5 mm KBr cells. The net absorbance data obtained with a 1.5 mm cell for the generic and for the ester peak were found to have an erratic behavior. Efforts were made to use the generic peak (2854 cm-1) for the preparation of the calibration curve with a 5 mm KBr cell but the data demonstrated a highly erratic and similar behavior of 1.5 mm KBr cell due to high background interferences by the solvent in the region of generic peak(s) in the infrared absorbance spectrum.

The net absorbance data obtained on the ester spectral peak with a 5 mm KBr cell is presented in Figure 3-22. The figure demonstrates that it is possible to detect 20 ppm or less of the total hydraulic fluid using the ester peak and a 5 mm KBr cell. However, R2 value of the absorbance data was found to be equal to 0.73.

IV-CONCLUSIONS

1. The results obtained on the quantification of hydraulic fluids in perchloroethylene has demonstrated that it is possible to detect high ppm levels of the analyte easily with the infrared method using a generic or any other absorbance spectral peak of the analyte. R squared is found to be higher than 0.97 for the range (50-500 ppm) used for the preparation of the calibration curves.

2. The calibration curves prepared for quantification of the hydraulic fluids at low ppm levels of concentration (20-100 ppm) in PCE have demonstrated that it is possible to detect about 20 ppm of the analyte in PCE under the experimental conditions of the test runs.

3. The data has demonstrated that the generic spectral peak for most of the samples can not be used under the present experimental conditions for the detection of low ppm of the analyte due to background noise generated in the generic peak area by the solvent tested.

4. The optimal sample path length is found to be between 1.5-5 mm.

5. The results have also demonstrated that it is possible to extend the applicability of the infrared method to low ppm (2-20 ppm) levels of detection of the hydraulic fluids in PCE. However, one must control certain variables (sample size, contamination and background noise) which may affect the interpretability of the results obtained.

V-RECOMMENDATIONS

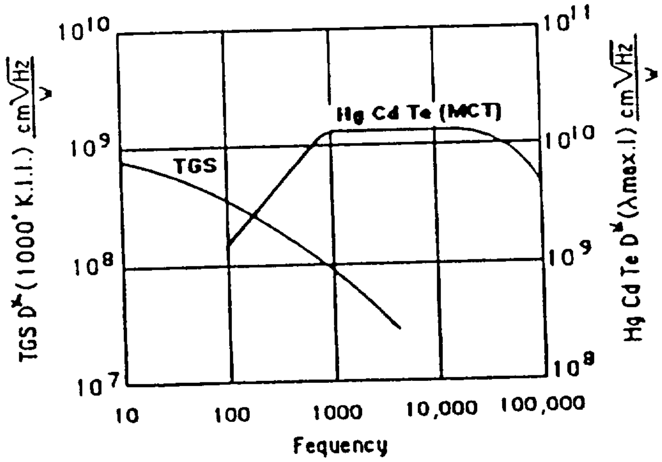
1. Infrared method, generally is not a quantitative method of analysis for the determination of analytes at low ppm levels of concentration. In order to extend its capability to low ppm level work, one must optimize certain variables which may directly affect the interpretability of the results.

   - One of them is the sample size. It is found that the optimum length of the sample lies somewhere between 1.5 mm and 5 mm. It is suggested to carry out the experimental work to collect the data with a new variable path length KBr or BaF2 (preferred since it does not fog) cell.

   - Another possible source of error in the detection of the analyte by the infrared method (or any other instrumental method) at low ppm levels may result from the use of contaminated supporting materials like auto pipettes. One of the auto-pipette (5ml range) used in the project had multi-users. Under the normal laboratory procedures, it is not possible to avoid contamination of the pipettes. It is suggested that pipettes and other supporting materials prone to contamination due to daily routine laboratory work should not be used for research projects.

   - The infrared detector used in this research project was a deuterated triglycine sulfate with cesium iodide windows. It may be worth a try to use a more sensitive liquid nitrogen cooled mercury-cadmium-telluride detector which has a constant S/N ratio between 1,000-10,000 wavenumber for the quantification work at low ppm level.

D*
- is a function of audio frequency being detected, and also a measure of S/N ratio associated with the detector.



D* for TGS and HgCdTe Detectors

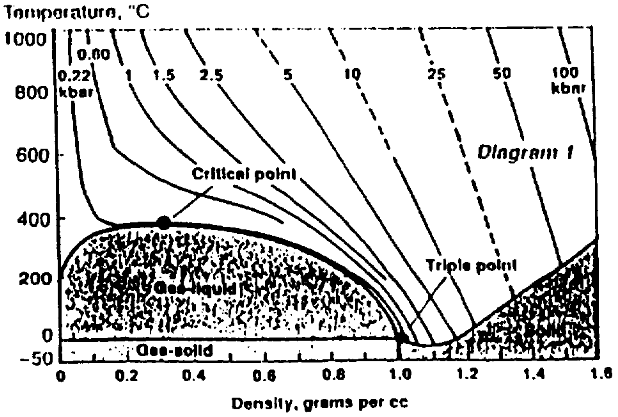
2. A careful evaluation of the recorded absorbance spectras revealed that sometimes the absorbance peak splits into two peaks or more depending on the characteristic bands of the compound. This evaluation on the spliting of the absorbance peaks reflect that their intensity (height) and position (wavenumber) varies with the concentration of the analyte especially at low ppm levels. It is suggested that peak area instead of peak height should be tried for the preparation of the calibration curves for the quantification of fluids at low ppm concentration levels of the analyte.

3. About 20 hydraulic fluids and greases are used at KSC. Some of them are silicon-based compounds which have limited solubility in PCE. It will not be possible to determine their concentration using infrared method. It is suggested to develop a model by running experiments on mixtures having fluids and greases by infrared method and also by the standard NVR method. The deviation in the results can be used to optimize a K factor in the following equation:

   Total Concentration = K x Conc. (Infrared method)

   where K is a predetermined ratio of the NVR method concentration to the Infrared method concentration, and is always greater than one. Since there are only a limited known types of fluids and greases, it won't be very difficult to optimize the K factor.

4. For the removal of the non-volatile residue (NVR) material for the clean validation process, it is recommended to explore the possibility of using water at or near supercritical conditions (SCW), since at these conditions, water has properties as of a fluid and a gas thus increasing its solvation power. Experimental runs should be carried out to optimize the temperature and pressure conditions for the maximum removal of the NVR materials.



ORIGINAL PAGE IS
OF POOR QUALITY

FIGURE 2-1

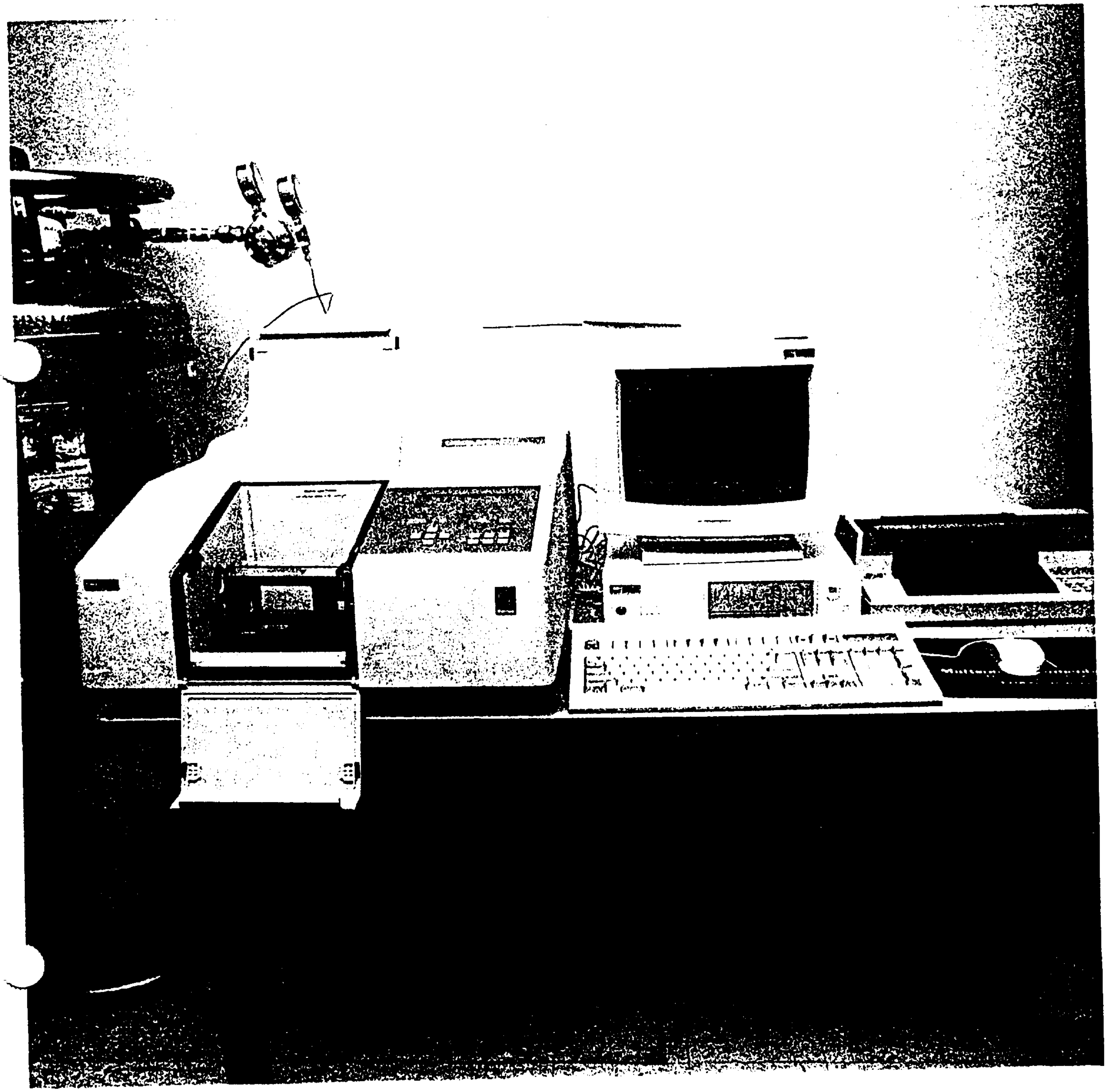


FIGURE 3-1

10% MOBILE JET II IN PCE

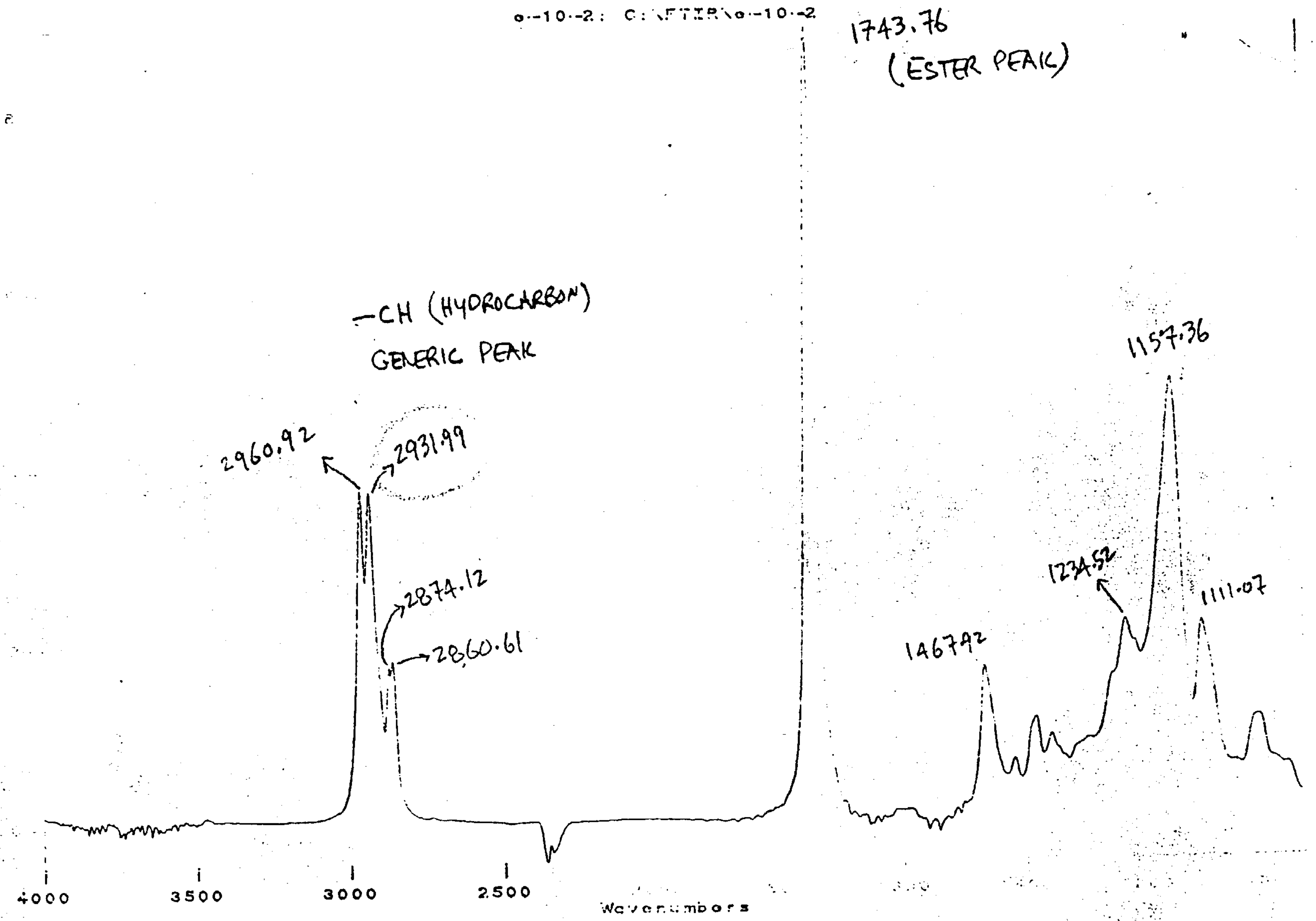


FIGURE 3-2

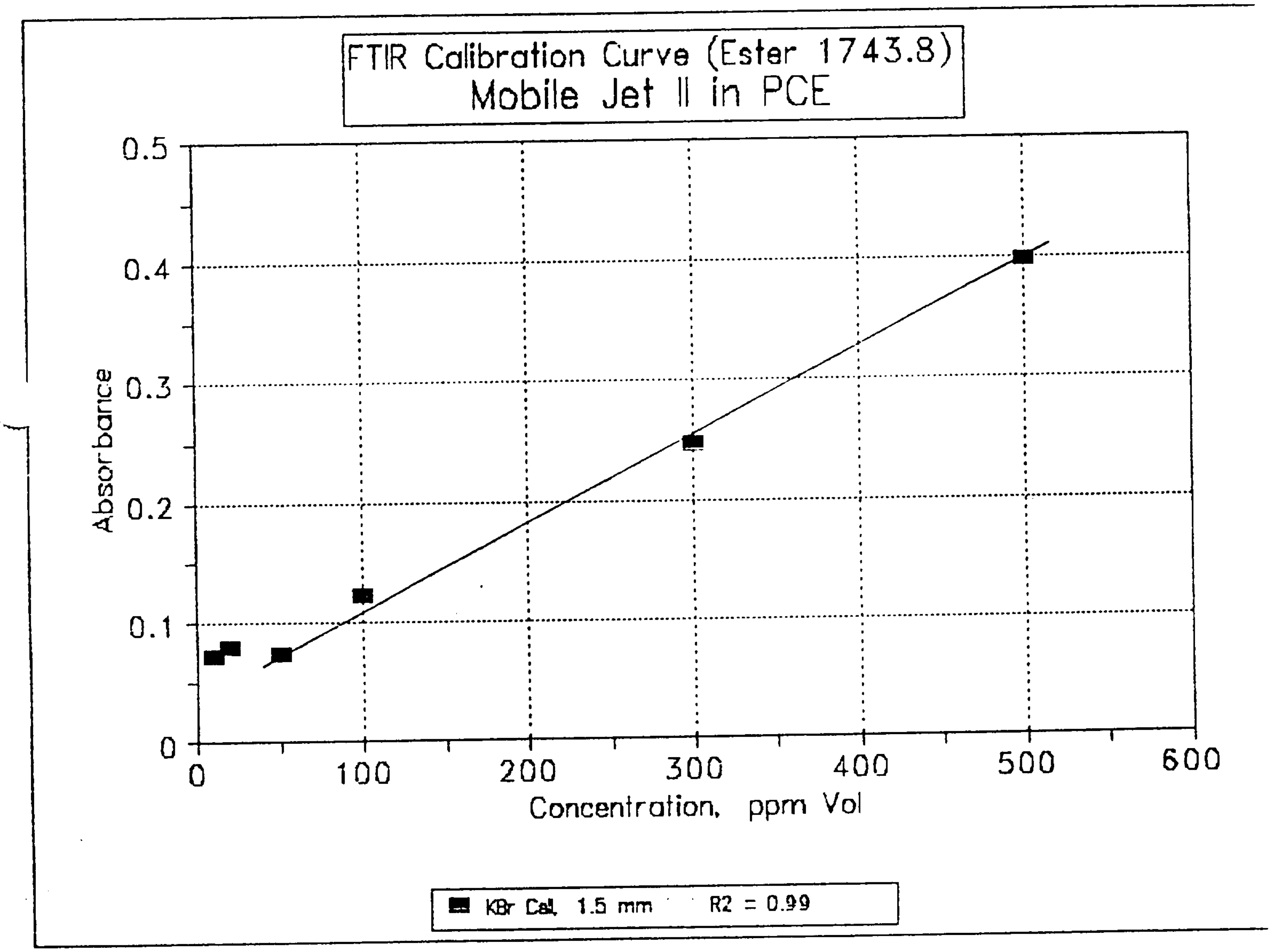

FTIR Calibration Curve (Ester 1743.8)
Mobile Jet II in PCE
Absorbance
0
0.1
0.2
0.3
0.4
0.5
0
100
200
300
400
500
600
Concentration, ppm Vol
■ KBr Cel. 1.5 mm
R2 = 0.99

FIGURE 3-3

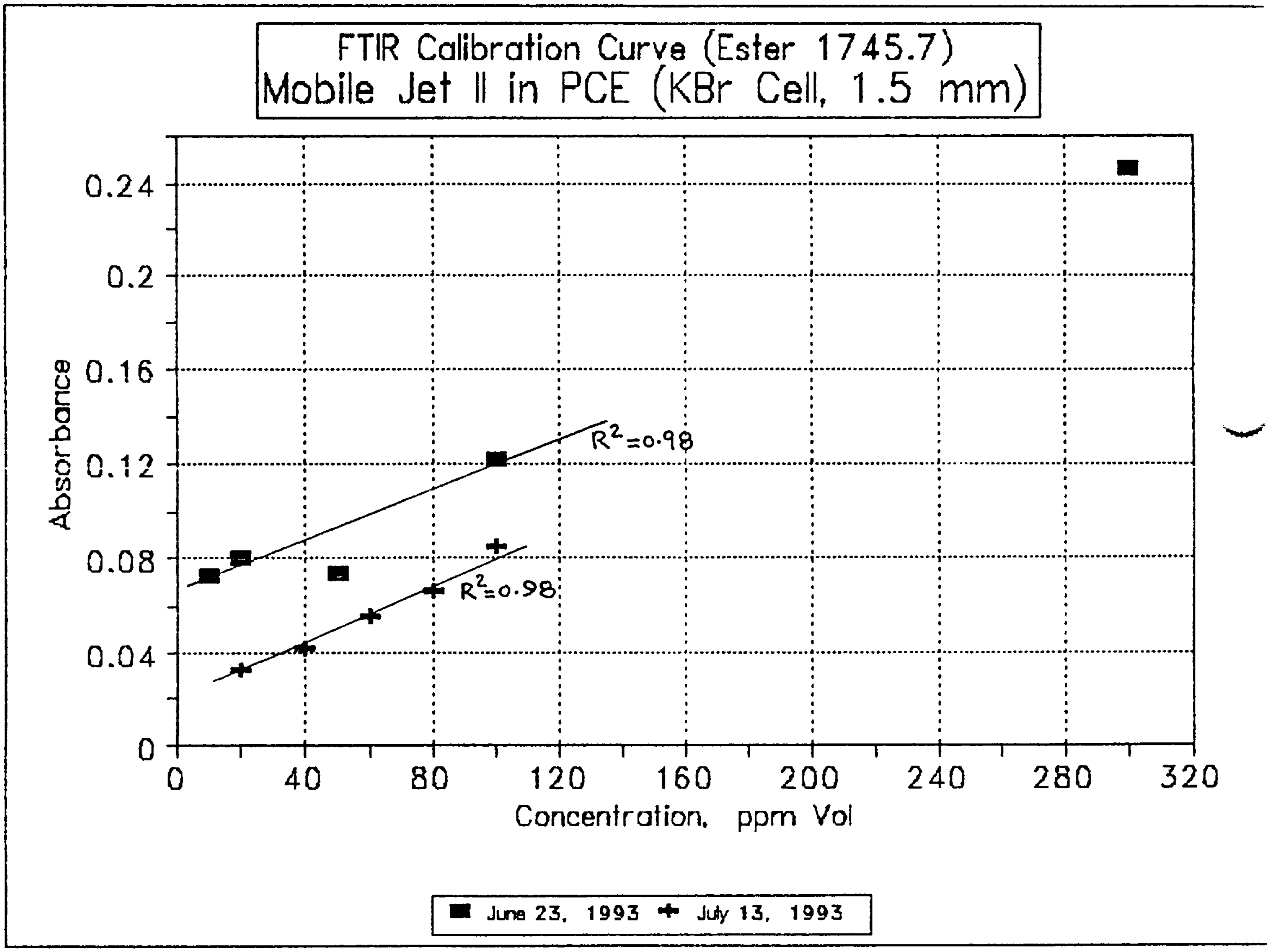

FTIR Calibration Curve (Ester 1745.7)
Mobile Jet II in PCE (KBr Cell, 1.5 mm)
Absorbance
0
0.04
0.08
0.12
0.16
0.2
0.24
0
40
80
120
160
200
240
280
320
Concentration, ppm Vol
R^2=0.98
R^2=0.98
■ June 23, 1993
+ July 13, 1993

FIGURE 3-4

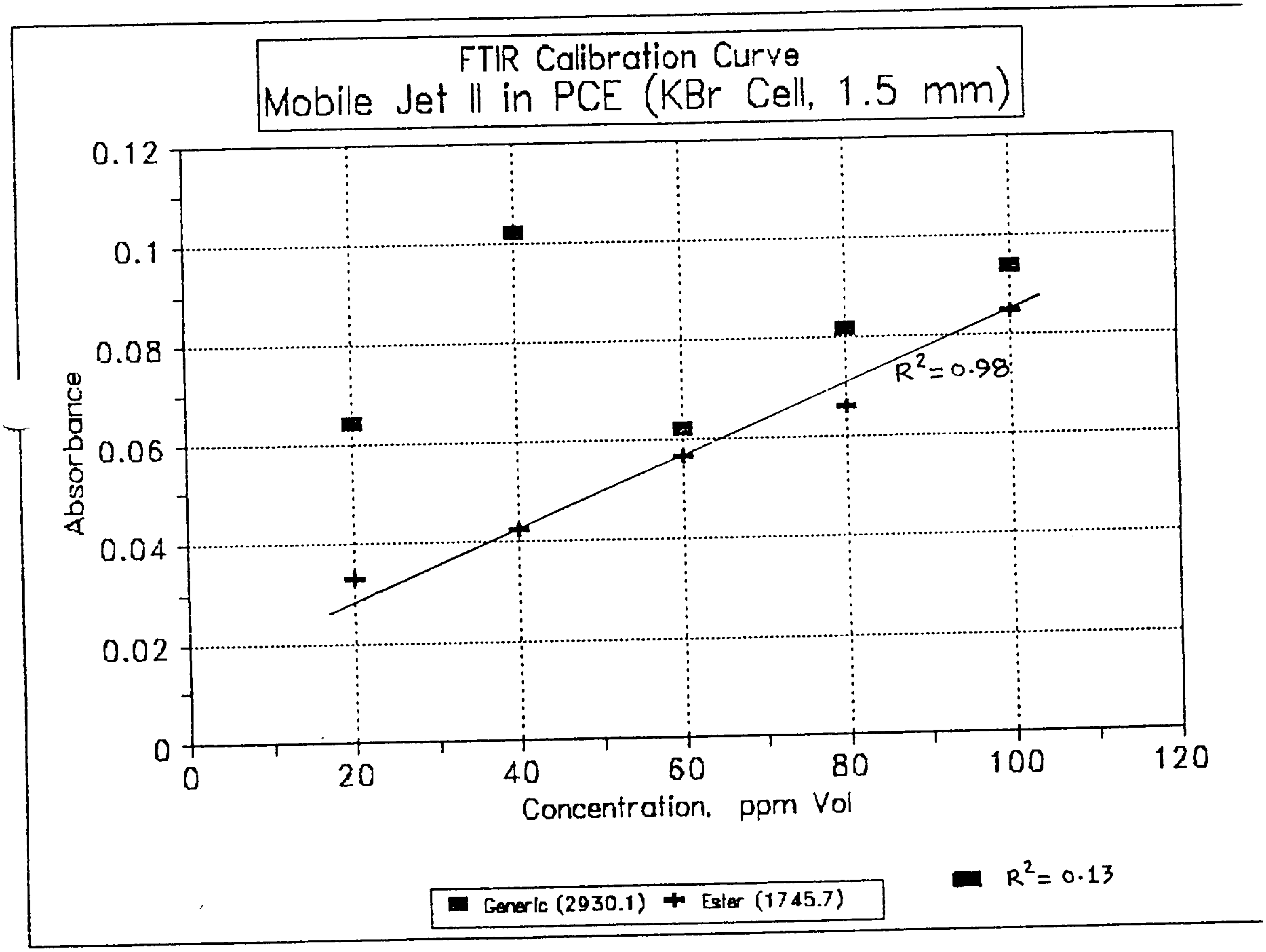

FTIR Calibration Curve
Mobile Jet II in PCE (KBr Cell, 1.5 mm)
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
Concentration, ppm Vol
$R^2 = 0.98$
■ $R^2 = 0.13$
■ Generic (2930.1) + Ester (1745.7)

FIGURE 3-5

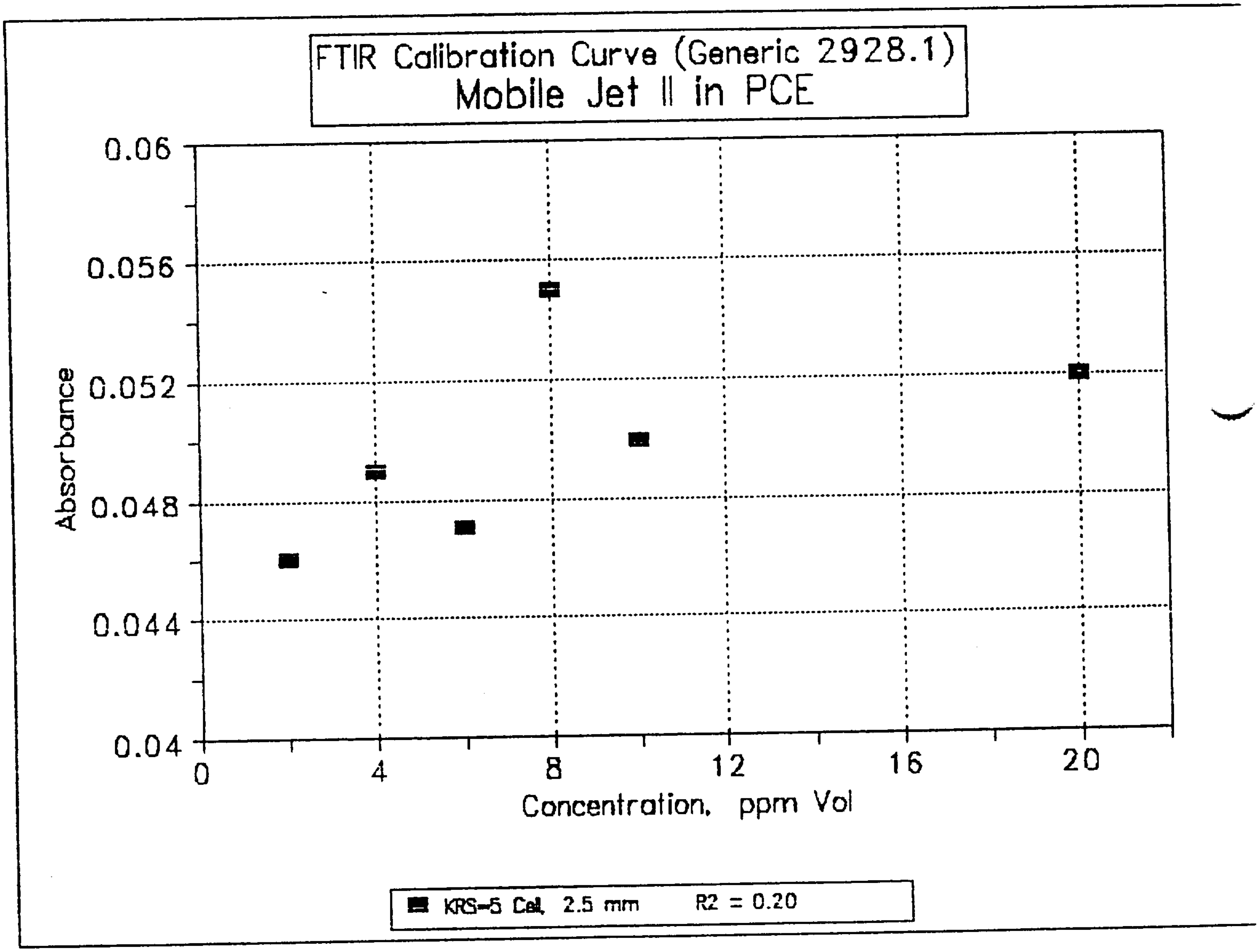

FTIR Calibration Curve (Generic 2928.1)
Mobile Jet II in PCE
Absorbance
0.06
0.056
0.052
0.048
0.044
0.04
0
4
8
12
16
20
Concentration, ppm Vol
■ KRS-5 Cell, 2.5 mm
R2 = 0.20

FIGURE 3-6

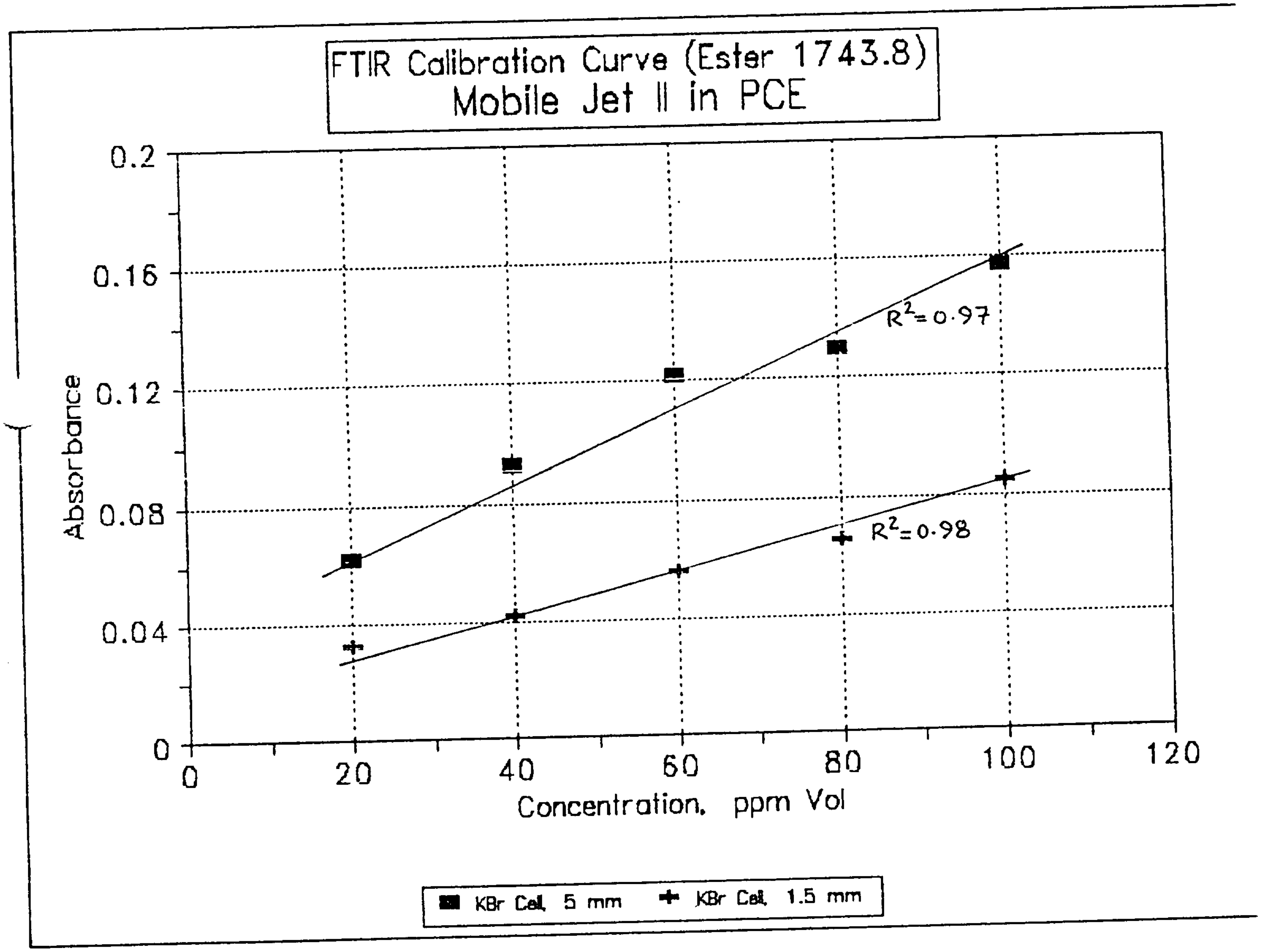
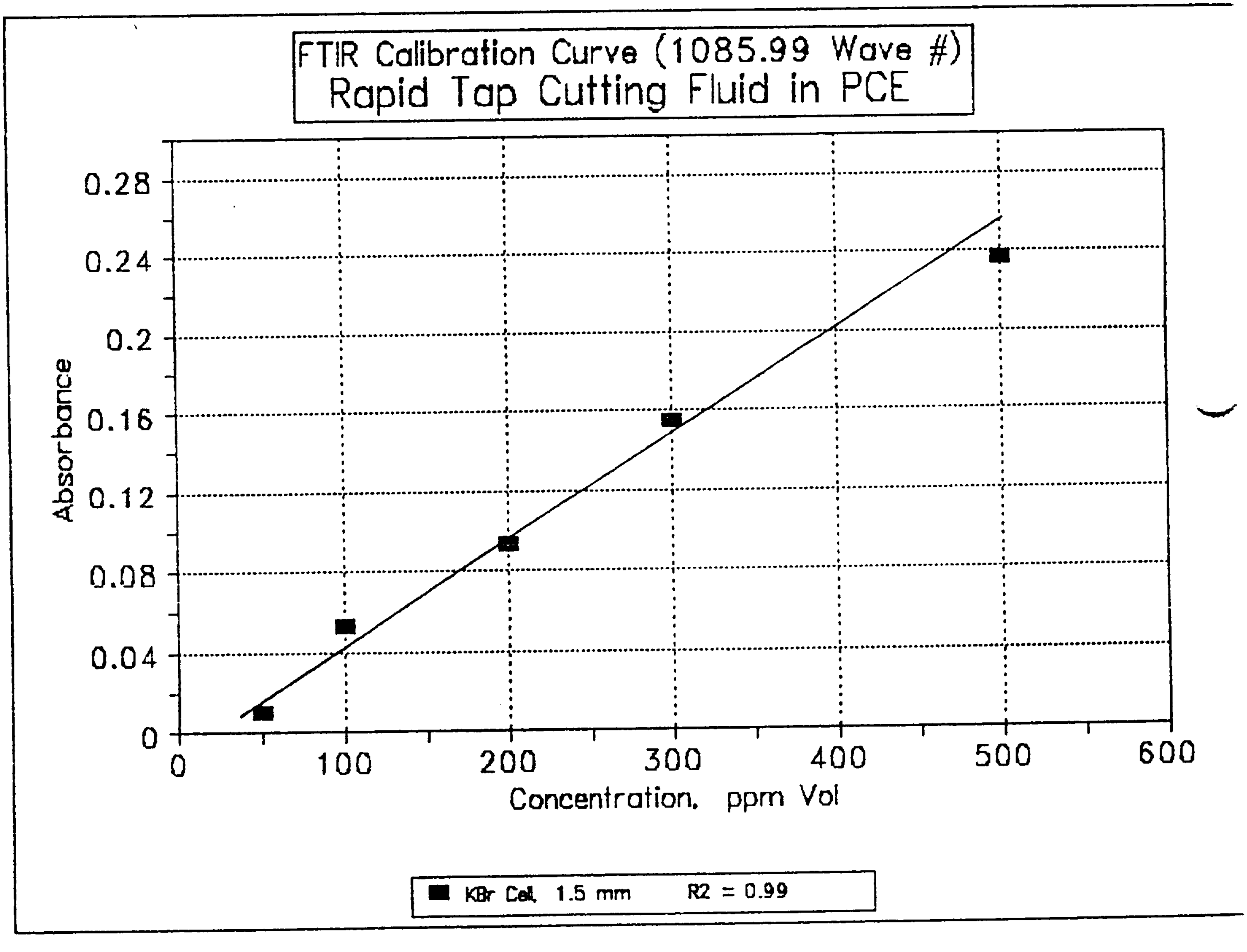

FTIR Calibration Curve (Ester 1743.8)
Mobile Jet II in PCE
0.2
0.16
0.12
0.08
0.04
0
Absorbance
0
20
40
60
80
100
120
Concentration, ppm Vol
R² = 0.97
R² = 0.98
■ KBr Cell, 5 mm
+ KBr Cell, 1.5 mm

FIGURE 3-7



FTIR Calibration Curve (1085.99 Wave #)
Rapid Tap Cutting Fluid in PCE
Absorbance
0.28
0.24
0.2
0.16
0.12
0.08
0.04
0
0
100
200
300
400
500
600
Concentration, ppm Vol
■ KBr Cell, 1.5 mm R2 = 0.99

FIGURE 3-8

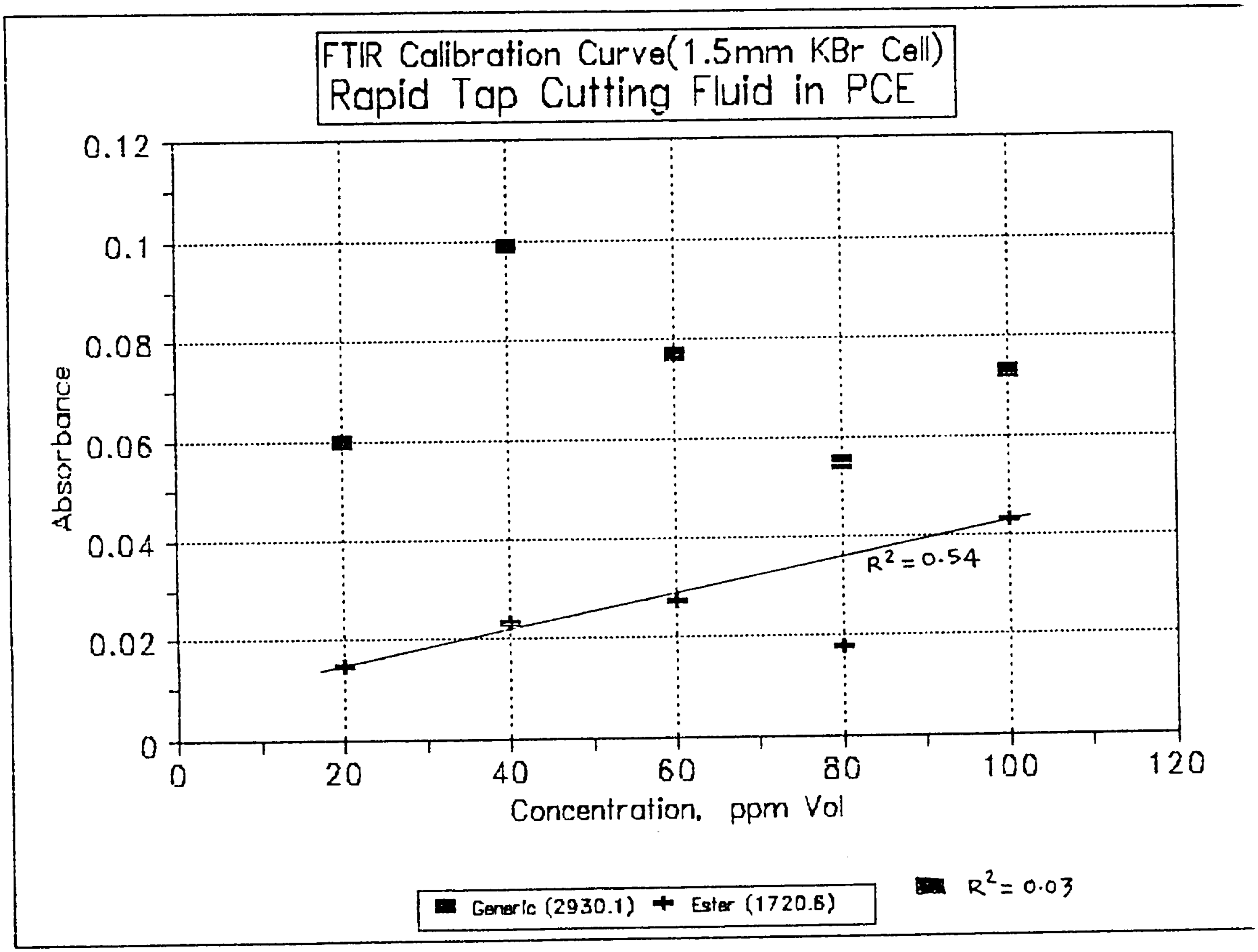

FTIR Calibration Curve(1.5mm KBr Cell)
Rapid Tap Cutting Fluid in PCE
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
Concentration, ppm Vol
$R^2 = 0.54$
■ Generic (2930.1)
+ Ester (1720.6)
■ $R^2 = 0.03$

FIGURE 3-9

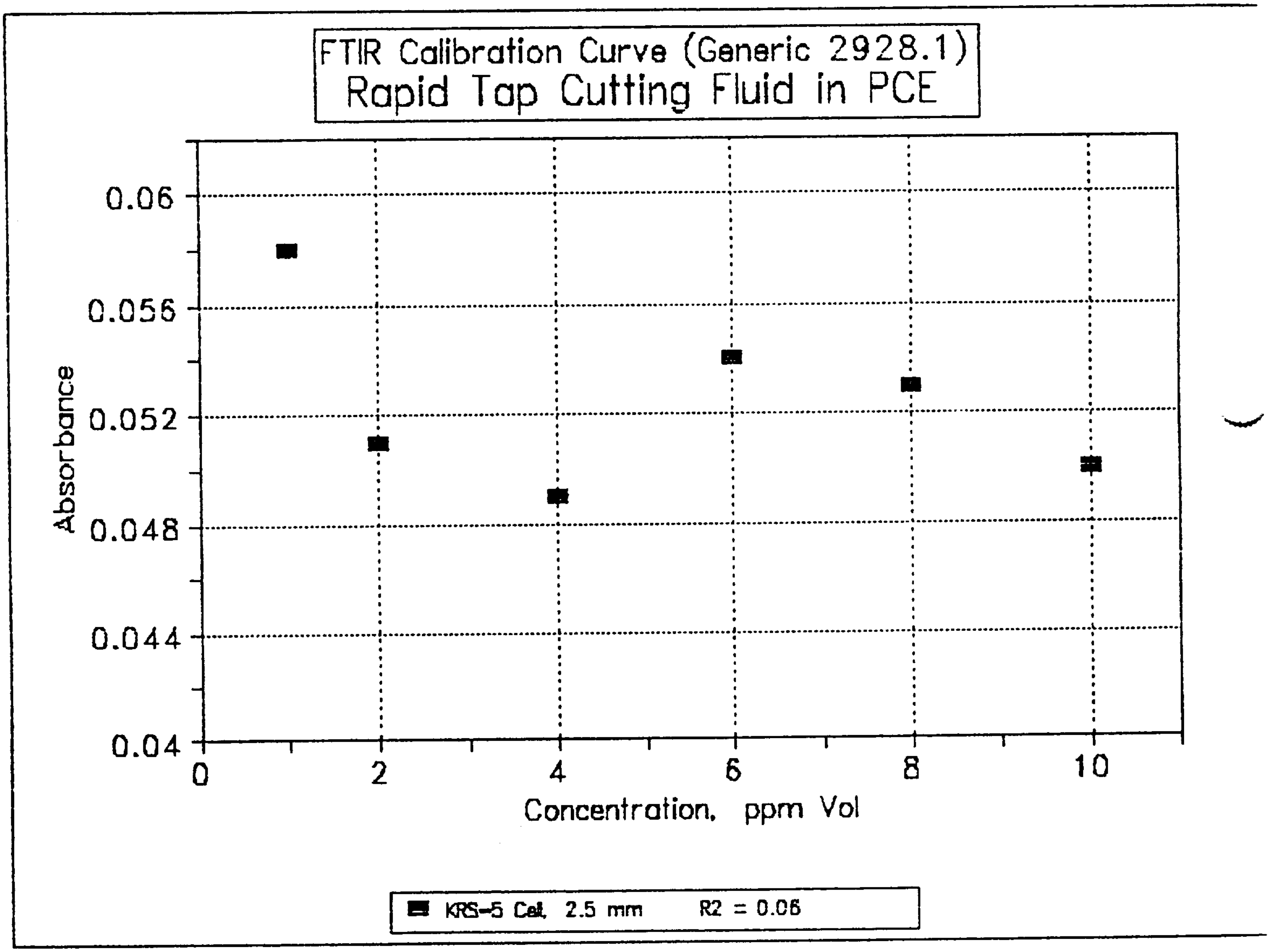
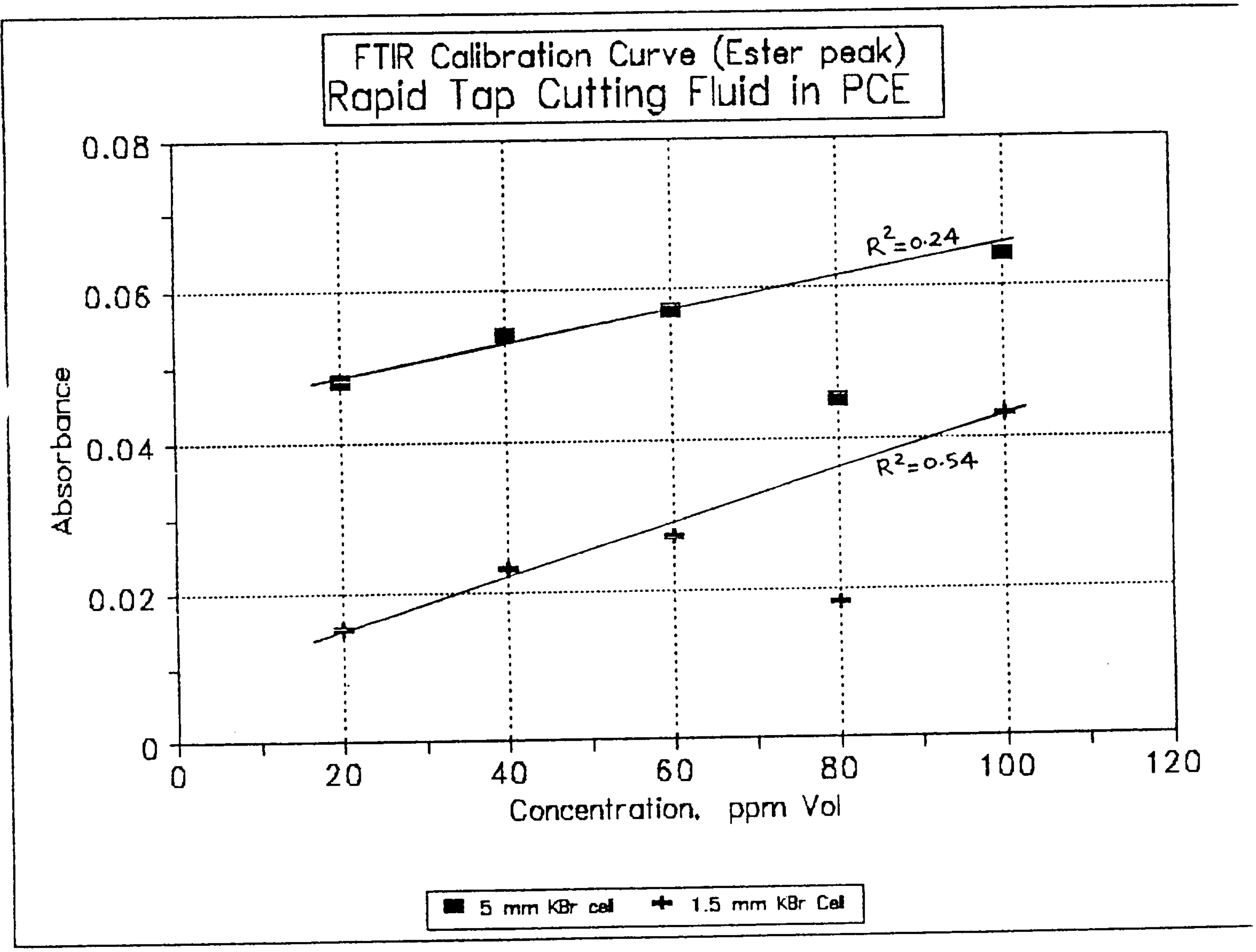

FTIR Calibration Curve (Generic 2928.1)
Rapid Tap Cutting Fluid in PCE
Absorbance
0.06
0.056
0.052
0.048
0.044
0.04
0
2
4
6
8
10
Concentration, ppm Vol
■ KRS-5 Cell, 2.5 mm R2 = 0.06

FIGURE 3-10



FTIR Calibration Curve (Ester peak)
Rapid Tap Cutting Fluid in PCE
0.08
0.06
0.04
0.02
0
Absorbance
0
20
40
60
80
100
120
Concentration, ppm Vol
R²=0.24
R²=0.54
■ 5 mm KBr cell
+ 1.5 mm KBr Cell

FIGURE 3-11

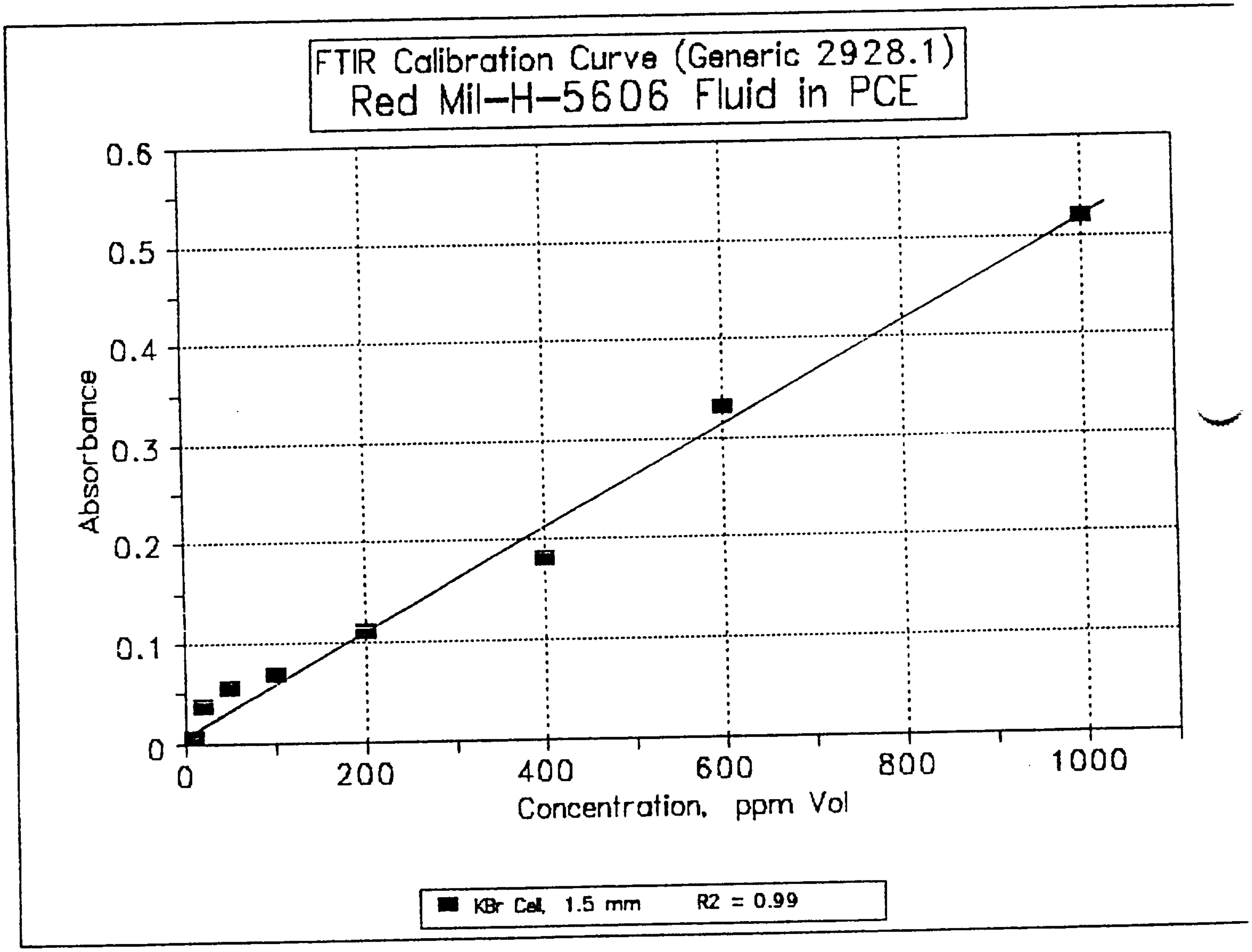

FTIR Calibration Curve (Generic 2928.1)
Red Mil-H-5606 Fluid in PCE
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
Concentration, ppm Vol
■ KBr Cell, 1.5 mm
R2 = 0.99

FIGURE 3-12

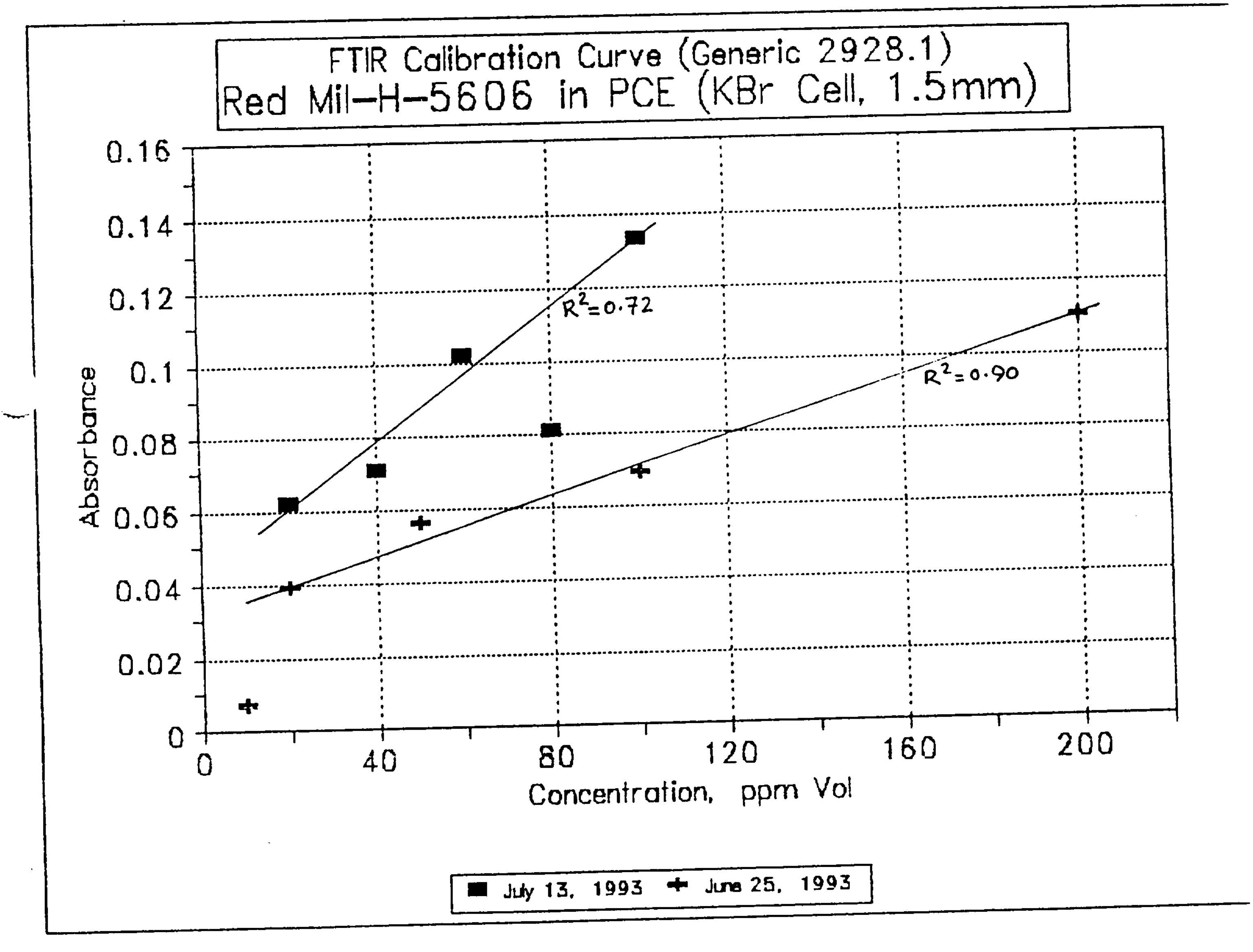

FTIR Calibration Curve (Generic 2928.1)
Red Mil-H-5606 in PCE (KBr Cell, 1.5mm)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Absorbance
0
40
80
120
160
200
Concentration, ppm Vol
R^2=0.72
R^2=0.90
■ July 13, 1993
✚ June 25, 1993

FIGURE 3-13

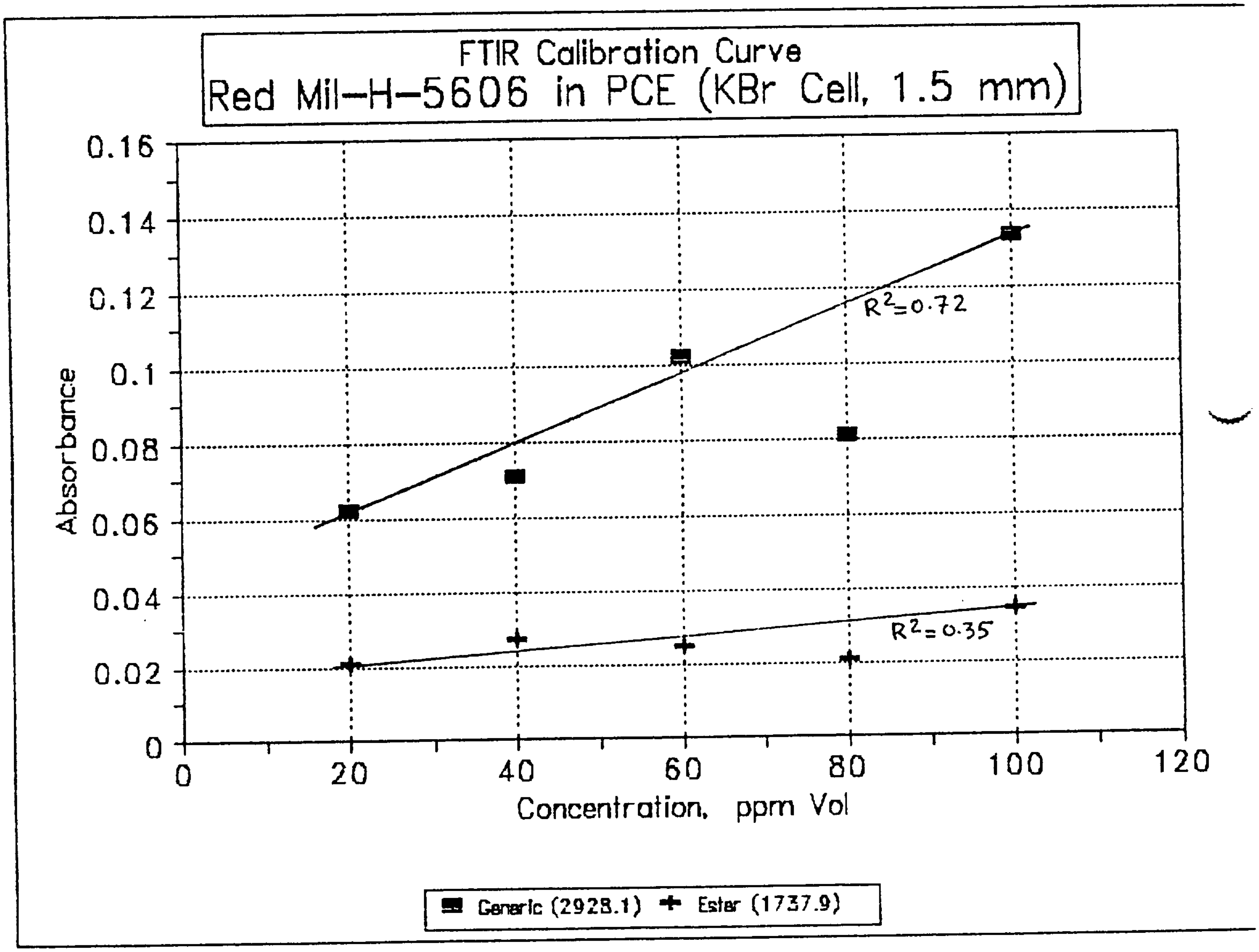

FTIR Calibration Curve
Red Mil-H-5606 in PCE (KBr Cell, 1.5 mm)
Absorbance
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
Concentration, ppm Vol
R²=0.72
R²=0.35
■ Generic (2928.1)
+ Ester (1737.9)

FIGURE 3-14

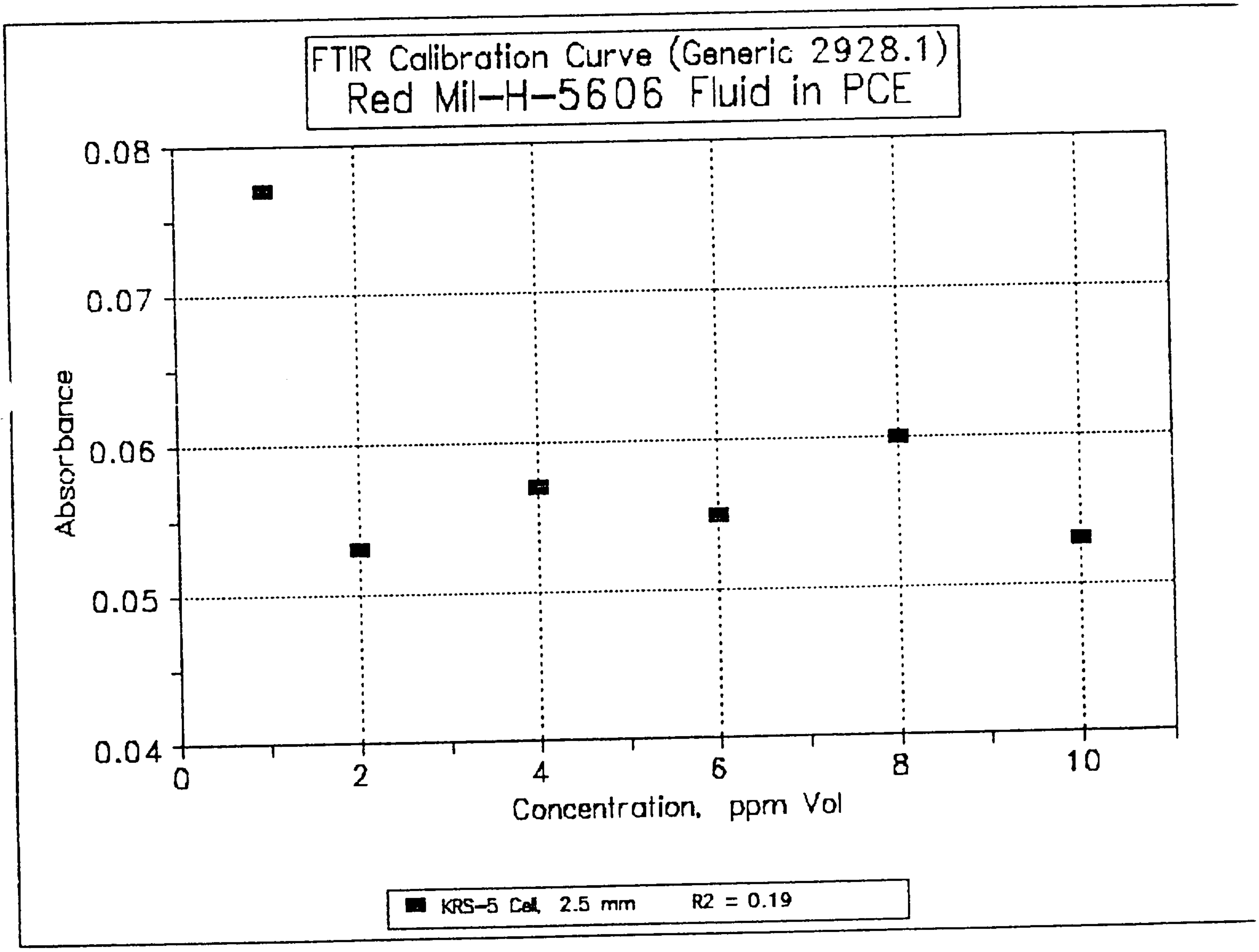

FTIR Calibration Curve (Generic 2928.1)
Red Mil-H-5606 Fluid in PCE
Absorbance
0.08
0.07
0.06
0.05
0.04
0
2
4
6
8
10
Concentration, ppm Vol
■ KRS-5 Cell, 2.5 mm
R2 = 0.19

FIGURE 3-15

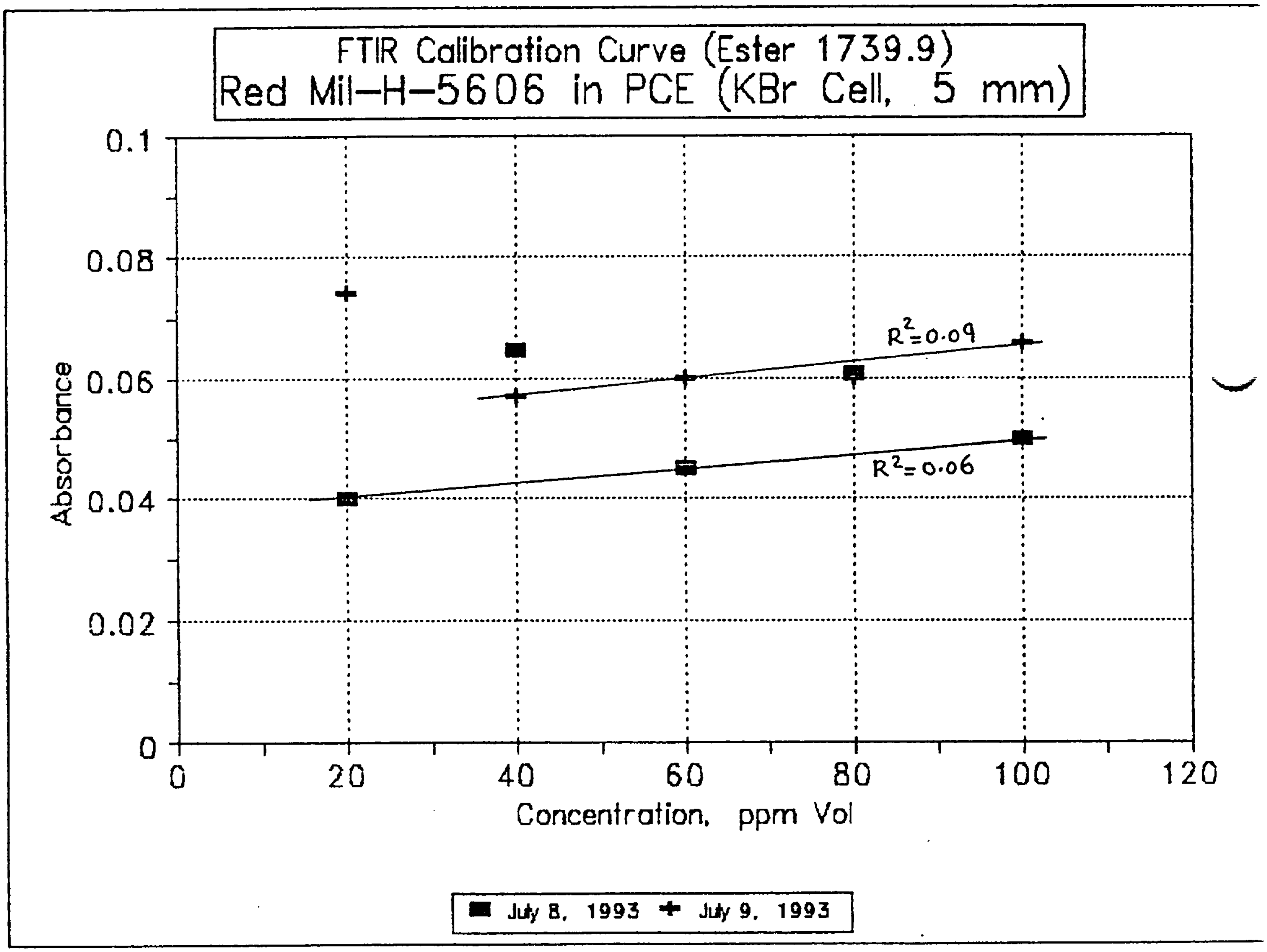

FTIR Calibration Curve (Ester 1739.9)
Red Mil-H-5606 in PCE (KBr Cell, 5 mm)
Absorbance
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
120
Concentration, ppm Vol
R² = 0.09
R² = 0.06
■ July 8, 1993
+ July 9, 1993

FIGURE 3-18

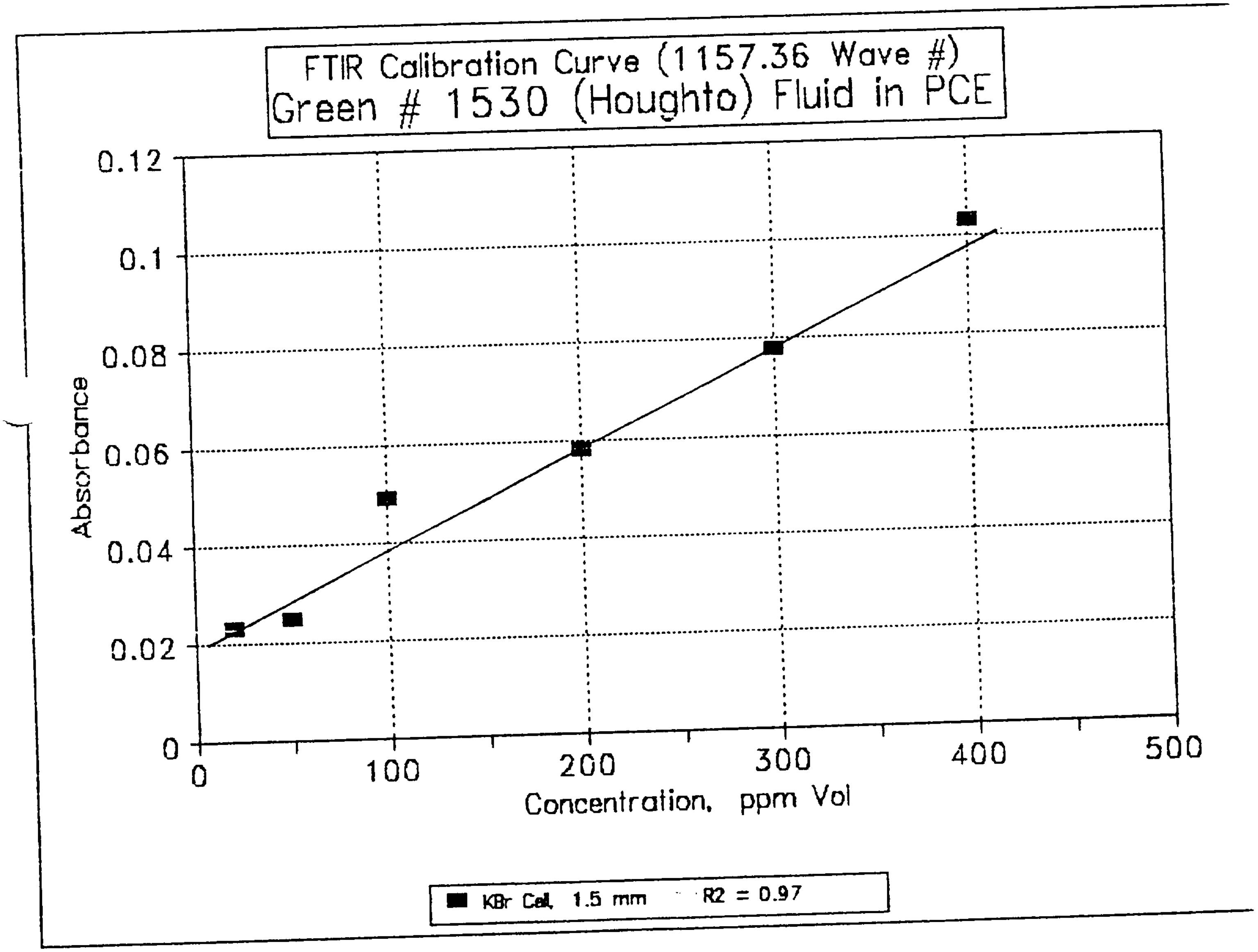

FTIR Calibration Curve (1157.36 Wave #)
Green # 1530 (Houghto) Fluid in PCE
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
100
200
300
400
500
Concentration, ppm Vol
■ KBr Cell, 1.5 mm
R2 = 0.97

FIGURE 3-17

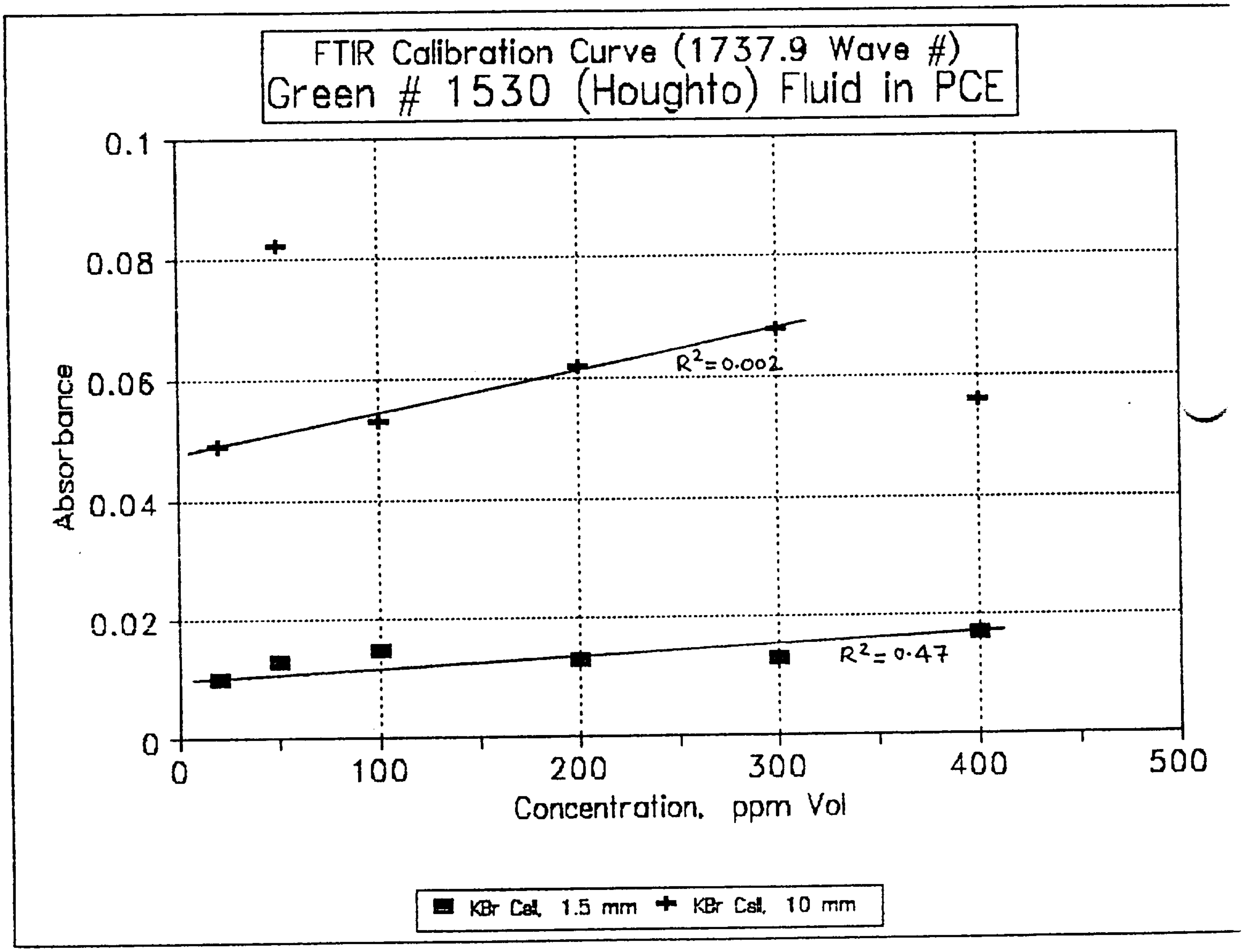

FTIR Calibration Curve (1737.9 Wave #)
Green # 1530 (Houghto) Fluid in PCE
Absorbance
0.1
0.08
0.06
0.04
0.02
0
0
100
200
300
400
500
Concentration, ppm Vol
$R^2 = 0.002$
$R^2 = 0.47$
■ KBr Cel, 1.5 mm
+ KBr Cel, 10 mm

FIGURE 3-18

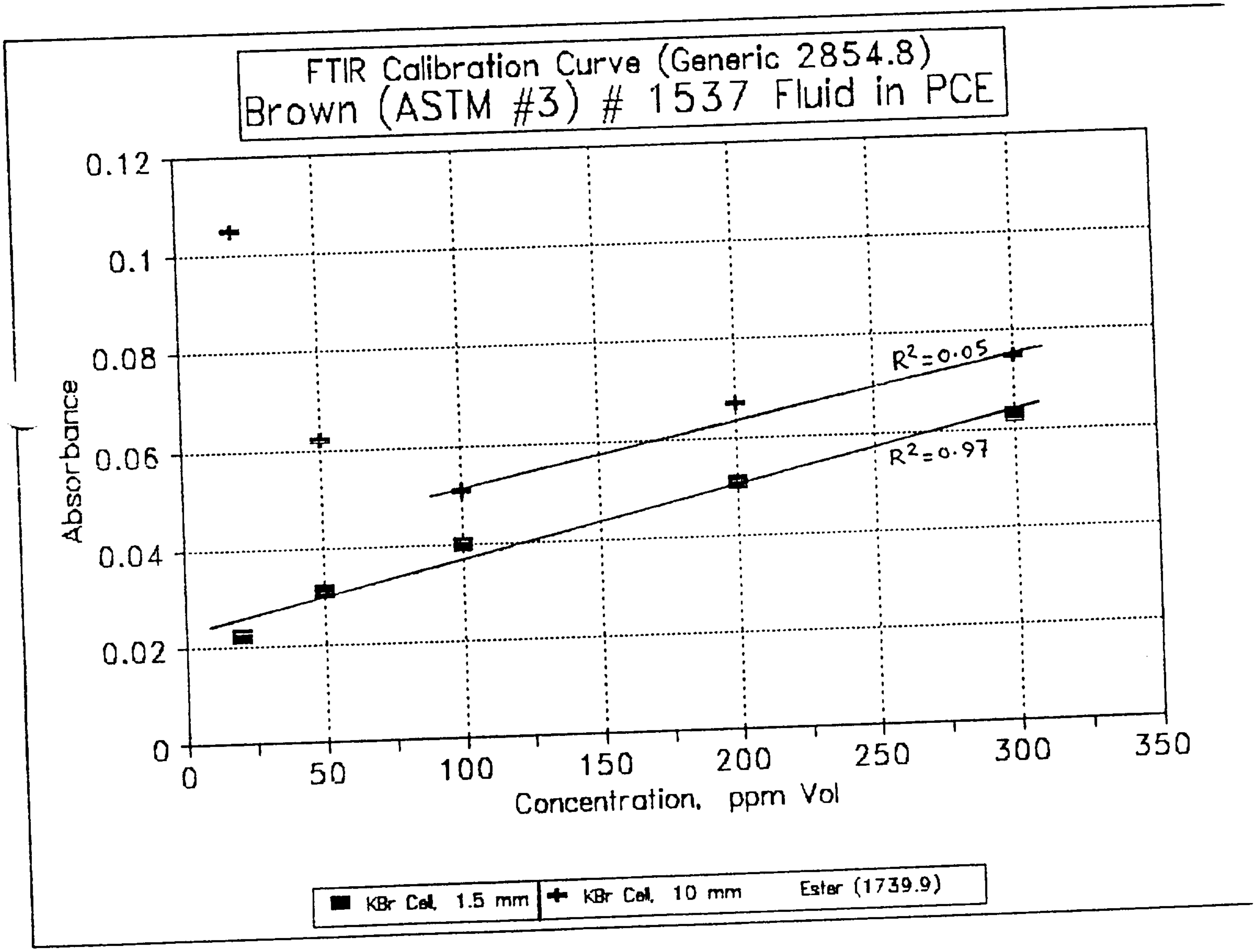

FTIR Calibration Curve (Generic 2854.8)
Brown (ASTM #3) # 1537 Fluid in PCE
0.12
0.1
0.08
0.06
0.04
0.02
0
Absorbance
0
50
100
150
200
250
300
350
Concentration, ppm Vol
$R^2 = 0.05$
$R^2 = 0.97$
■ KBr Cell, 1.5 mm
+ KBr Cell, 10 mm
Ester (1739.9)

FIGURE 3-18

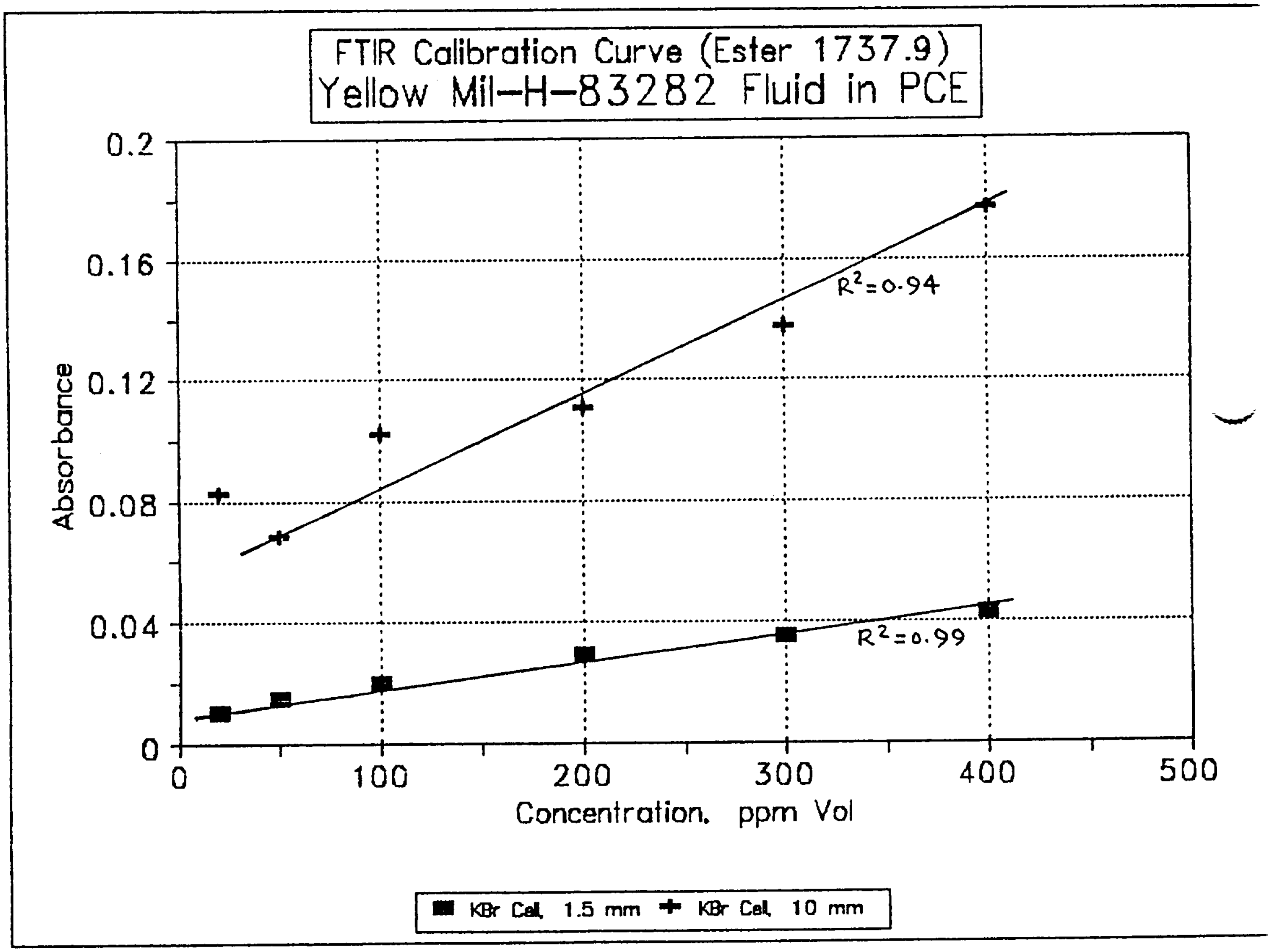
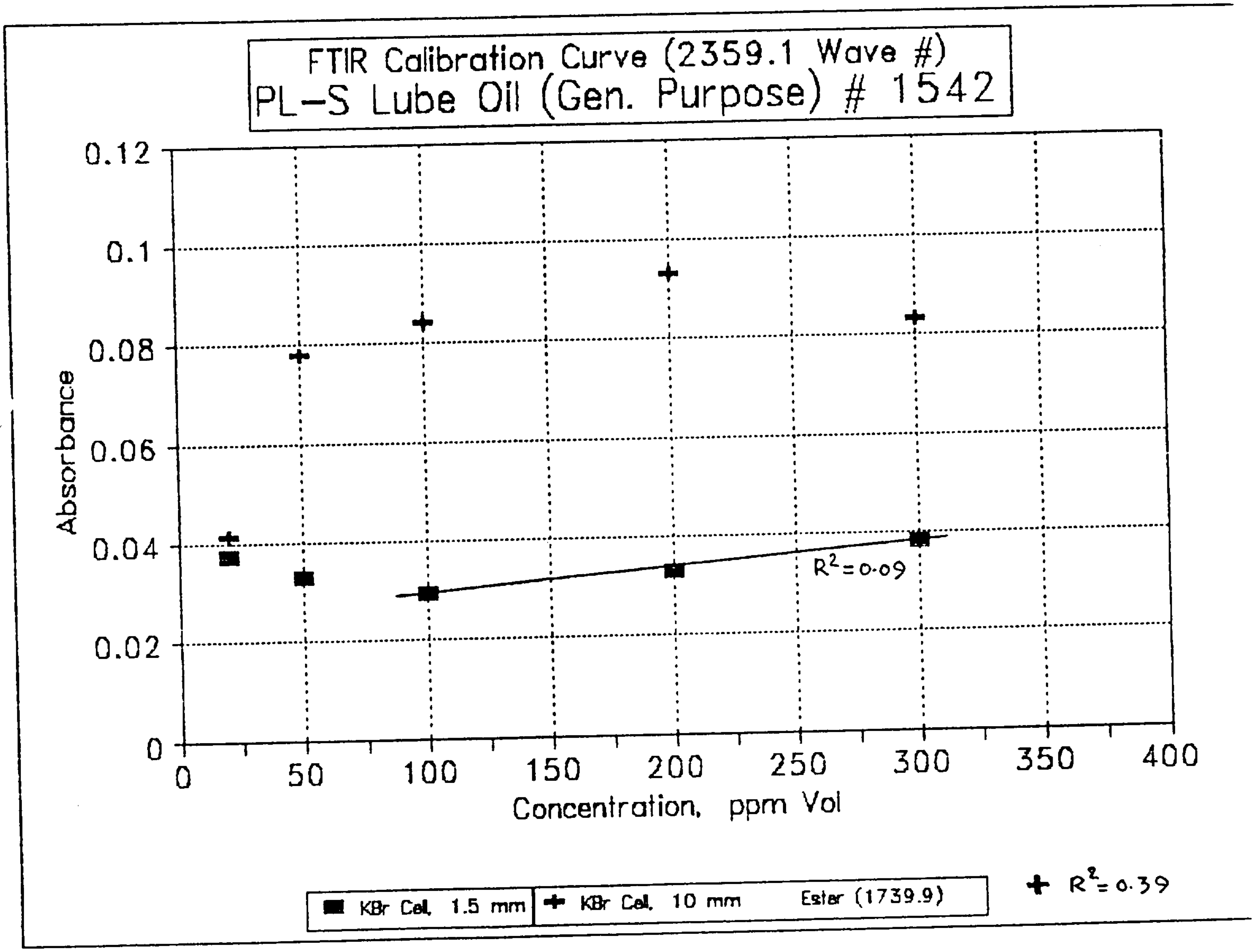

FTIR Calibration Curve (Ester 1737.9)
Yellow Mil-H-83282 Fluid in PCE
0.2
0.16
0.12
0.08
0.04
0
Absorbance
0
100
200
300
400
500
Concentration, ppm Vol
R^2=0.94
R^2=0.99
■ KBr Cell, 1.5 mm
+ KBr Cell, 10 mm

FIGURE 3-20



FTIR Calibration Curve (2359.1 Wave #)
PL-S Lube Oil (Gen. Purpose) # 1542
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
50
100
150
200
250
300
350
400
Concentration, ppm Vol
$R^2 = 0.09$
■ KBr Cell, 1.5 mm
+ KBr Cell, 10 mm
Ester (1739.9)
+ $R^2 = 0.39$

FIGURE 3-21

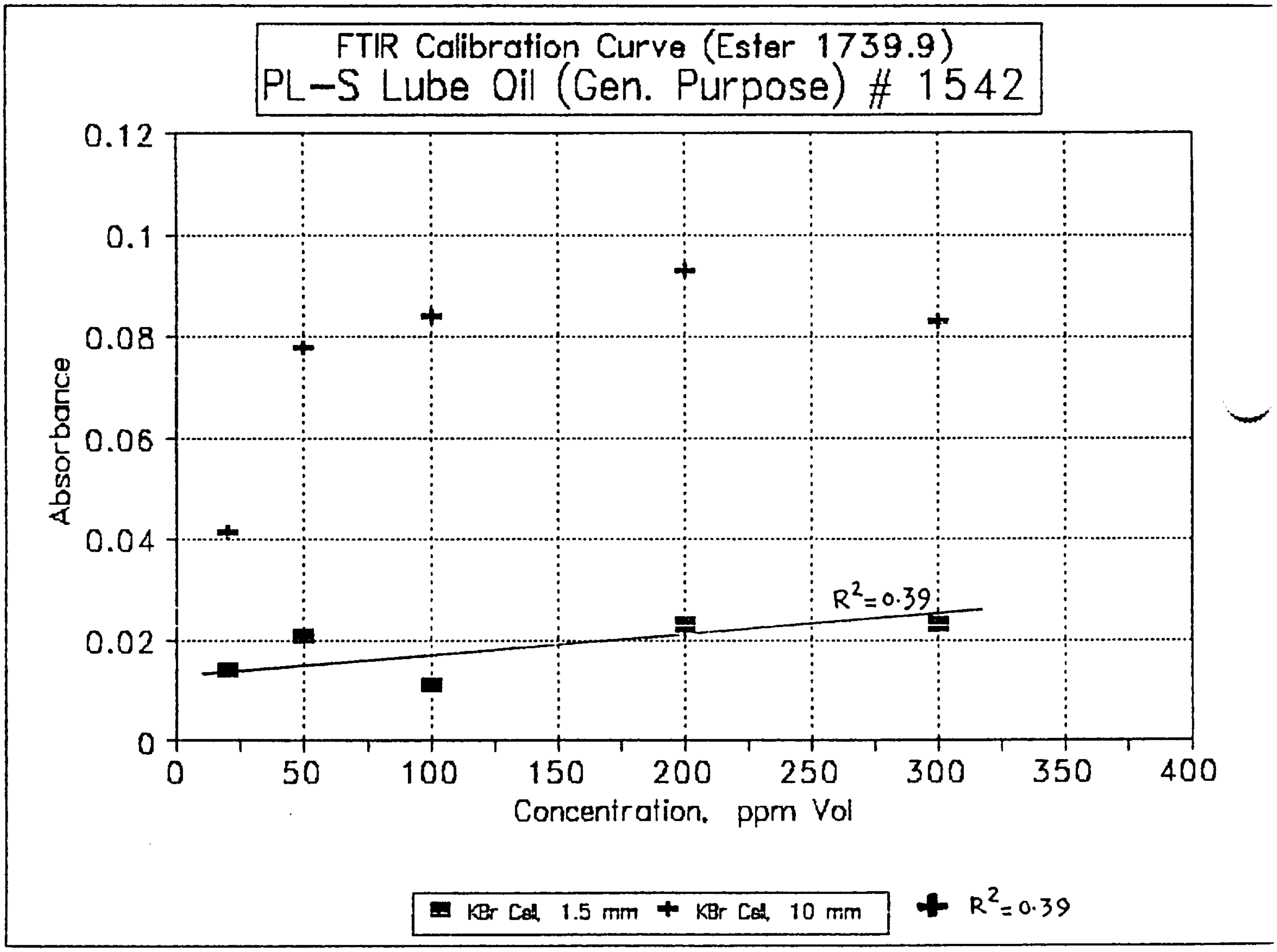
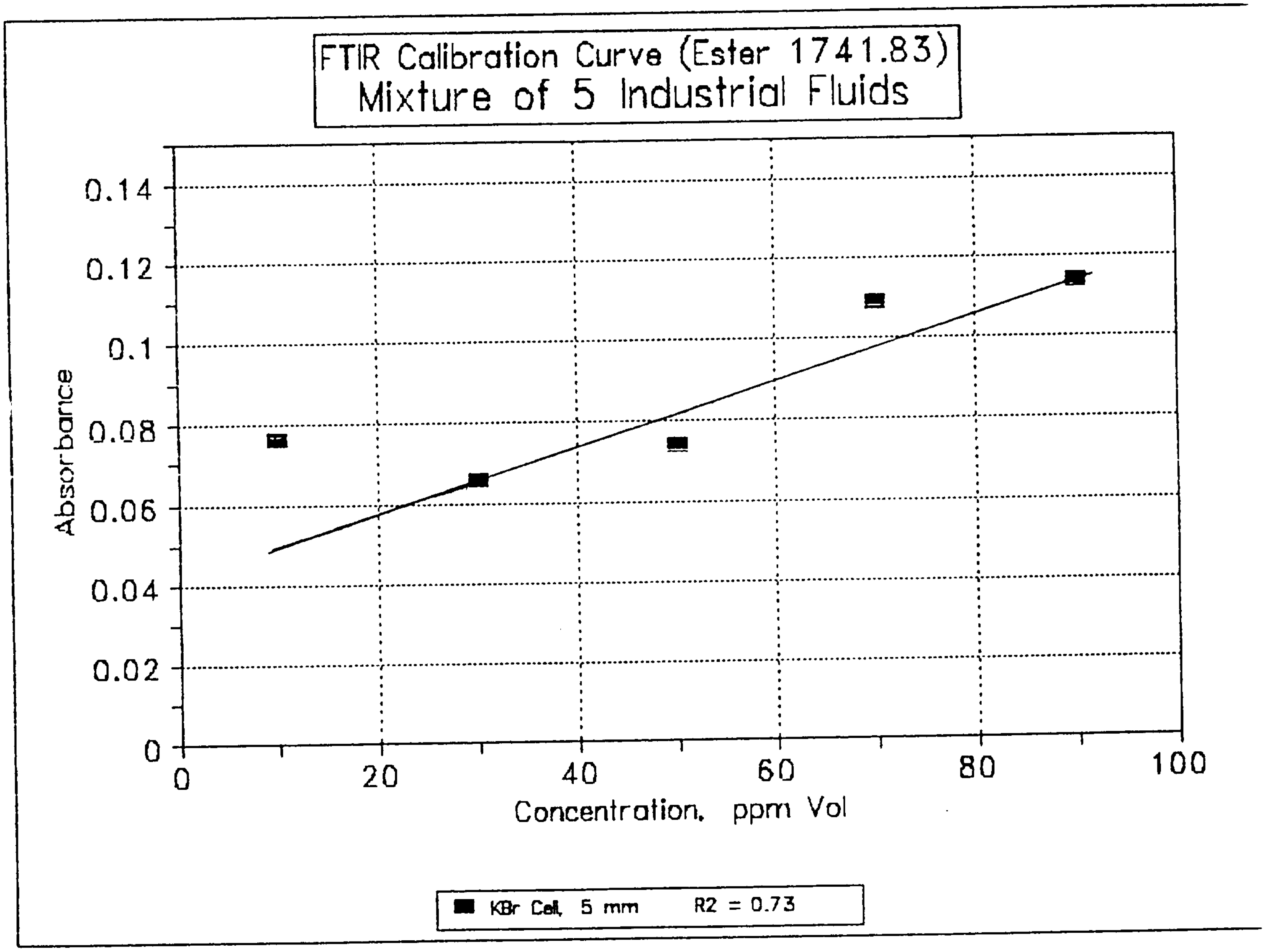

FTIR Calibration Curve (Ester 1739.9)
PL-S Lube Oil (Gen. Purpose) # 1542
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
50
100
150
200
250
300
350
400
Concentration, ppm Vol
R² = 0.39
■ KBr Cell, 1.5 mm
+ KBr Cell, 10 mm
+ R² = 0.39

FIGURE 3-22


FTIR Calibration Curve (Ester 1741.83)
Mixture of 5 Industrial Fluids
Absorbance
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
Concentration, ppm Vol
■ KBr Cell, 5 mm
R2 = 0.73