

LIBRARY

Michigan State University

PLACE IN RETURN BOX
 to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
JAN 11 2000		
AUG 00 2000		

**THE DIFFERENTIATION OF LASER PRINTER TONERS
USING DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM
SPECTROPHOTOMETRY**

By

Troy Jonathan Ernst

A THESIS

**Submitted to Michigan State University
in partial fulfillment of the requirements
for the degree of**

MASTER OF SCIENCE

School of Criminal Justice

1997

ABSTRACT

THE DIFFERENTIATION OF LASER PRINTER TONERS USING DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROPHOTOMETRY

By

Troy J. Ernst

In this project, laser printer toners were analyzed using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The purpose of this research was to evaluate DRIFTS as a method for differentiating laser printer toners. The spectra were collected, differentiated, and classified based on distinguishing peaks of absorption. A library of spectra of laser printer toners was produced, which was tested by re-running several samples and comparing their spectra to the library.

ACKNOWLEDGMENTS

I would like to extend my appreciation to Dr. Jay A. Siegel, who provided a plan, knowledge of the subject and of the instrumentation, and helped things to run as smoothly as a research project can. His guidance and assistance enabled the research to overcome several obstacles and ultimately reach a conclusion.

Also, thanks go out to Jerry Bockes, who was my primary source for toners.

TABLE OF CONTENTS

LIST OF FIGURES	v
LIST OF ABBREVIATIONS	vi
INTRODUCTION	1
Laser Printers.....	2
DRIFTS.....	4
Past Research Focusing on Differentiation of Toners.....	5
PROCEDURE	8
RESULTS	11
DISCUSSION	23
APPENDIX A – NAMES OF TONERS	28
APPENDIX B – TONER GROUPS	29
APPENDIX C – INFRARED SPECTRA OF TONERS	31
BIBLIOGRAPHY	57

LIST OF FIGURES

Figure 1 – Path of Laser in DRIFTS Unit	4
Figure 2 – Groups I through VII	13
Figure 3 – Groups VIII through XIII	14
Figure 4 – Spectra of Top Matches from Library	16
Figure 5 – Spectra of Top Matches from File	17
Figure 6 – Overlays of Unknown with T008 and T004	19
Figure 7 – Overlays of Unknown with T003 and T002	20
Figure 8 – Overlays of Unknown with T015 and T001	21
Figure 9 – Overlays of Unknown with T009 and T007	22

LIST OF ABBREVIATIONS

cm⁻¹ – wavenumbers

DRIFTS – Diffuse Reflectance Infrared Fourier Transform Spectrophotometry

FTIR – Fourier Transform Infrared

GC/MS – Gas Chromatography / Mass Spectrometry

HPLC – High Performance Liquid Chromatography

IR – Infrared

KBr – Potassium Bromide

INTRODUCTION

In the field of forensic science, there is much room for empirical research. This research focuses on questioned document analysis, which is a discipline within the forensic sciences. The term "questioned document" refers to any document of which the source is unknown (Saferstein, 1990). Examples of questioned documents include forgeries, notes of extortion, and letters of threat.

Questioned documents can be handwritten, typewritten, copied, or printed by an ink-jet printer, a laser printer, etc. Another form is the document that is made by cutting letters out of magazines and newspapers and affixing them to paper to form the desired words.

Each form of questioned document requires a different method of examination. A handwritten document is compared to exemplars taken from suspects, in order to determine the similarities and differences in the printing or writing styles between the documents. An analyst of a typewritten document compares the typefaces used and the irregularities in certain letters due to the normal wear and damage to the typewriter's moving parts in the questioned document with a specimen collected on the suspect's typewriter. Questioned documents prepared on a copier or computer printer may be analyzed by studying the makeup of the toners or inks present on the paper. Cut-and-paste questioned documents allow for the comparison of adhesives found on the paper with adhesives obtained from the suspect.

The research presented in this thesis focuses solely on the analysis of questioned documents prepared by a laser printer. Because laser printers and

electrostatic copiers operate on the same principles, the conclusions of this research apply to copier toner analysis as well.

With the rise in technology and the lowering of prices for advancements in printing and copying procedures, a growing number of people have greater access to equipment that can produce printed documents of seeming anonymity. A result of this situation is the need for improved measures for the differentiation of these documents.

Laser Printers

Laser printing requires several steps to produce the final printout. First, a cylindrical photosensitive drum receives a cleaning from the last image it made by a cleaning blade and an erase light. The blade removes excess toner, and the light erases any prior images. A negative 600-volt charge is given to the drum by a thin wire called the primary corona. It is then ready for a new image, which is drawn on the drum with a laser beam reflected by a movable mirror. The new image is made wherever the laser strikes the drum by changing the voltage to negative 100 volts. Because the toner has magnetic properties, the toner is deposited on the drum where there is a more positive surface. This is done when the drum rotates past the toner particles. The next step is the transfer of the toner to the paper, which has been given a positive 600-volt charge by another thin wire, the transfer corona. Because of the paper's positive charge, the toner is transferred to the paper. The paper then undergoes a reduction in charge. The final step is fusion of toner onto the paper. The paper is rolled through a metal roller at a temperature of 180 degrees Celsius, which melts the toner onto the paper (Minasa, 1992).

Laser printer toners are comprised of varying amounts of pigments, binding agents, and various additives that depend on the brand and function of

the toner. The pigments give the toner its color. The most common pigment is carbon black, although additional pigments are sometimes added. The binding agent affixes the pigment to the paper and is a mixture of synthetic organic resins. Additives ensure the toner particles have the correct polarity to remain on the charged paper before the fusion of the toner and the paper takes place (Mazzella, Lennard, & Margot, May 1991).

Laser printers are sufficiently common that attempting to trace a printed paper to a particular source is not normally feasible. Only when a particular printer leaves unique marks on every page of paper it prints could individualization of a document to a specific printer take place (Brunelle, 1982). Since individualization is the exception, methods need to be developed that can associate a printed paper with a class of laser printers. The class could include a single brand and model of printer, or a variety of brands and models, each producing the same distinguishing features.

Analysis of the toner on the printed paper represents one method to classify documents. Laser printer models specify which type of toner is to be used in printing. For example, one model of laser printers may specify Oasis Eclipse laser printer toner to be used in it, while another model may call for Laser1 Aspen Toner. If a method could be found that could differentiate between the toners, then a document examiner could compare the test results of an unknown source to the results of known toners. The result would be that some laser printers would be eliminated as the possible source of the questioned document, narrowing the scope of the criminal investigation. If it could be shown that the suspect had access to a laser printer with toner that matched the questioned document, then it is a piece of corroborative evidence, linking the suspect to the crime.

DRIFTS

Diffuse reflectance infrared Fourier transform spectrophotometry (DRIFTS) uses properties of molecules when they are irradiated with infrared radiation. Radiation in this region includes the wavenumbers from 4000 to 650 cm^{-1} . A laser beam provides this energy. The beam is directed at an oblique angle onto a powdered sample using a series of mirrors (Figure 1). The powdered sample is mixed with a background such as potassium bromide (KBr), which does not absorb radiation in the infrared region (Skoog & Leary, 1992).

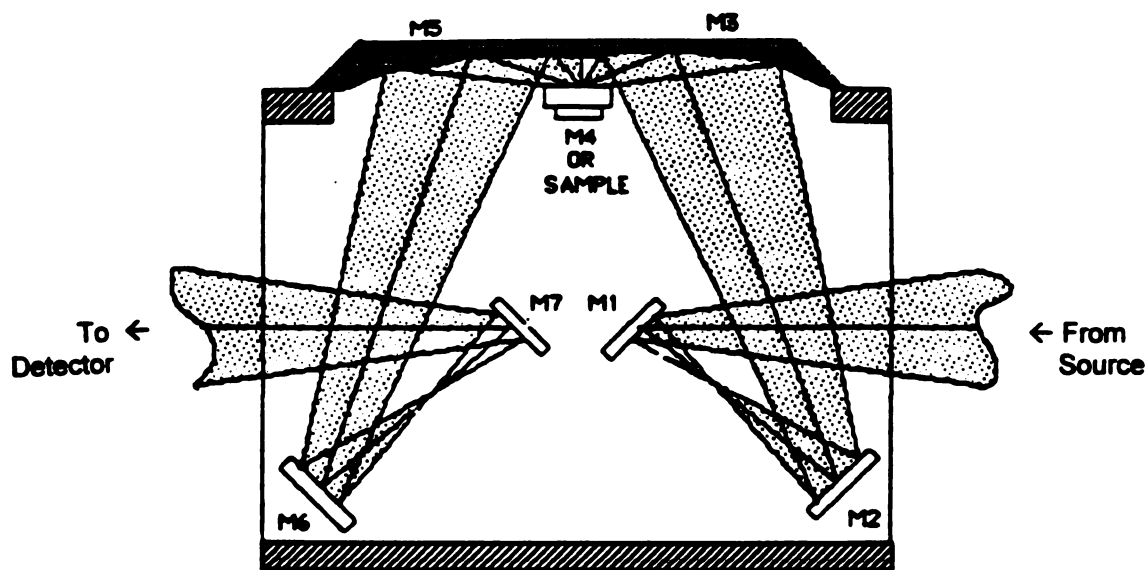


Figure 1 – Path of Laser in DRIFTS Unit

Molecules absorb energy at wavenumbers that correspond to the required energy needed to excite vibrational modes. These wavenumbers are highly specific. Energy at wavenumbers that is not absorbed is scattered in all directions. The scattered radiation is reflected through another series of mirrors to a detector, which measures the wavenumbers of energy that reaches it. The computer records this information for every scan that is made of the reflected energy. The sample is replaced by a microcup containing only the background and the same number of scans are run on it. The Fourier transform function of the machine subtracts the average reflectance of the scans of the sample with background from the average reflectance of the scans of the background to obtain the infrared spectrum of the sample (reflectance v. wavenumber). The reflectance spectrum is converted to absorbance through a mathematical function and a highly specific absorbance v. wavenumber spectrum for that sample is obtained (Skoog & Leary, 1992).

Past Research Focusing on Differentiation of Toners

A few studies of methods attempting to classify and differentiate toners have been attempted. These have analyzed primarily copier toners, but their conclusions are relevant to laser printer toners as well. Past studies have attempted normal infrared spectrophotometry, pyrolysis gas chromatography / mass spectrometry (GC/MS), and DRIFTS to classify toners.

Normal infrared spectrophotometry of toners was studied by Kemp and Totty (1981), with some discrimination between different toners. However, their research indicated differences in the spectrum of the raw toner versus that of the toner extracted from a printed paper. Therefore, it could not conclusively link the two types (raw and extracted) to be from the same source, even when, in fact, they were. The rationale given for this finding was that the process of binding the

toner to the paper caused a chemical change to take place, thereby causing a different spectrum to be produced. This theory does not prove to be the case, however. Later studies have shown that spectra of a toner in its raw and extracted forms are indistinguishable.

Pyrolysis GC/MS experiments on toners were published by Levy and Wampler in 1986. Only nine samples from four manufacturers were tested. The results showed that toners from different manufacturers were distinguishable, while toners made by the same manufacturer had similar spectra. Pyrolysis GC/MS, therefore, may be capable of classifying a toner by the manufacturer. A larger sample size is needed to verify this conclusion, however.

A combination of IR spectrophotometry and pyrolysis gas chromatography was used by Zimmerman, Mooney, and Kimmett (1986) in an effort to characterize copier toners. They placed 35 toners into 18 categories based on their IR spectra. Their next step used pyrolysis gas chromatography to further break down the categories. In their largest category based on IR absorbance, which included eight toners, differences in the pyrolysis gas chromatography spectra distinguished between each of them.

DRIFTS on toners was first studied in 1990 (Mazzella et al., March 1991). 149 toners were classified into 36 distinct groups, based on differences in the infrared spectrum. In this study, 119 black copier toners were analyzed, along with several color toners and laser printer toners. Characteristic peaks were found in the wavenumber region between 2100 cm^{-1} to 700 cm^{-1} .

Raw and extracted samples of the same toner were analyzed and compared, giving identical spectra. Tests on specific toners used in different copiers yielded matching spectra also (Mazzella, et al., May 1991). These two findings are significant. The first allows for comparison tests to be done between raw toners as the known source and extracted toners as the unknown. The

second indicates that different copy machines do not cause the same type of toner to produce different spectra. The data for laser printer toners was suggestive of similar results.

Clearly, more research is needed with regards to the analysis of toners. Relying on a small set of studies has inherent dangers. Without studies of confirmation of results and conclusions, assumptions by future researchers based on past studies may be faulty. These assumptions may then lead to flawed or irrelevant studies conducted and incorrect conclusions reached.

The following research attempts to extend the analysis of toners by DRIFTS to include a greater number of laser printer toners.

PROCEDURE

Laser printer toners are collected in both the raw and printed form. The raw toners need only to be mixed with KBr to be prepared for analysis. The toners in the printed form first need to be extracted from the paper. This is done by heating a microscope slide on a hot plate, placing the slide on the printed paper, and removing the slide. The toner is melted by the hot slide and lifted off the paper. The toner on the microscope slide is then scraped off using a razor blade and mixed with KBr.

A small amount of KBr is ground using a Wig-L-Bug® for approximately 15 seconds. This grinds the KBr into a fine powder, which is desirable for DRIFTS. A portion of the ground KBr is placed into a microcup, which is approximately three mm in diameter and two mm deep. The toner sample is then added to the unused portion of KBr in an estimated 10:1 ratio of KBr:toner. This mixture is ground with the Wig-L-Bug® for an additional 15 seconds to produce a fine, intimate mixture. This sample is placed in another microcup. Both microcups are taken to the DRIFTS unit for analysis.

For the first nine toner samples, a Nicolet FTIR fitted with a DRIFTS unit was used for the testing. With this machine, the main bench and the DRIFTS unit use the same fitting apparatus, which means that the main bench needs to be replaced by the DRIFTS unit every time testing is done. After placing the DRIFTS unit in the machine, the laser beam needs aligning in order to be aimed at the sample in such a way as to permit the most reflectance of infrared radiation. This is accomplished by raising or lowering the apparatus on which the

microcups are seated.

When the bench is aligned, the sample is placed on the microcup seat and the door to the DRIFTS unit is closed. Because water and carbon dioxide distort spectra significantly, a wait of approximately 15 minutes is involved to allow the gases in the chamber to purge. After the fifteen minutes elapse, 200 scans of the toner sample are taken. The toner sample is replaced by the background sample and, after 15 minutes of purging, 200 scans of the background are taken. The computer Fourier transforms the spectra of the samples, and the infrared spectrum of the toner is seen.

This spectrum needs to be converted to absorbance using a function of the computer. The spectrum's baseline then needs correcting, as it is prone to drifting during the run. A straight baseline is obtained in order to compare two or more spectra. The baseline scale is then set so that the minimum absorbance is equal to zero, since the computer's software did not contain this function.

After these nine spectra were collected, the computer system supporting the FTIR crashed, preventing any additional spectra from being taken. A newer Nicolet model, with more advanced computer programming was ordered, which allowed the spectra on the old model to be transferred without the loss of data. Five of the samples which were analyzed on the old model were again analyzed on the new model in order to test the consistency between the models. In each case, the original spectrum and the new spectrum were indistinguishable. With these results, testing continued.

The newer model has the DRIFTS unit in a compartment by itself, which means that it is permanently mounted and requires aligning only once. The new DRIFTS unit has a detector that requires extremely low temperatures to operate at a satisfactory level. Liquid nitrogen needs to be added to the detector at the beginning of every day of research, and after every two or three hours of use.

The remaining toners were analyzed on the newer model, using the same procedures as before, except there is no wait for the gases to purge. The new model has a function that eliminates the water and carbon dioxide peaks without having to purge for fifteen minutes, and this function is set up according to the manual.

The toners' spectra are saved on the hard drive, and a library of laser printer toners is formed of the 26 toners. A report form is made for the toners to print out the whole spectrum (4000 - 650 wavenumbers), with the "fingerprint" region (2000 - 650 wavenumbers) directly beneath it. The 26 spectra are printed using this report form.

Another function of the computer displays the wavenumber of all of the peaks above a certain threshold. These results are noted for comparative purposes, and the toners are placed into groups according to distinguishing peaks.

Raw toners were labeled T001 through T016, and toners extracted from paper were labeled T101 through T109.

When the collection of toner spectra ended and the spectra were entered into a searchable library, several toners were retested and checked against the library. Promising, yet cautionary, results were obtained, which will be discussed later. In addition, tests were performed to check the accuracy of assigning toners to groups.

RESULTS

The 26 toners displayed several different spectra. Based on distinguishing peaks, 13 groups were formed. The largest group contained four toners, and six of the toners were placed into an individual category. Twenty-three of the toners shared eleven prominent peaks, and were broken down by the presence or lack of additional peaks. The remaining three toners had little in common with the others, but shared some similarities with each other.

It should be noted that there are error margins for the peaks. Sharp peaks may vary by up to two wavenumbers, while broad peaks may vary by as many as ten wavenumbers. The reason for the variations is that the computer's resolution is two wavenumbers. This means that peaks differing by two wavenumbers or less are not able to be distinguished by the computer. The broad peaks' error margin results from the absorbance of radiation throughout a broad region of the infrared spectrum. When the computer labels a broad peak at a certain wavenumber, it chooses the highest point of the peak as the spectrum is displayed. A slight adjustment of the baseline may alter the point at which the computer labels the peak.

Group I consists of a single toner that contains only the eleven basic peaks (Figure 2). Toner in Groups II through X consist of the eleven basic peaks plus the additional peaks that set them apart from the rest. Toner in Group II contain a peak at 1780 wavenumbers (Figure 2). Toner in Group III absorb at 1780 and 1376 wavenumbers (Figure 2). Group IV toners have a small peak at 1269 and have no significant absorbance at 1376 (Figure 2).

Toners in Group V have a small peak at 1376, no significant peak at 1269, and a significant peak at 1114 (Figure 2). Group VI toners have a large peak at 1376 and no peak at 1269. A small peak is present at 1114, but it is much less pronounced than that in Group V (Figure 2). Group VII toners have significant peaks at 1376, 1269, and 1114 (Figure 3). Toners in Group VIII contain Group VII's peaks, but the peak at 1269 is much smaller than the peak at 1160 (Figure 3). Also, a small peak at 1780 may be present. Group IX toners have the same peaks as Group VII, and also a significant peak at 1347 (Figure 3). Toners in Group X contain similar peaks to those in Group VII, but two of the peaks are shifted more than the two wavenumbers allowed for narrow peaks and ten wavenumbers for broad peaks. There is absorption at 1724, and not 1729; there is absorption at 1180, and not 1160. In addition, there is a peak at 970 (Figure 3).

Groups XI through XIII contain toners that differ markedly from those in Groups I through X. Further, Group XI and XII toners have very few peaks in common with each other (Figure 3). The toner that makes up Group XIII shares several peaks with the Group XI toner, and several others with the Group XII toner (Figure 3).

The groups, with the toner labels and distinguishing peaks are printed in Appendix B.

A limited blind test was conducted to test the library's ability to match the new spectrum with the spectra in the library and to test the grouping of the toners discussed previously. This blind test was not a true blind test. The toner was known to be one that was collected and placed in the library. Therefore, the chance that the toner would not match any within the library was not present, as it should be in a true blind test.

When a spectrum is compared to the library of toners, the computer lists

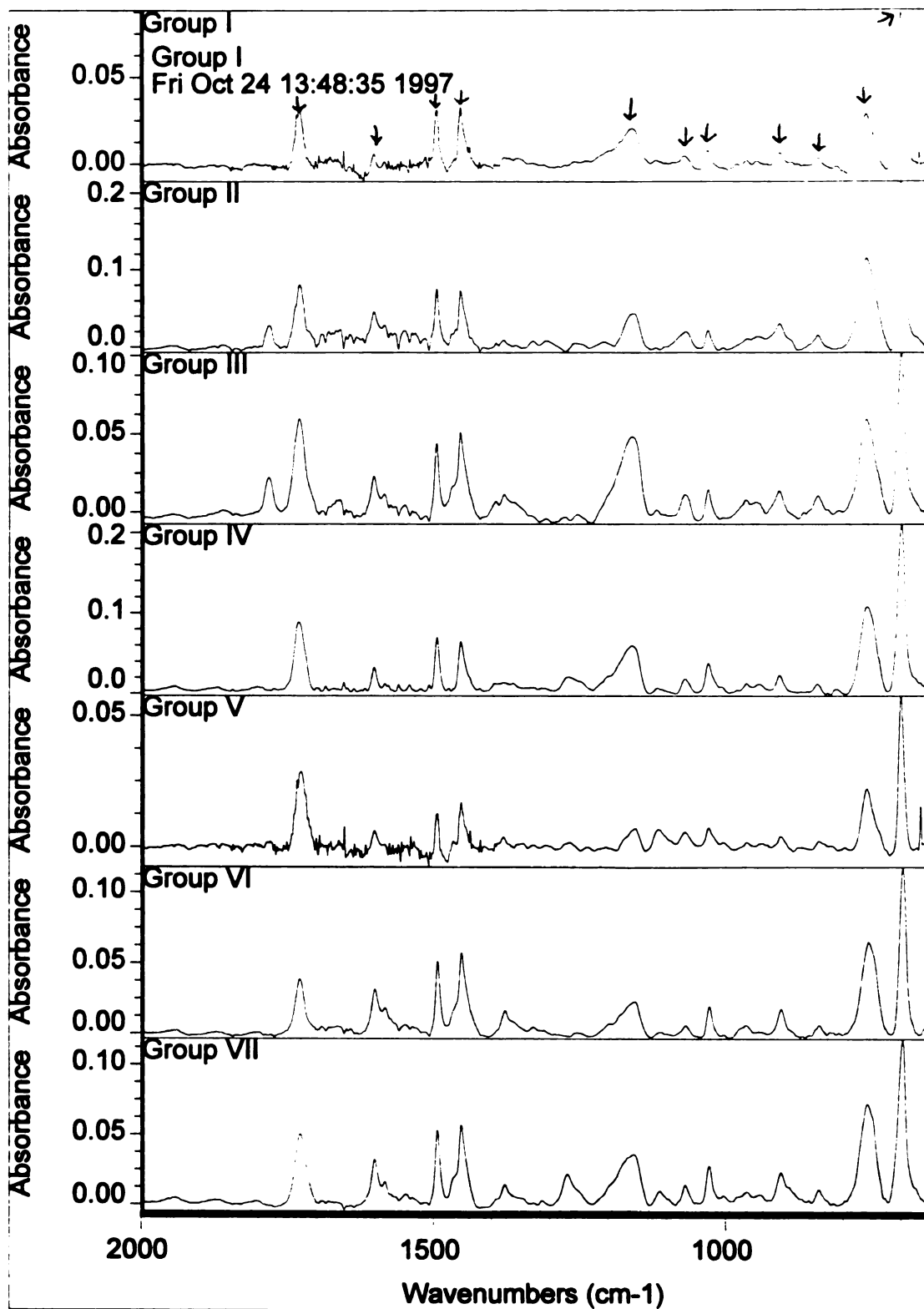


Figure 2 – Groups I through VII

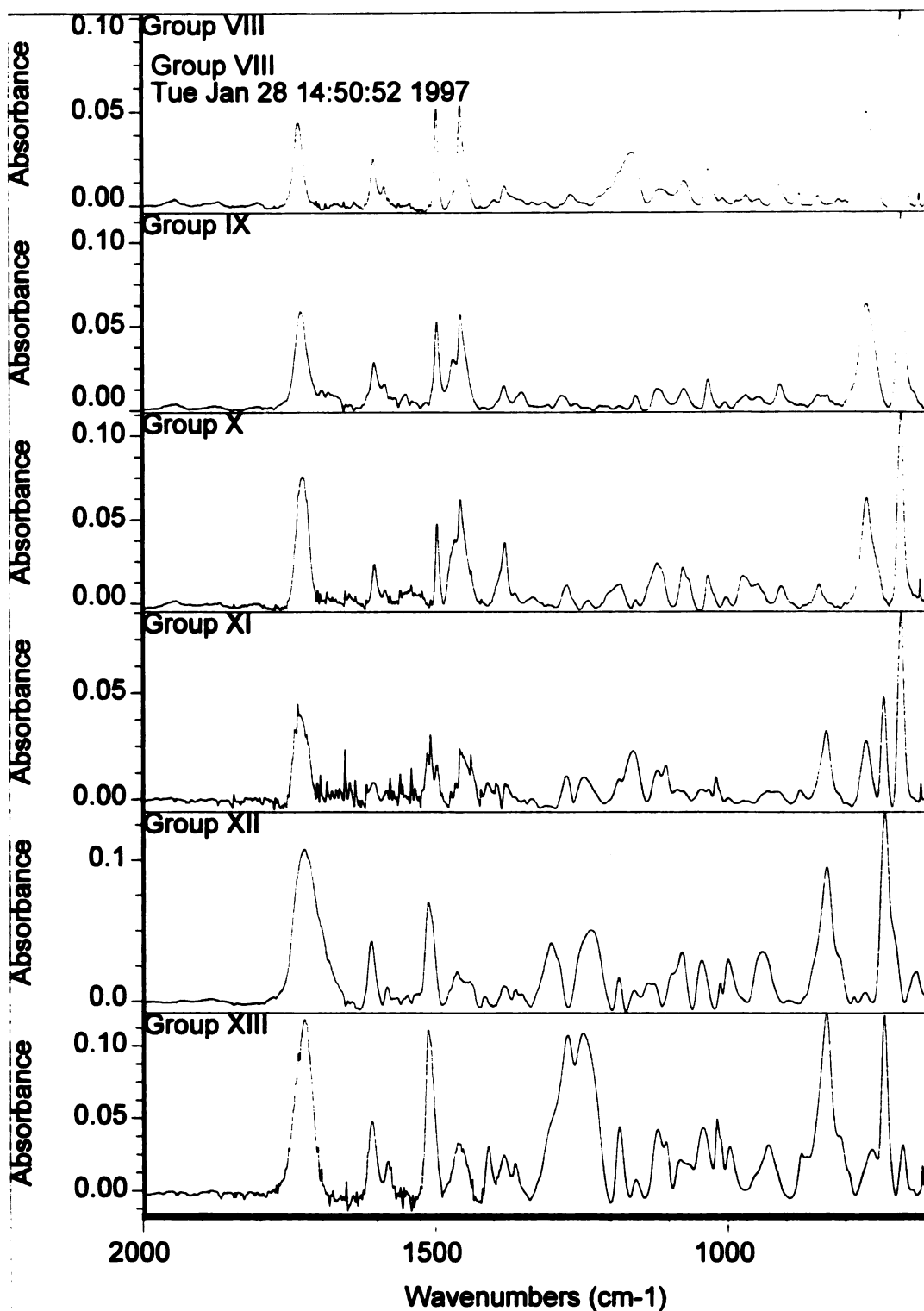


Figure 3 – Groups VIII through XIII

the top ten matches based on a 100-point scale. A match rating of 100 indicates a perfect match of the spectra. This scale is a quantitative matching based on the location and intensity of peaks. Out of these ten matches, the top four are displayed below the new spectrum.

When the blind test of a toner was performed in order to test the library, the library displayed the names and ratings of the top ten matches. Because T008 was accidentally added to the library in triplicate, three of these matches were for T008. Exclusion of two of these from further evaluation led to a total of eight toners which were compared to the unknown spectrum. Instead of comparing only the library's top four matches, the top eight were compared (Figure 4).

Because the spectra in the library have much poorer resolution than those saved on the hard drive, the according files were opened for a more telling comparison (Figure 5). By comparing the unknown toner with each of the library's top matches, some of the toners could be eliminated as the probable source. The toners are eliminated when the spectrum of the unknown is distinguishable from the spectrum of the known toner. The presence of a peak in one spectrum that is not present in the other spectrum is grounds for ruling that the two are from different toners.

A toner is not eliminated when its spectrum is indistinguishable from that of the unknown toner. Two spectra are indistinguishable when all of their peaks are found within the error margin of two wavenumbers. Further, the relative intensities of the peaks should be similar. In this research, relative intensities were considered in major peaks, that is, those that are at least ten percent of the height of the largest peak. Differences in relative intensities were considered distinguishable when one peak was at least twice as high as the other peak.

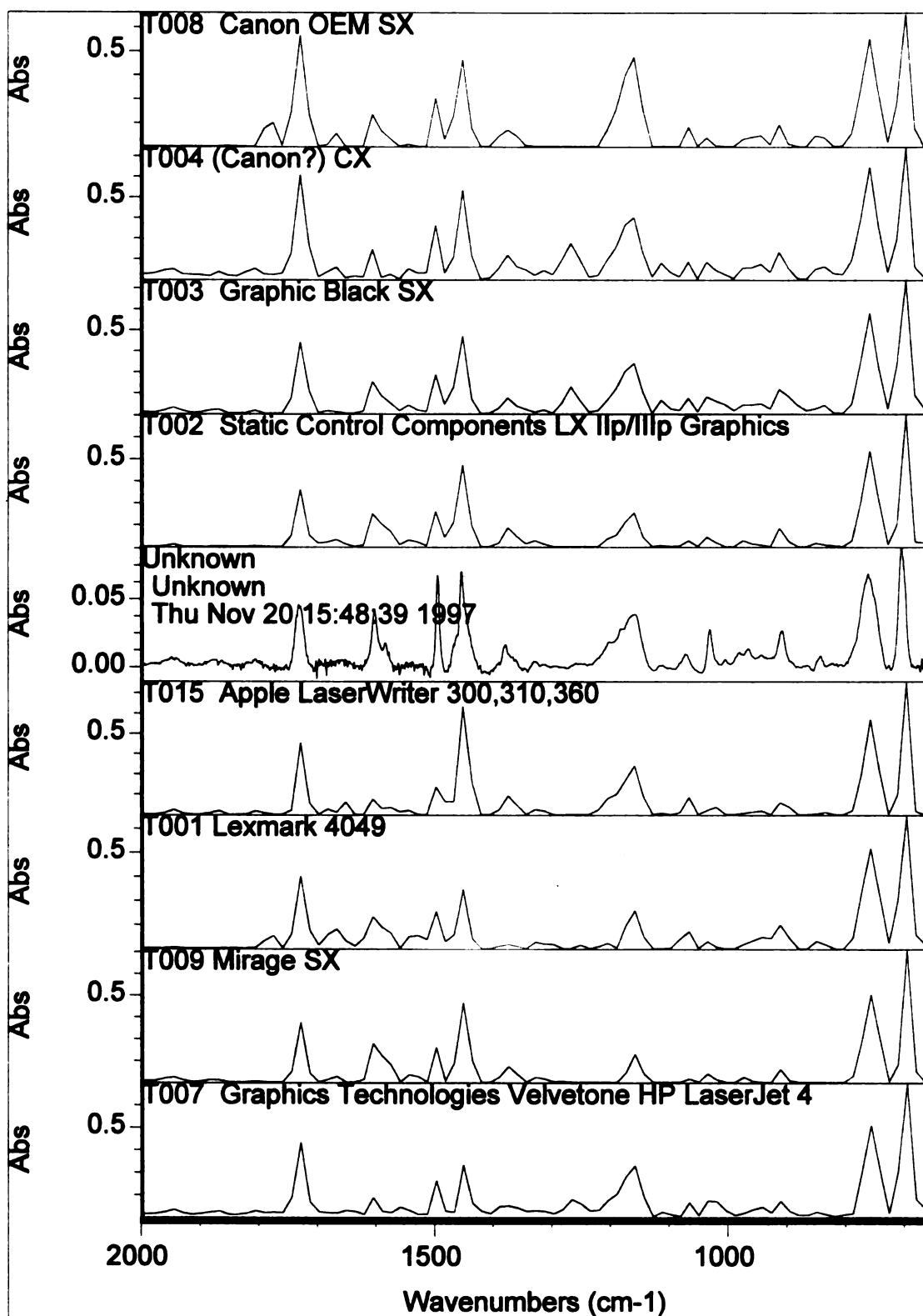


Figure 4 – Spectra of Top Matches from Library

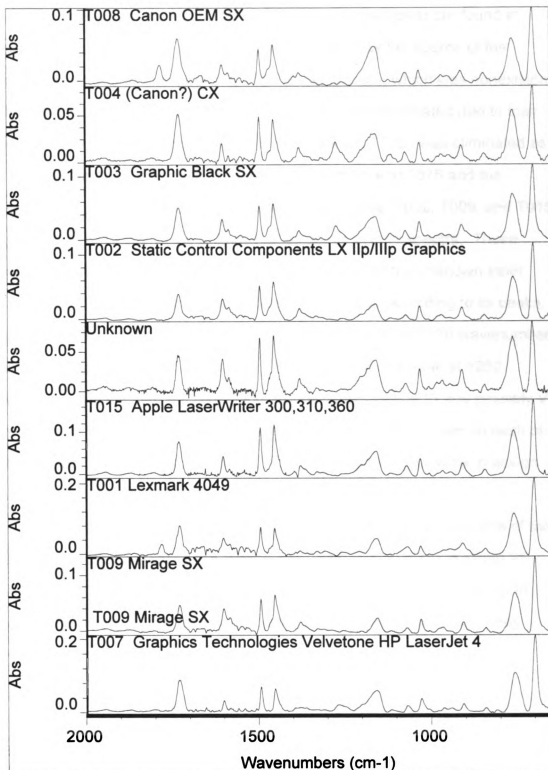


Figure 5 – Spectra of Top Matches from File

The overlays of the top matches with the unknown toner are found in Figures 6 through 9. T008 and T001 were eliminated as the source of the unknown toner due to their peaks at 1780 wavenumbers, which was nonexistent in the unknown toner's spectrum. T004 and T003 were eliminated due to their peaks at 1269, which was not present in the unknown. T007 was eliminated as the possible source by the lack of significant absorbance at 1376 and the presence of a peak at 1269. The three remaining toners, T002, T009, and T015, displayed peaks similar to the unknown at all points in their spectra. These three, therefore, could not be eliminated as the source of the unknown toner.

Next, the unknown toner was placed into a group according to its peaks. In addition to the eleven basic peaks, it possessed a peak at 1376 wavenumbers. This eliminated Groups I, II, IV, and XI – XIII. The lack of a peak at 1269 wavenumbers eliminated the remaining groups except Group VI and possibly V. By comparing the unknown's absorbance at 1114 with that of toners in each of these groups, Group V was eliminated. The logical choice would be to assign the unknown toner to Group VI.

In fact, the unknown toner was learned to be T009, which was one of the three finalists after searching the library, and which is a member of group VI. The other finalists in the library search, T002 and T015, are also in Group VI, which further validates the grouping of laser printer toners discussed in this thesis.

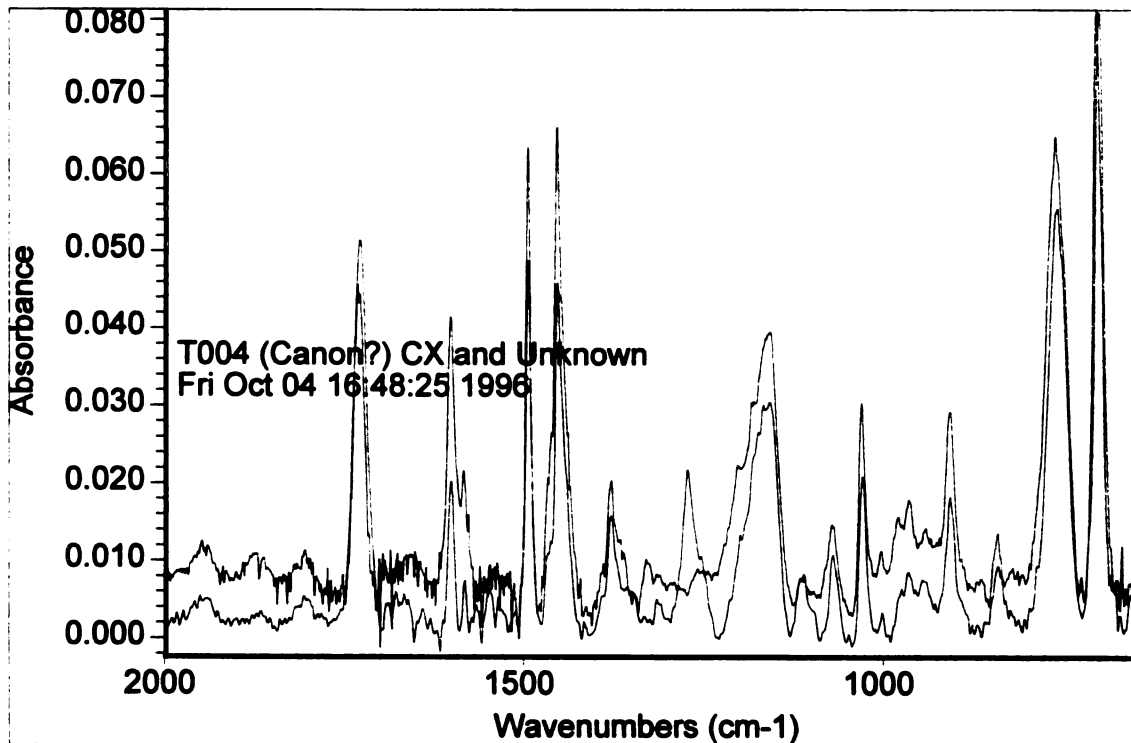
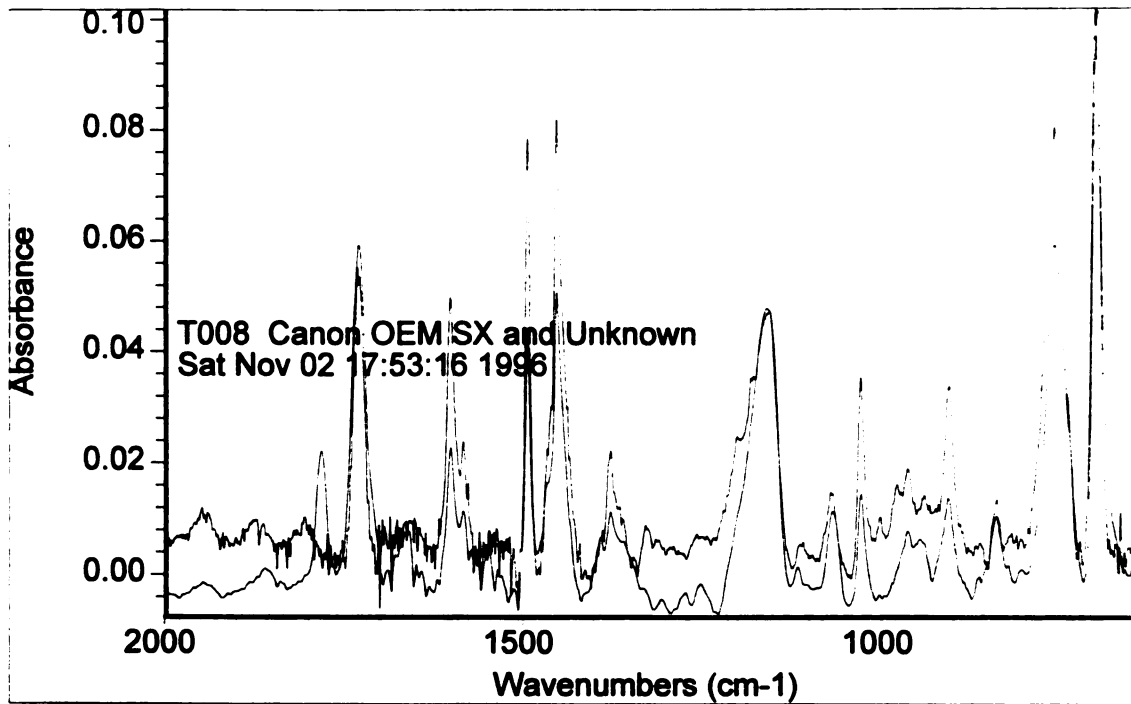


Figure 6 – Overlays of Unknown with T008 and T004

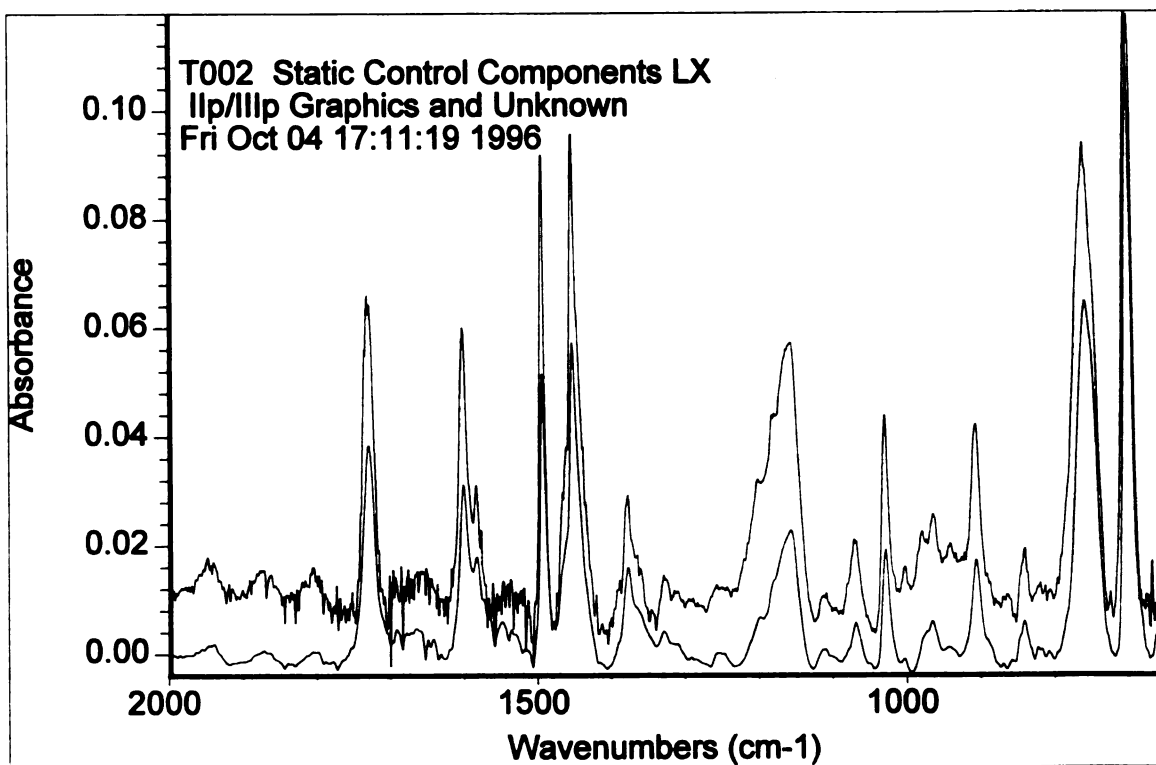
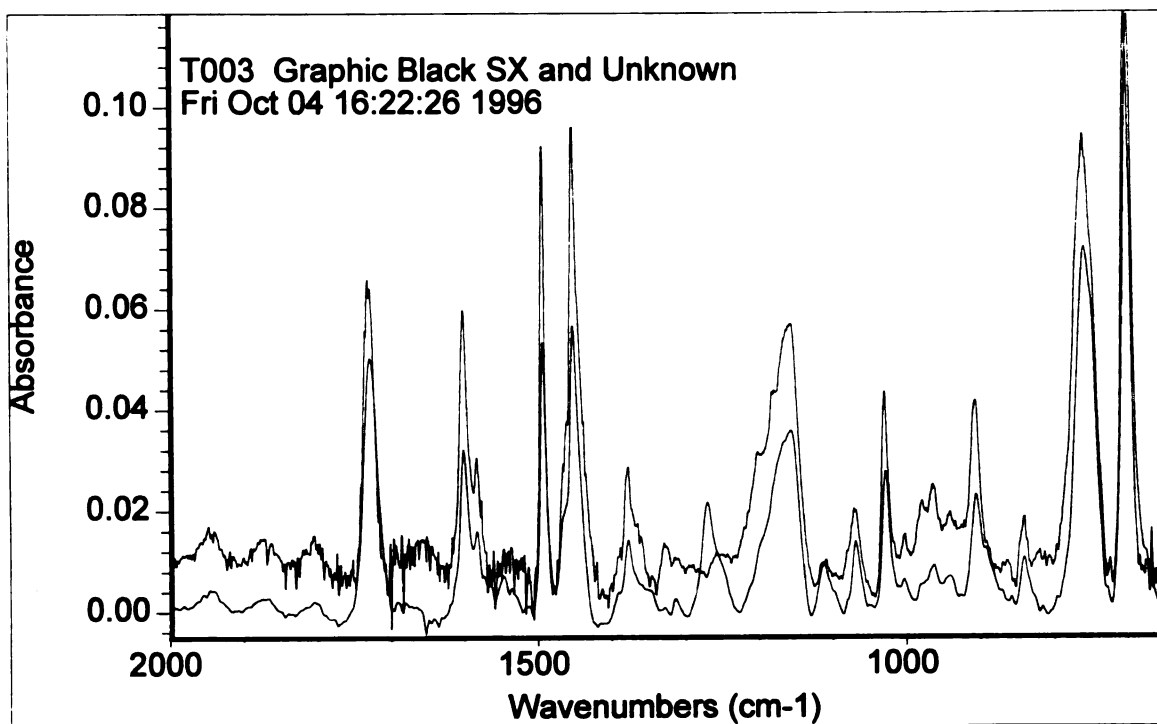


Figure 7 – Overlays of Unknown with T003 and T002

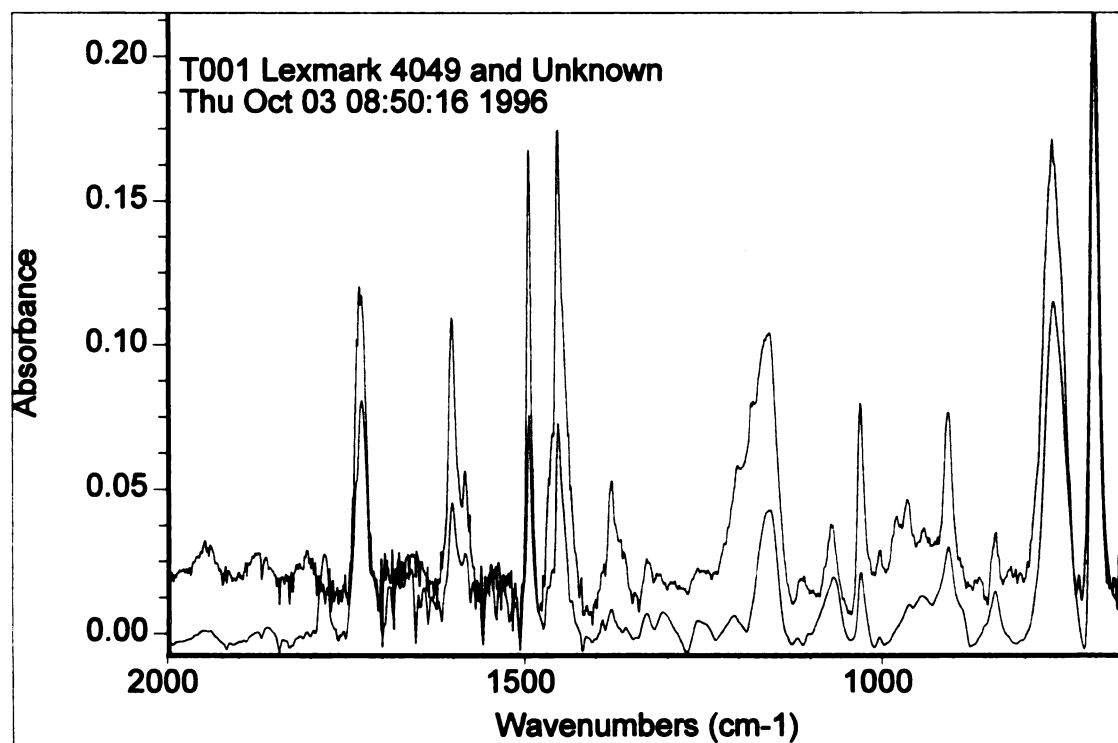
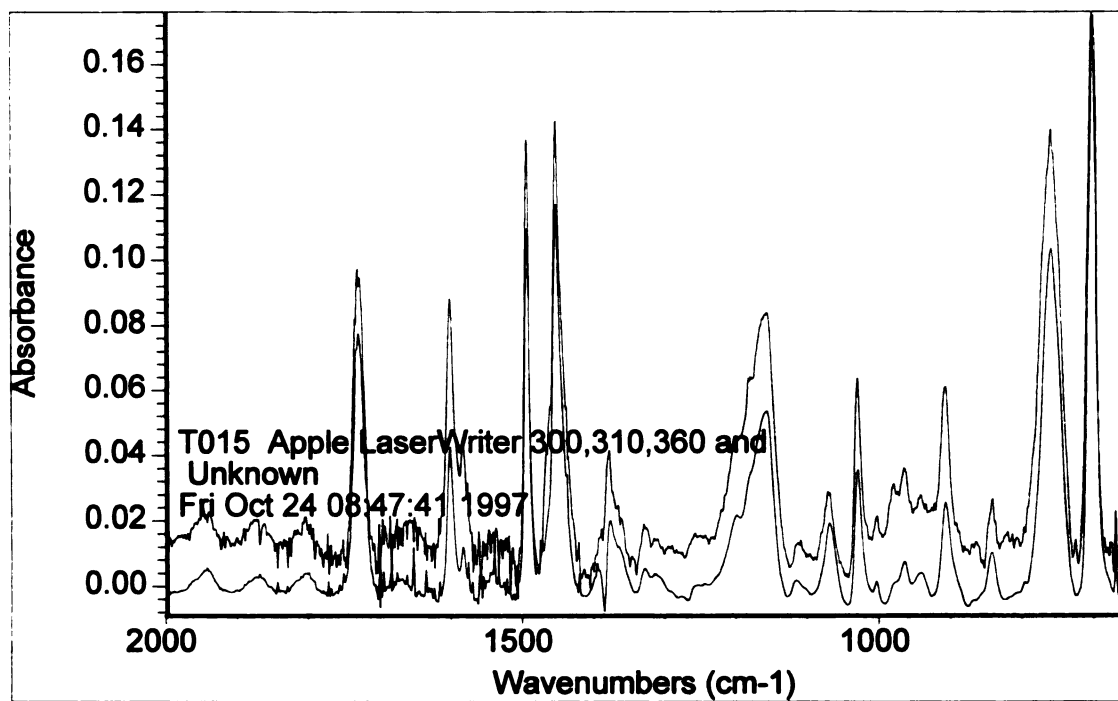


Figure 8 – Overlays of Unknown with T015 and T001

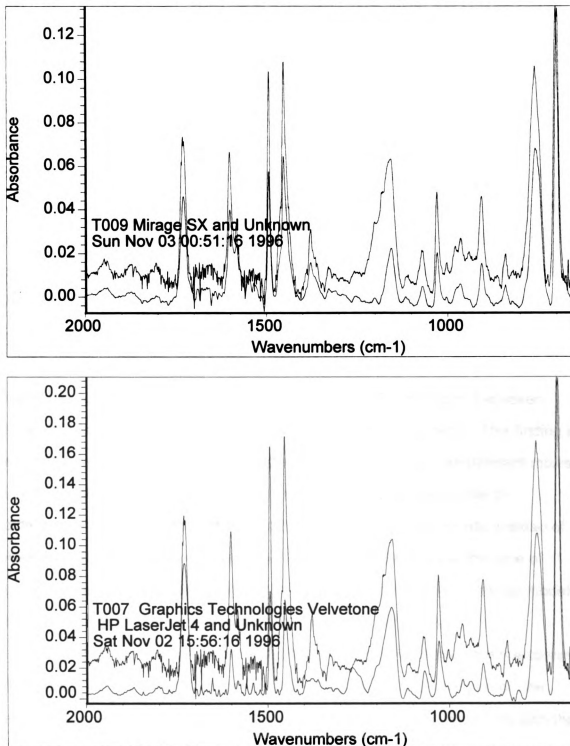


Figure 9 – Overlays of Unknown with T009 and T007

DISCUSSION

The goal of this project was to evaluate DRIFTS as a method to differentiate laser printer toners. This research has shown that DRIFTS is a valuable technique in distinguishing between laser printer toners. Laser printer toners contain differences in chemical makeup, which can be used to differentiate between them using DRIFTS. The toners did not all display unique spectra, but were broken down into classes containing between one and four toners.

It is interesting to note that the toners which were known to be of the same brand did not necessarily fall into the same groups. For example, the seven Hewlett Packard laser printer toners were placed into four groups. This finding is evidence that the companies that produce laser printer toner use different mixes in their types of toners. Knowing this, it is possible for the researcher to differentiate not by company, but by individual toner. In other words, instead of identifying the company who made the toner, the results indicate the type of toner. Since the type of toner is specific to a single or small set of printer models, the spectrum links the sample to this set of laser printer models.

In forensic science, almost all tests are comparison tests. In a questioned documents case in which the document was prepared on a laser printer, the examination would be to compare the toner of the questioned document with that of a document of a known source to determine if they could have come from the same source. This research provides evidence that laser printer toners can be distinguished using DRIFTS, and would prove useful for this examination. If the

spectra of the two documents' toners were distinguishable from each other, the known source could be eliminated as the possible source of the questioned document. If, on the other hand, the spectra were indistinguishable, the source of the known document could not be ruled out as the source of the unknown. With class evidence, which is what this evidence is, the value comes in excluding possible sources of the questioned document. This research has shown that DRIFTS can exclude toners on the basis of their infrared spectra.

Another notable finding is that toners manufactured by different companies for use in the same printer model produced distinguishable infrared absorbance spectra. For example, in addition to the toner made by Hewlett Packard for their LaserJet 4 printers, Graphics Technologies makes a toner designed for this printer. The spectra of these two toners are distinguishable. This means that the same manufacturer is not used among toner companies for toners made for the same model. The significance of this finding is that if a certain printer can use two different toners, and an unknown toner sample's spectrum is indistinguishable from one of these, then the printers using the other toner can be eliminated as the source of the unknown. In the example from above, if a spectrum indistinguishable from that of Graphics Technologies' toner for the LaserJet 4 was obtained from a questioned document, laser printers that contained toner from Hewlett Packard could be eliminated as the possible source of the questioned document. However, this only holds for printers that have used only one of the two types of toners during the timespan in question.

Of the eight toners that were retested and compared to the toner library, the library search results indicated that the correct toner was the first or second best match five of these times. On two occasions, however, the correct toner was not in the top five choices, as given by the computer's rating of the degree of match between the tested toner and the toners in the library. The reason for this

is that the resolution of the spectra that are saved in the toner library is much lower than that of the toners when they are tested. When a spectrum is saved to a library, the resolution is decreased in order to accommodate more spectra in the same amount of memory. The result of this is that the spectra in the library may be missing small peaks or may contain peaks shifted by up to eight wavenumbers.

When the computer searches the library to compare a recently acquired spectrum, it is not infallible. Discretion must be exercised by the operator in determining whether there is a match or not. When the computer provides the spectra that are most like the new spectrum, the operator should open the files that correspond to these spectra to compare the original spectra. This practice reduces the shifting of peaks to a maximum of two wavenumbers. When a narrow peak from one spectrum is three wavenumbers different than a peak on a second spectrum, there is a difference between the spectra.

Although a database of 26 laser printer toners is by no means exhaustive, this provides a solid base for future research and for practical use. Researchers in the future may add spectra from additional toners as the toners become available. The new toners may be placed into the groups defined in this research or, if other distinguishing peaks are present, new groups may be formed.

In theory, spectra from DRIFTS collected from one instrument should be interchangeable with DRIFTS spectra from other instruments. In other words, a spectrum of a toner from one DRIFTS unit should be similar to a spectrum of the same toner produced on another DRIFTS unit. The presence of searchable libraries of spectra obtained from infrared analysis indicates that FTIR instruments produce interchangeable spectra. Also, the spectra obtained in this research came from two different units, which produced indistinguishable spectra when testing the same toner.

The reason interchangeable spectra are produced is because DRIFTS does not depend on the settings of the machines such as temperature, flow rate, or length or type of column. Instead, DRIFTS measures a physical characteristic of matter, infrared absorption, that is present at any given time. Any differences between spectra from DRIFTS units would possibly be the result of different resolutions of the detector, which would affect the sharpness of the peaks, but not the wavenumbers at which the infrared radiation is absorbed.

The practical use of this research comes in questioned document analysis. When a document that has been printed with a laser printer is analyzed, the examiner may perform DRIFTS of the toner and compare its spectrum to that of known sources. If the toners display distinguishable spectra, then the sources of the two documents are different.

In cases in which there is no known source with which to compare the questioned document, this research provides a base from which to begin. The laboratory conducting the examination could obtain a disk with the 26 toners' spectra, and the spectrum from the toner of the questioned document could be compared to those on file. If the spectrum was indistinguishable from any of the toners, then the laser printers that use these toners are possible sources. All of the printers that use toners whose spectra are distinguished from the questioned document's toner's spectrum would be eliminated as the source. Although this research is most useful in providing evidence of the characterizability of laser printer toners using DRIFTS in order to distinguish a questioned document from possible known sources, it can provide a starting point in a case that contains no suspected sources.

This research would be more useful in this regard if the entire population of laser printer toners were analyzed. Unfortunately, laser printer toners are not easily obtained from the companies that manufacture or distribute them. This

research contains 26 of the estimated 50 toners on the market in the United States.

An examiner would yield the optimum results if DRIFTS analysis of toners was used in conjunction with another differentiating method, such as pyrolysis GC/MS. The toners could be analyzed first by DRIFTS and placed in a group. The next step would involve subjecting the toners with spectra that match the questioned document to pyrolysis GC/MS, which possibly could differentiate between the toners within the group.

Future research in this area should focus on extending the database of DRIFTS spectra and attempting other tests to differentiate between toners within the groups defined in this study. Pyrolysis GC/MS has provided promising results to meet this need. High-performance liquid chromatography (HPLC) could possibly be used to differentiate toners based on the synthetic organic resins present in the toners.

This research showed that it is possible to differentiate laser printer toners based on infrared absorption using DRIFTS. The results did not show that the toners were individualizable, but many different spectra were seen, and the toners were grouped accordingly. The field of questioned document analysis benefits from this research. Documents printed by a laser printer are able to be differentiated by the type of toner, and therefore by the brand and model of printer. This is an additional piece of evidence that may be used to determine the outcome of the case, which is the ultimate goal of all forensic science examinations.

APPENDICES

APPENDIX A

T001 Lexmark 4049
T002 Static Control Components LX – IIP/IIIP Graphics
T003 Graphic Black SX
T004 (Canon?) CX
T005 Laser1 Aspen Toner
T006 Graphics Technologies Legend HP LX Graphics
T007 Graphics Technologies Velvetone HP LaserJet 4
T008 Canon OEM SX
T009 Mirage SX
T010 No Brand – SX only
T011 Oasis Eclipse EX
T012 Older LX – Unknown Brand
T013 Static Control Components SX – Ultra Graphics
T014 Ricoh FT Type 410
T015 Apple LaserWriter 300,310,360
T016 IBM 4019
T017 Oasis Mirage 5P/VX
T101 Hewlett Packard LaserJet C3903A
T102 Hewlett Packard LaserJet 92298A
T103 Hewlett Packard LaserJet 92291A
T104 Hewlett Packard LaserJet 92274A
T105 Hewlett Packard LaserJet 92295A
T106 Hewlett Packard LaserJet C3900A
T107 Hewlett Packard LaserJet C3909A
T108 Brother TN-200HL
T109 Lexmark 1382150

APPENDIX B

Group I: T104
peaks: 1729 1601 1493 1452 1160 1070 1028 906 842 758 699

Group II: T001 T101 T105 T107
peaks: peaks from Group I; 1780

Group III: T008 T017
peaks: peaks from Group I; 1780 1376

Group IV: T007 T016 T109
peaks: peaks from Group I; small 1269; not significant 1376

Group V: T102 T103
peaks: peaks from Group I; small 1376; 1114; not significant 1269

Group VI: T002 T009 T015
peaks: peaks from Group I; large 1376; no 1269

Group VII: T003 T004 T013
peaks: peaks from Group I; 1376 1269 1114

Group VIII: T011 T012 T106
peaks: peaks from Group VII, but 1269 much smaller than 1160; small 1780 may be present

Group IX: T006
peaks: peaks from Group VII; 1347

Group X: T010
peaks: peaks from Group VII; 1724, not 1729; 1180, not 1160; 970

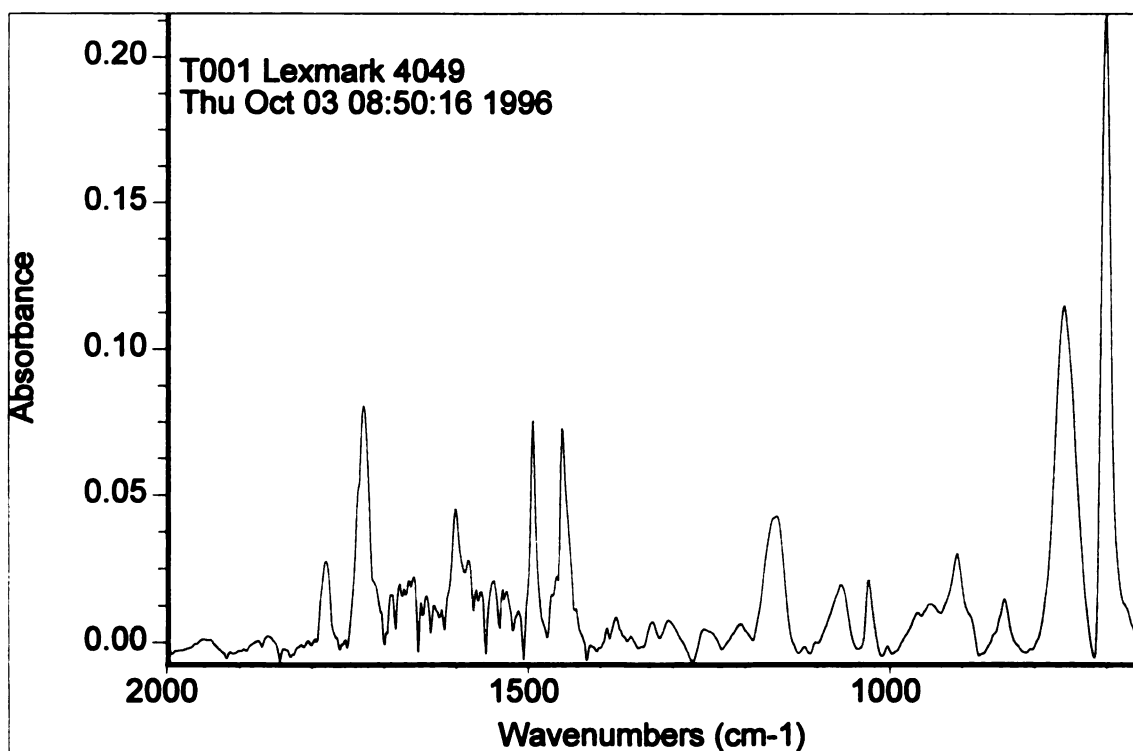
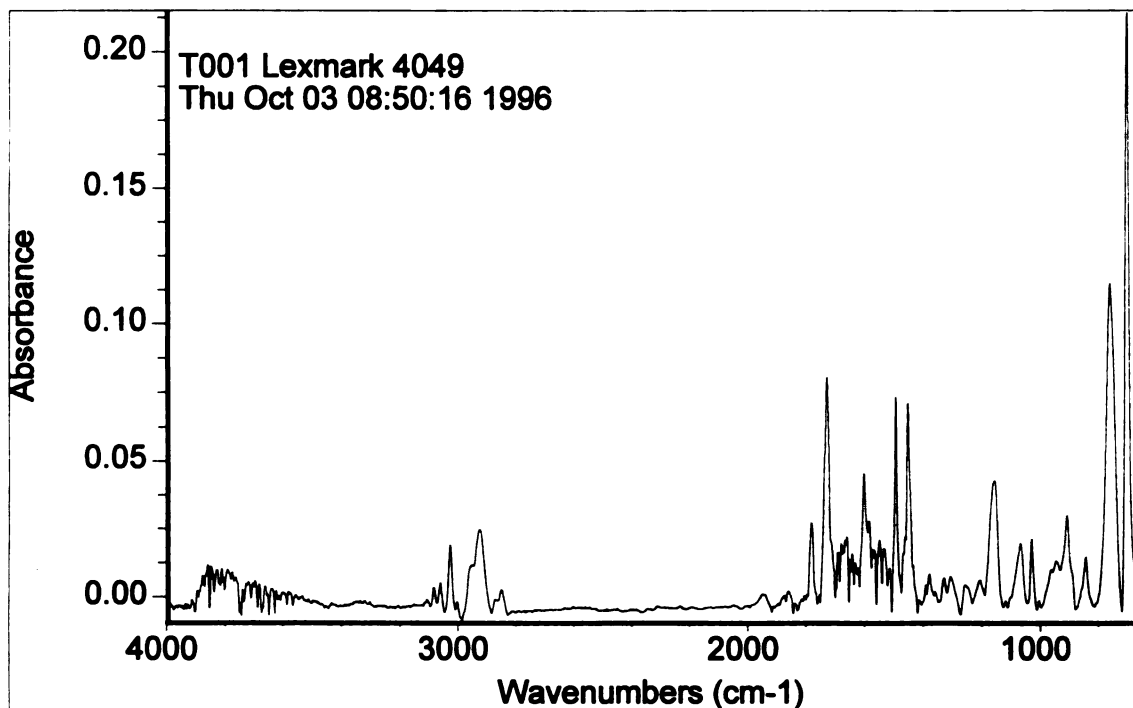
Group XI: T014
peaks: 1729 ~1500 ~1450 1272 1242 1158 1117 1103 1017 829 761
730 700

Group XII: T005
peaks: 1722 1607 1510 1461 1299 1231 1183 1075 1042 997 939 829
729 676

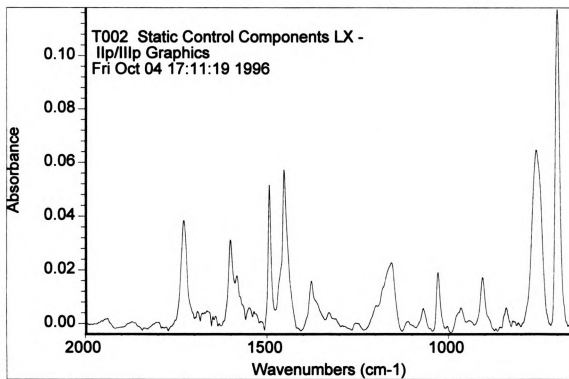
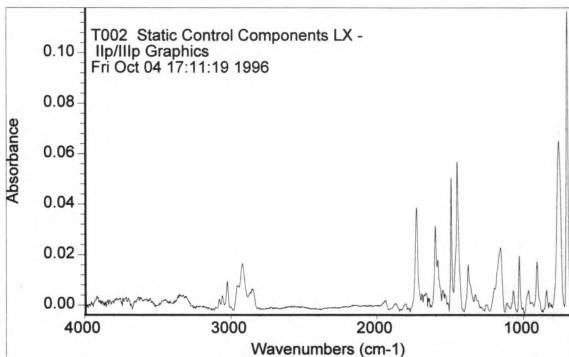
Group XIII: T108

**peaks: 1722 1607 1510 ~1456 1408 1271 1245 1183 1118 1041 1017
996 931 830 731 700**

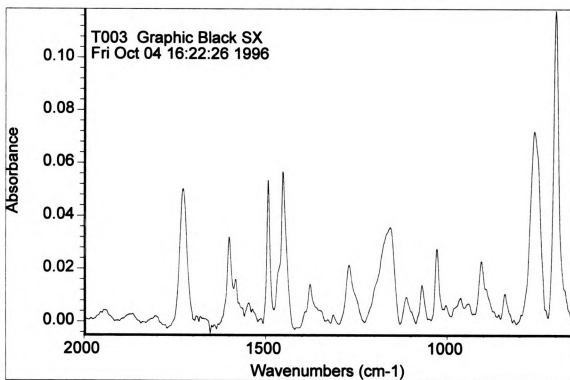
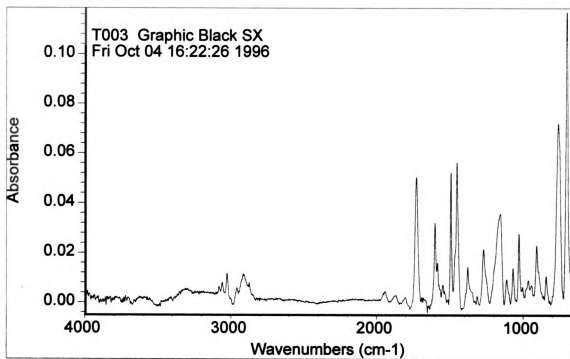
APPENDIX C



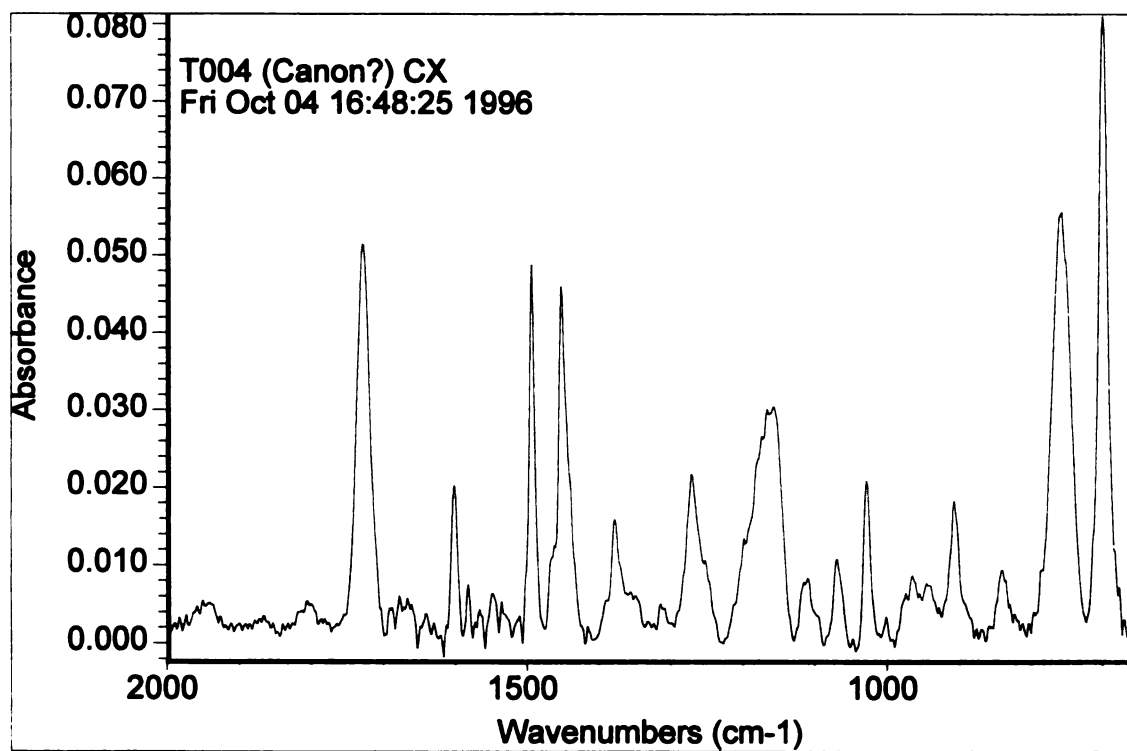
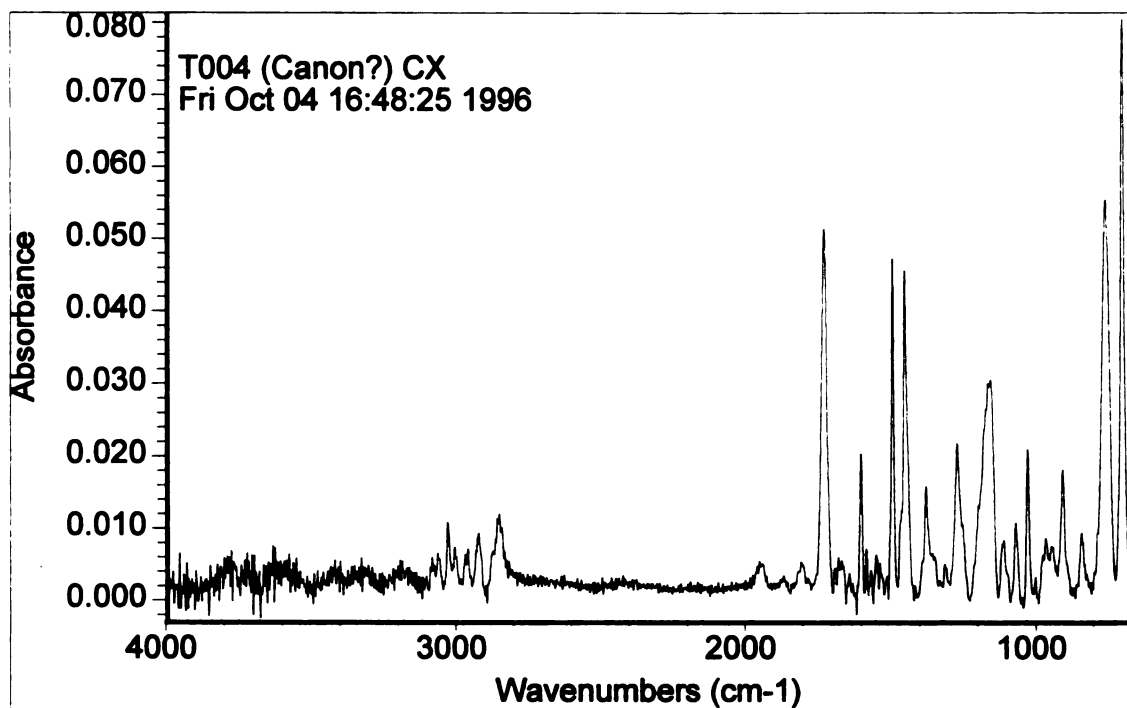
T001 Lexmark 4049



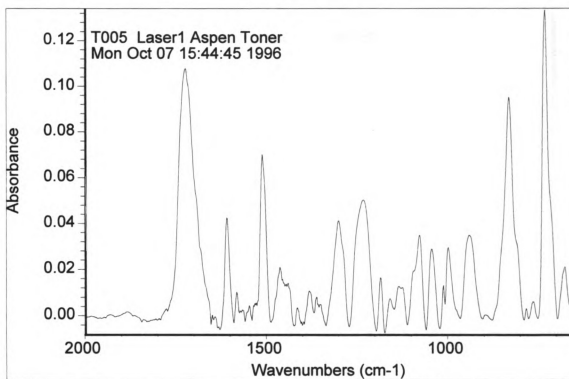
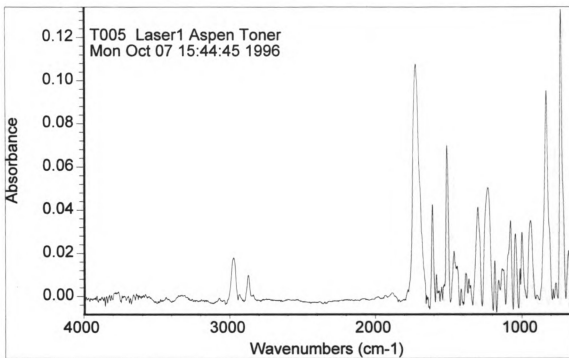
T002 Static Control Components LX - Ilp/Ilp Graphics



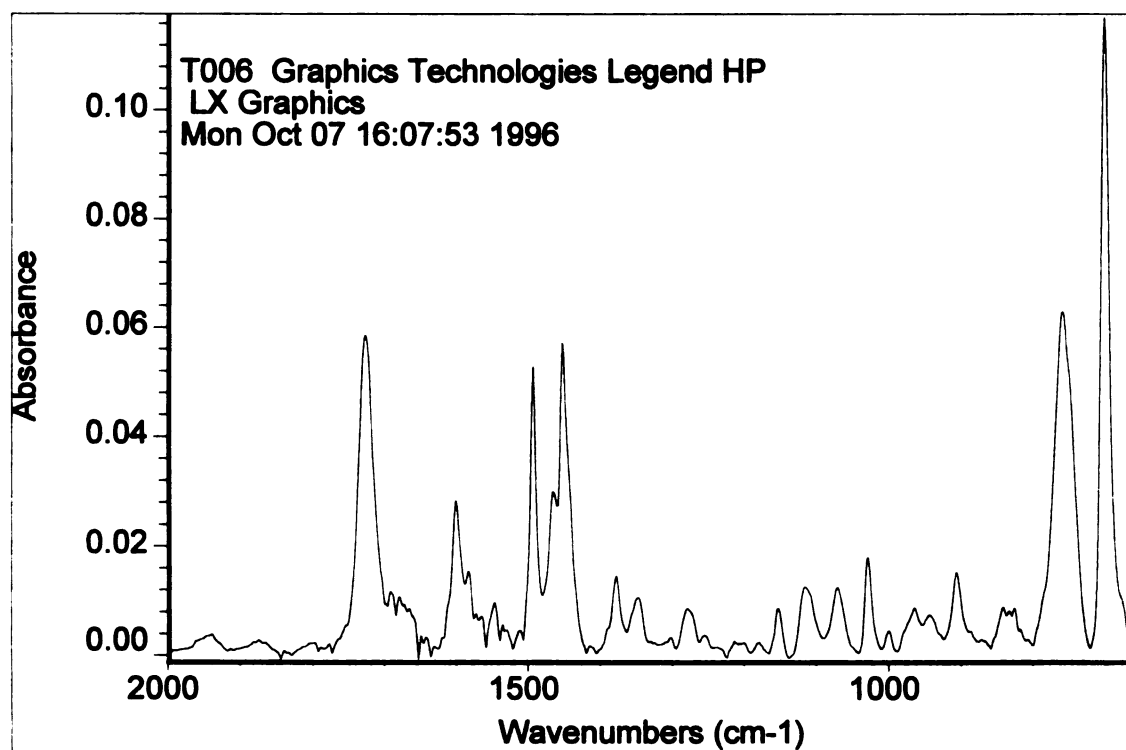
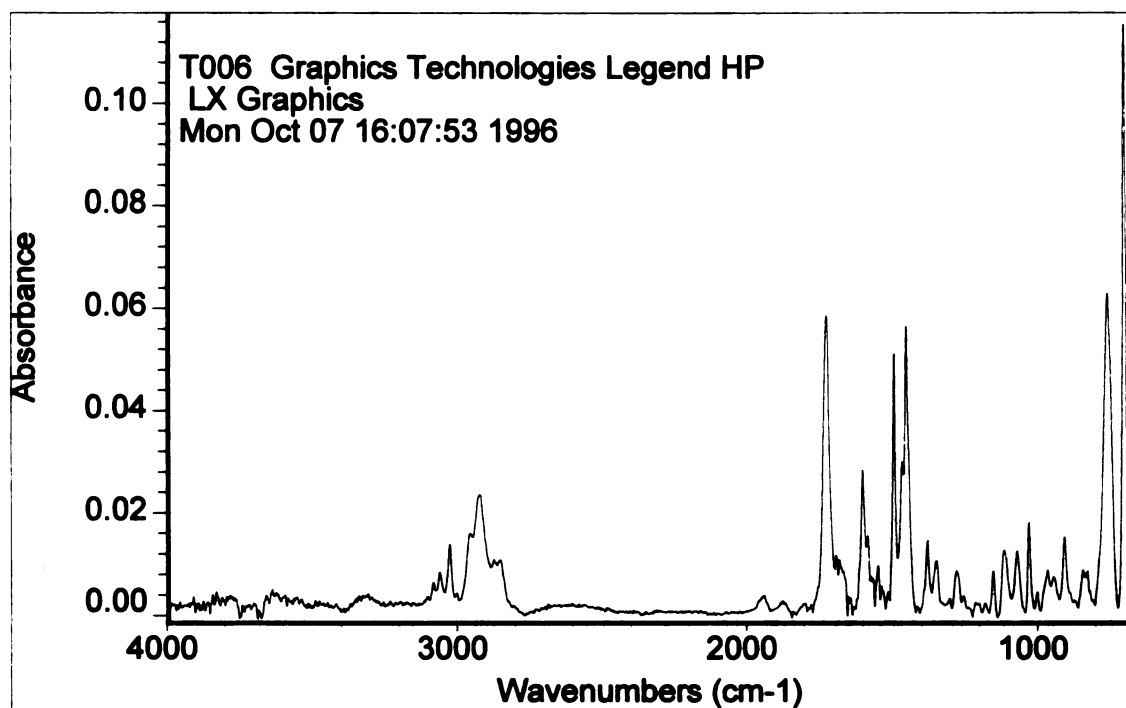
T003 Graphic Black SX



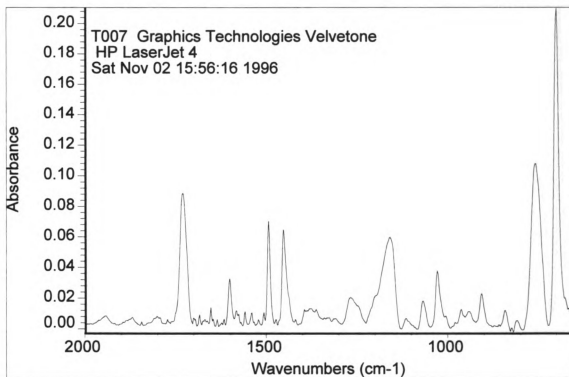
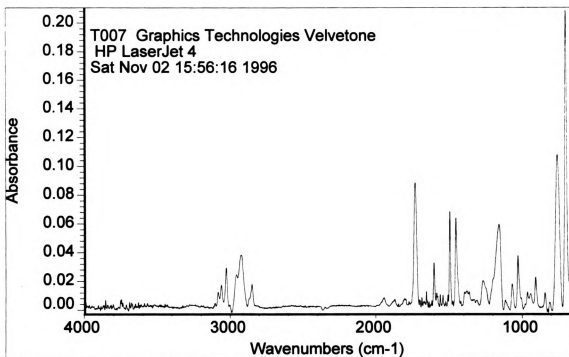
T004 (Canon?) CX



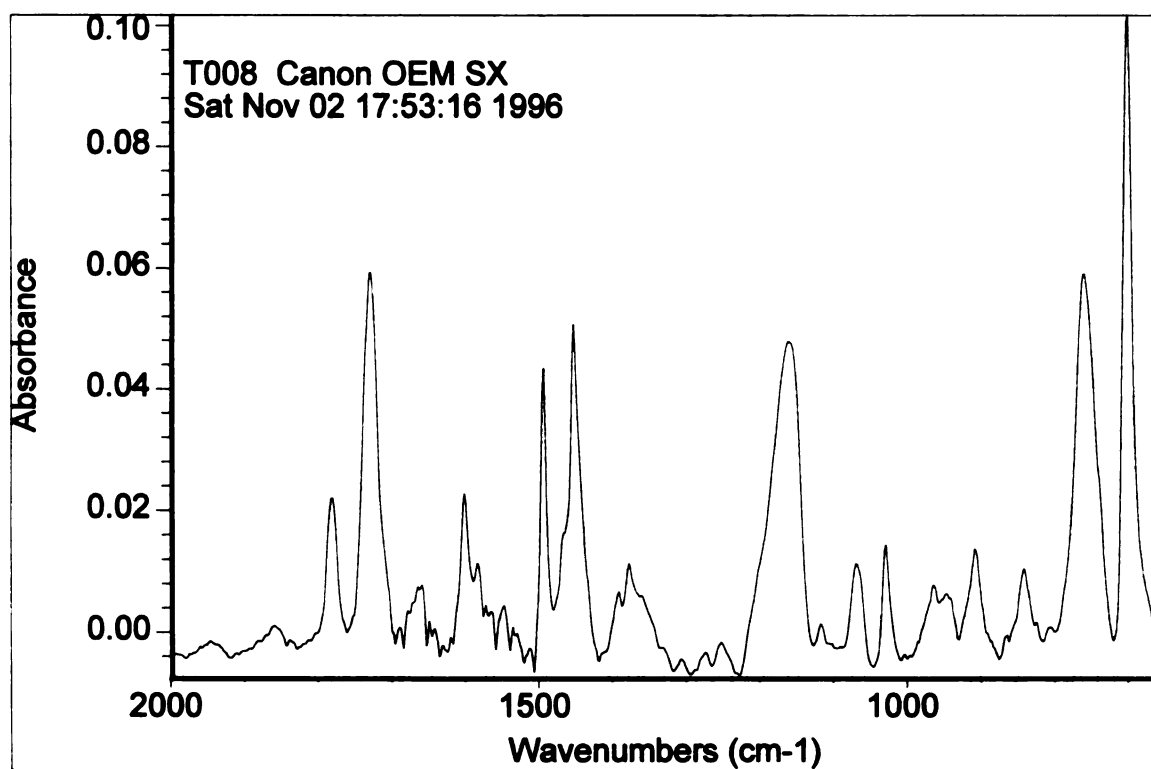
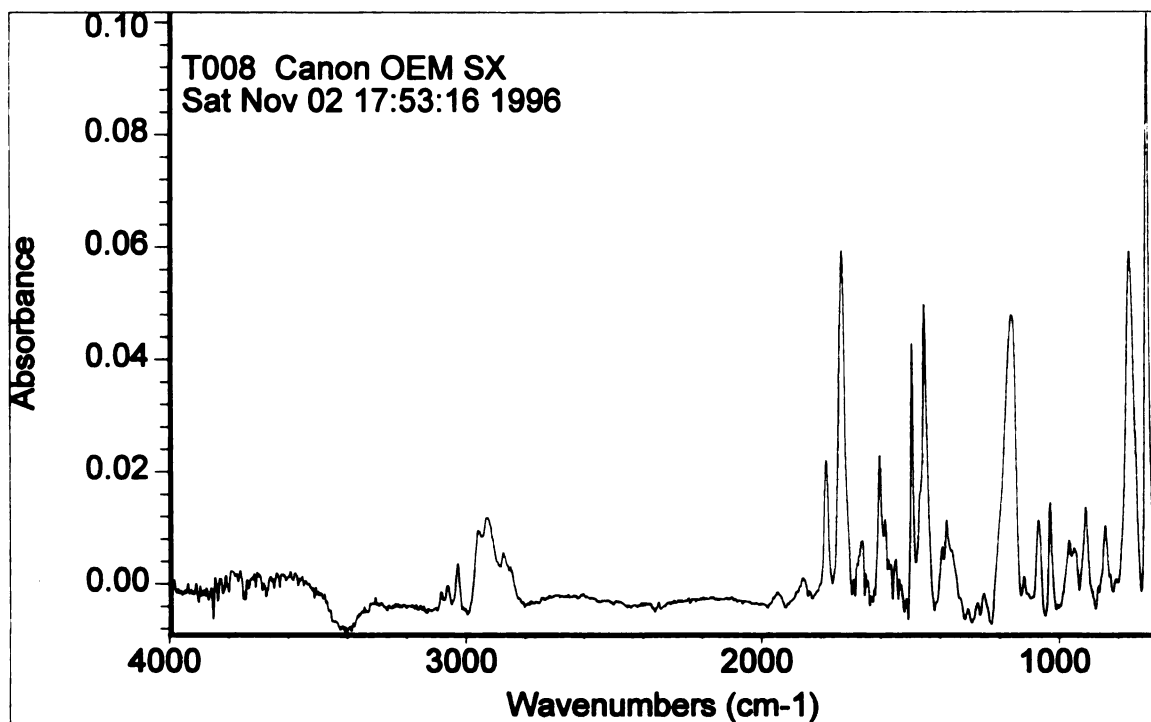
T005 Laser1 Aspen Toner



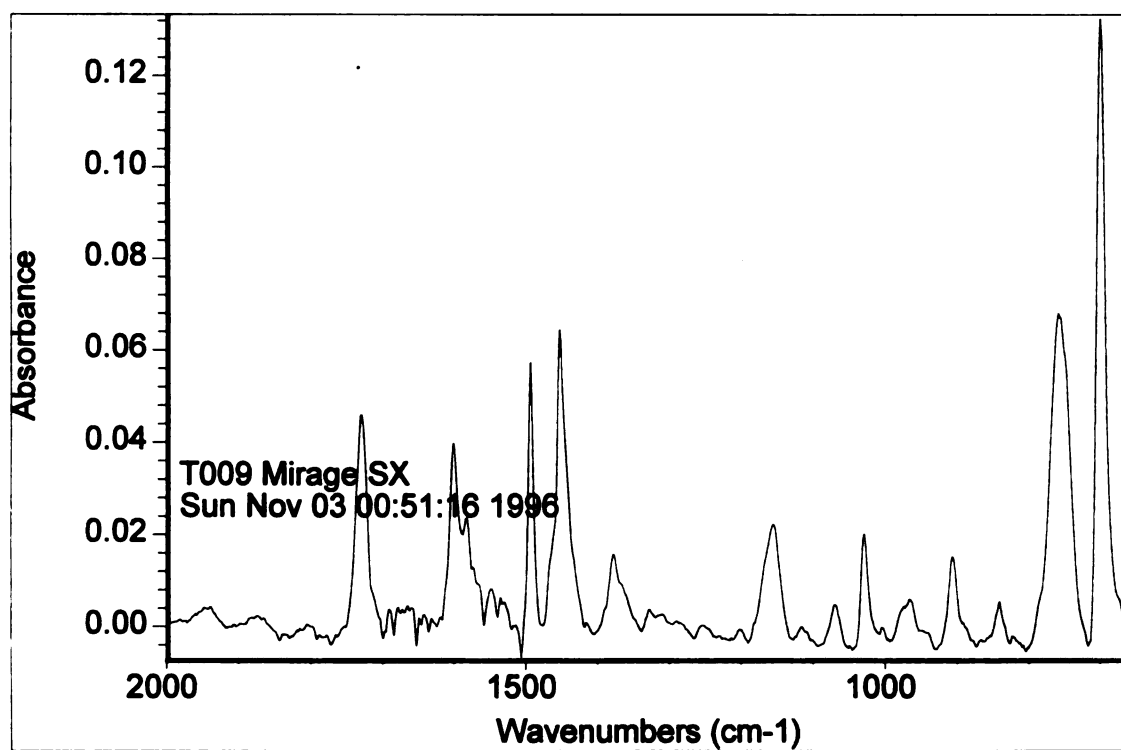
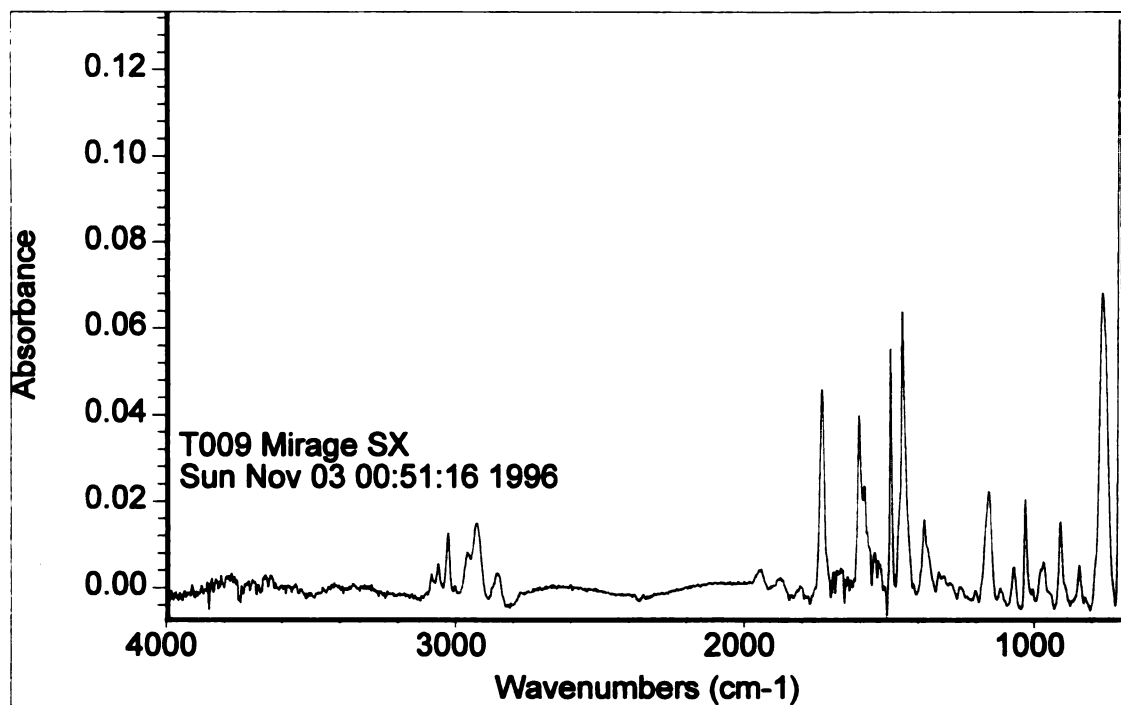
T006 Graphics Technologies Legend HP LX Graphics



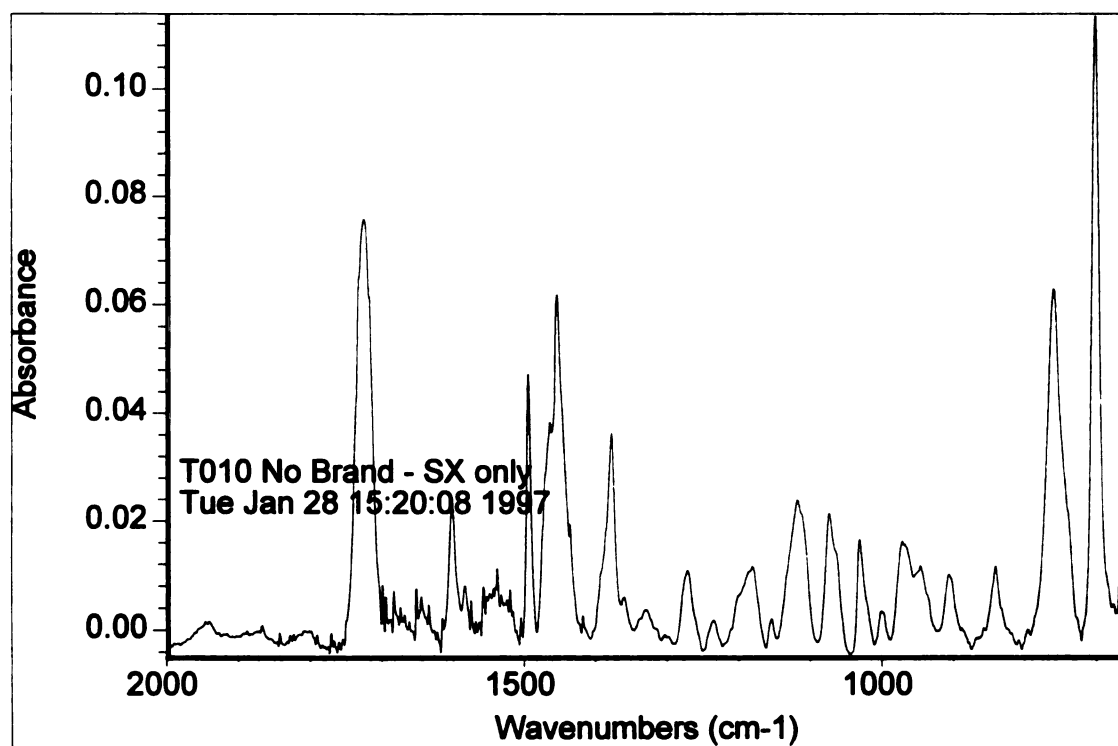
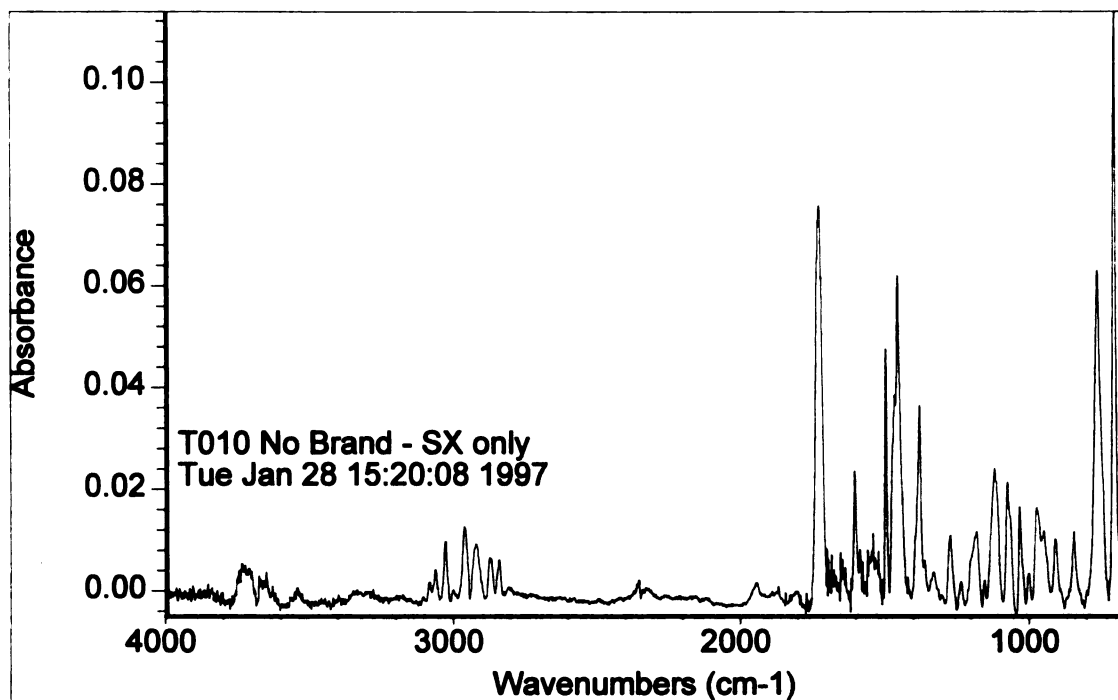
T007 Graphics Technologies Velvetone HP LaserJet 4



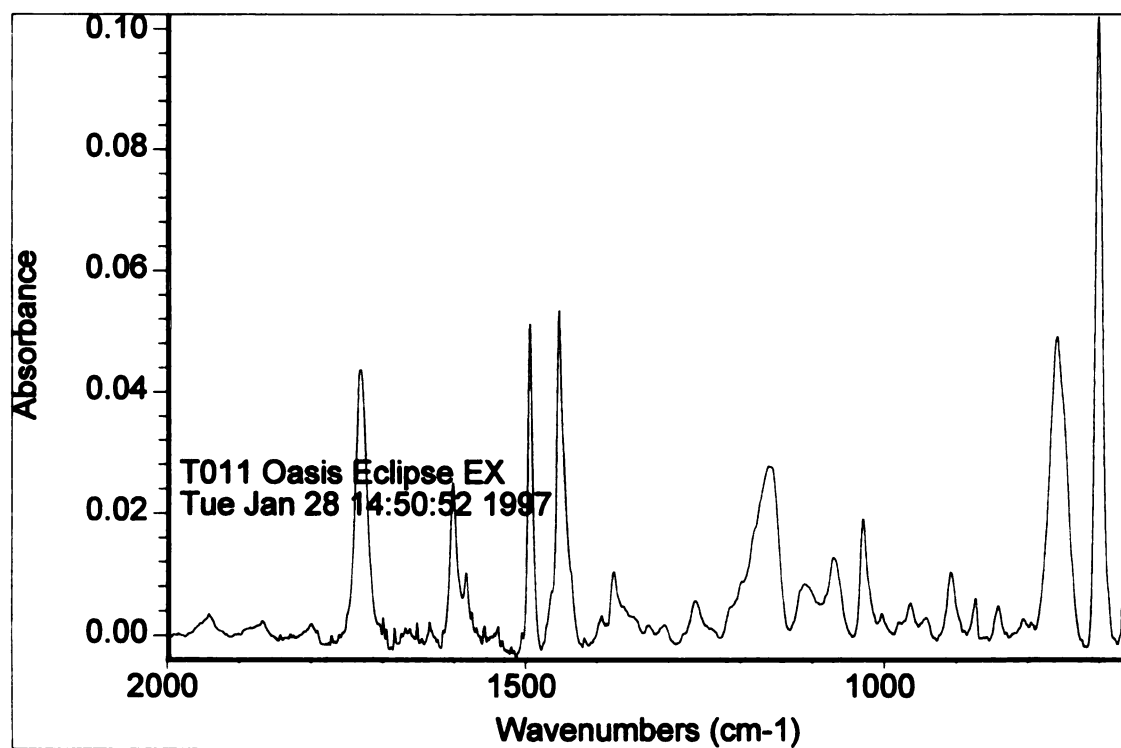
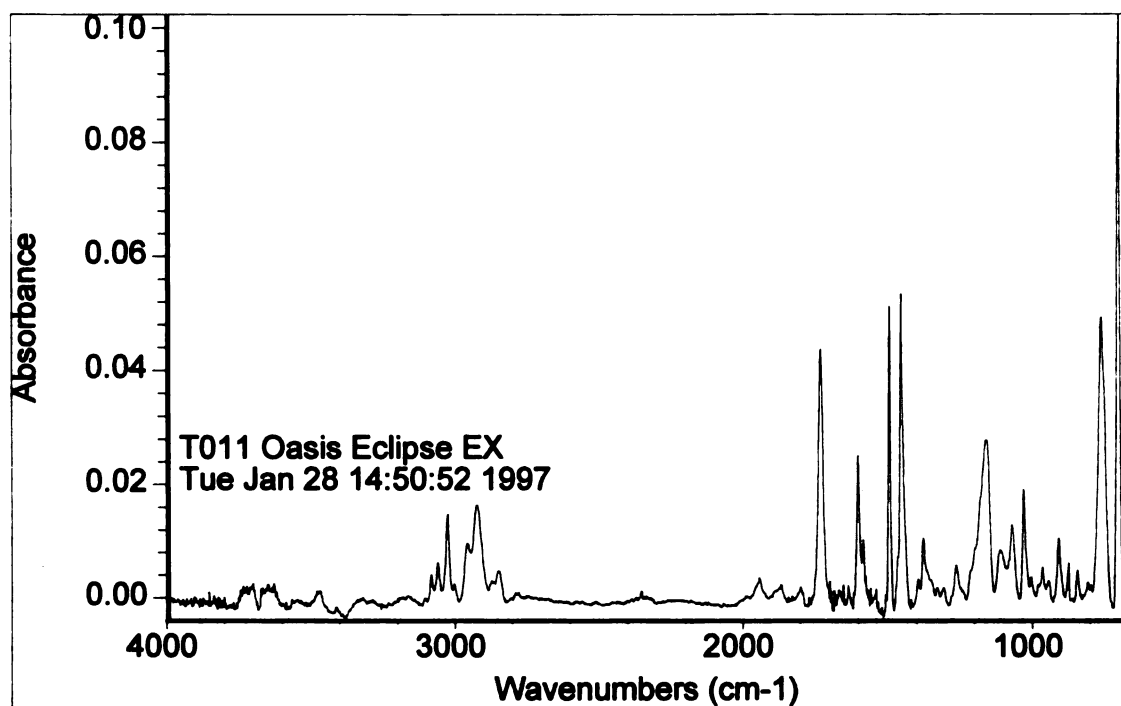
T008 Canon OEM SX



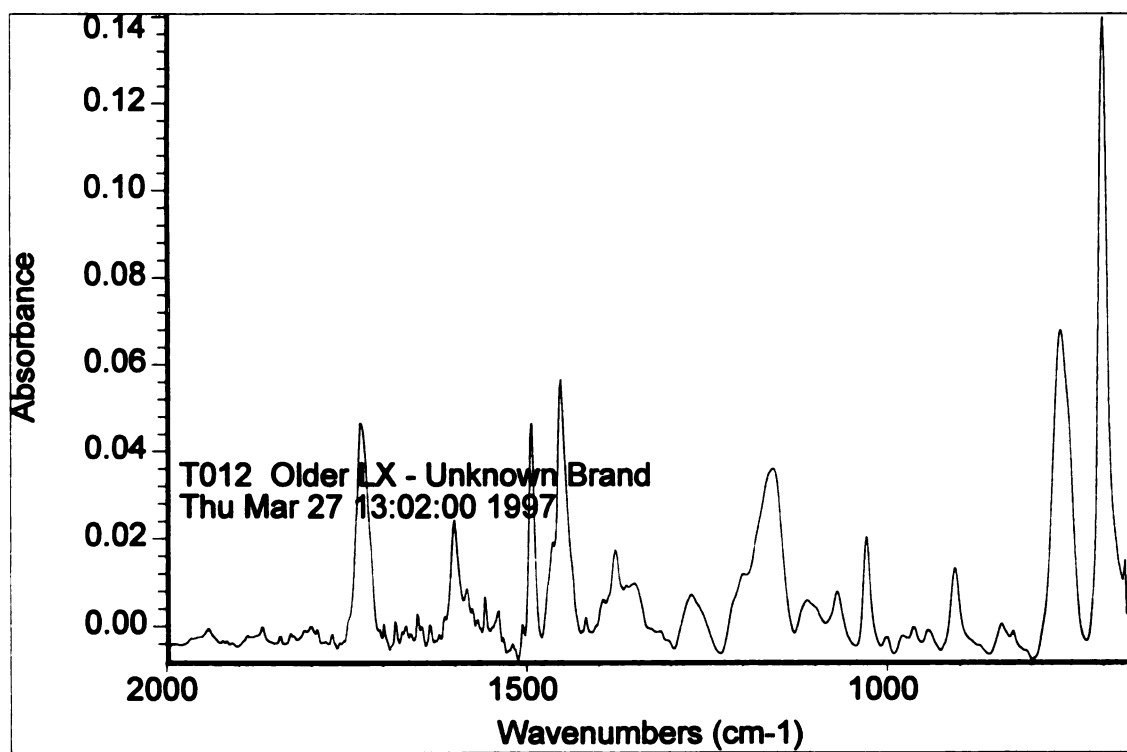
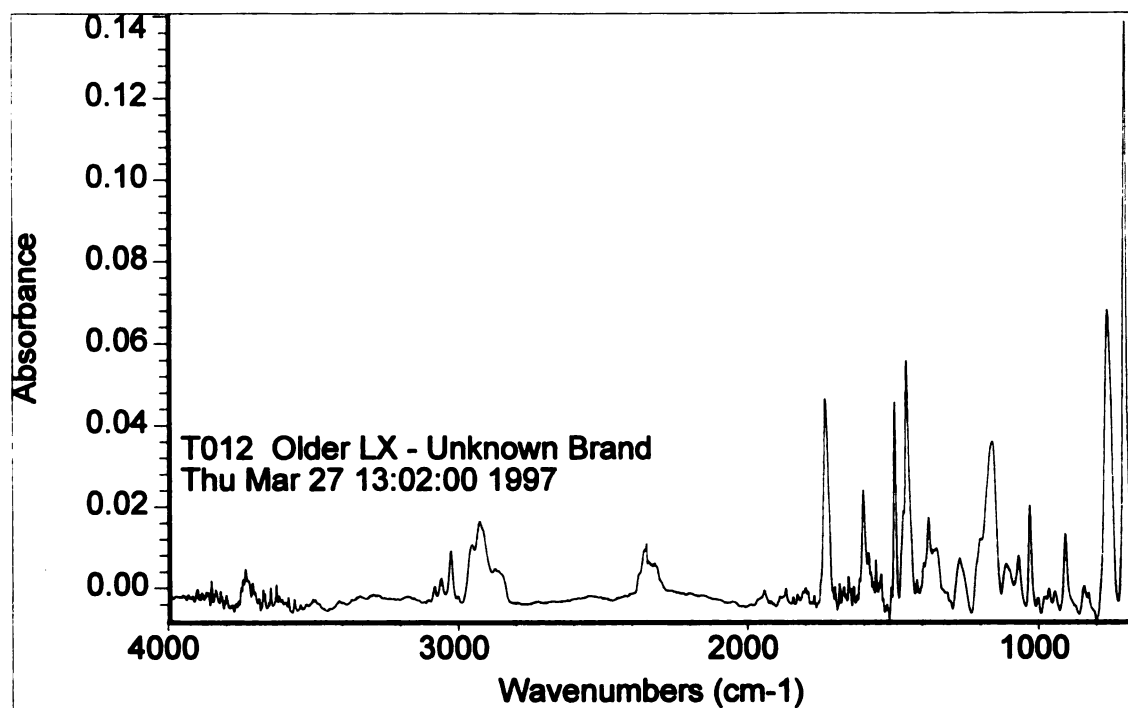
T009 Mirage SX



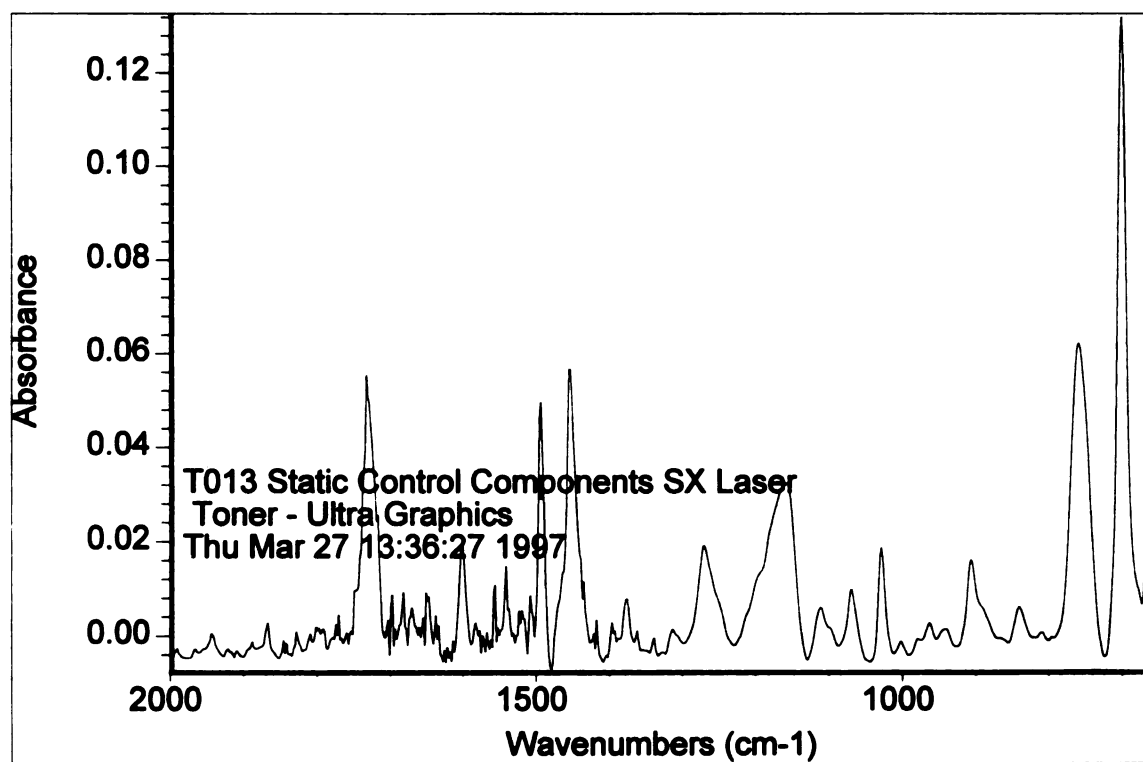
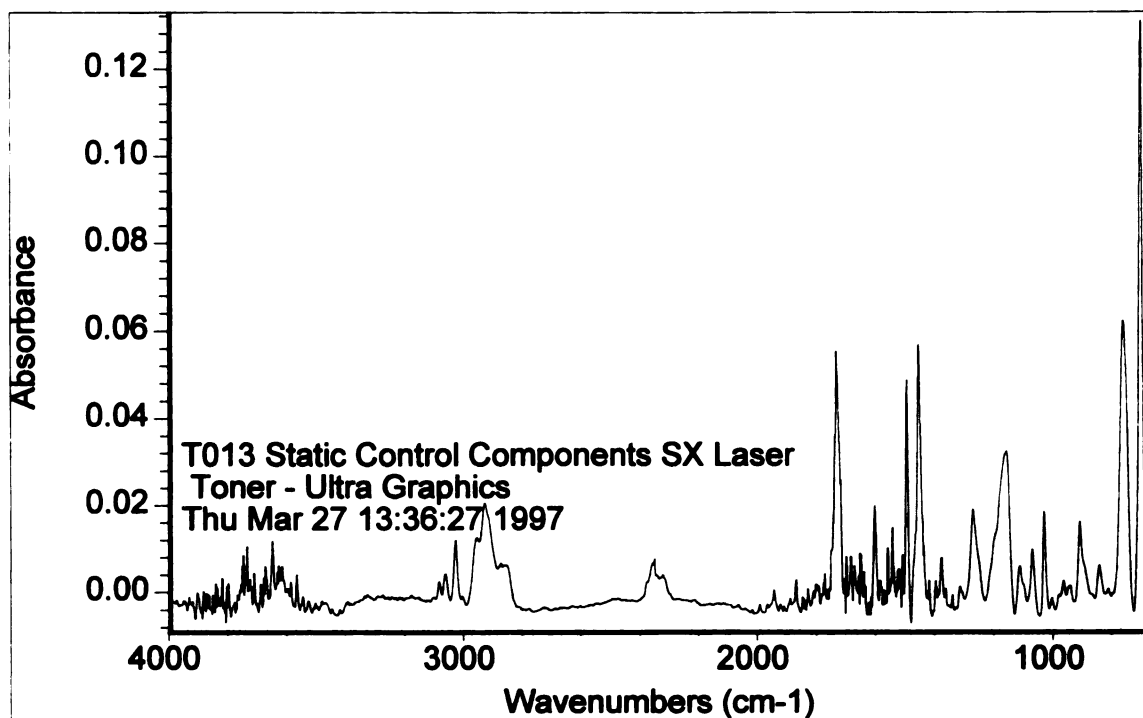
T010 No Brand - SX only



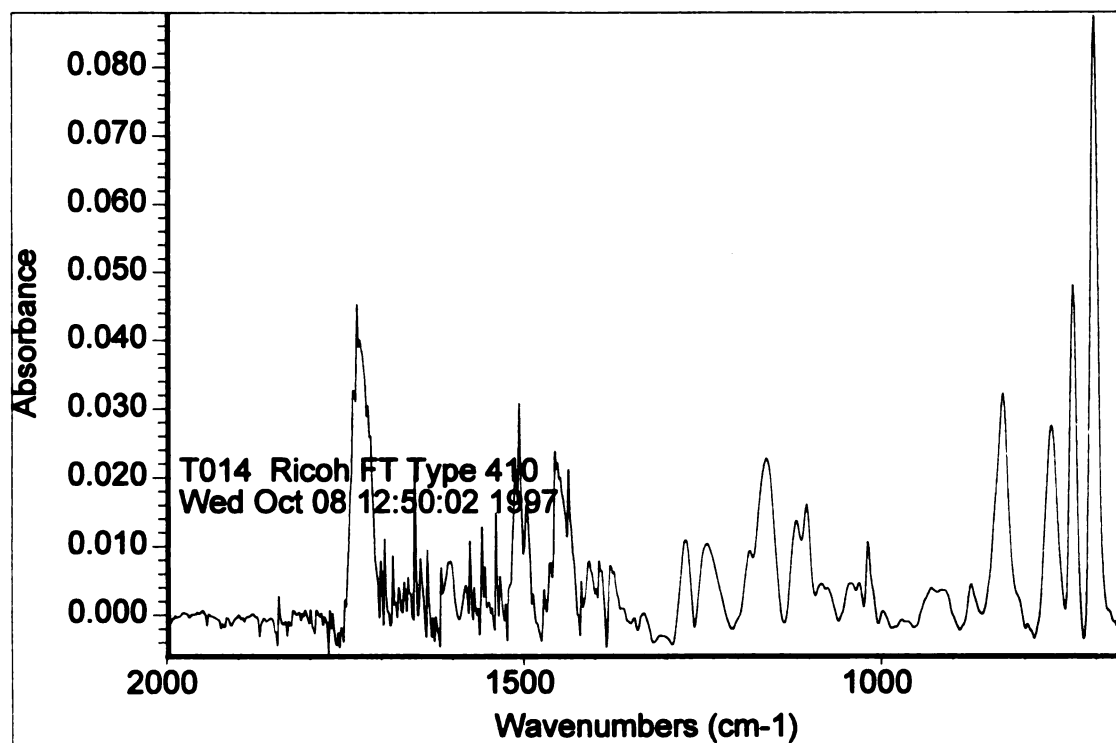
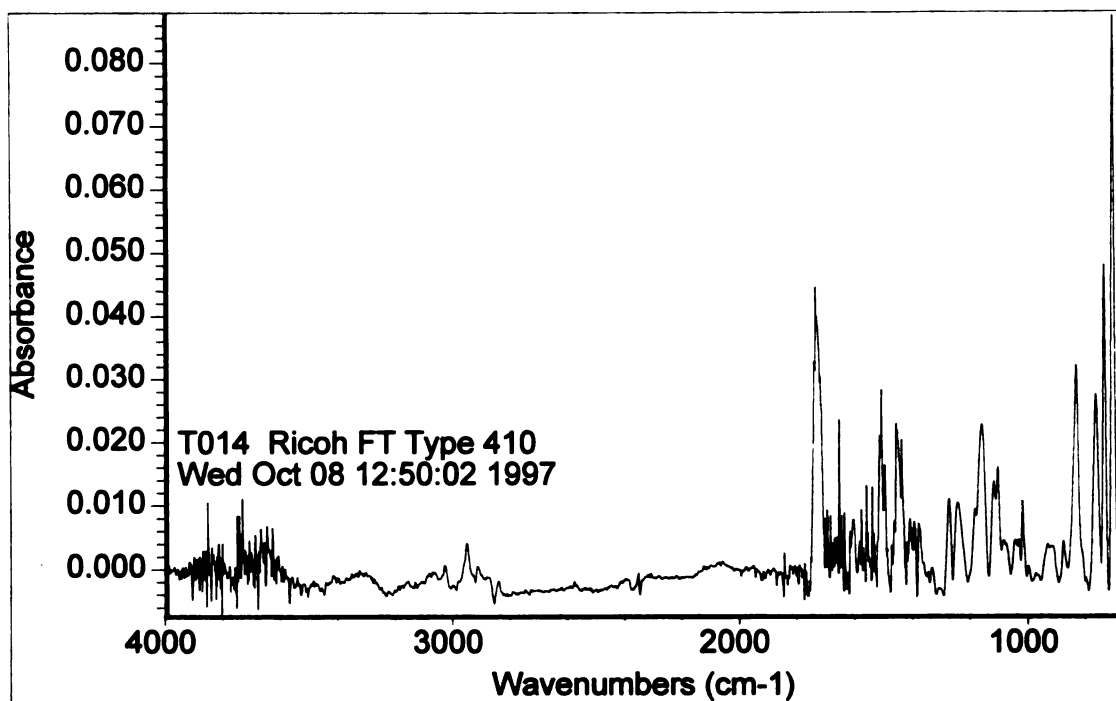
T011 Oasis Eclipse EX



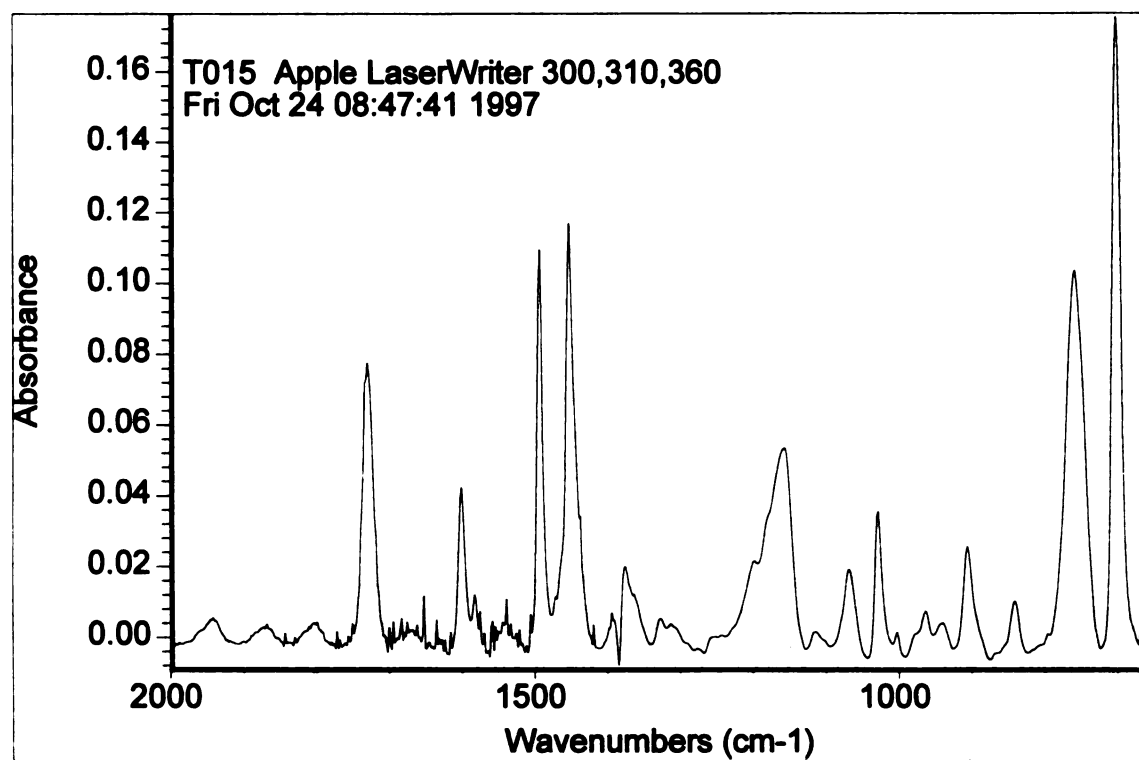
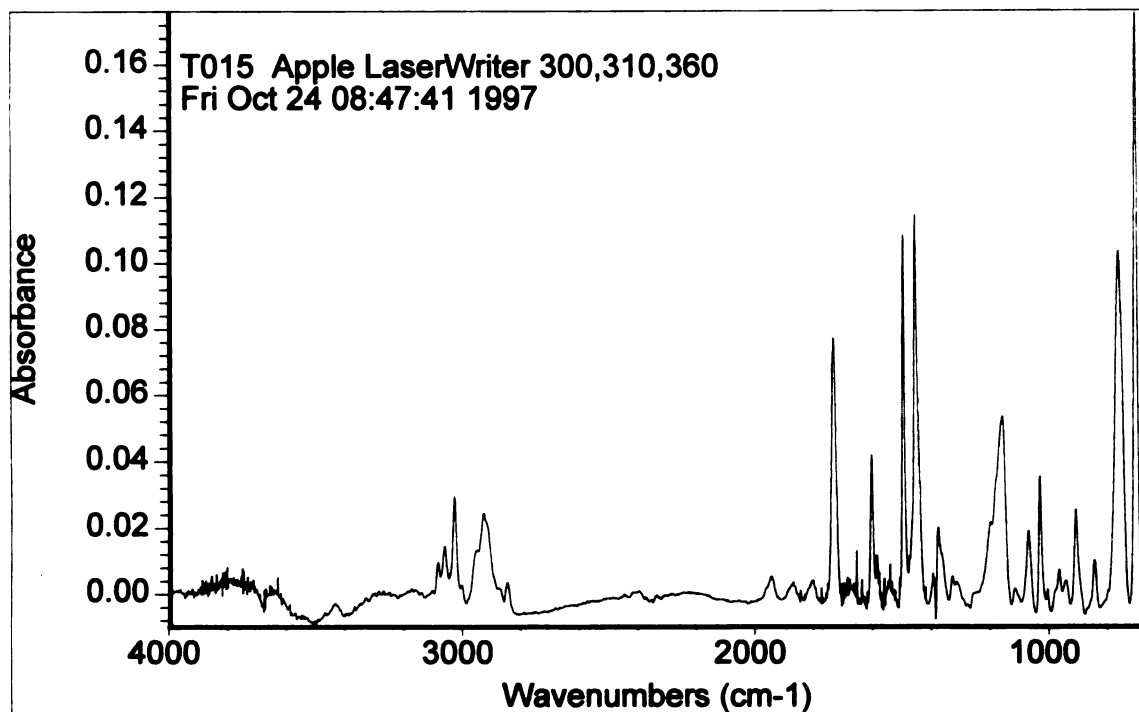
T012 Older LX - Unknown Brand



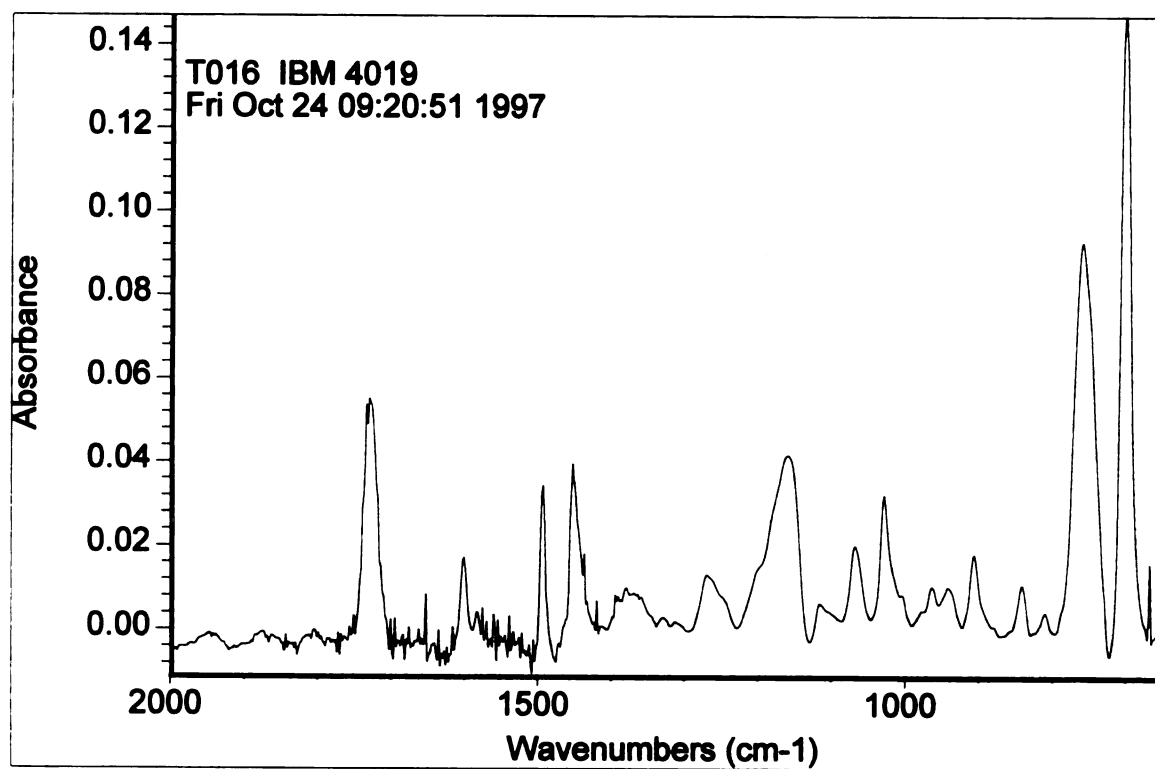
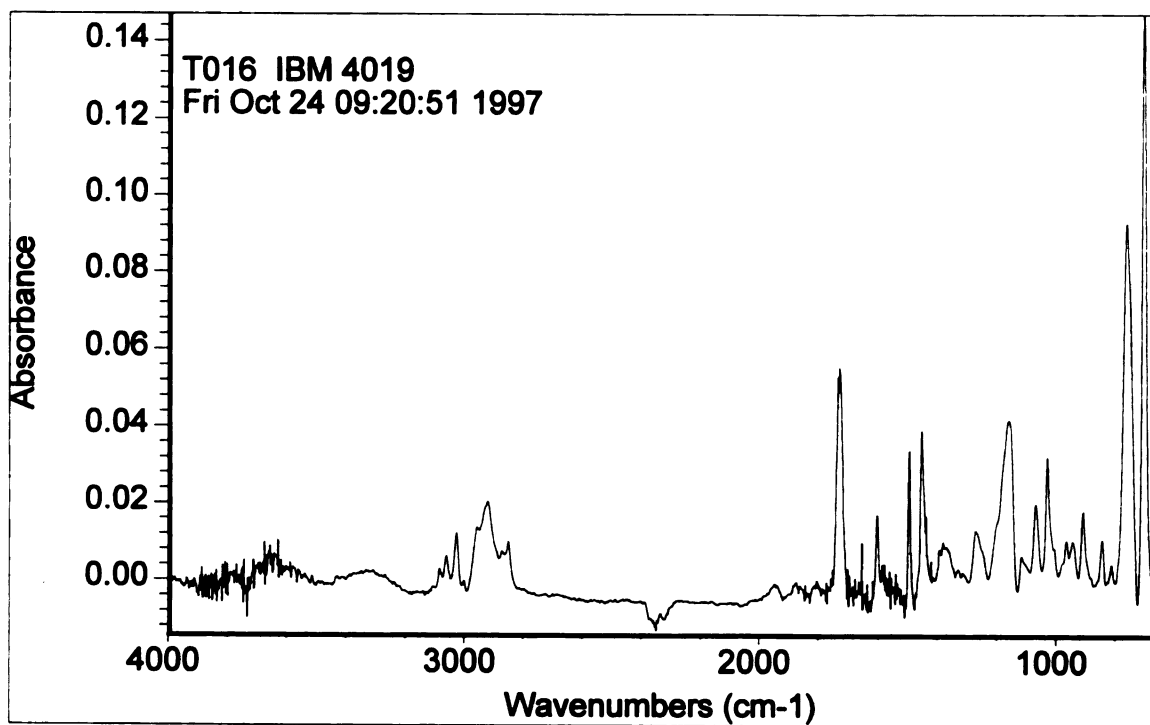
T013 Static Control Components SX Laser Toner - Ultra Graphics



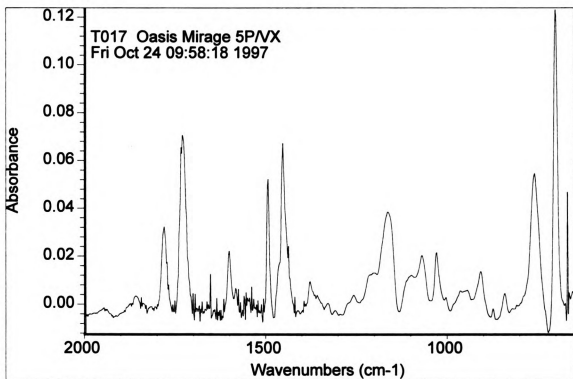
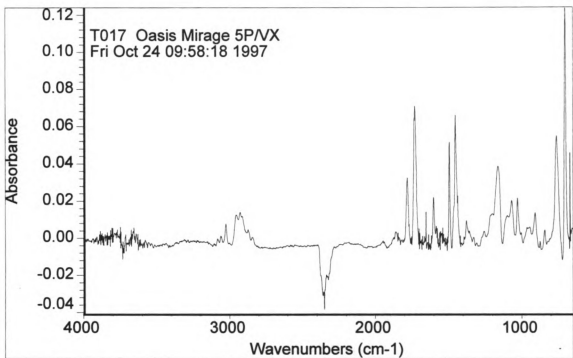
T014 Ricoh FT Type 410



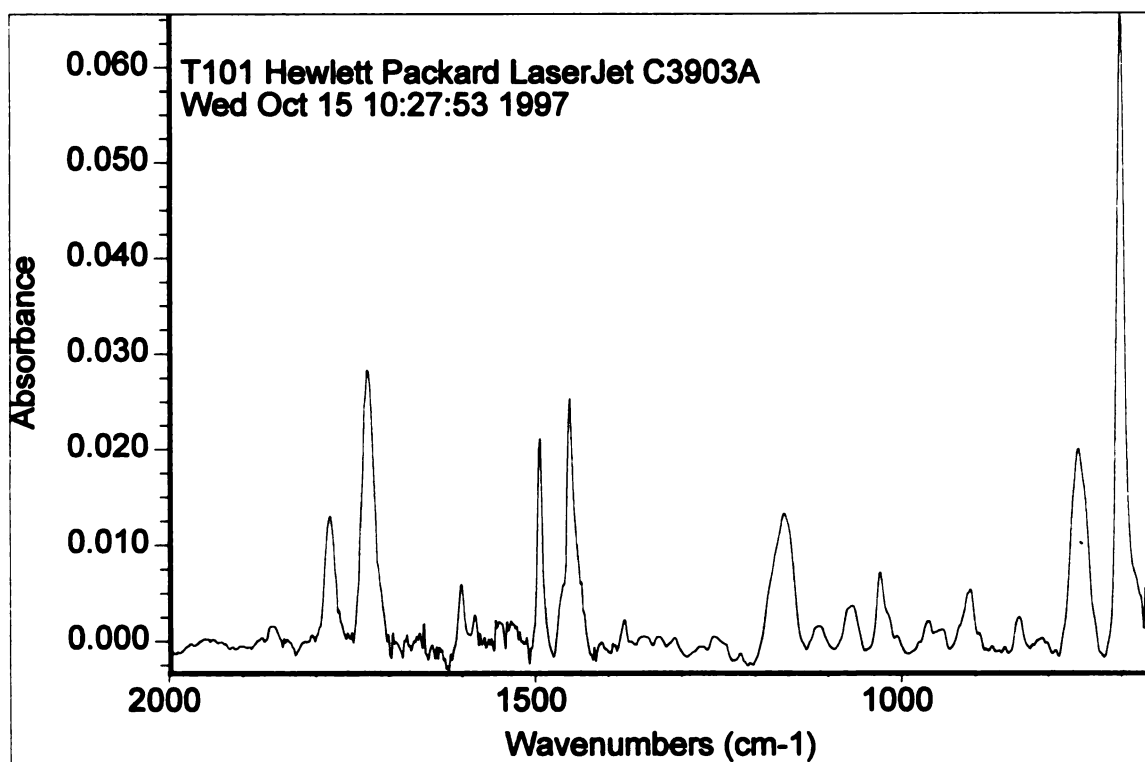
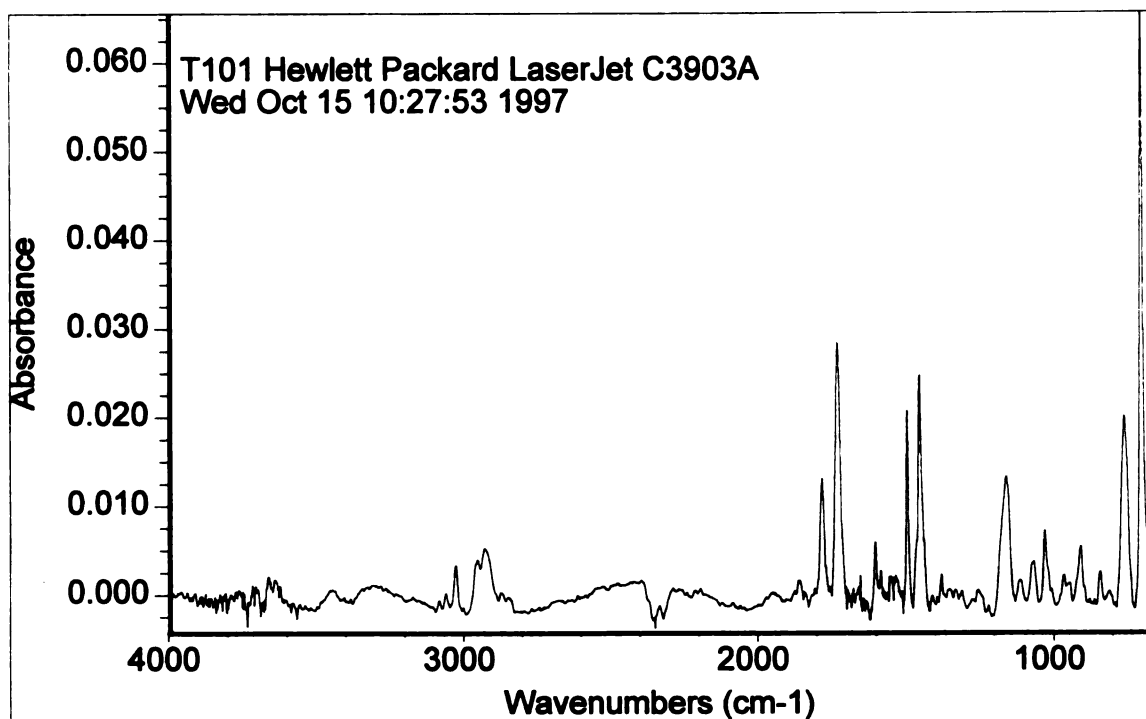
T015 Apple LaserWriter 300,310,360



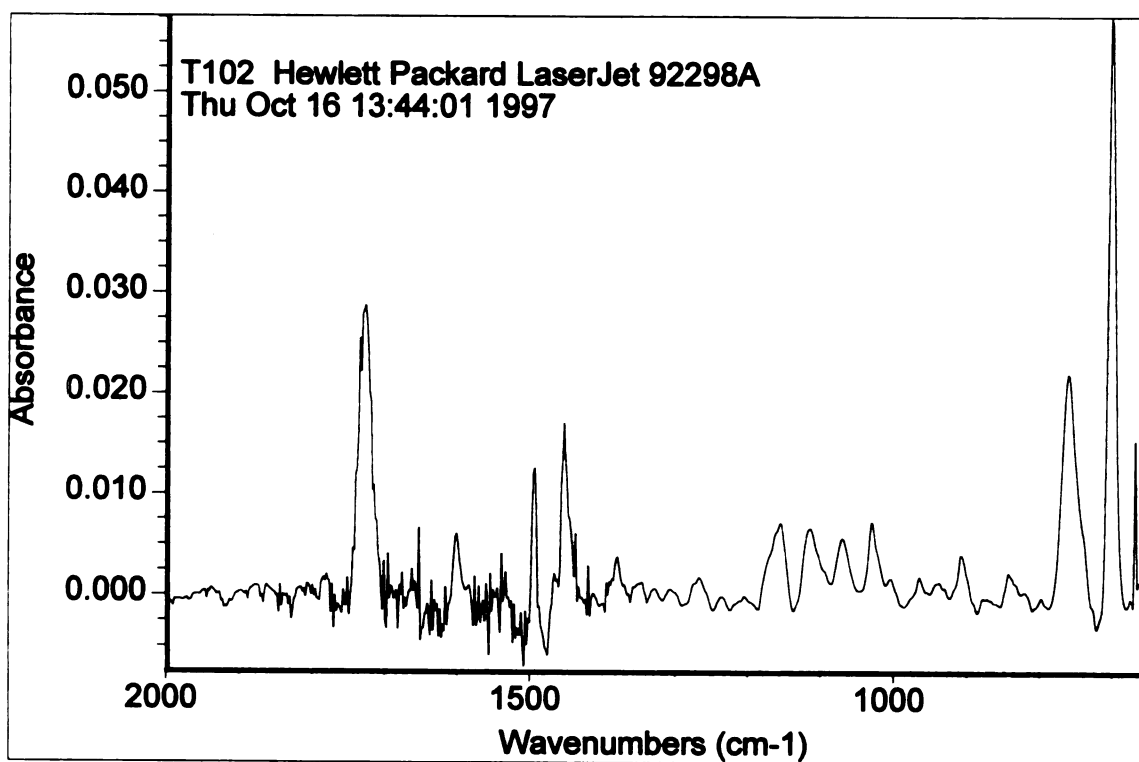
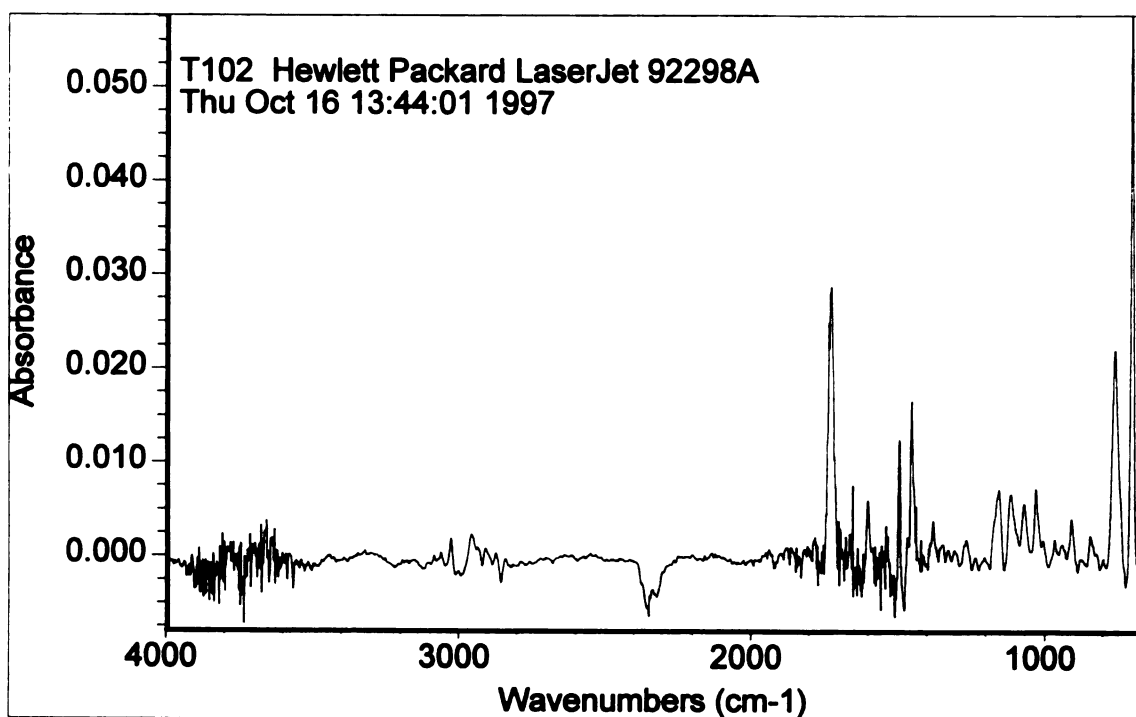
T016 IBM 4019



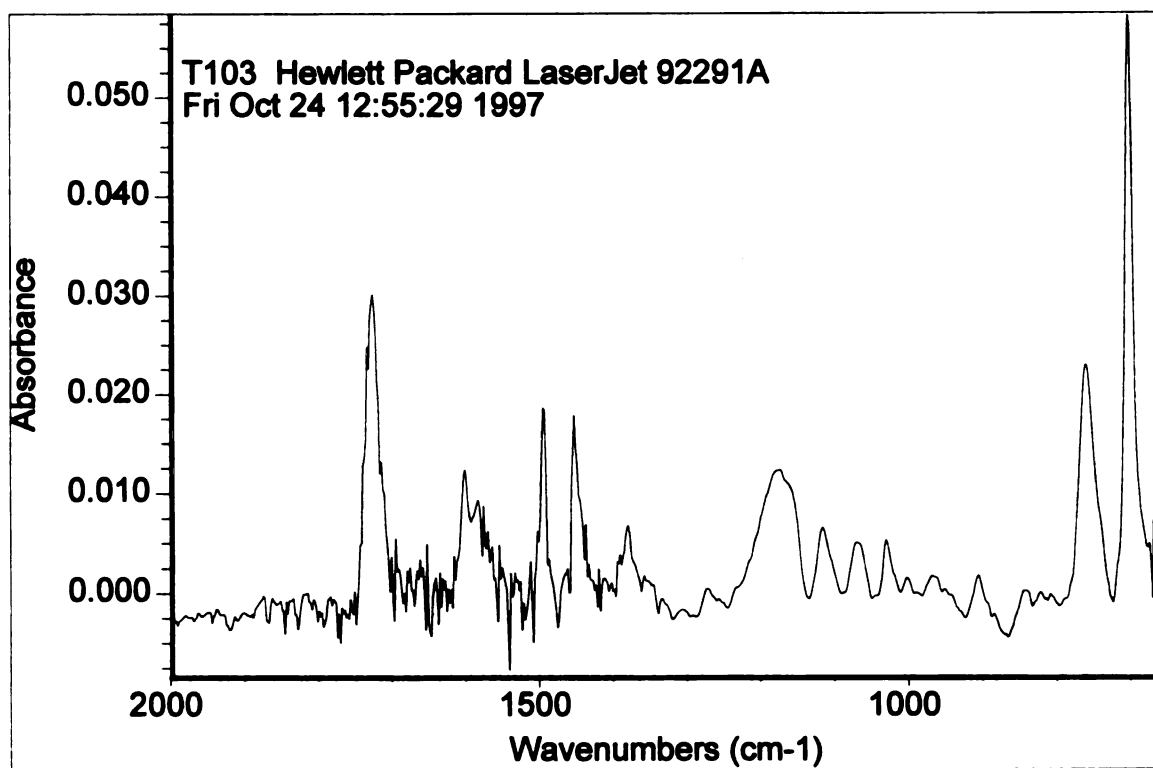
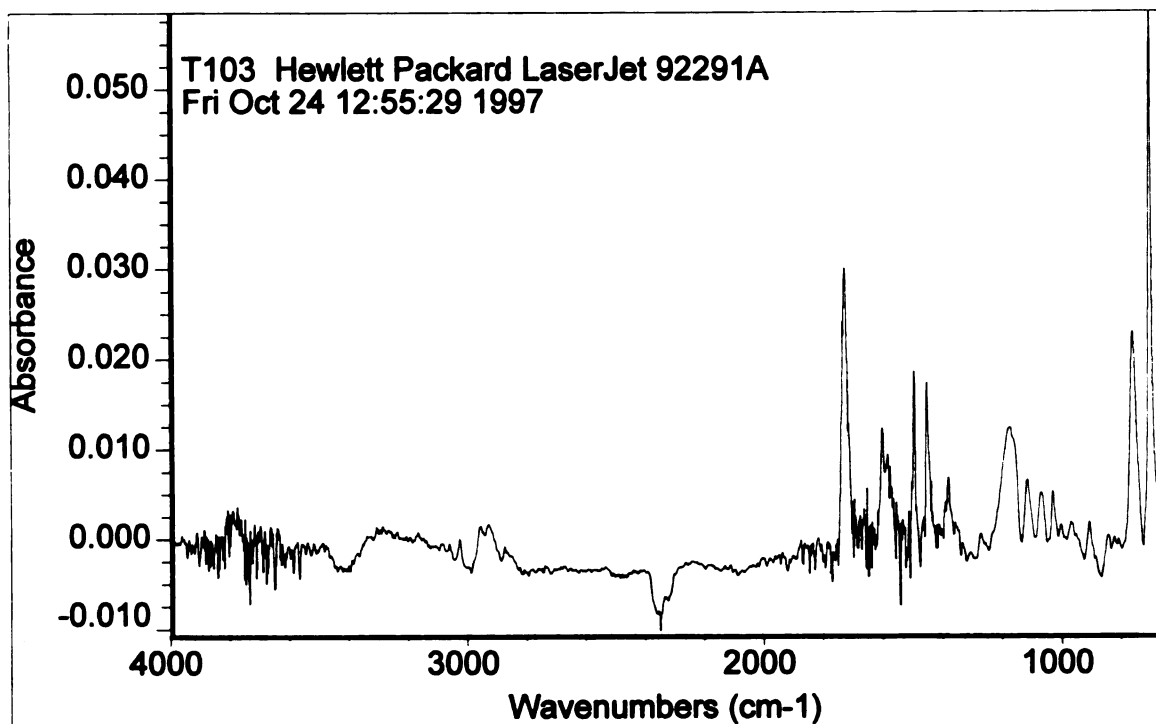
T017 Oasis Mirage 5P/VX



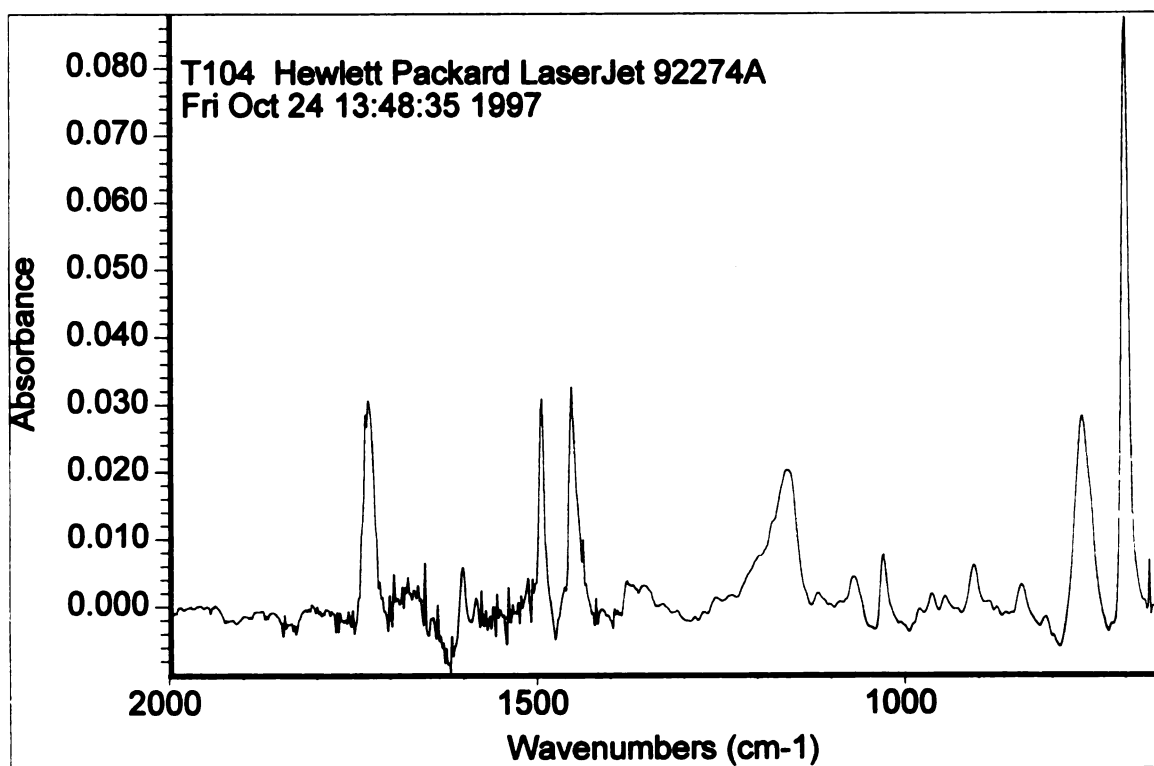
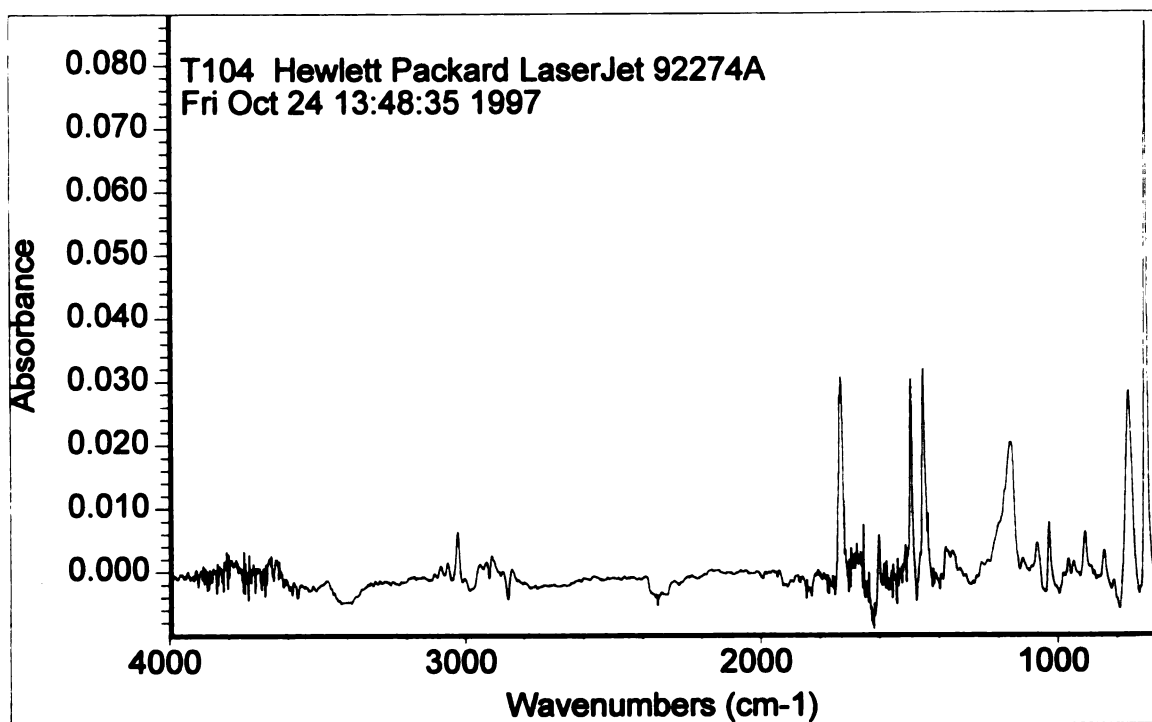
T101 Hewlett Packard LaserJet C3903A



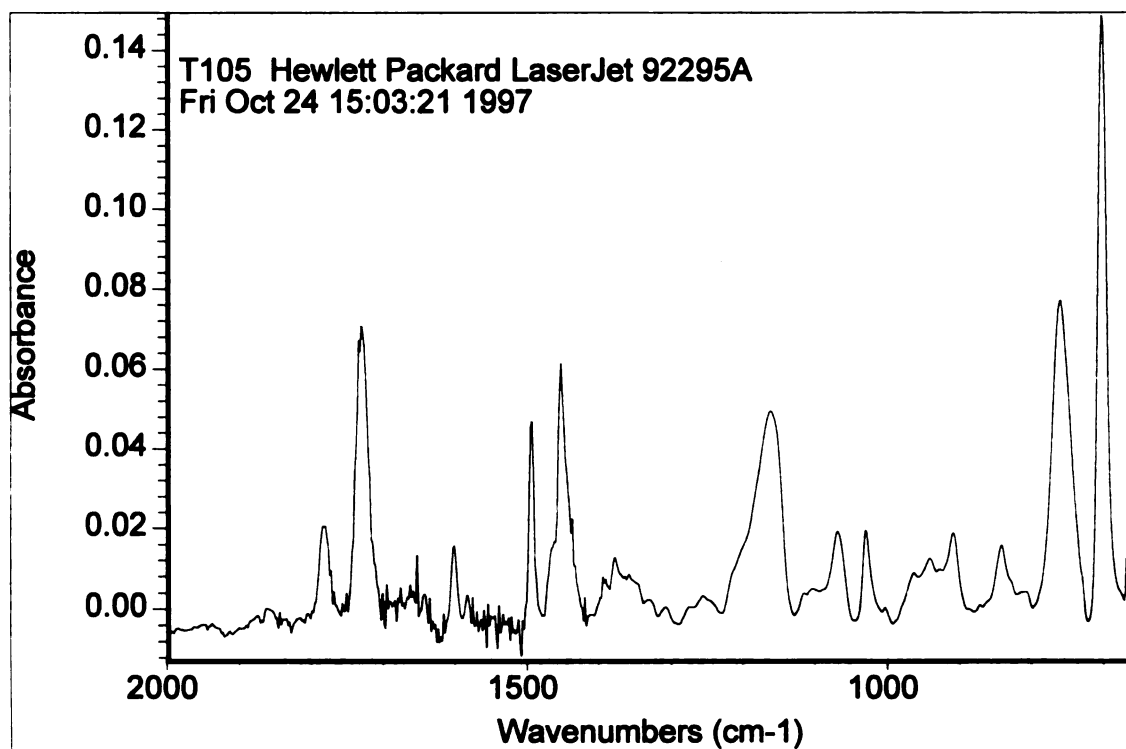
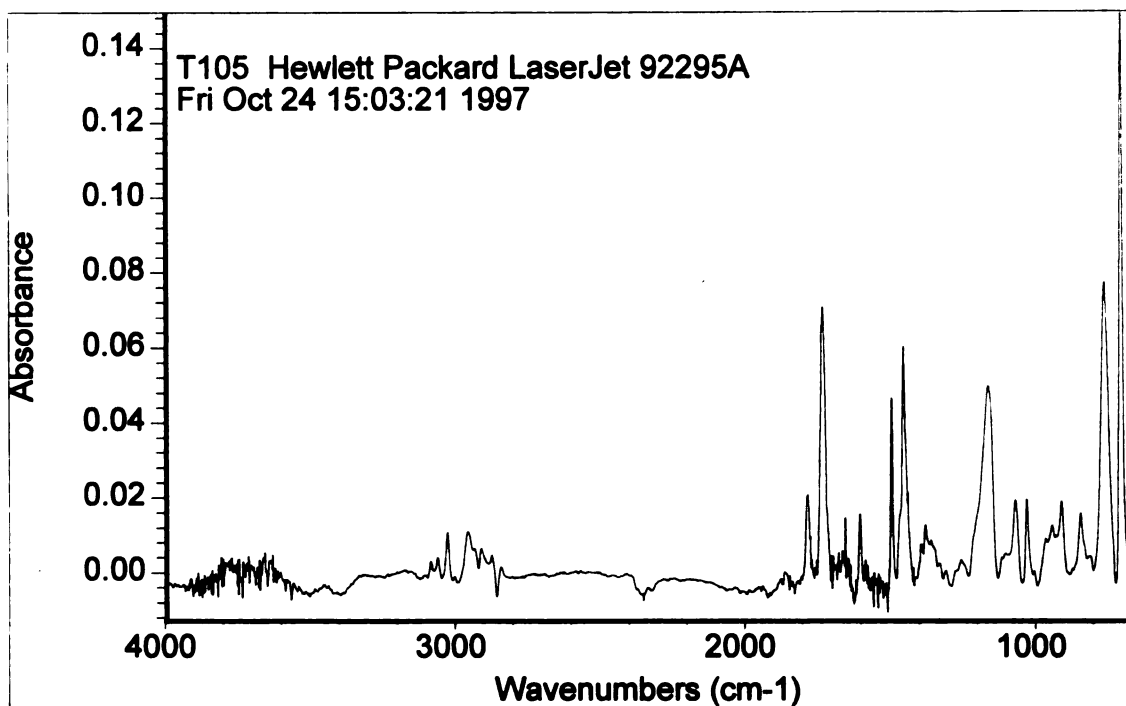
T102 Hewlett Packard LaserJet 92298A



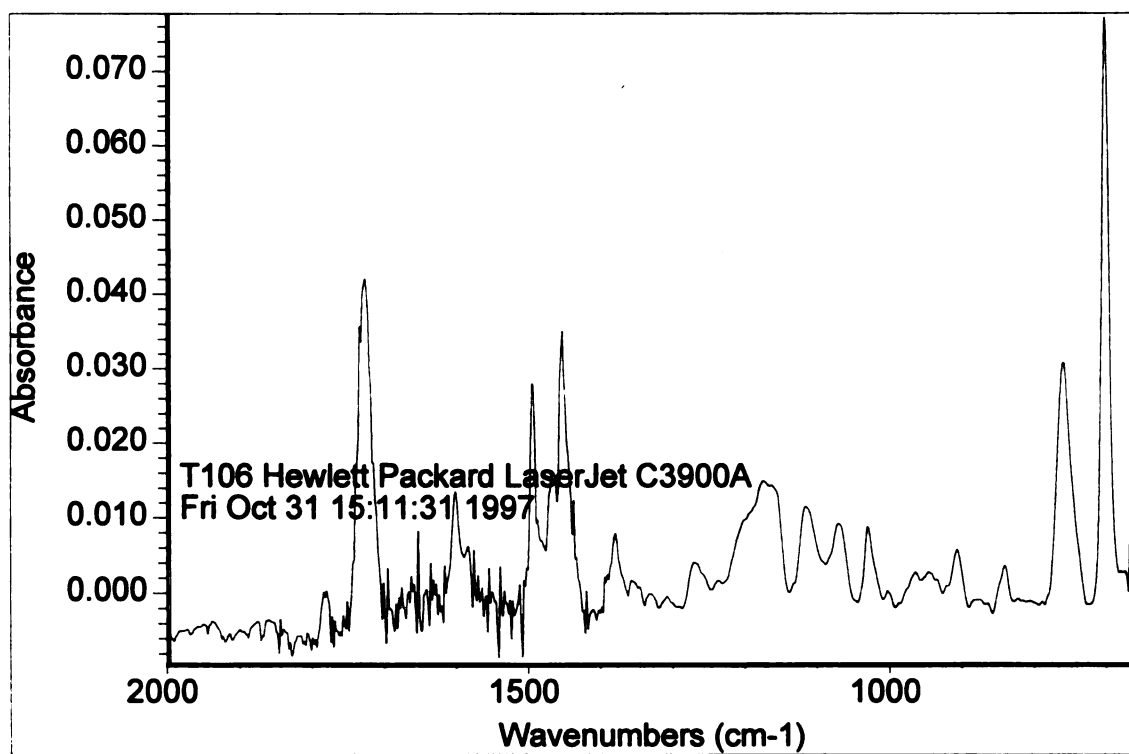
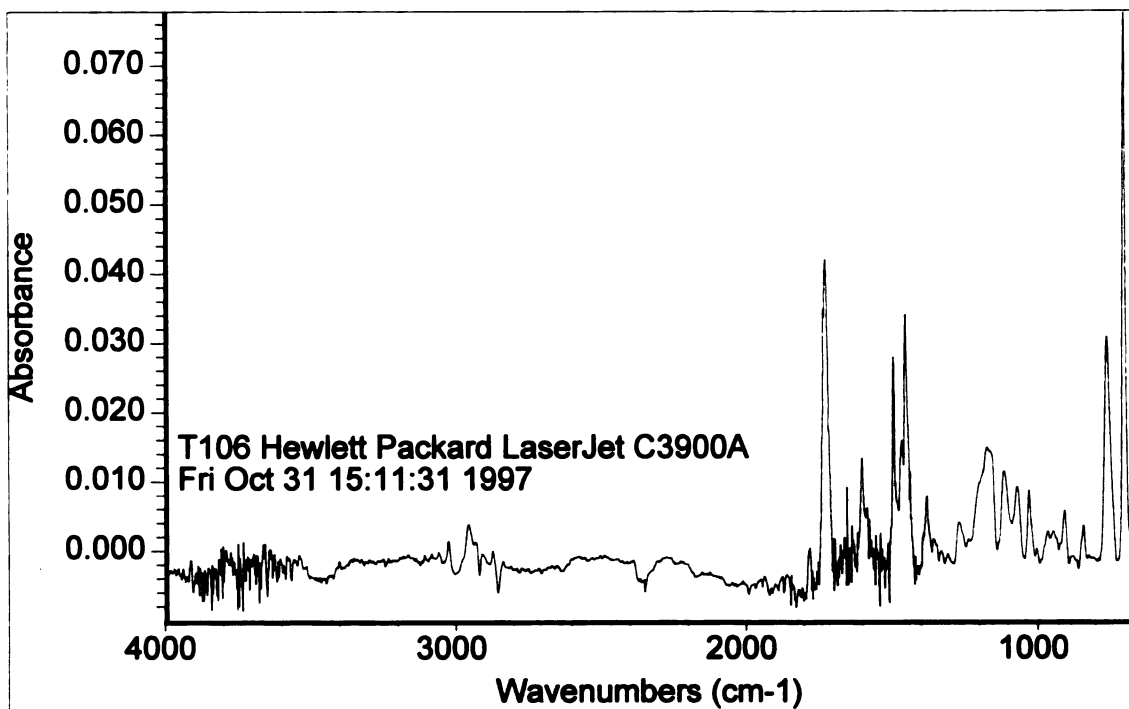
T103 Hewlett Packard LaserJet 92291A



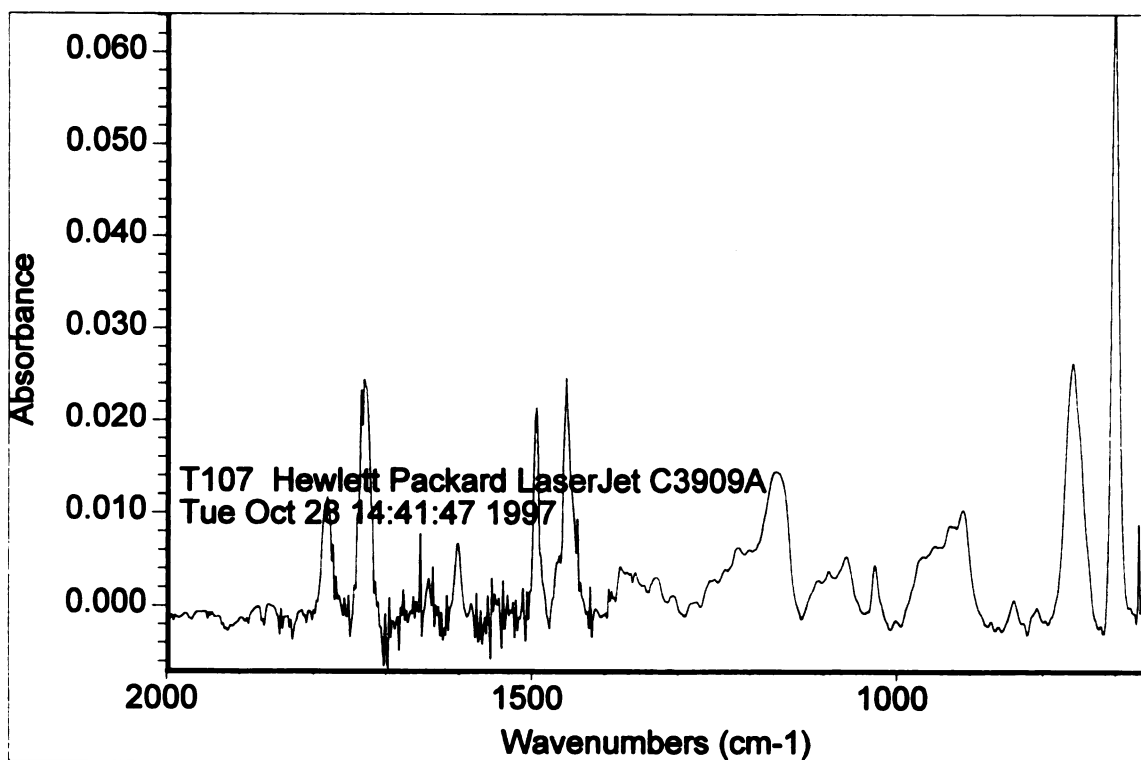
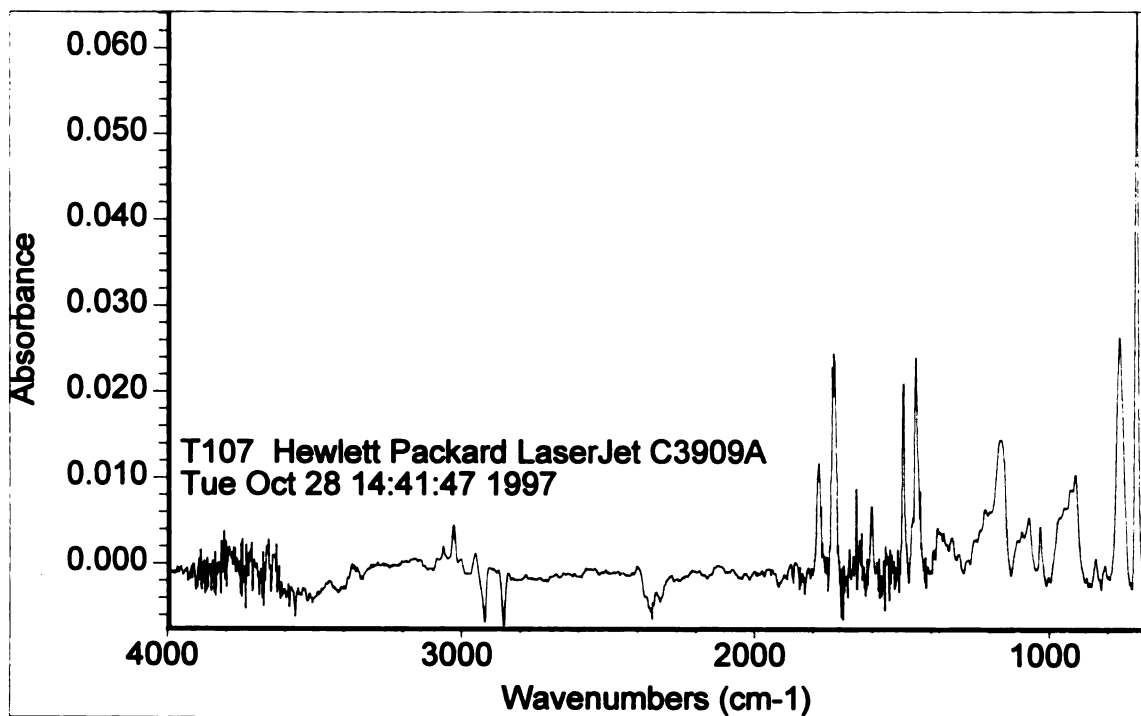
T104 Hewlett Packard LaserJet 92274A



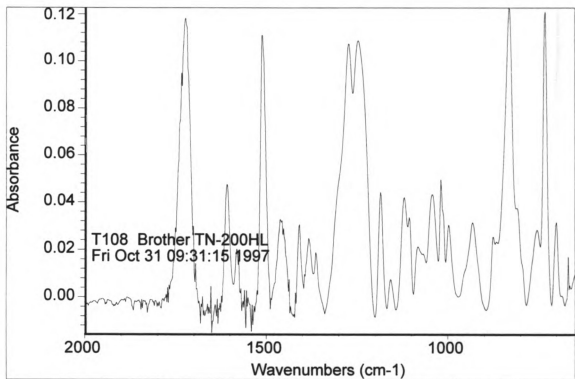
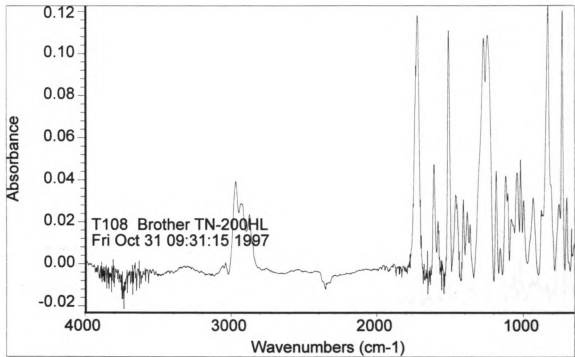
T105 Hewlett Packard LaserJet 92295A



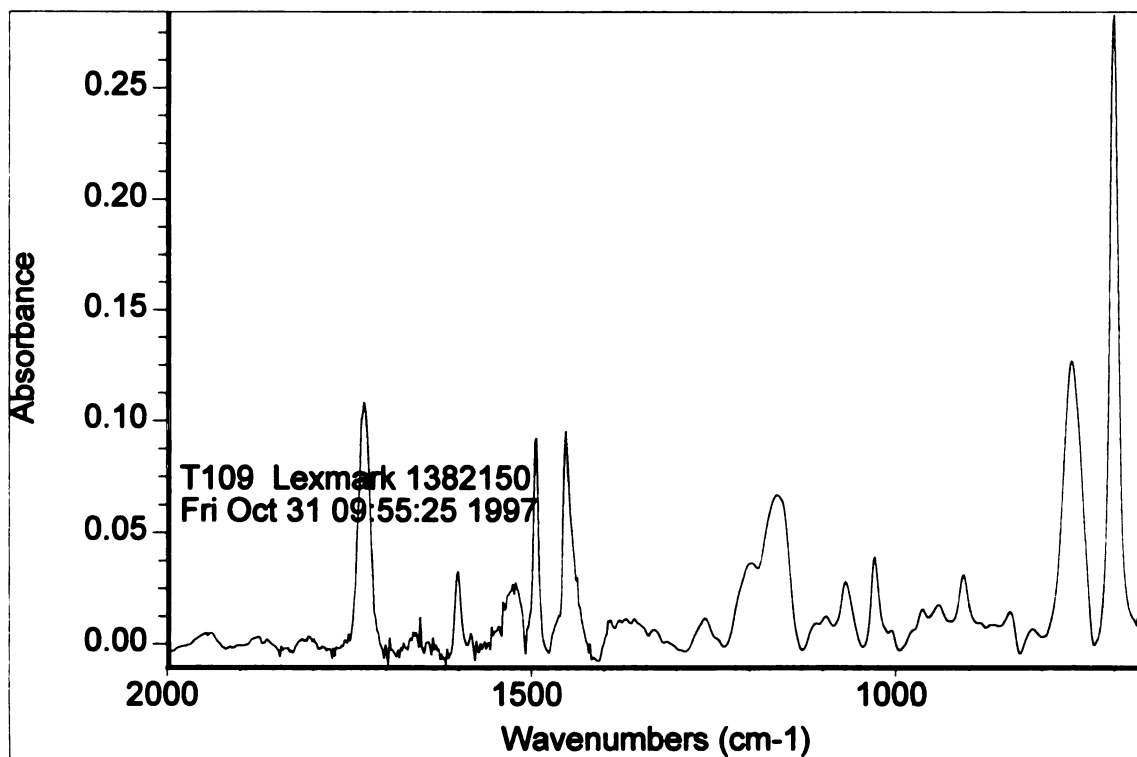
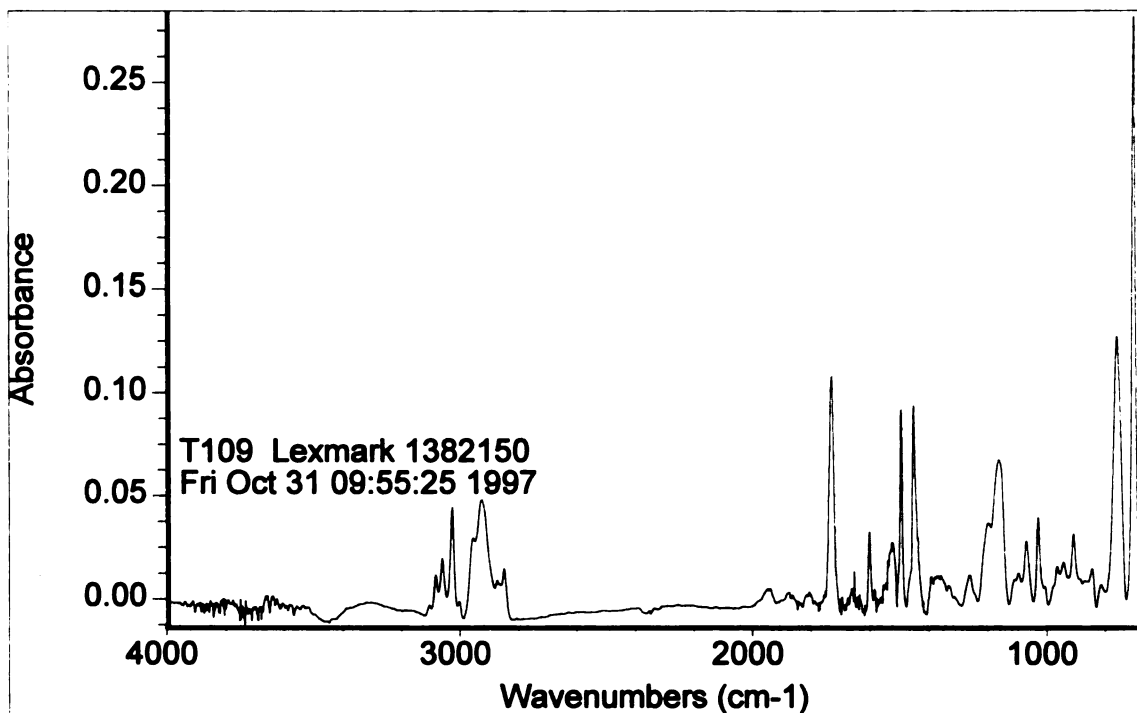
T106 Hewlett Packard LaserJet C3900A



T107 Hewlett Packard LaserJet C3909A



T108 Brother TN-200HL



T109 Lexmark 1382150

BIBLIOGRAPHY

BIBLIOGRAPHY

Brunelle, R.L. Forensic Science Handbook, Vol. I., Chapter 14, edited by Saferstein, R. Prentice-Hall: Englewood Cliffs, NJ, 1982.

Kemp, G.S. and Totty, R.N. "The Differentiation of Toners Used in Photocopy Processes by Infrared Spectroscopy." *Forensic Science International*, Vol. 22. 1983, pp. 75-83.

Levy, E.J. and Wampler, T.P. "Application of Pyrolysis Gas Chromatography/Mass Spectrometry to Toner Materials from Photocopiers." *Journal of Forensic Sciences*, JFSCA, Vol. 31, No. 1. Jan 1986, pp. 258-271.

Mazzella, W.D., Lennard, C.J., and Margot, P.A. "Classification and Identification of Photocopying Toners by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): I. Preliminary Results." *Journal of Forensic Sciences*, JFSCA, Vol. 36, No. 2. March 1991, pp. 449-465.

Mazzella, W.D., Lennard, C.J., and Margot, P.A. "Classification and Identification of Photocopying Toners by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): II. Final Report." *Journal of Forensic Sciences*, JFSCA, Vol. 36, No. 3. May 1991, pp. 820-837.

Minasi, M. "Hardware Clinic: You Look Marvelous." *Compute*. Jan 1992, pp. 68+.

Skoog, D.A. and Leary, J.J. Principles of Instrumental Analysis, 4th ed. Saunders College Publishing: Fort Worth, TX, et al. 1992.

Totty, R.N. "Analysis and Differentiation of Photocopy Toners." *Forensic Science Review*, Vol. 2, No. 1. June 1990.

Saferstein, R. Criminalistics: An Introduction to Forensic Science, 4th ed. Prentice-Hall: Englewood Cliffs, NJ, 1990.

Zimmerman J., Mooney D., and Kimmet, M.J. "Preliminary Examination of Machine Copier Toners by Infrared Spectrophotometry and Pyrolysis Gas Chromatography." *Journal of Forensic Sciences*, JFSCA, Vol. 31, No. 2. April 1986, pp. 489-493.

MICHIGAN STATE UNIV. LIBRARIES



31293016884698