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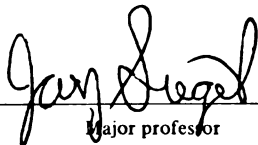
THE ANALYSIS AND COMPARISON OF ADHESIVES BY  
PYROLYSIS GAS CHROMATOGRAPHY/MASS SPECTROMETRY

presented by

Kirsten Renee James

has been accepted towards fulfillment  
of the requirements for

M.S. degree in Criminal Justice  
Specializing in Forensic Science

  
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Kirsten Renee James

A THESIS

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

MASTER OF SCIENCE

School of Criminal Justice

2003

## **ABSTRACT**

### **ANALYSIS AND COMPARISON OF ADHESIVES BY PYROLYSIS GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

By

Kirsten Renée James

Pyrolysis gas chromatography-mass spectrometry, or PyGC/MS, is a sensitive technique used to compare complex compounds. This research evaluated PyGC/MS as a method for characterizing adhesives. It is a technique that has not commonly been used in forensic science to analyze various types and brands of adhesives. 48 brands were dried overnight before analysis. A minimum sample size of 100µg was placed in a quartz tube with both ends sealed with quartz wool. Samples were pyrolyzed to obtain pyrograms indicative of each sample's chemical components. Using the general patterns of the pyrograms the adhesives were compared and distinguished by brand and type. The adhesives were grouped into eight classes according to their general use. These eight classes of adhesives include: All - purpose glues, Contact Cement, Caulk, Fabric glues, Hot melt glue sticks, Super glues, Twist & Paste Glue Sticks, and Wood glues.

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2003

I dedicate this work to our God for blessing me to bring it to completion.  
To my husband Sonny, and our sons Robert and Lemuel for their love and support.

## ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to Dr. Jay Siegel for teaching me, and advising me at Michigan State University, and for hanging in there with me over the past few years. Much thanks to Jennifer Rizk for her dedication and assistance on this research. Sincere gratitude and thanks to Elizabeth Murray of the College of Mt. St. Joseph for her editorial assistance and for inspiring me to pursue a career in forensic science. Thanks to Jeff Kindig, Doug Heitkemper, Fred Fricke, Duane Satzger, Karen Wolnik and the staff of the U.S. Food and Drug Administration's Forensic Chemistry Center (FCC) for giving me the opportunity to gain hands-on experience in the field. I would also like to thank Thomas Wampler with Chemical Data Systems (CDS) and Ray Huang of the Michigan State University Chemistry Department for their technical support. Last but not least, I would like to extend a special thanks to my parents, Harold and Emily Stewart, for their years of love, support, and encouragement.



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## KEY TO ABBREVIATIONS

CDS - Chemical Data Systems

DRIFTS - Diffuse Reflectance Infrared Fourier Transform Spectroscopy

FTIR - Fourier Transform Infrared Spectroscopy

GC - Gas Chromatograph(y)

GC/MS - Gas Chromatography/Mass Spectrometry

GPC - Gel Permeation Chromatography

HP - Hewlett Packard

HPLC - High Performance Liquid Chromatography

IR - Infrared Spectroscopy

MS - Mass Spectrometry

PyGC - Pyrolysis Gas Chromatography

PyGC/MS - Pyrolysis Gas Chromatography/Mass Spectrometry

PyMS - Pyrolysis Mass Spectrometry

## INTRODUCTION

Evidentiary materials in forensic science can be found in a variety of forms. These forms range from something as small as a fiber, a hair, or paint flake to something as complex as ink, plastic, copier toners, and in the case of this research, adhesives. When this evidence is brought into the lab, it is the goal of the forensic scientist to identify these materials and to link them to their source of origin. Connecting evidence to its origin can only be done by analyzing and comparing the unknown (questioned) sample, which comes from the crime scene, to the known (control) sample, which is the material suspected to be the source of origin. For example, a white powder collected at a crime scene is thought to be cocaine (unknown sample). A small bag of white powder, similar to that retrieved at the crime scene, was found in the possession of the person suspected of committing the crime (possible known sample). So, the two samples of powder are analyzed and compared. It is concluded that the sample at the crime scene(unknown) could have in fact come from the sample obtained from the suspect (known). Since chemical evidence rarely comes into the forensic lab as a pure substance it is the job of the forensic scientist to break down these substances into their chemical components. By doing so two different samples can be compared one component at a time. This will better assist the lab personnel to better connect the evidence to its source of origin.

There are several analytical methods used to identify and characterize various types of physical evidence. One technique commonly used to analyze fibers, paints, and other polymers is Pyrolysis Gas Chromatography-Mass Spectrometry, or PyGC/MS. The intent of this research was to evaluate PyGC/MS by determining the extent to which it

can differentiate household adhesives. This was an exploratory pilot study to determine the feasibility of even using PyGC/MS to analyze adhesives. The interest of this study lied in generating peak patterns for a variety of adhesives. Forty-eight in all were purchased in craft and grocery stores. These samples were obtained from local stores where most people can conveniently select from a diverse supply of adhesives each with a particular function. Each sample was smeared on a microscope slide and dried overnight. A small piece of sample, 100 $\mu$ g, was placed in a quartz tube which was then plugged with quartz wool. Sample-filled tubes were pyrolyzed in a Pyroprobe 1000® which was mounted to a Chemical Data Systems (CDS) 1500 valved interface. Both pieces of equipment were coupled to a Hewlett Packard 5971 Series Gas Chromatograph and Mass Spectrometer.

Pyrolysis is the chemical breakdown of macromolecules by heat in the absence of oxygen(1). During the pyrolysis process there are other chemical reactions going on besides the degradation of polymers. The chemical bonds of these molecules can depolymerize, or “unzip”; an elimination can occur in which there is the loss of a small, neutral molecule; then there is random cleavage which makes rearrangement reactions impossible if a polymer consists of bond energies that are similar (2). Helium which is the carrier gas used in this research is often used to minimize secondary degradation reactions (3). As the gaseous residues elute off the column via the Helium each component of the original sample is picked up by the detector, which creates a pattern of peaks specific to that sample. The output of the PyGC is the pyrogram, which shows the breakdown of the sample’s chemical fragments in the form of a peak pattern. The

pyrograms were compared to determine consistencies between samples.

What was found were peak patterns common to a specific type, or group of adhesive. Many of the adhesives could be individualized, however, without the run of a blank between samples there may have been some carry over from previous adhesives pyrolyzed. This may have contributed to the difficulty in determining some differences/similarities between samples. So, the adhesives could be classified into eight groups, by type, and distinguished one type from another (i.e. Super glues vs. Wood glues). There were, however, a few exceptions within some groups that were labeled as sub-classes for the purpose of differentiation.

Some cases and situations in which this type of evaluation could be useful include package tampering and mail fraud. For instance, a package-tampering case may involve the opening of a package with the motive of contaminating its contents. The suspect, in an effort to conceal the opening of the package, reseals the package with a different adhesive. The analysis of such a case would include: 1) collecting a sample of adhesive from the suspect package (unknown sample); 2) adhesive from an unaltered package that looks like the suspect package would come from the manufacturer (control); and, 3) if possible, the adhesive the suspect used (known sample) to reseal the tampered package. The pyrograms of the two adhesives on the tampered package should correlate to the pyrograms of the two known adhesives found in the possession of the suspect and from the manufacturer. Package tampering is encountered in the pharmaceutical industry when individual boxes containing medicine are opened to get to the enclosed bottle. In the food industry, labels can be counterfeited and placed on cans that did not come from the manufacturer, or on expired products. These labels are applied to the surface of cans

using a different adhesive from the manufacturer's adhesive. The postal service can also use this analytical technique in the event letters and packages have been opened illegally, then resealed.



## LITERATURE REVIEW

Throughout history people have made adhesives from a variety of materials including beeswax, egg yolks, tree sap, protein from animal hides, hooves, and blood (4). Now, most adhesives are made from polymers and other synthetic materials. To determine the composition of the aforementioned materials, adhesives were analyzed by several methods. For this research PyGC/MS was the method of focus.

Even throughout the literature it was common to see PyGC and PyMS being used as separate analytical techniques. Although GC/MS was discussed in some of the papers it was rare to come across the coupling of PyGC and MS. PyGC is an analytical method that can distinguish materials belonging to the same group, or class. Combine the sensitivity of the PyGC and its ability to specify components in a substance with the MS's "fingerprinting" ability and speed of processing data, the result is a powerful forensic analytical technique called Pyrolysis Gas Chromatography - Mass Spectrometry (PyGC/MS).

PyGC/MS is the degradation of non - volatile polymers into smaller more volatile fragments (5), Gas Chromatography (GC) performs the separation of those same fragments, and the identification of those fragments is determined by the Mass Spectrometer. PyGC/MS is such a sensitive analytical technique that it requires only a small amount of sample (1 - 100 ug) (6). It practically eliminates tedious and time consuming sample preparation because it is responsive to both soluble and insoluble samples. This analytical technique employs a pyrolyzer interfaced to a GC that's coupled to a Mass Spectrometer (MS). At an extremely high temperature the pyrolyzer breaks

down non -volatile polymeric substances into smaller, volatile molecules (7). This mixture of smaller molecules flows through the GC, via a capillary column, where its components are separated into fragments. The MS detects each fragment and sends a signal to the computer as each molecule elutes off the GC column. The computer records these signals as peaks. So, every peak represents a different molecule. The set of peaks creates a pattern that acts as a blueprint for the substance that was originally analyzed (8). These blueprints, or output, are called pyrograms.

The field of applications of PyGC/MS is extremely wide and diverse. This method has been used to determine the composition of something as diverse as the natural resins used as adhesives in art materials (9) to something as complex as polymer blends found in food wraps, coated freezer paper, and the clear film on cigarette packages (10). It is frequently applied to industrial processes involving large scale pyrolysis such as municipal solid waste processing and scrap automotive tire recycling (11). One study (12) used PyGC/MS to examine the pyrolysis of energetic materials which consist of hazardous waste containing explosives and propellants. The goal of the aforementioned study was to compare pyrolytic products of incomplete combustion to incineration by - products in order to determine if the two techniques have similar outcomes. If so, PyGC/MS would be an acceptable means to dispose of the energetic materials without causing environmental pollution that open incineration causes.

Before PyGC/MS was implemented as an analytical tool for adhesives there were a few other techniques used to characterize these materials such as Infrared Spectroscopy (IR), Pyrolysis Gas Chromatography (PyGC), and Gas Chromatography - Mass Spectrometry (GC - MS). All of these analytical methods have their benefits and

disadvantages. However, PyGC/MS possesses a combination of some of the better benefits of many of these analytical techniques. The GC - MS often used for drug analysis by most forensic laboratories, can easily be adapted for pyrolysis by mounting an interface to the GC injector (13).

When examining the advantages of polymer identification using PyGC over IR, the qualitative application of PyGC is actually “fingerprinting” for the comparison of pyrograms to those of a reference library, usually accomplished using GC and retention time data or MS spectral identification (14). Unlike the Fourier Transform Infrared Spectral Library of Commercial adhesives created by Jeff Kindig (15) and Steve Borowski (16), the goal of this research was not to create an adhesive library for PyGC - MS, but to compare the results of pyrolyzed adhesives. The lack of standard pyrolytic and chromatographic parameters amongst forensic labs has kept the creation of pyrogram libraries from reaching its potential (17). These libraries would be helpful in identifying and characterizing adhesives and other physical evidence. A new combined technique which respectively analyzes adhesive samples via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and PyGC is becoming a highly discriminating scheme of analysis (18). An actual forensic case employing this technique confirmed the similarity between the adhesive on the flaps of yellow envelopes that held counterfeit American bank notes, to yellow envelopes in the suspect’s possession. Infrared Spectroscopy (IR) also has its limitations when it comes to identifying complex materials. IR can identify the presence of functional groups, but it is difficult to characterize insoluble samples using IR (19).

Both PyGC and IR are commonly used to analyze polymers. Between the two,

PyGC was found to be much more efficient in analyzing materials. PyGC has the ability to analyze insoluble materials whereas, IR cannot analyze such materials without additional sample preparation (20). By breaking down samples, the pyrolyzates would be swept into the GC eventually resulting in pyrograms that provide the analytical information. PyGC cannot only specify functional groups but it can also identify specific compounds. Adhesives on tapes used to bind materials together have been analyzed by PyGC. The adhesive on polyvinyl chloride (PVC) tapes (21), used to tape detonation devices to bombs, has been successfully compared before and after explosions. After an explosion, small fragments of tape could be linked to the original roll. For reasons such as this, PyGC is an excellent technique for analyzing minute samples. PyGC has also been used to analyze cooking fat from the stomach of a murder victim. Gum from the skin of a murder victim and suspect have been linked (22). This diverse evidence indicates types of polymeric substances that PyGC can successfully analyze. Though PyGC is a highly effective analytical method, it has a few limitations such as the slow separation of a sample, a variation in column/instrument conditions makes it difficult to replicate retention time data and process pyrograms, inter - laboratory standardization is almost impossible due to multiple stationary phases, and variation in PyGC data make computer treatment difficult.

Although PyMS predates PyGC, forensic science laboratories use PyGC for economic reasons (23). PyMS is not prone to the same limitation as PyGC, but it may be difficult to determine the composition of a pyrolyzate, and the instrumentation is expensive. PyMS is considered a rapid, sensitive analytical method. Like the PyGC, PyMS breaks down the sample, but doesn't perform a separation of the pyrolyzate prior to

entering the mass spectrometer. Here the pyrolyzates are ionized and mass spectral scans are made. With the aid of data processing software spectra are integrated and mass pyrograms are plotted (24).

Over the past 20 years, adhesives have been one of the least common forensic samples analyzed by PyGC, PyMS and more recently, PyGC - MS (25). Adhesives are often referred to as glues or resins. However, In this study the terms “glue” and “adhesives” were used interchangeably. An adhesive is a substance capable of bonding surfaces together (26). The ability of an adhesive to bond relies primarily on its molecular weight or the size of its molecules. So, the higher the molecular weight, the stronger the bond (27). Adhesives belong to a family of materials called polymers. Polymers are composed of repeating chemical units called monomers that are linked together in a couple of formations. The chemical makeup of adhesives has been characterized by a variety of techniques which include nuclear magnetic resonance, IR methods, gel permeation chromatography (GPC), and High Performance Liquid Chromatography (HPLC) (28). One study used PyGC and IR to classify adhesives. A few samples from each class of adhesive were analyzed by PyGC, then reference spectra of each adhesive were obtained from IR to confirm the results (29).

## METHODS AND MATERIALS

### *Sampling Technique*

Forty-eight household adhesives (Refer to Table1) were chosen for evaluation by Pyrolysis Gas Chromatography - Mass Spectrometry (PyGC/MS). They were chosen based on them being easily accessible by the public in grocery and craft stores. Each adhesive was smeared, as evenly as possible using a wooden applicator, on opposing ends of a microscope slide. The adhesives were then allowed to dry overnight. The dried adhesive was cut or scraped, with a straightedge razor from the surface of the microscope slide. A capillary tube was used to push the sample to the center of a quartz tube, then both ends of the tube were sealed with quartz wool. Gloves were worn throughout the sample preparation to prevent the contamination of the quartz tubes, quartz wool and samples, with oils from the hands.

The initial sampling began by filling quartz tubes full of adhesives for insertion into the PyGC/MS. Over half of the adhesives were sampled in this manner. By weighing the estimated amount of sample used to fill the quartz tubes, it was determined that the first set of samples weighed between 1100 $\mu$ g and 1200 $\mu$ g. After sampling initially with these amounts of adhesive per pyrolysis run some broad peaks were noticed on the pyrograms that were not characteristic of the adhesives. This was because too much adhesive was being deposited on the column. It was determined that only a small amount of sample was needed for each run on this particular instrument. As a result, the Gas Chromatograph's (GC) capillary column had to be changed. Once the column had been replaced normal peak patterns and retention times were restored. To determine the best sample size a test was conducted to compare sample sizes of 100  $\mu$ g, 500  $\mu$ g, and

**Table 1 Adhesives Evaluated by PyGC/MS**

BRAND NAME	COLOR	TYPES	SUBCLASS
Modge Podge Waterbase Sealant	white	All-Purpose (AP)*	
Ross All-Purpose White Glue	white	AP*	
Rose Art Washable School Glue	white	AP*	
Tacky Glue	white	AP*	
Elmer's Glue-All X06D1	white	AP	AP-1
Elmer's Glue-All	white	AP	AP-1
Elmer's Glue-All B21C1	white	AP	AP-1
Elmer's Green Glue	green	AP*	
Contact Cement	clear	Contact Cement (CC)*	
Elmer's Neoprene Based Contact Cement	clear	CC*	
Duro Safe Contact Cement	clear	CC*	
Duro Safe Contact Cement 61C1429A	clear	CC*	
Elmer's Silicone Acrylic Latex Squeeze N Caulk	almond	Caulk (CK)	C-1
Elmer's Silicone Acrylic Latex Squeeze N Caulk	clear	CK	C-1
Elmer's Squeeze N Caulk B2711	almond	CK	C-2
Elmer's Squeeze N Caulk C0861	dries white	CK	C-2
Dow Corning Adhesive	white	CK	C-3
Silicone Sealer T-HC	white	CK	C-3
Bathtub Sealer	white	CK	C-3
Adhesive Caulk	white	CK	C-4
Kwik Seal	white	CK	C-4
ALEX Plus	white	CK	C-4
Titebond Polyurethane Glue 7K5131	white	CK*	
Weldbond	white	CK*	
Flexible Stretchable Fabric Glue	white	Fabric (F)*	
No Sew Fabric Glue	white	F*	
OK to Wash-It Permanent Fabric Bond	white	F*	
Stanley Dualmelt Glue Sticks	clear	Glue Gun Glue Sticks (GS)	
Greystone Craft & Hobby Low Temp Glue Sticks 5154	clear	GS	
Fingerprint Developer	clear	Super Glue (SG)*	
Loctite Quicktite	clear	SG*	
Quick Setting Epoxy Adhesive Super Glue	clear	SG*	
High Performance Future Glue (Superglue Corp)	clear	SG*	
Meijer Super Glue Gel	clear	SG	SG-1
Instant Krazy Glue All-Purpose	clear	SG	SG-1
Super Glue for Leather & Wood C13A	clear	SG	SG-1
Elmer's Wonder Bond Super Glue	clear	SG	SG-1

\*Samples distinguishable from other samples within the same class of adhesives

**Table 1 (cont'd) Adhesives Evaluated by PyGC/MS**

BRAND NAME	COLOR	TYPES	SUBCLASS
AVSG	clear	SG	SG-2
Surebond <sup>er</sup>	clear	SG	SG-2
Elmer's Washable glue stick (Dries clear)	blue	Twist & Paste Glue Sticks (TP)*	
Elmer's Washable School Glue Stick (Dries clear)	blue	TP*	
Elmer's All-Purpose Glue Stick (Dries clear)	white	TP*	
Scotch Glue Stick	white	TP*	
Avery Permanent Glue Stick	white	TP*	
Franklin Wood Glue exp. Dec. 95 <sup>^</sup>	almond	Wood glue (W)*	
Franklin Wood Glue exp, Sept. 92 <sup>^</sup>	almond	W*	
Liquid Nails for Woodwork		W*	
Carpenter's Wood Glue		W*	

<sup>^</sup> For the purpose of comparing the consistency of batches, dates printed on the package were used in place of batch numbers not printed on the label.

1100 µg. After testing, the sample size was reduced to 100 µg in an effort to lessen the amount of pyrolyzates, or residual adhesive components, which had been congesting the gas chromatograph's capillary column. 100 µg was the maximum useful sample size, not the optimum sample size. Any sample size from 100 µg or less could have been used to achieve similar results.

The 100 µg sample size was found to be equivalent to a 2mm x 2mm square area of dried adhesive. This measurement was determined by measuring pieces of paper, of various sizes, with a ruler. The pieces were then weighed to determine what area of sample weighed 100µg. After weighing the 2mm x 2mm piece of paper, a piece of adhesive the same size was weighed to determine if its weight for that particular area was comparable to that of the paper. The weight and area of the adhesive were comparable to that of the paper. The pre-measured square of paper was then used as a template to size



the remaining samples. After sizing a few samples with the piece of paper, the approximate size of each sample was estimated without the template.

### *Instrumentation*

Pyrograms of the adhesives were obtained using PyGC/MS. For the analysis of the adhesives, each sample-filled quartz tube was loaded into the platinum coil of the pyroprobe, then inserted into the interface of the Gas Chromatograph-Mass Spectrometer, or GC-MS. An “Adhesive Method” was developed, based on parameters from literature, to program the pyrolysis unit and GC-MS for a sample run time of 36 minutes, along with the following temperature settings. The PYROPROBE 1000® was programmed to pyrolyze samples at 700°C for 10 seconds. The pyroprobe (Figure 1), with quartz tube inserted, was screwed into a Chemical Data Systems (CDS) 1500 valved interface mounted on top of a Hewlett Packard (HP) 5890 Series II Gas Chromatograph (Figure 2) coupled to an HP 5971 Series Mass spectrometer. The temperature of the interface was set to 275°C (Refer to Table 2).

The gas chromatograph was fitted with a 30m Alltech EC-5 capillary column. The column, 32  $\mu\text{m}$  in diameter, contained SE-54 stationary phase with a film thickness of 1.0  $\mu\text{m}$ . Helium was used as a carrier gas at a flow of 1 ml/mn. For all adhesives analyzed, the GC-MS was employed with a split injection ratio of 50:1.

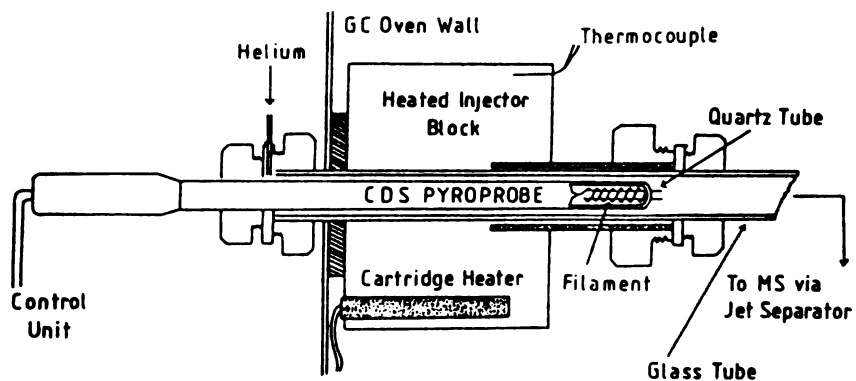


Figure 1: Diagram of a CDS Pyroprobe. (From Yinon, Jehuda, (editor), *Forensic Applications of Mass Spectrometry, Forensic Applications of Pyrolysis - Mass Spectrometry*, Munson, Thomas, Boca Raton, FL., CRC Press, Inc. 1995.)

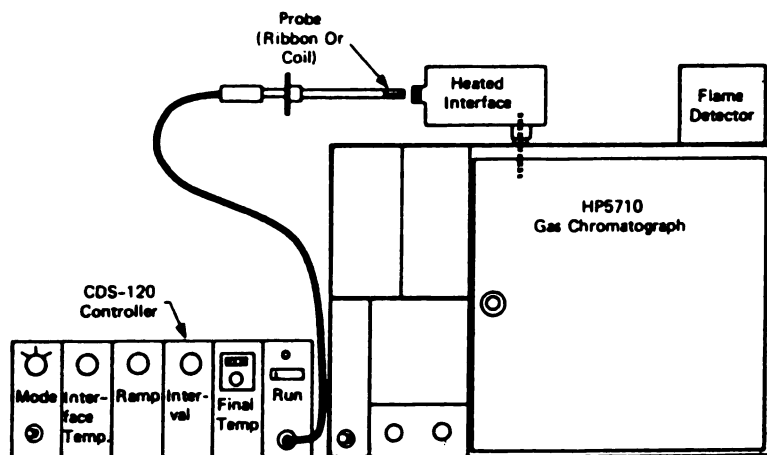


Figure 2: Diagram of CDS-120 Pyrolysis - GC Instrumentation. (From Voorhees, Kent J., (editor), *Analytical Pyrolysis Techniques and Applications, Practical Analytical Pyrolysis Applications for Polymer Industry*, Smith, Charles G., London, Butterworth & Co., 1984.)

**Table 2 Pyrolytic Parameters**

<b>PYROLYSIS CONDITIONS</b>
-----------------------------

Interface Oven:	275°C
Pyrolysis Temperature:	700°C
Pyrolysis Interval:	10 seconds

<b>CHROMATOGRAPHIC CONDITIONS</b>
-----------------------------------

Column:	30m x 32 µm EC - 5 Capillary (Alltech)
Injector Temp.:	275°C
Split Ratio:	50:1
Carrier Gas:	He
Carrier Flow Rate:	1ml/min.
Oven Program:	50°C for 1.00 min, then 10.0°C/min to 250°C

<b>MASS SPECTROMETER SCAN PARAMETERS</b>
--

Mass Range:	50 to 550 Scans/sec. 1.2
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## RESULTS AND DISCUSSION

After running samples through the PyGC/MS each run was given a filename and saved on a computer disc. A pyrogram was obtained as the data for each adhesive. All pyrograms were assessed visibly by comparing the overall peak patterns, retention times, and abundance. The pyrograms were examined by overlaying at least two, but no more than three, pyrograms at a time on a light table often used for tracing pictures or viewing negatives. The pyrograms of samples within the same family of adhesive were compared one to another first (i.e. Glue sticks vs. Glue sticks). Then the pyrograms of one type, or family, of adhesives were compared to those in the other types of adhesives (i.e. Woodglue vs. Fabric glue). This was done to ultimately conclude if adhesives could be differentiated using PyGC/MS.

The 48 adhesives analyzed could not all be individually characterized so they were grouped in classes according to their useful purpose; and into subclasses based on their being comparable to adhesives within their class. There were eight general classes in which the pyrolyzed adhesives could be grouped (Refer to Appendix A for all pyrograms). The groups include: Caulking glues, Contact Cement, Fabric glues, Hot Melt glue sticks, Super Glue (Cyanoacrylate), Twist and Paste Glue Sticks, All - Purpose glue, and Wood glue. The adhesives were grouped according to their general purpose. A representative pyrogram for each of these types of adhesives can be found in Figures 3 - 6. Within the classes there were some adhesives that were not easily distinguished, so subclasses were created for those particular adhesives. In addition to the comparison between samples in the same class, and the evaluation to differentiate between the classes of adhesives, there were a few other points of interest taken into consideration during

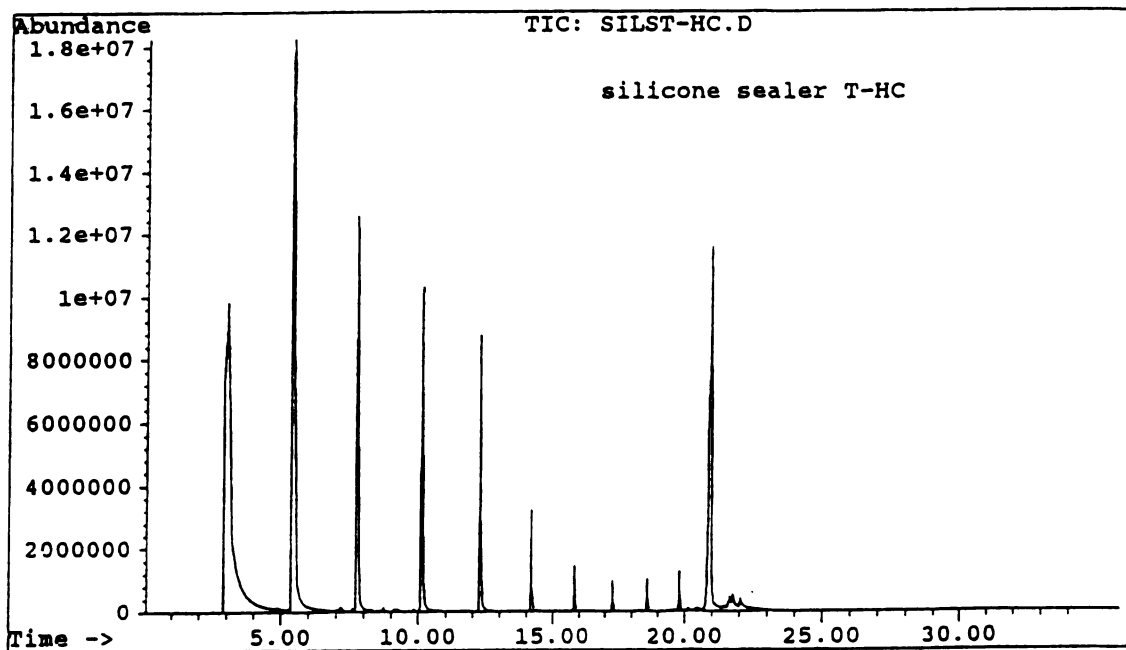
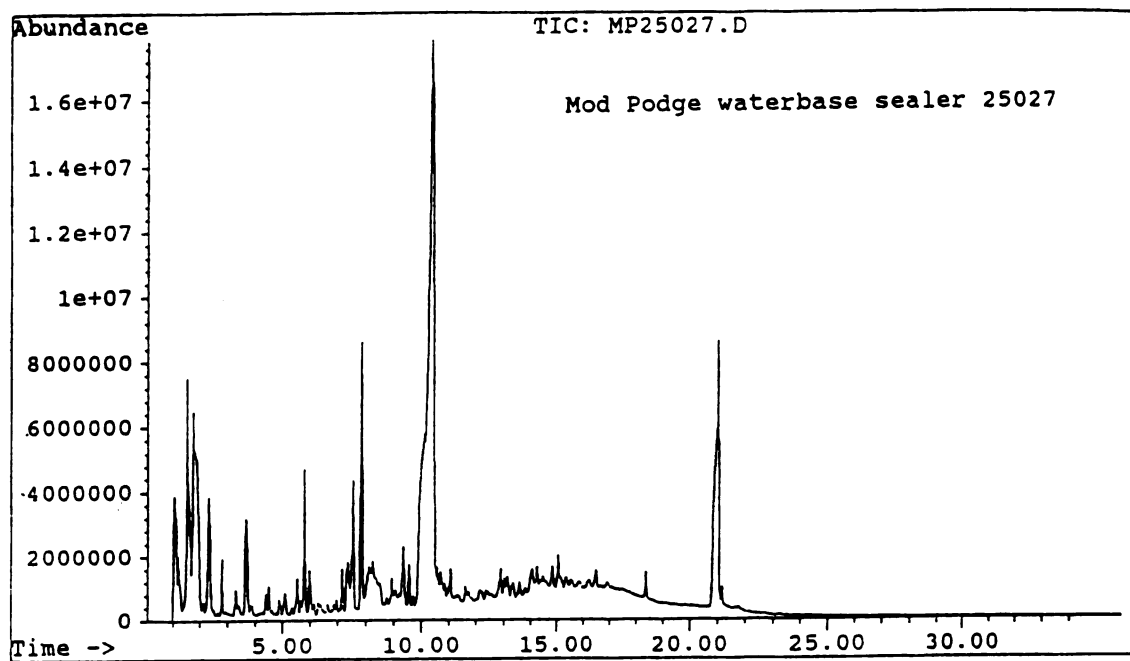


Figure 3: Representative Pyrograms for (Top) All - purpose Glues and (Bottom) Caulking Adhesives.

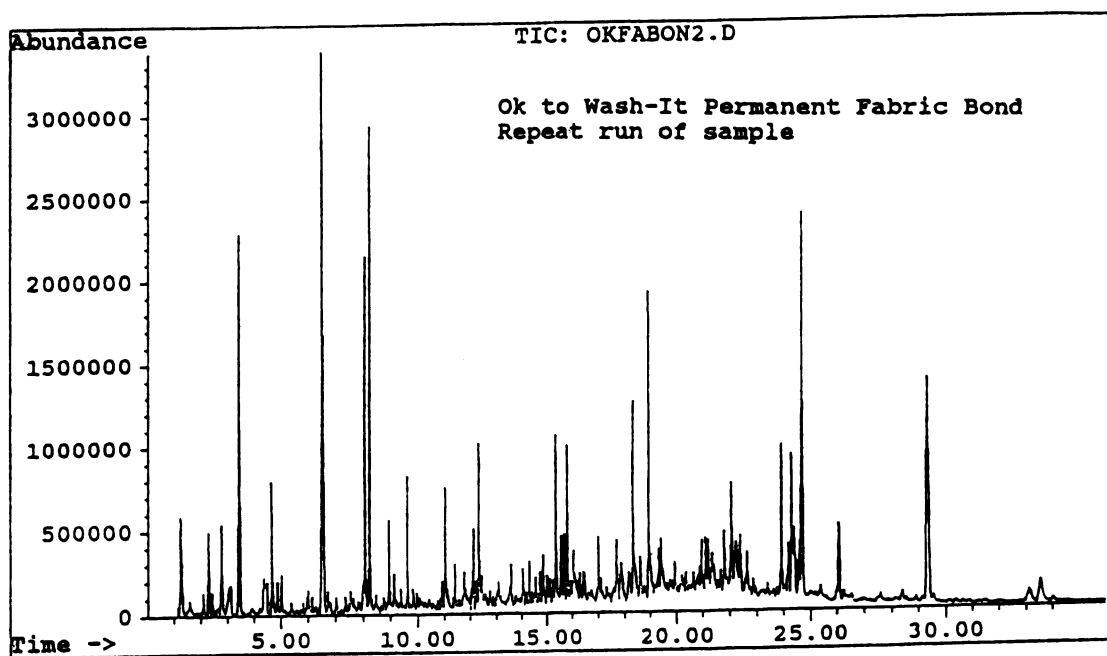
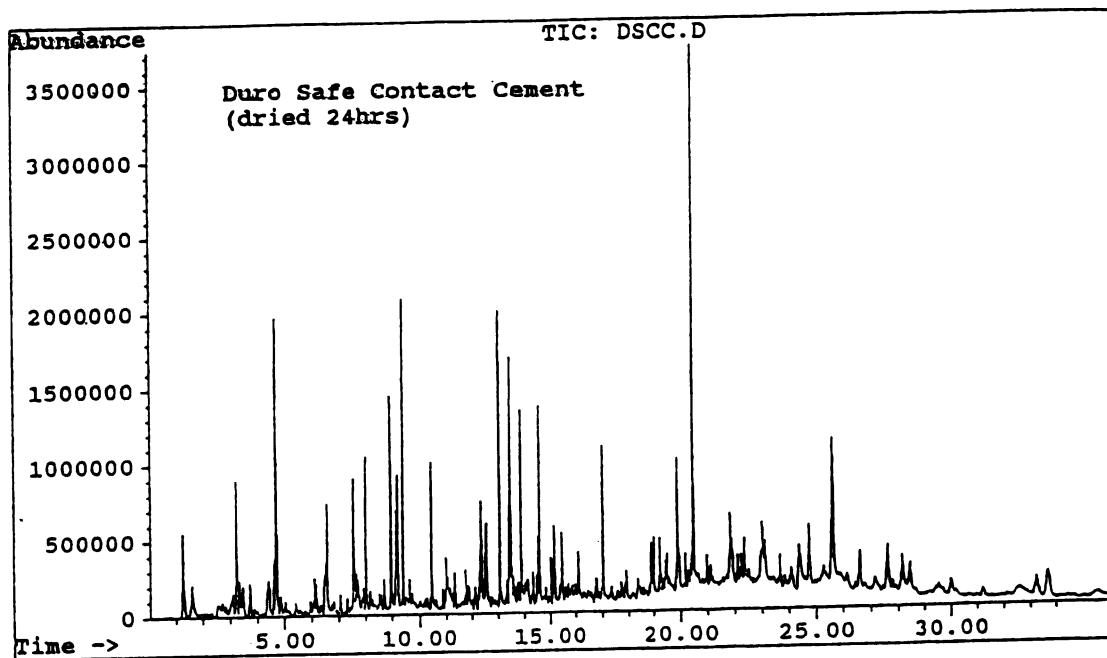


Figure 4: Representative Pyrograms for (Top) Contact Cement and (Bottom) Fabric Glues.

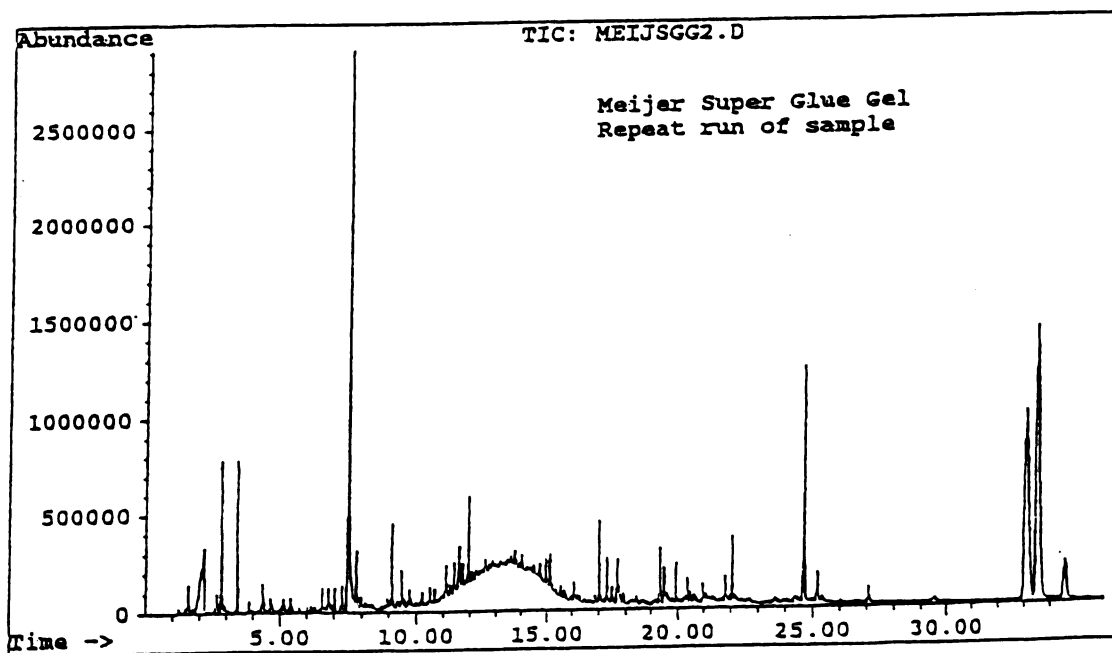
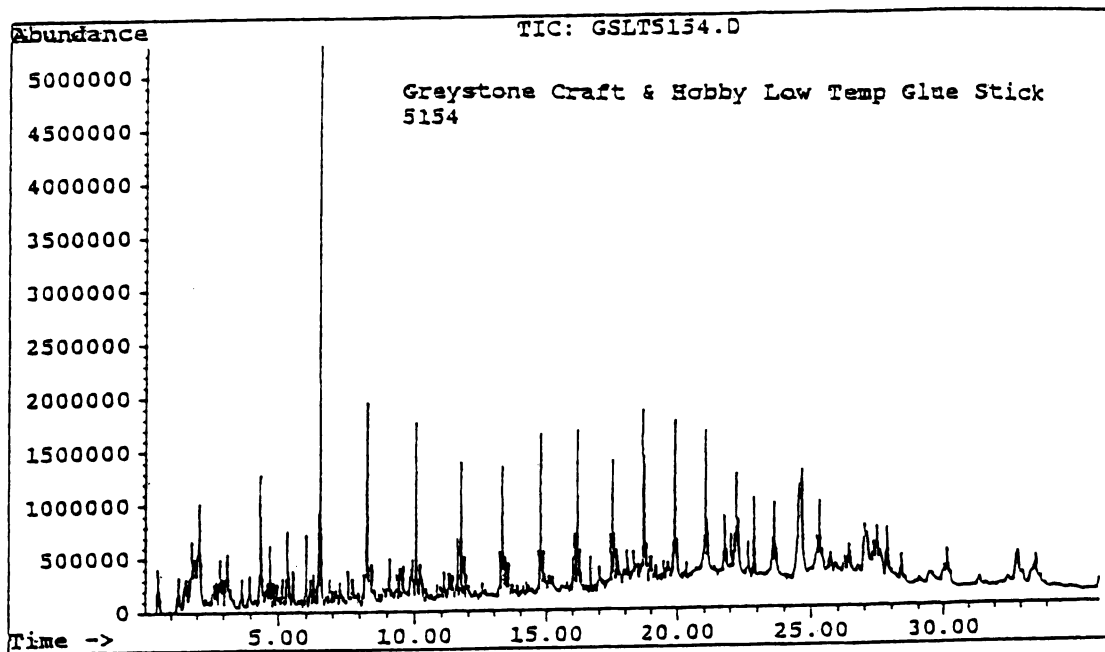


Figure 5: Representative Pyrograms for (Top) Hot Melt Glue Sticks and (Bottom) Superglues.

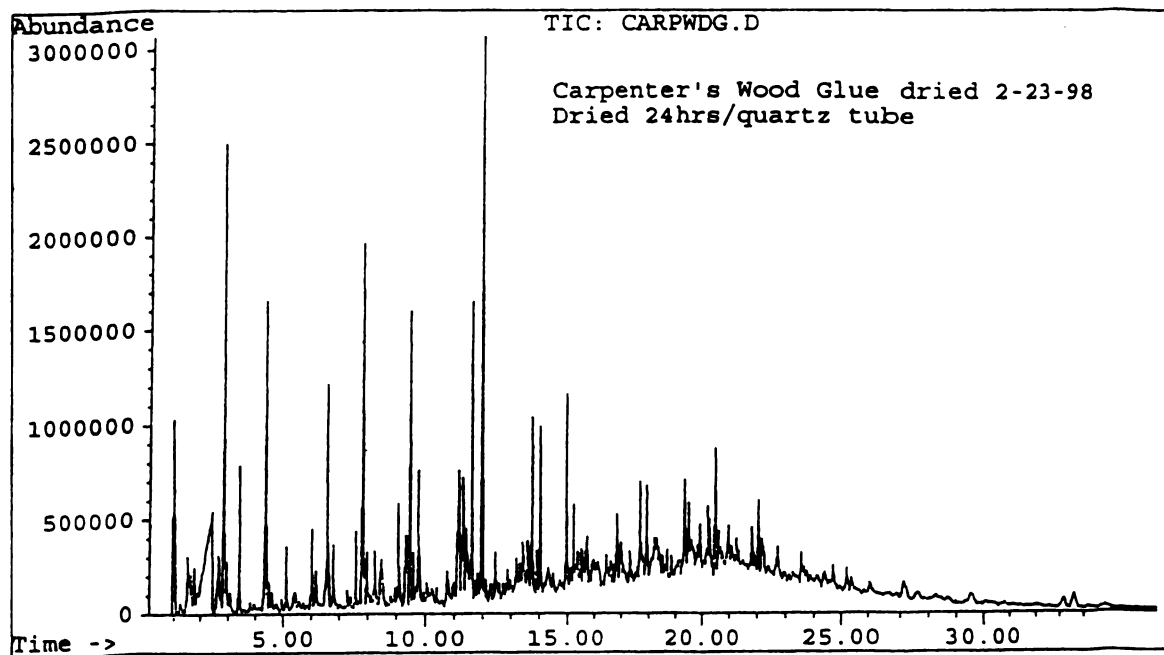
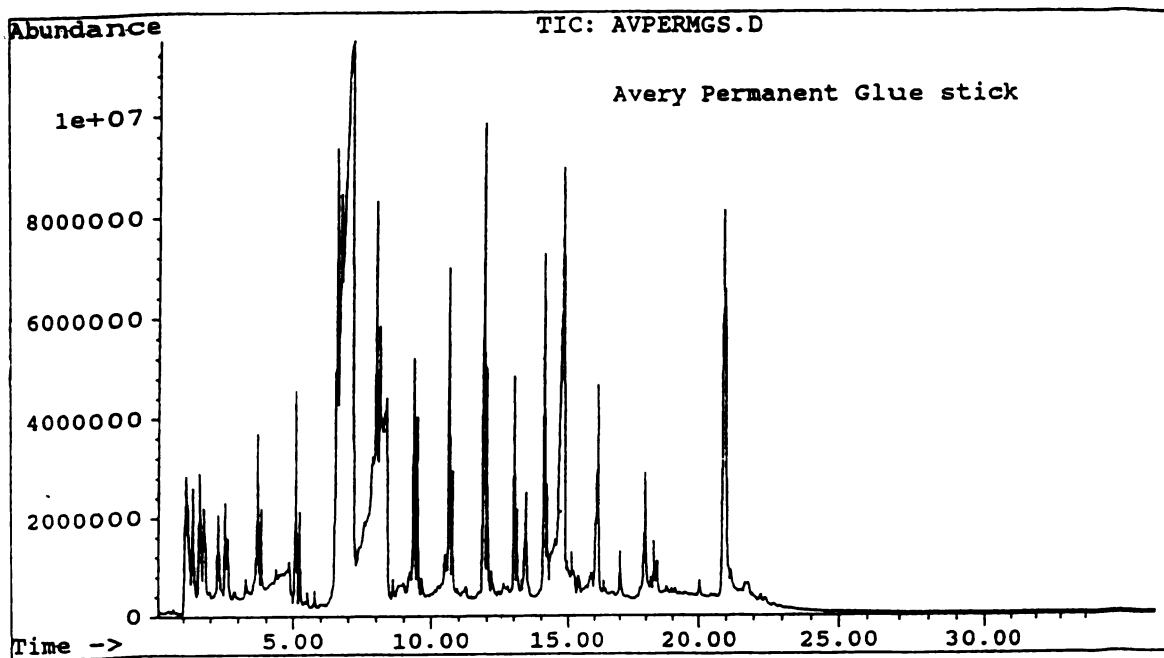


Figure 6: Representative Pyrograms for (Top) Twist & Paste Glue Sticks and (Bottom) Wood Glues.



the comparison. These points of interest include adhesives of the same type and brand sampled from different batches and color, the affect sample size has on the data, and a “repeatability” study that examined the affects of drying time on a sample.

#### *Fabric Glues*

All three of the fabric glues share some common peaks, but all of them had distinct pyrograms. Although the Flexible Stretchable Fabric Glue and the No Sew Fabric Glue share a similar peak pattern up to five minutes into the run, they can still be distinguished from one another.

#### *Twist & Paste Glue Sticks*

There were five adhesives analyzed. Three of which were distinguishable. Two of the samples were of the same type and brand, but different colors. Their peaks were grouped at intervals about every 1.5 min. - 2.0 min. Despite the difference in color their pyrograms almost matched peak for peak. So, the color didn't play much of a factor in differentiating the brands.

#### *All - Purpose Glue*

The all - purpose glues, in general, have been used for basic crafts and school projects. However, they can be used for adhering a variety of things. Out of eight samples analyzed three were indistinguishable. The remainder were distinguishable.

#### *Hot Melt Glue Sticks*

There were only two types of Glue Sticks pyrolyzed. These particular glue sticks are used in hot glue guns for crafts. Aside from a couple of extra peaks on one pyrogram there was little difference between the two samples. One of the samples was pyrolyzed in a quartz tube, then in a glass tube of similar dimensions. This was done to determine if

glass tubes could be used in place of quartz tubes when pyrolyzing samples. There was no significant difference between the glass and the quartz tubes. The decision was made to continue pyrolyzing samples in quartz tubes since quartz tube had been the primary vessels for holding samples during pyrolysis.

#### *Caulking Adhesives*

This class of adhesives is often used to “fill joints, gaps, and cavities between two or more similar or dissimilar substrates” (27). Caulking adhesives could be grouped into four subclasses (See Table 1) because some of the samples were not easily distinguished within this particular class of adhesives. A total of 12 samples were analyzed. Since only two of the 12 could be differentiated by brand they weren’t placed in subclasses.

#### *Super Glues (Cyanoacrylates)*

Out of the 10 glues, eight possessed broad “humps” characteristic only to the cyanoacrylates. Upon request, Thomas Wampler of Chemical Data Systems (CDS), ran a couple of cyanoacrylates by PyGC/Ms and found similar results (28). It was not completely certain what caused the peak broadening in the pyrograms of the super glues. It was presumed that these “humps” are homogeneous and not a mixture of unresolved peaks.

#### *Wood Glues*

These glues are used to bind wooden substrates together, often in carpentry or when performing simple repairs on wooden structures. Contact cements are viscous, tacky glues often used in making crafts. The pyrograms within each of these classes of adhesive were distinguishable one from another.

### *Color & Batch Number Study*

The purpose of this study was to conclude if there were any distinctions in samples that were offered in more than one color. The other goal of this study was to note the consistency of samples taken from different batches of the same brand of adhesive. The lot number, or batch number, was recorded for each sample. If one was not present then the date on the package was used. A total of 10 adhesives from four classes were examined in this study (Refer to Table 3 & Appendix B). Samples taken from different batches did not pose much difference in their pyrograms. Around the twenty minute retention mark there appears to be some contamination. There were some minor distinctions in color, also. The Elmer's Squeeze & Caulk Almond and White caulking glues also showed some differences in there pyograms.

### *Sample Size Study*

Three different brands of adhesives were examined at varied approximate weights (Refer to Table 3). After each sample was dried they were run consecutively on the PyGC/MS. Elmer's All - Purpose glue stick was dried for five days and pyrolyzed at weights of 100 ug, 500 ug, and 1100 ug. At 1100 ug the sample managed to hold its peak definition. However, the best peak resolution of this sample was seen at 500 ug. Rose Art washable school glue was dried for 24 hours and pyrolyzed at weights of 100 ug, 1100 ug, and 1900 ug. The peak resolution for this sample was best at 100 ug. Although the baseline for the 100 ug and 1900 ug samples shifted, the peaks stilll correspond between runs. The Modge Podge water based sealer was also dried for 24 hours and pyrolyzed at 100 ug and 1100 ug. The baseline again was distorted in these two pyrograms for some unknown reason, and the peaks only correspond up to about 22.00 minutes. The

distortion in the baseline could be due to too much sample being applied to the column at once. As the literature stated, a sufficient amount of sample would consist of 100 ug, or less. Overall, this study shows that with an increase in sample weight the abundance, or constituents' concentration, may have increased, but it is possible to maintain some peak definition (Figure 7). However, it's best to use the minimum sample weight that gives the best resolution and prevent damaging the column, which can attribute to distortion in the pyrograms.

#### *Repeatability and Drying Time Study*

This study took into account the affects of drying time and how well consecutive runs of a sample were repeated with similar results. According to literature (32), "Repeatability" is the precision in one lab, by one analyst, and on one instrument. "Reproducibility" on the other hand refers to precision between different labs, different analysts, and different instruments. It is for this inconsistency with instrumentation and parameters that forensic labs lack standardization. So, for clarification the term "Repeatability" was used since it best described the repetitive results of this section.

Three aliquots of the sample were dried overnight and three aliquots were dried for 11 days. (Refer to Table 3) After the samples were dried they were run consecutively on the PyGC/MS. Aside from one peak visible at 20.00 min. for the second and third runs of the 24 hour sample the extension of drying time didn't improve the definition of the sample's peaks. However, the resolution, or the separation of each sample's constituent parts increased with each successive run from the retention range of 13.00 min. to 21.00 min.

To improve the overall resolution and consistency of pyrogram patterns it would

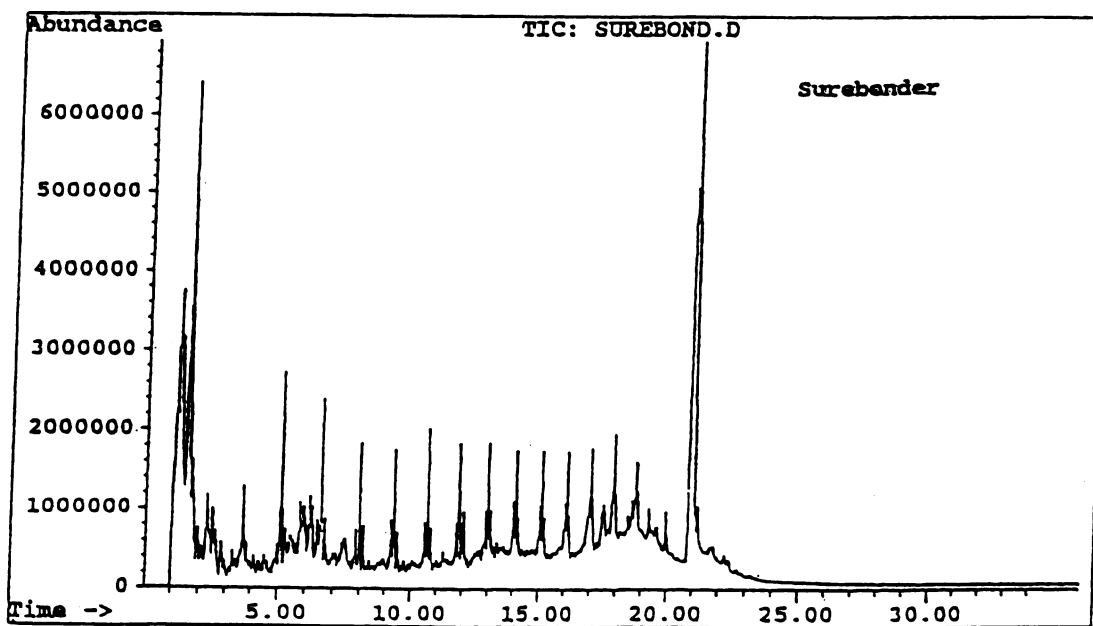
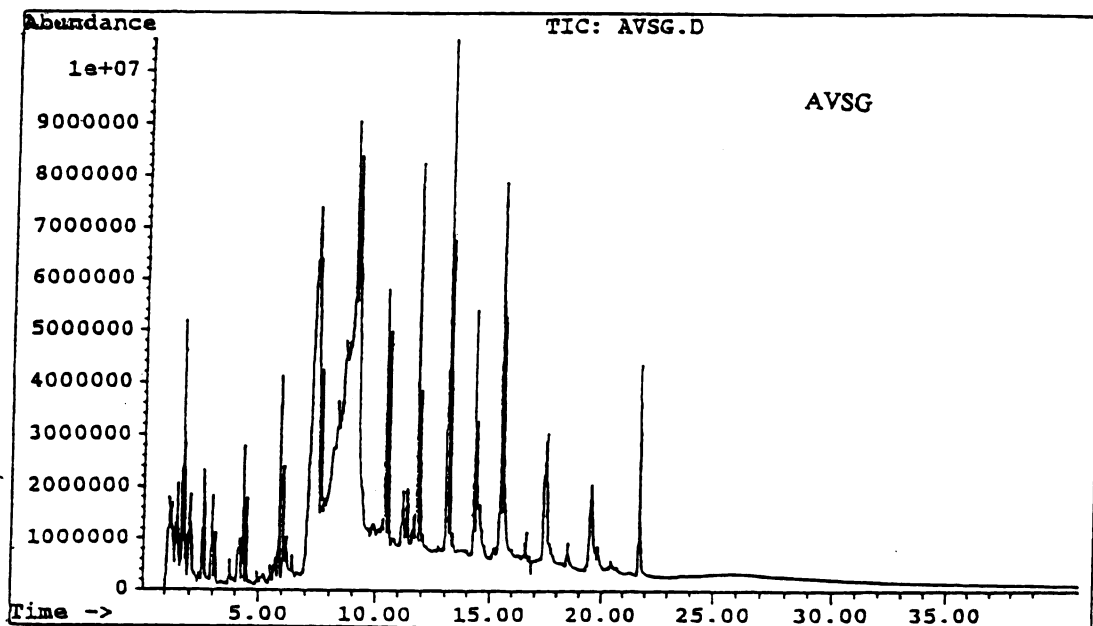


Figure 7: (Top) Pyrogram of a sample with a greater weight and abundance.  
(Bottom) Pyrogram of a sample with a smaller weight and abundance.

be best to ensure the complete elution of components and consistent sample size. This would ensure that there are no contaminants from previous samples eluting off with subsequent samples run. To make sure all of the adhesive components are eluting off the column between pyrolysis runs, conduct a run with a blank tube injected into the GC - MS. If any peaks appear on the pyrograms, then it will be evident that all of the sample is not flowing off the capillary column. Performing this blank run between samples may help preserve the life of the GC column. Too many residual components deposited on the column could over saturate the stationary phase of the column, thus causing broadening of peaks. If blanks were run between samples during this study, having to replace the column could have possibly been prevented. A consistent sample size throughout the analysis would provide an abundance set at a particular level. This would make comparing pyrograms of different adhesives a little easier because the peak patterns would have been about the same proportion. None the less, samples with varying abundance can still be compared because only the concentration, not the chemical makeup changes.

Although it was found that adhesives cannot be individualized 100% by pyrolysis, the fact that they can be narrowed down to their particular class , or type, of adhesive still makes it a pertinent form of analysis in forensic science.

**Table 3 Adhesive Studies**

REPEATABILITY AND AFFECTS OF DRYING TIME STUDY			
Adhesive	Color	Drying Time	Sample Weight♦
Ross All Purpose Glue	white	24 hours*	100µg
Ross All Purpose Glue	white	24 hours	100µg
Ross All Purpose Glue	white	24 hours	100µg
Ross All Purpose Glue	white	11 days	100µg
Ross All Purpose Glue	white	11 days	100µg
Ross All Purpose Glue	white	11 days	100µg

SAMPLE SIZE STUDY			
Adhesive	Color	Drying Time	Sample Weight♦
Elmer's All Purpose Glue Stick	white	5 days	100µg
Elmer's All Purpose Glue Stick	white	5 days	500µg
Elmer's All Purpose Glue Stick	white	5 days	1100µg
Rose Art Washable School Glue	white	24 hours	100µg
Rose Art Washable School Glue	white	24 hours	1100µg
Rose Art Washable School Glue	white	24 hours	1900µg
Modge Podge Waterbase Sealer	white	24 hours	100µg
Modge Podge Waterbase Sealer	white	24 hours	1100µg

COLOR AND BATCH NUMBER STUDY				
Adhesive	Batch Number†	Color	Drying Time	Sample Weight♦
Elmer's Glue		green	24 hours	100µg
Elmer's Glue All	X06D1	white	24 hours	100µg
Elmer's Glue All		white	24 hours	100µg
Elmer's Glue All	B21C1	white	24 hours	100µg
Franklin Wood Glue	exp. Dec. 95	off white	24 hours	100µg
Franklin Wood Glue	exp. Sept. 92	off white	24 hours	100µg
Uhu Stic	3082	purple	24 hours	100µg
Uhu Stic	4049	white	24 hours	100µg
Elmer's Squeeze N Caulk	B2711	almond	24 hours	100µg
Elmer's Squeeze N Caulk	C0861	white	24 hours	100µg

\*24 hours is an approximate drying period for samples dried overnight.

†Batch number not always available. The brand name, color, or date were used to identify samples.

♦Samples were weighed on an analytical scale.

## CONCLUSION

Py GC/MS is a practical analytical technique because it involves very little sample preparation, this instrument can receive both soluble and insoluble materials, its sensitivity allows for minute sample sizes ranging from 100 ug or less, and it provides a simple and economical process to interface a pyrolyzer unit to a GC - MS. It was also noted that PyGC/MS produces repeatable results, especially when running the same sample consecutively.

The majority of the adhesives analyzed, as predicted, were grouped in classes specific to their type (i.e. Fabric glues with Fabric glues). About half of the adhesives could be differentiated from other adhesives, even within their own class (Refer to Table 1). The absence or presence of a few peaks were the minor factors separating many of these adhesives from others in the same group. Subclasses were also created within some of the adhesive families for those samples that were not easily differentiated, but could be matched to other adhesives within their particular class (Refer to Table 1). There were also some minor distinctions between samples with different colors and those taken from various batches.

A larger sample size constitutes for a greater abundance, or concentration, for the group of samples pyrolyzed before the GC column was changed midway through the research. This may have made it possible for some more resolved peaks seen, for example, in a 100 ug sample to be obscured amongst a group of peaks in an 1100 ug sample (Figure 7). Although there was little difference in the peak patterns of samples with a greater weight versus those at 100 ug, it would be best to keep the sample size the



same throughout.

PyGC/MS by itself isn't 100% identifiable, but a scheme of analysis including FTIR and PyGC/MS could categorize and individualize complex samples like adhesives. This would be particularly effective if more adhesives were added to the library created by Jeff Kindig, against which an unknown adhesive brand and type could be confirmed. All of the samples noted as "indistinguishable" aren't all exactly the same, some differences with repeated runs and blank runs may be revealed as significant. Further research is needed with the cyanoacrylates to determine the composition of the unidentified "humps" in the cyanoacrylate pyrograms. In the future this comparison of pyrolyzed adhesives could be extended to classes of adhesives not run in this study, such as spray adhesives, nail glue, adhesives used by makeup artists, adhesive on the backing of tapes, and resins used to bind porcelain to teeth in dentistry (33).

## APPENDICES

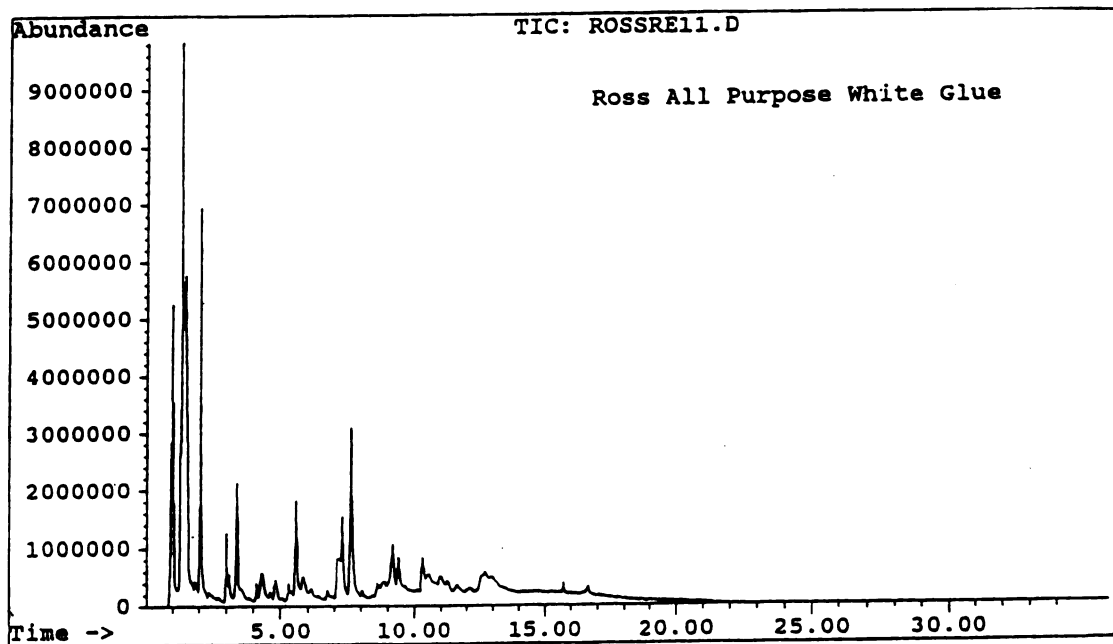
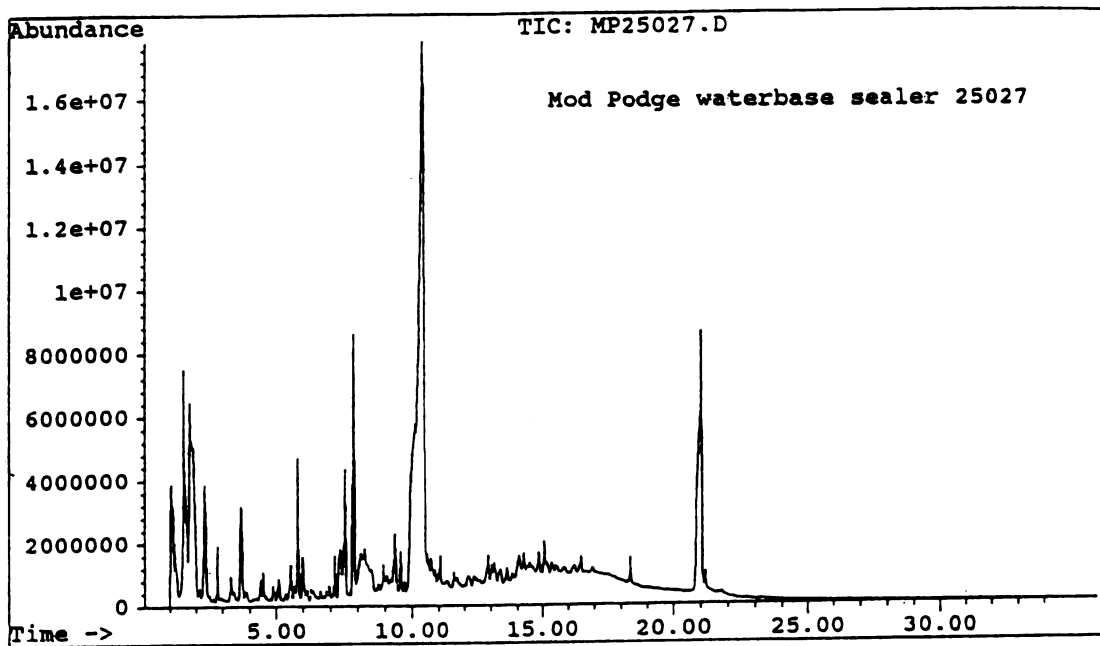
## APPENDIX A

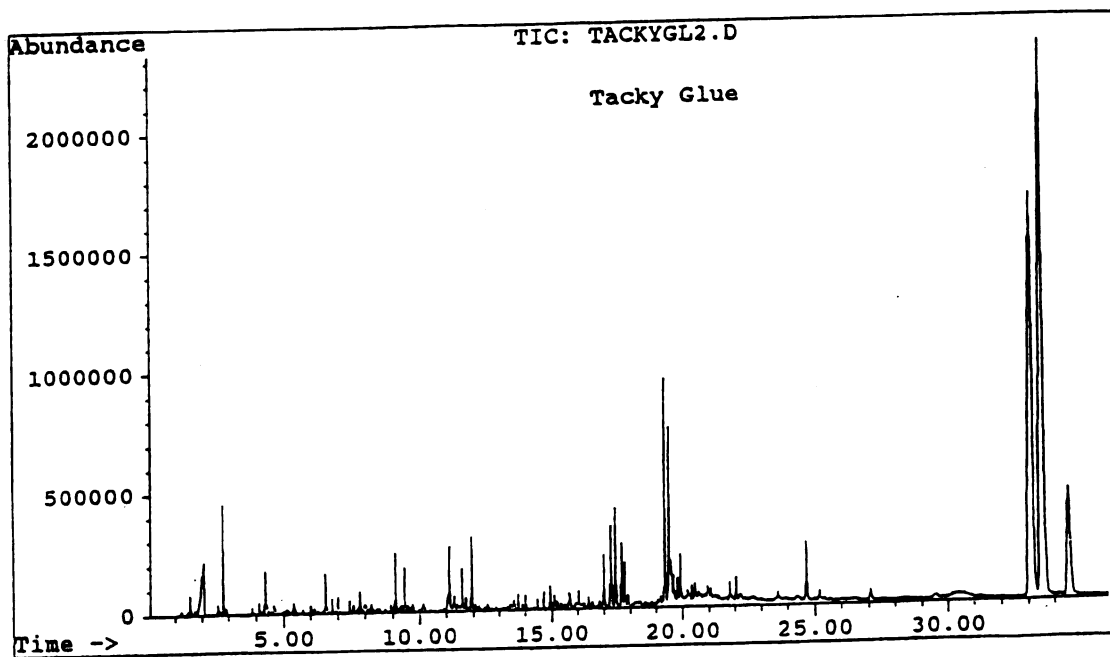
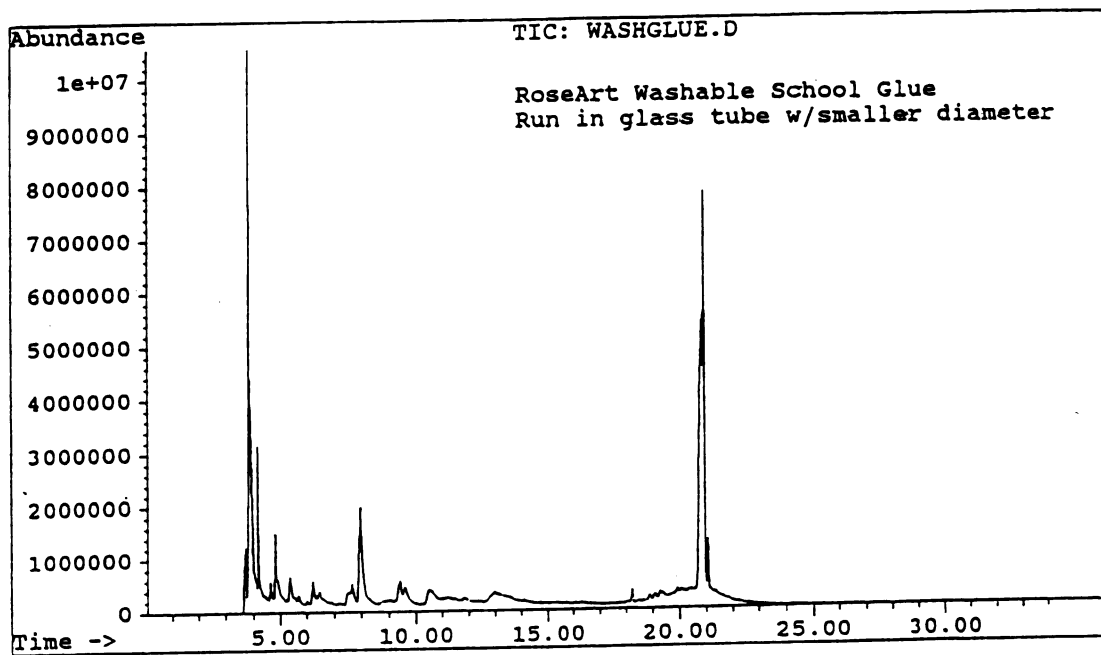
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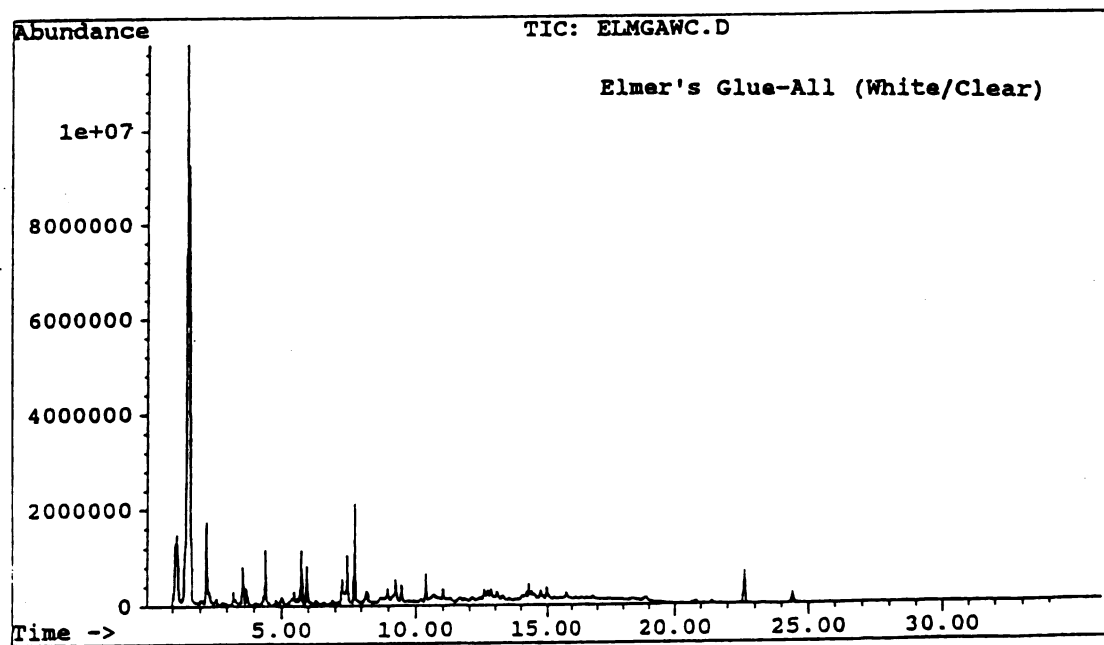
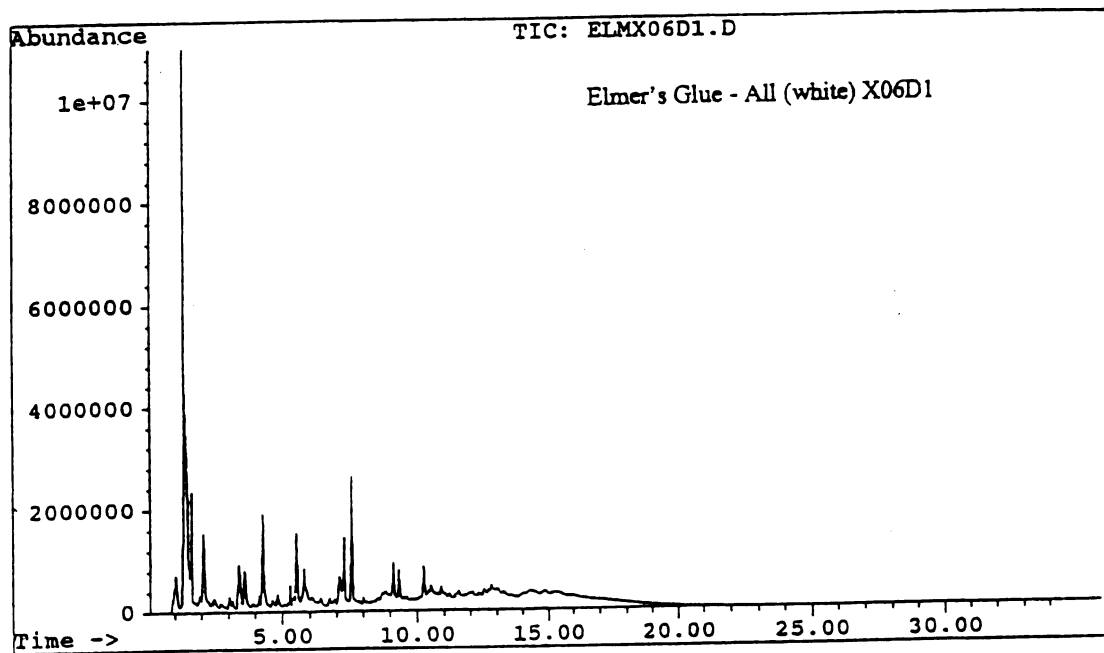
#### Eight Groups Evaluated

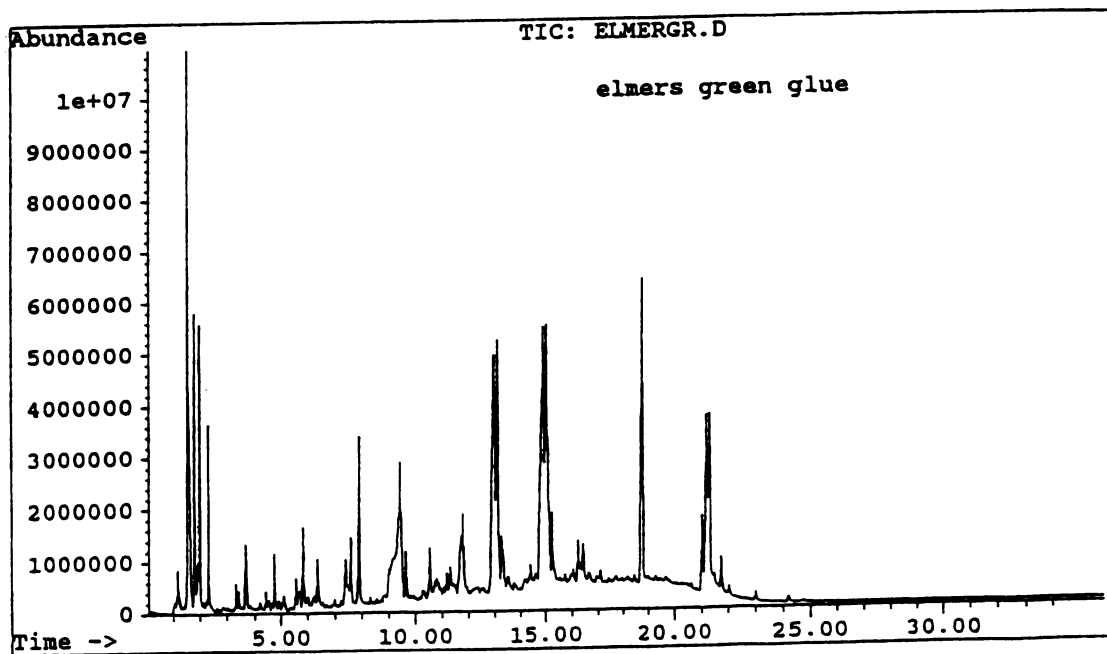
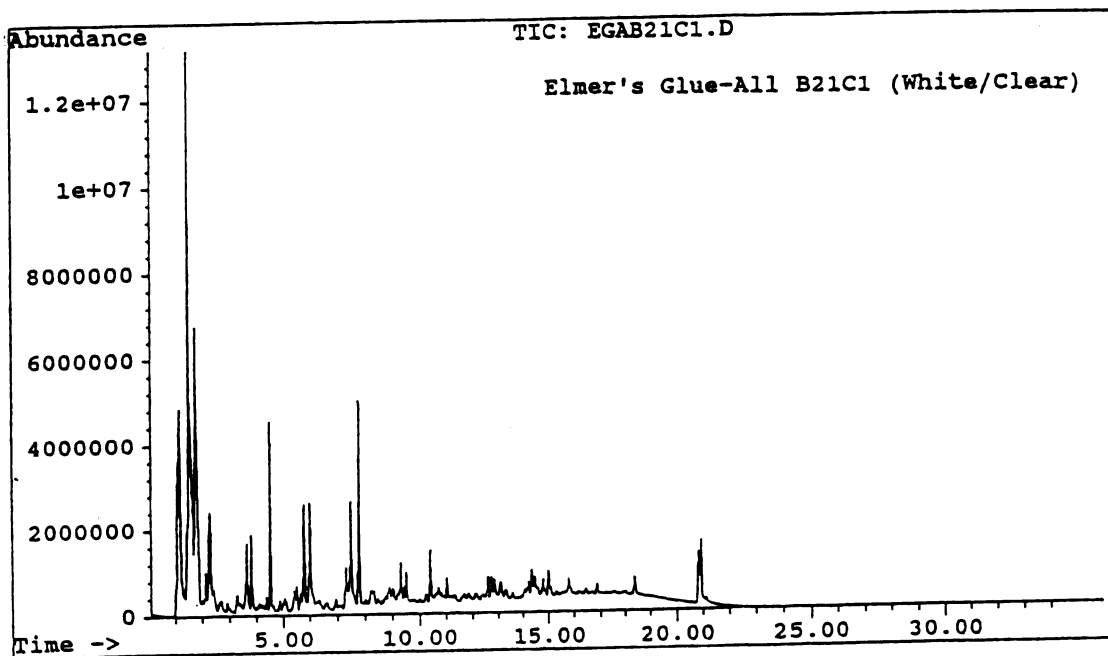
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2. Caulking Glues
3. Contact Cement
4. Fabric Glues
5. Hot Melt Glue Sticks
6. Super Glues (Cyanoacrylates)
7. Twist & Paste Glue Sticks
8. Wood Glues

## All Purpose Glues



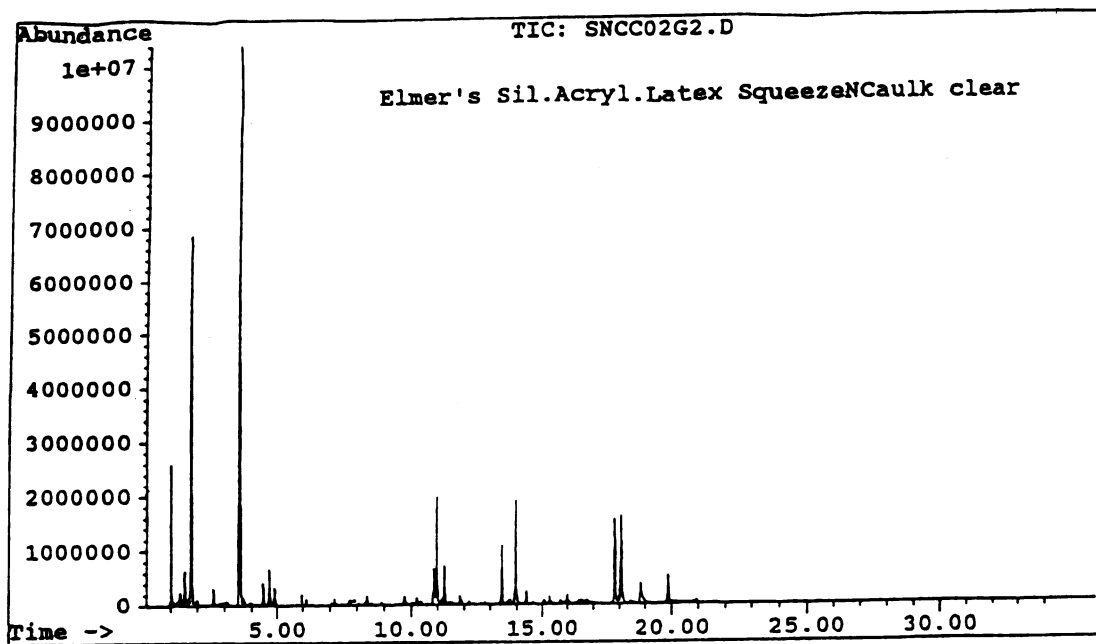
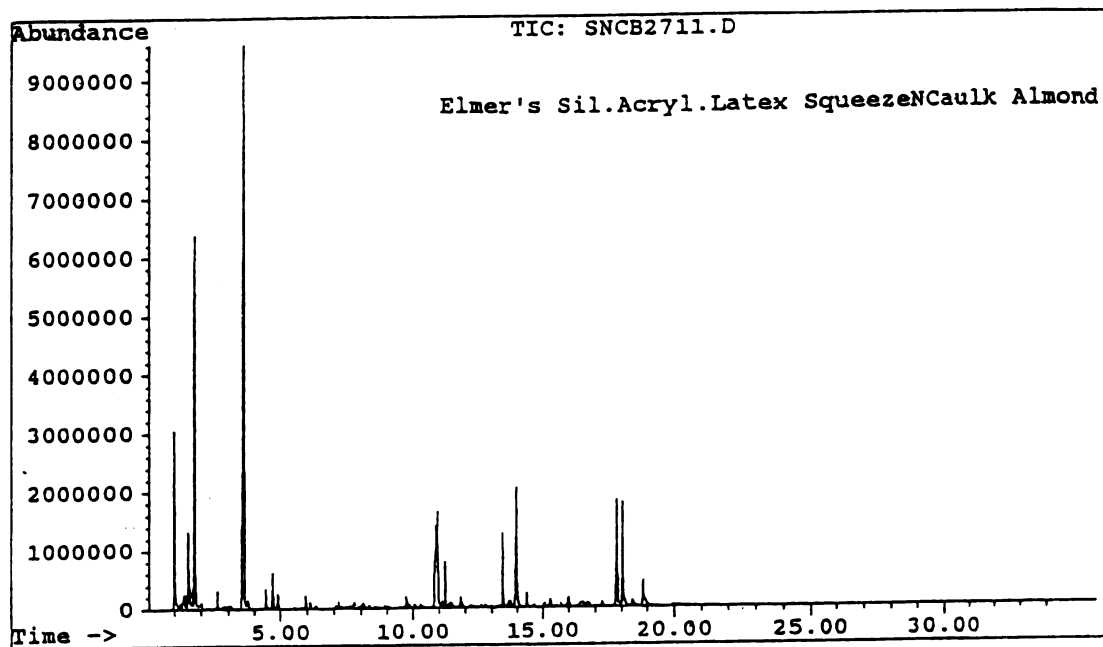


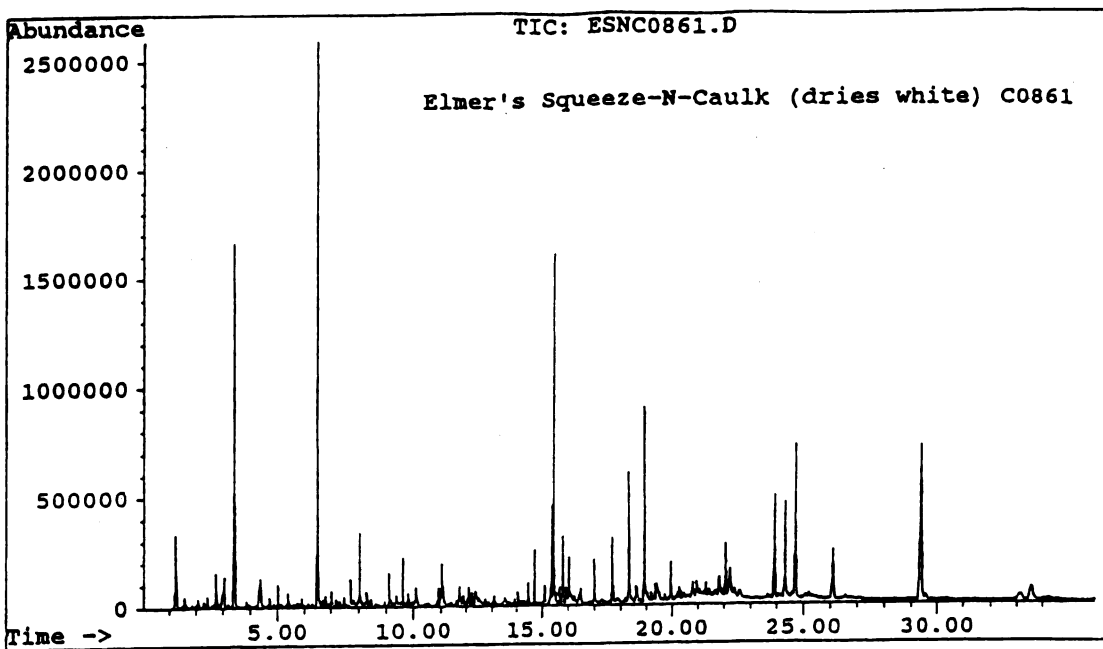
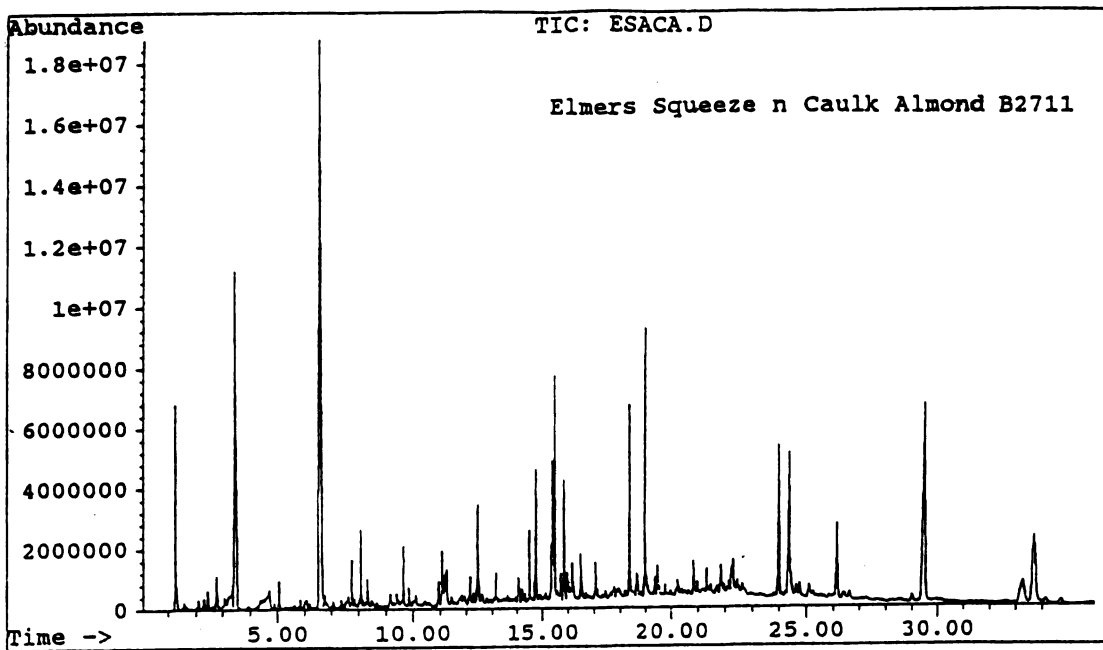


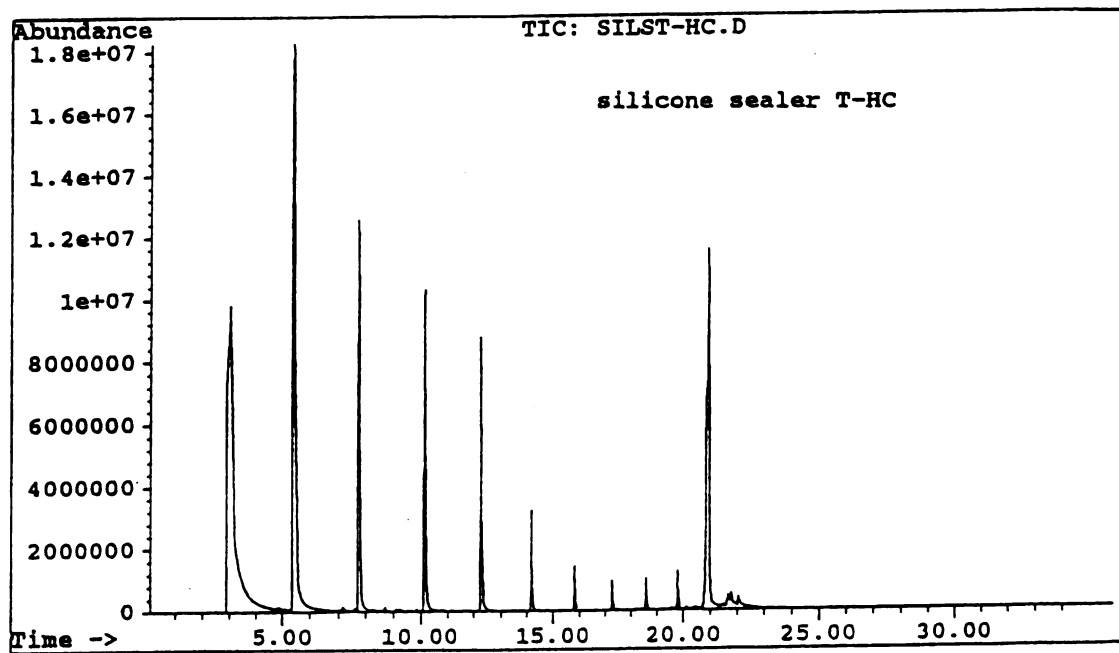
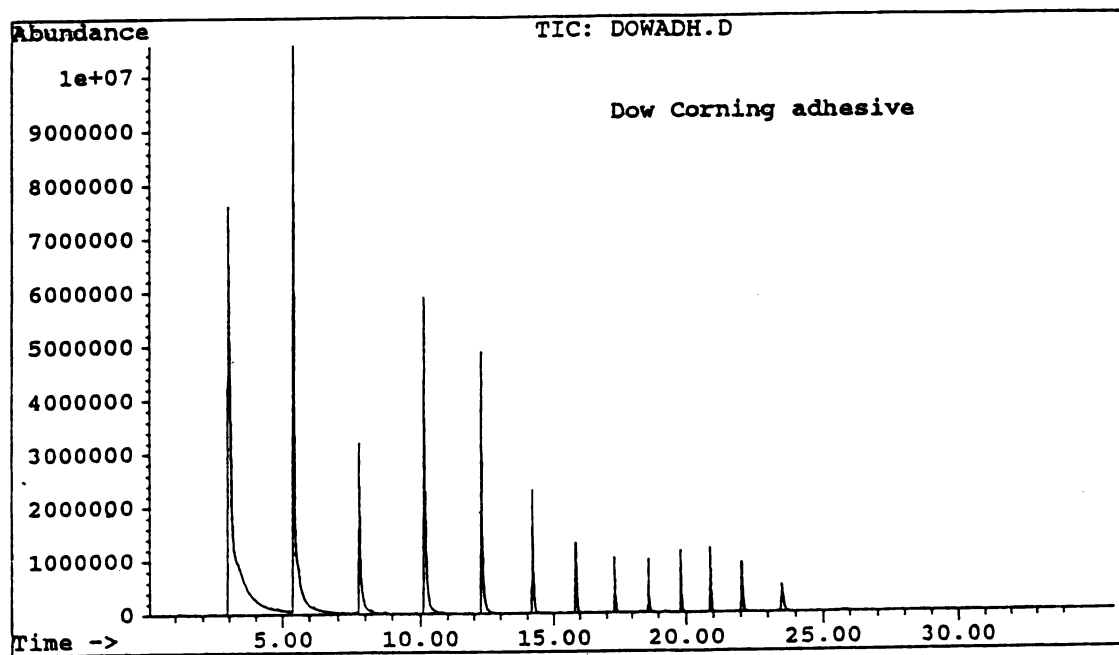


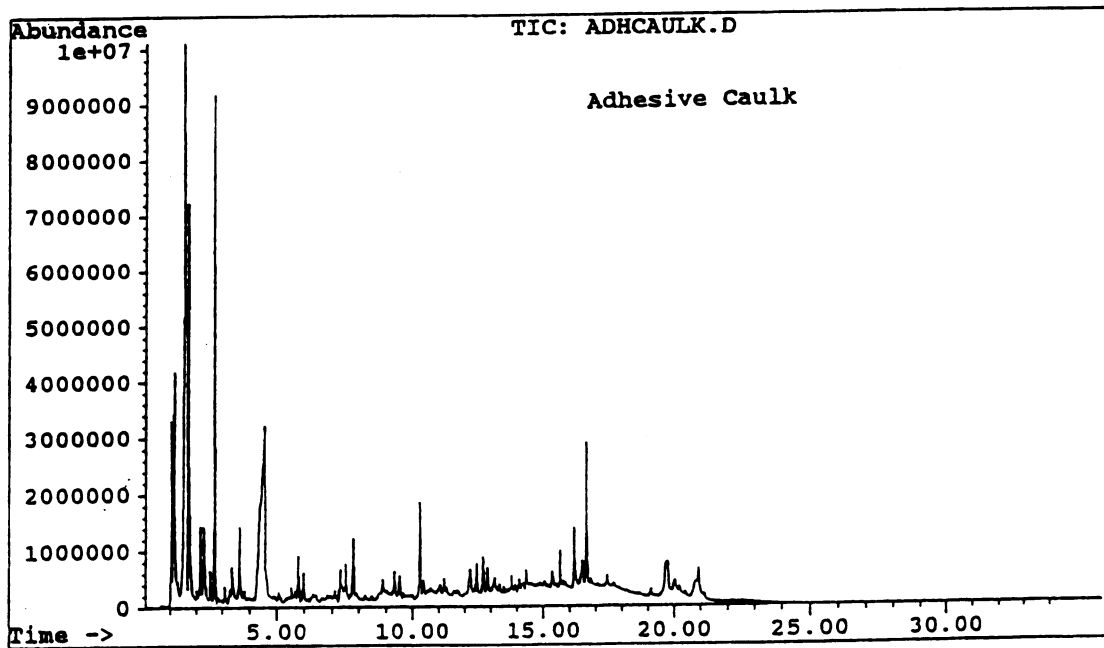
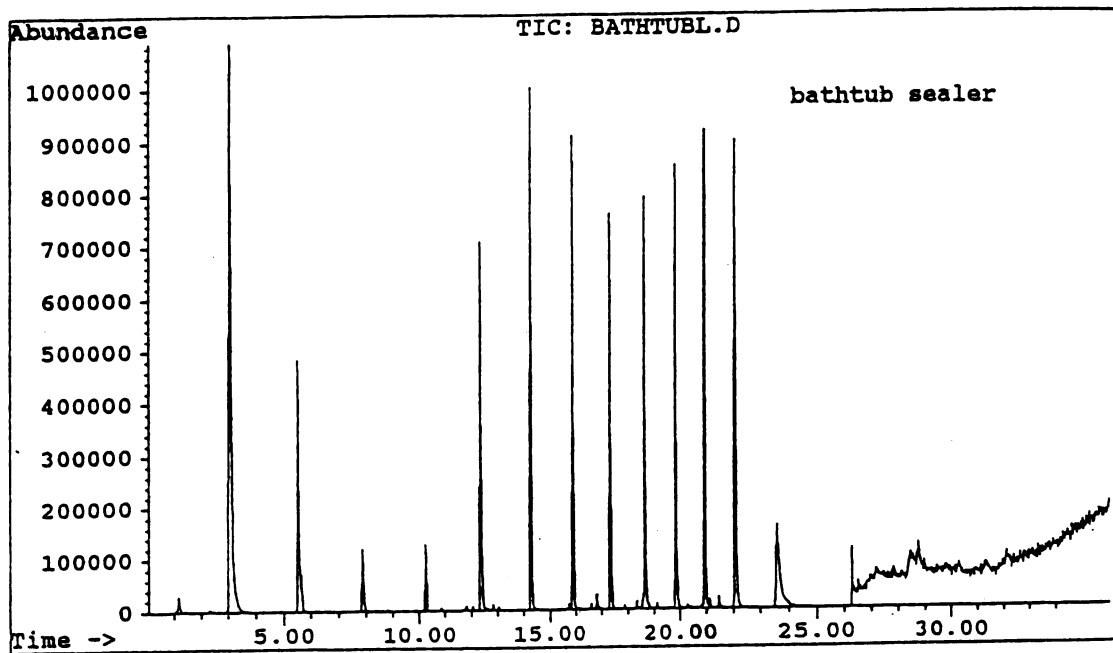


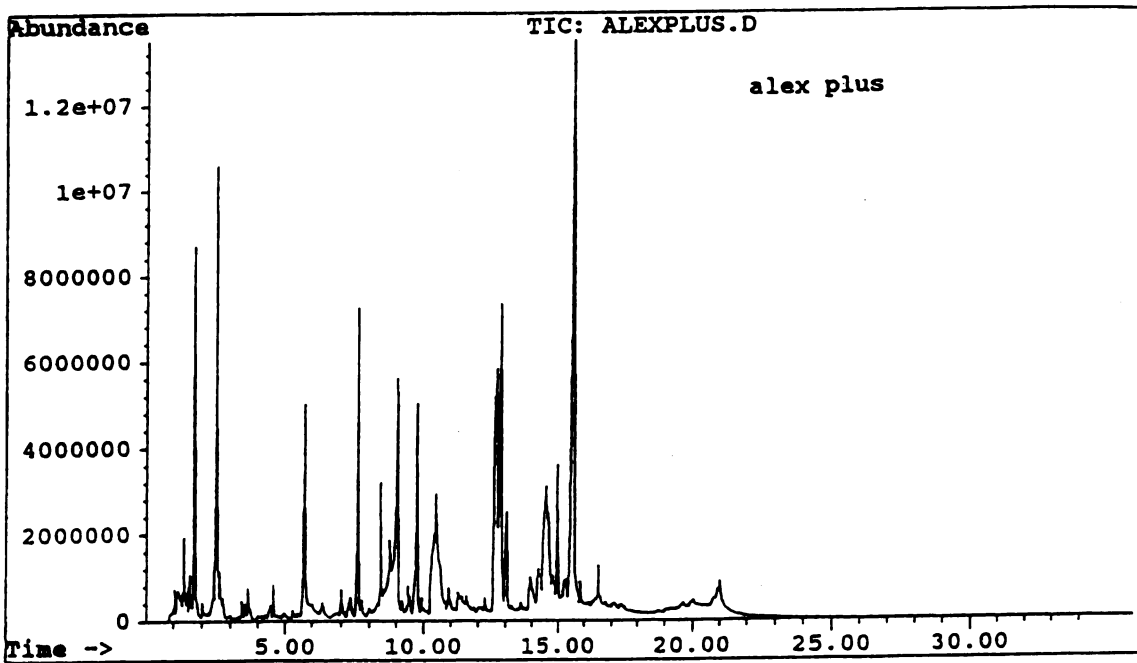
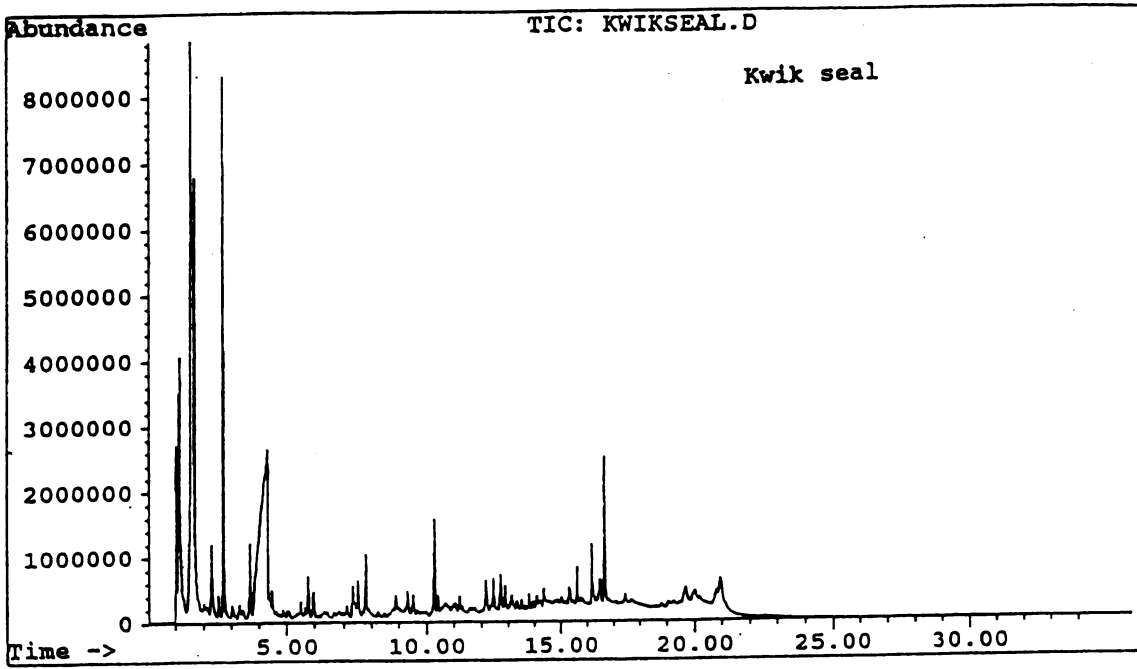
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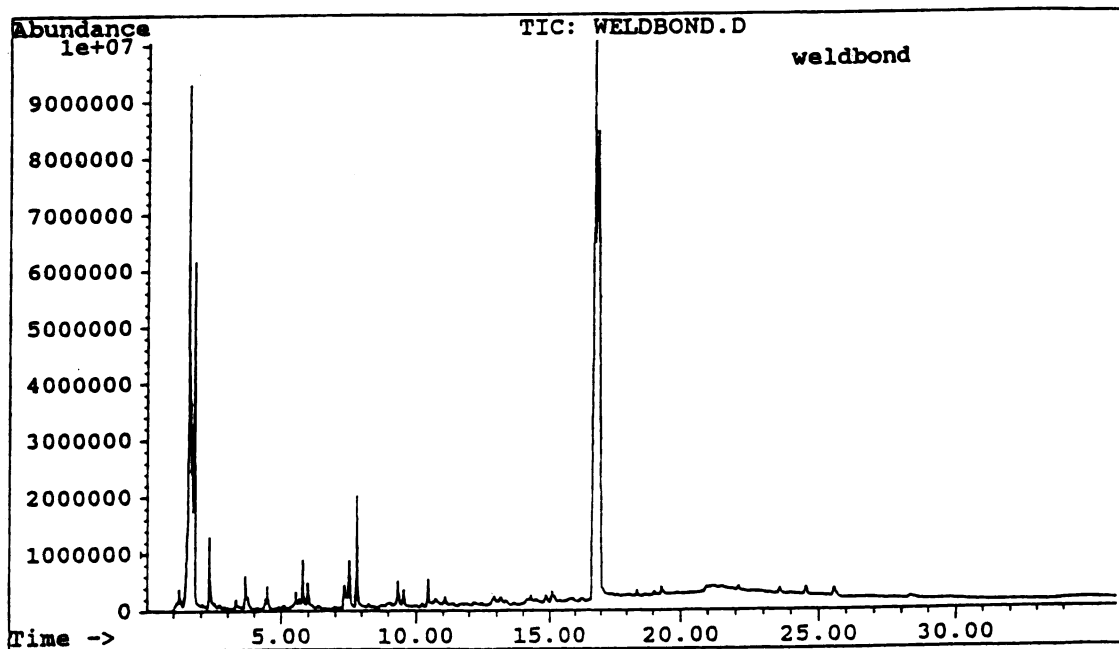
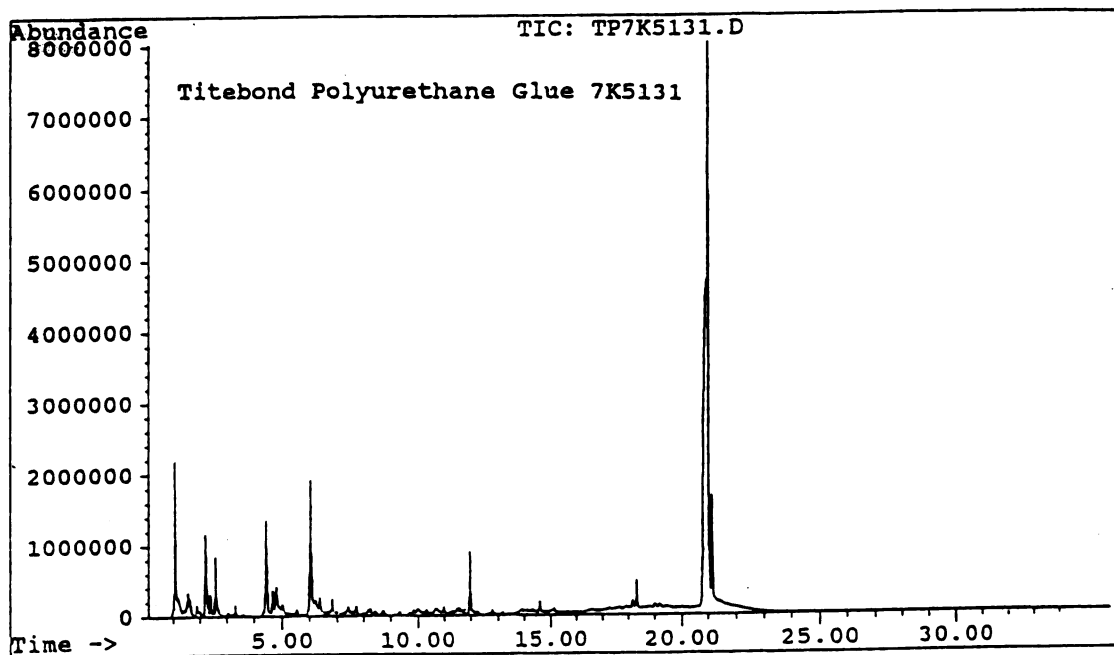






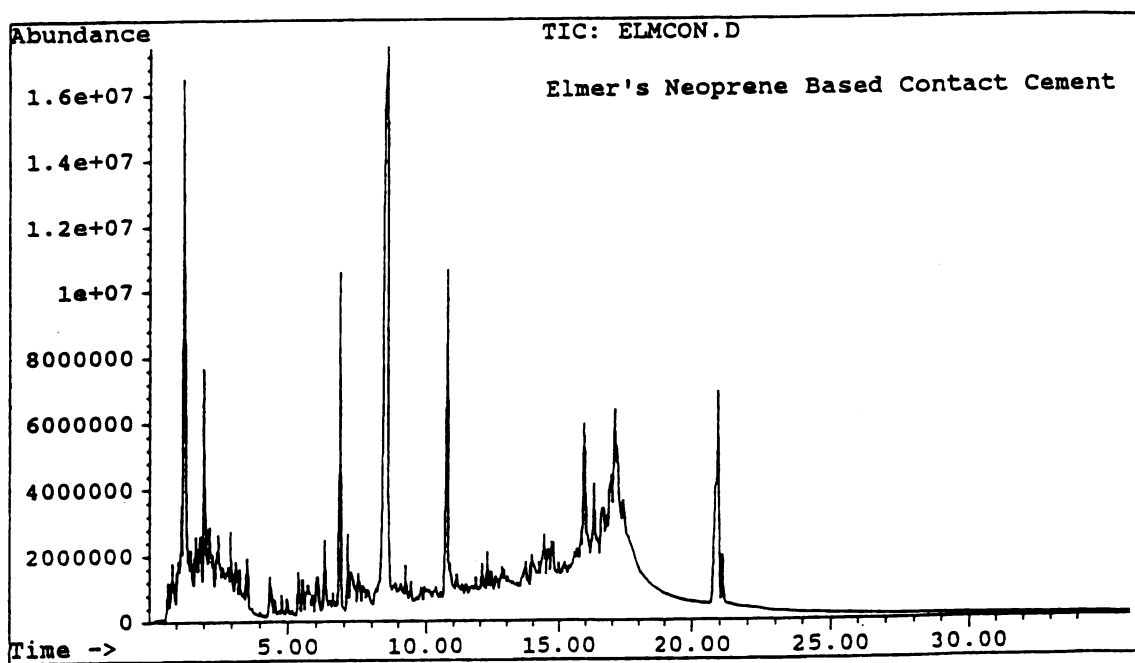
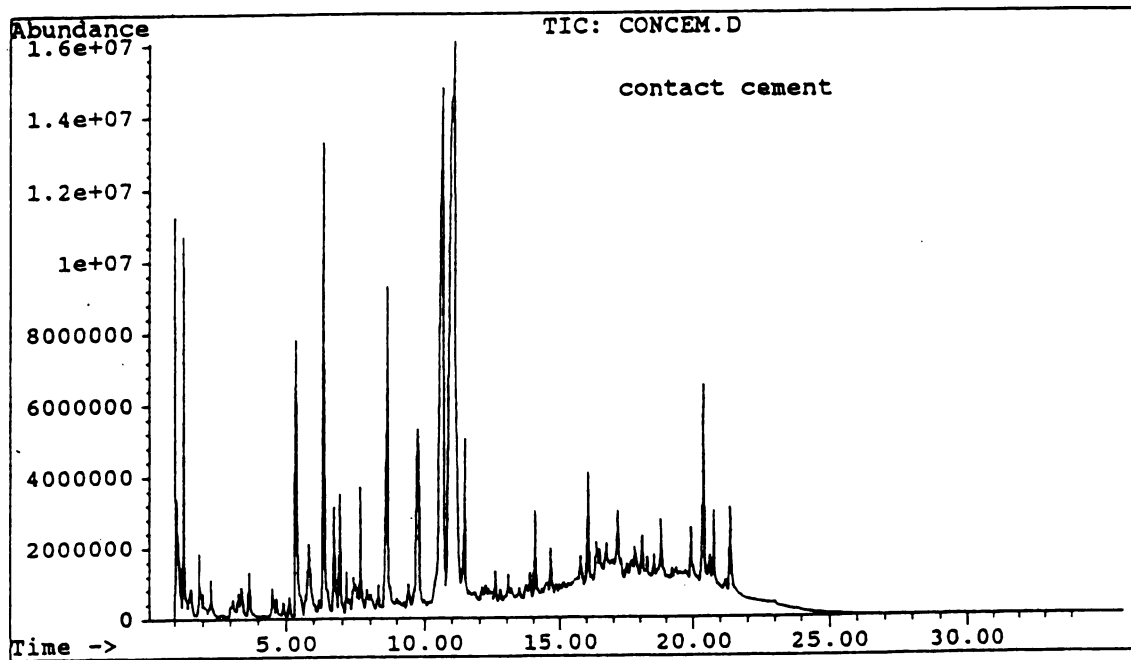


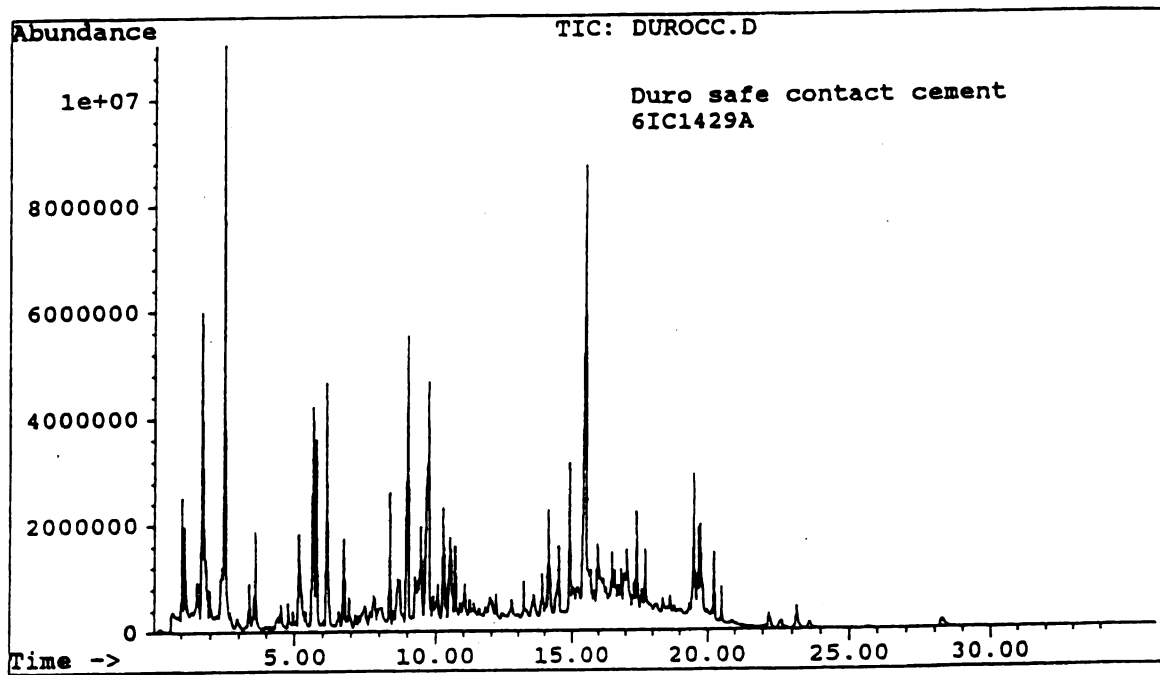
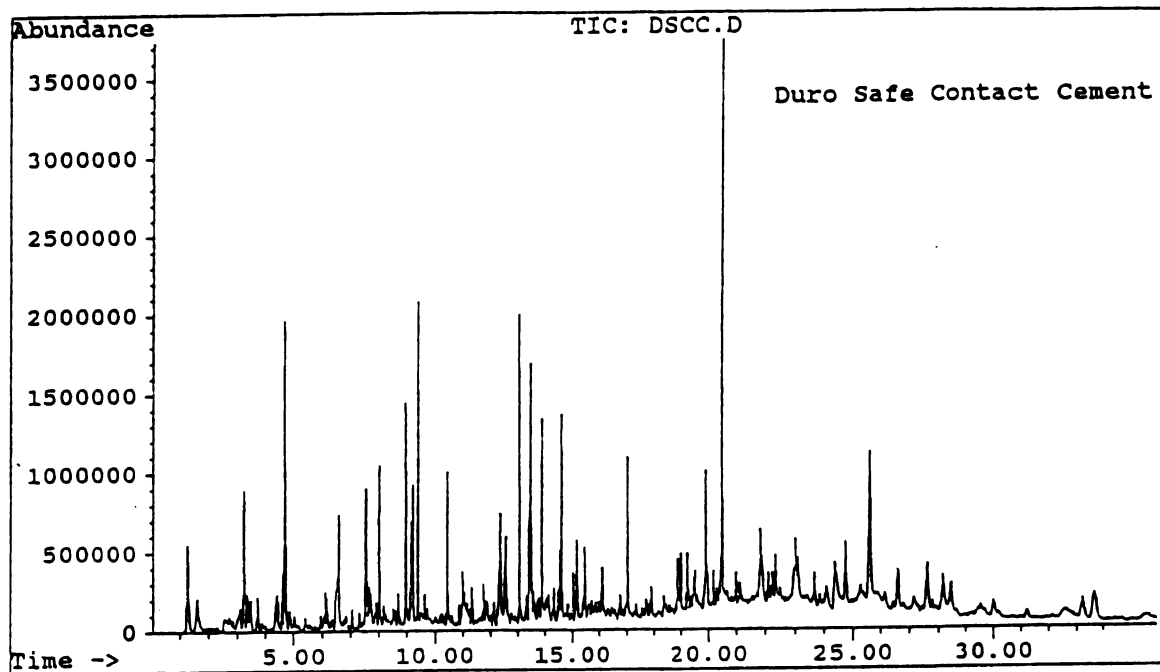




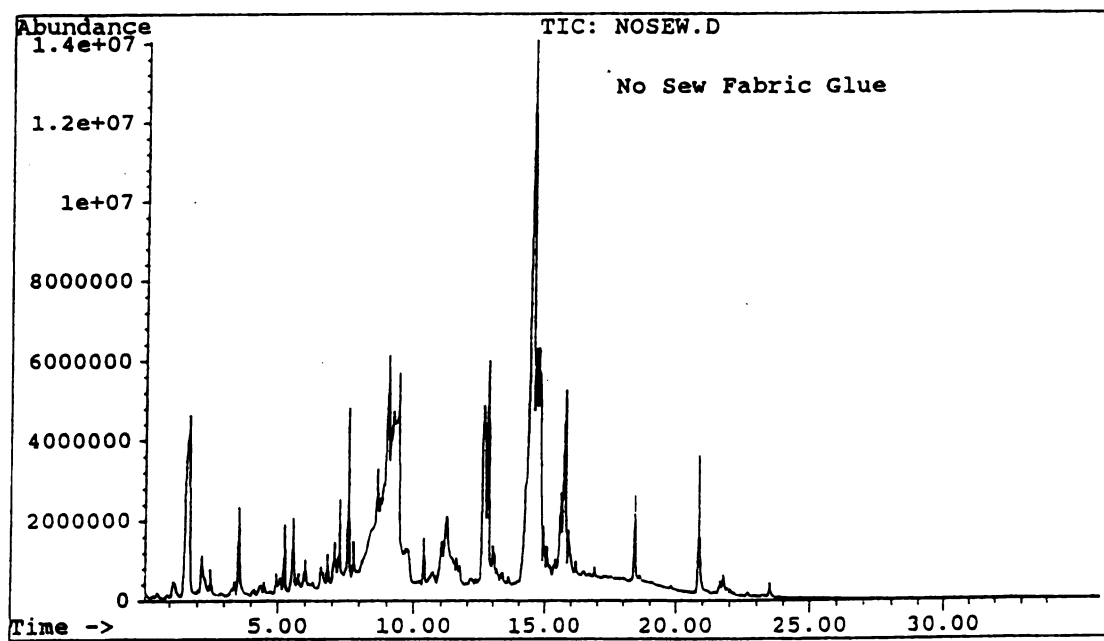
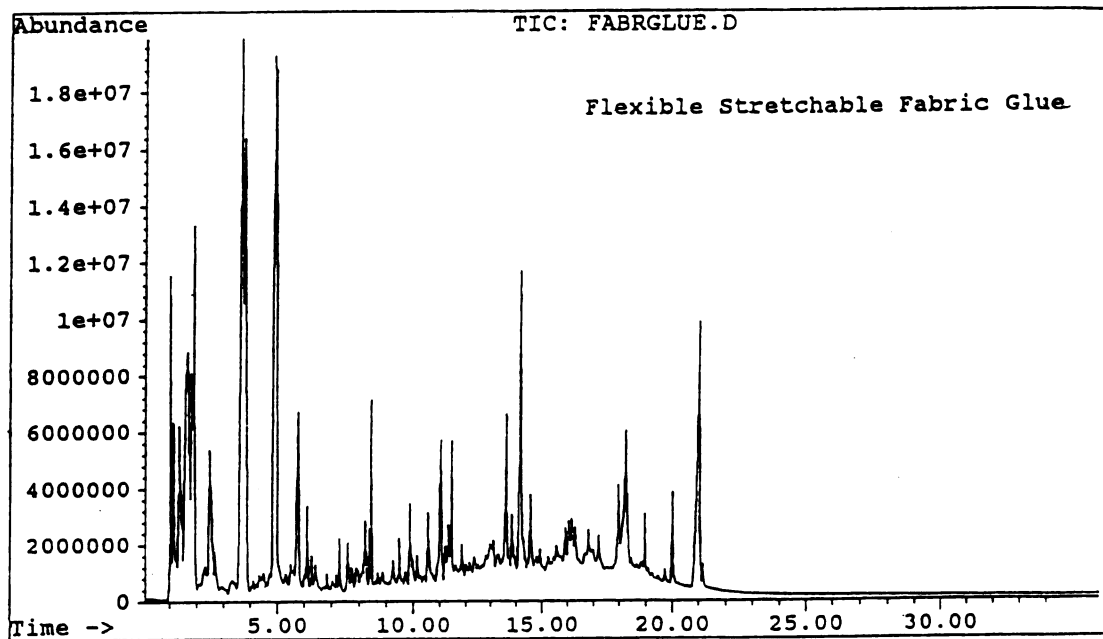
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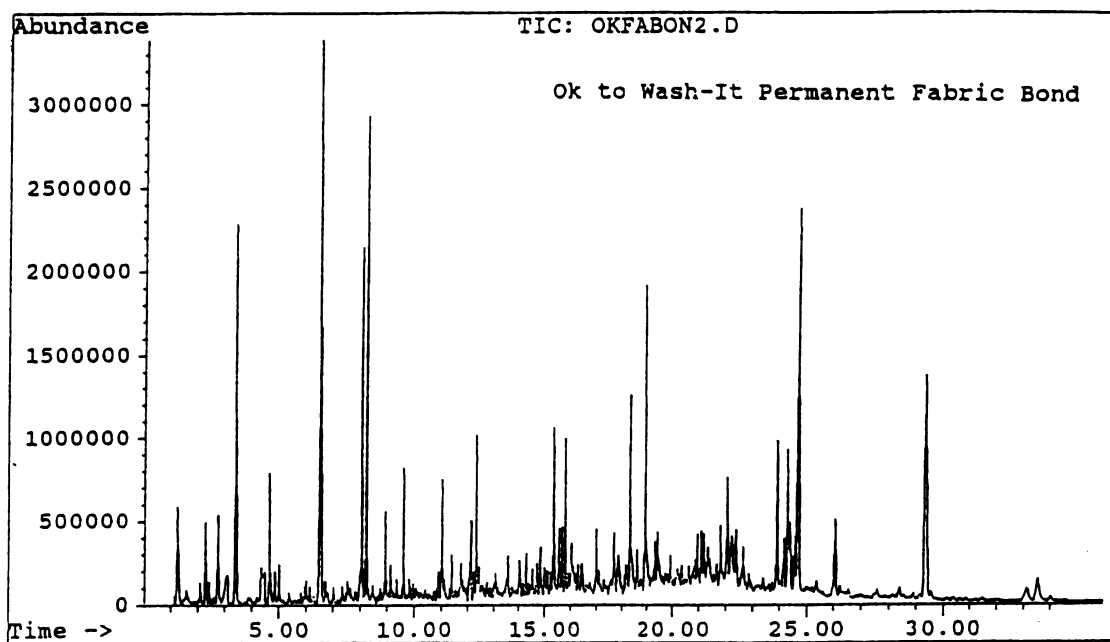




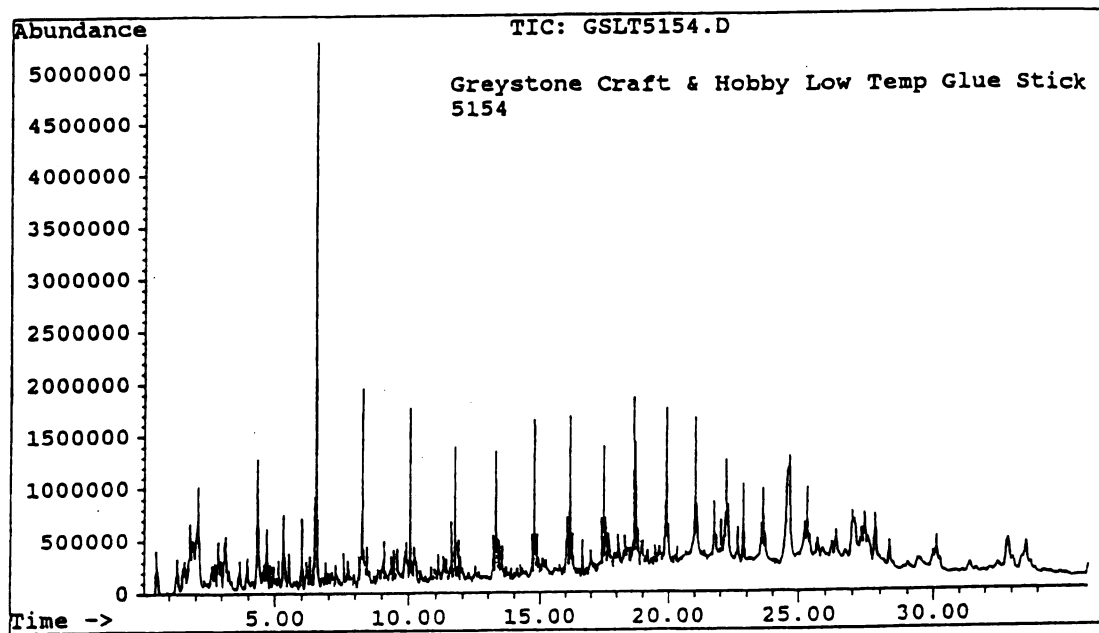
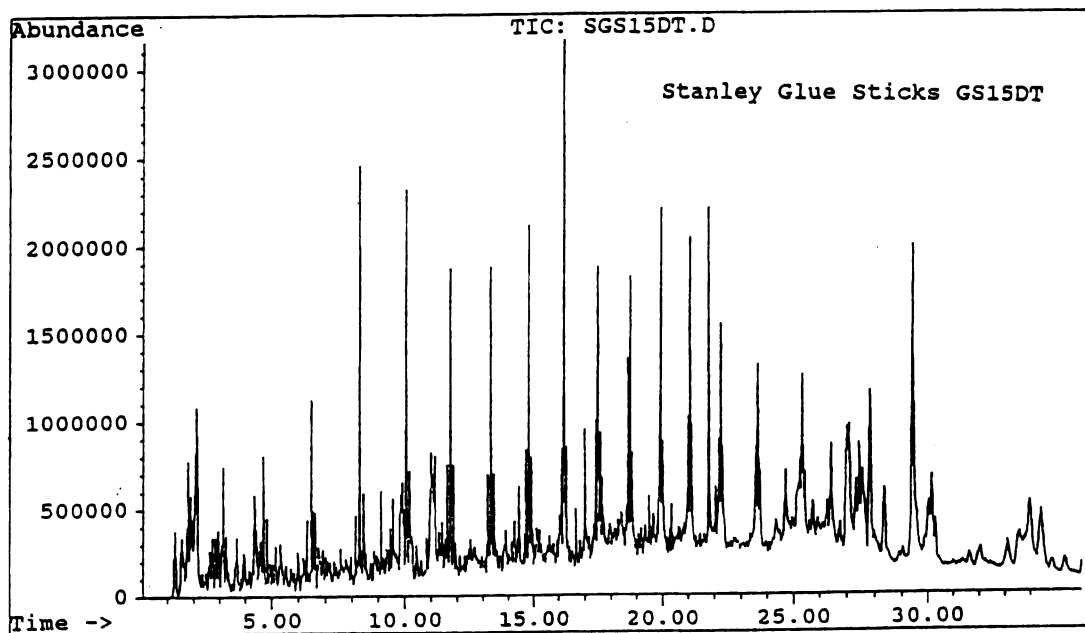


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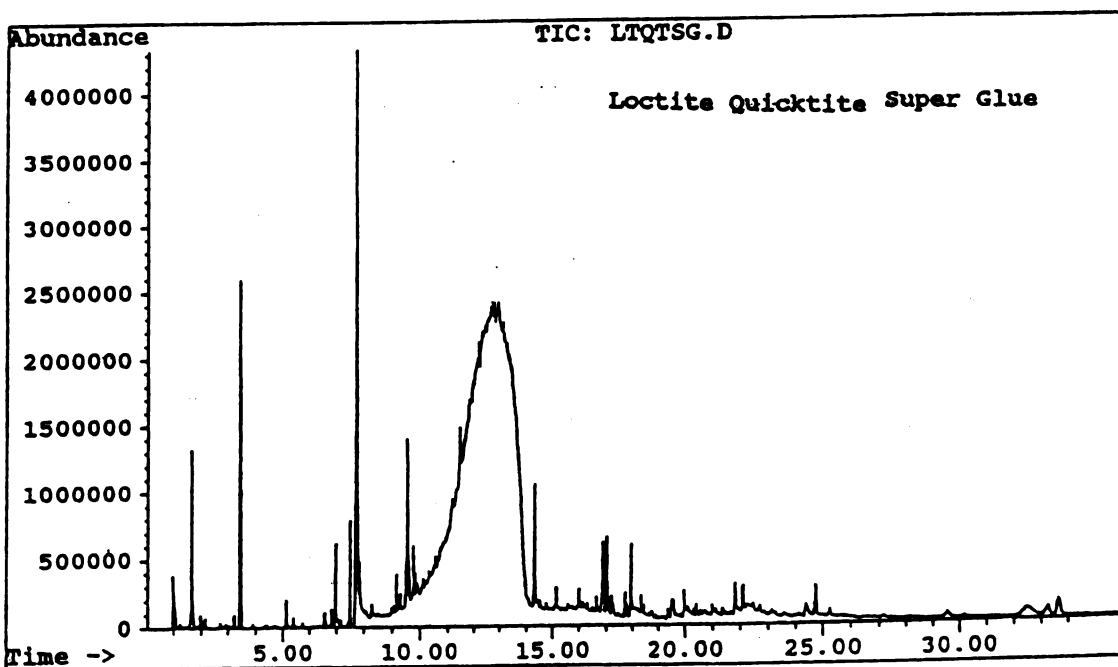
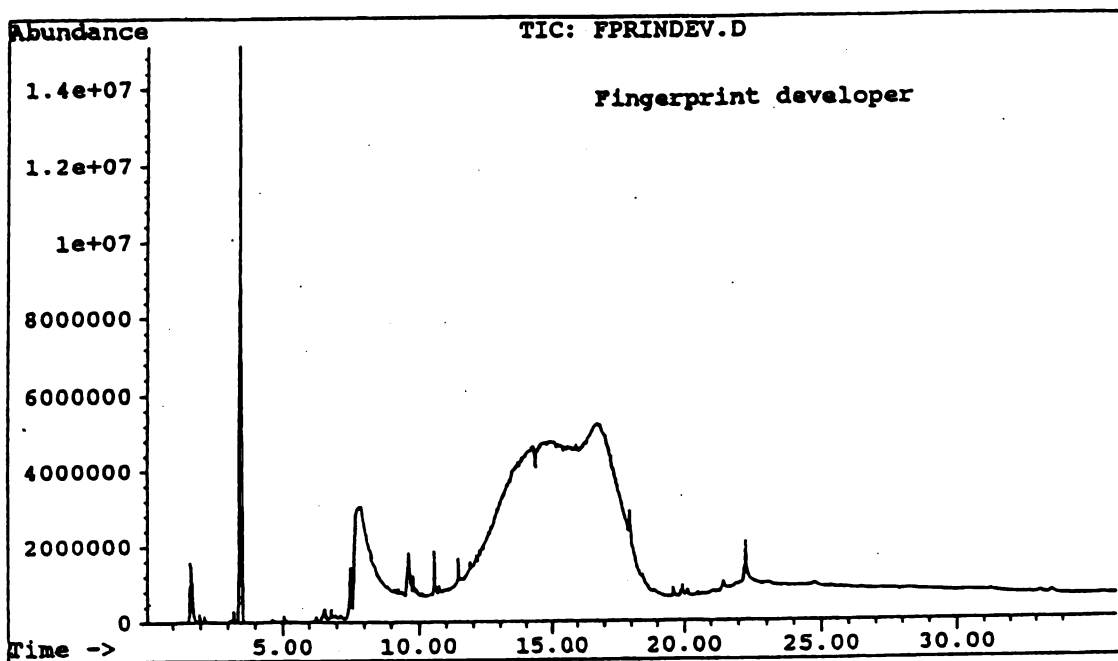


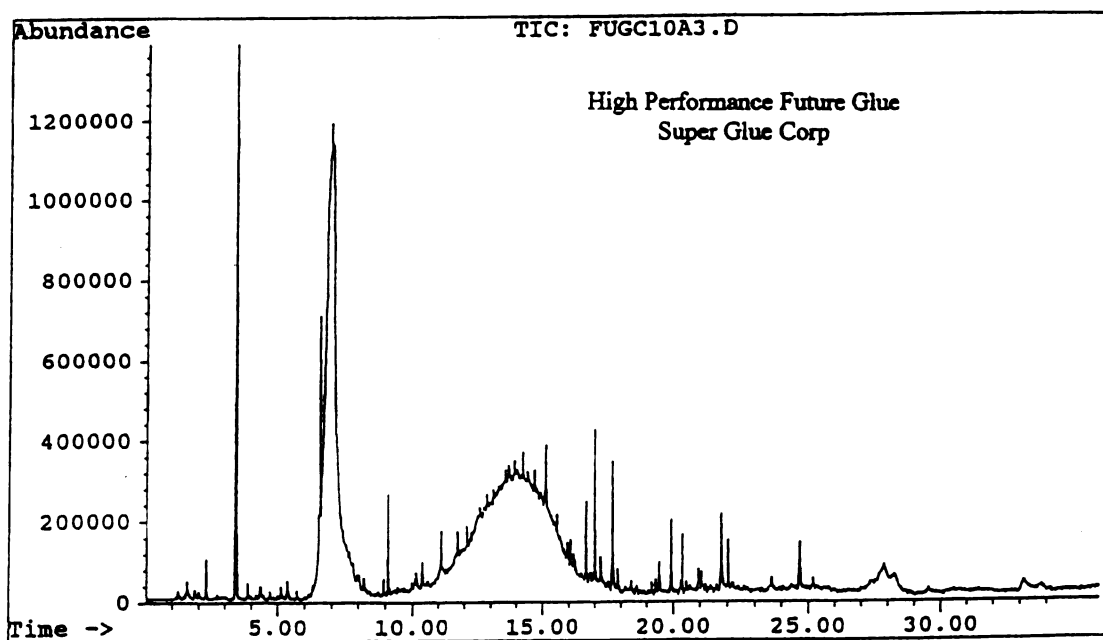
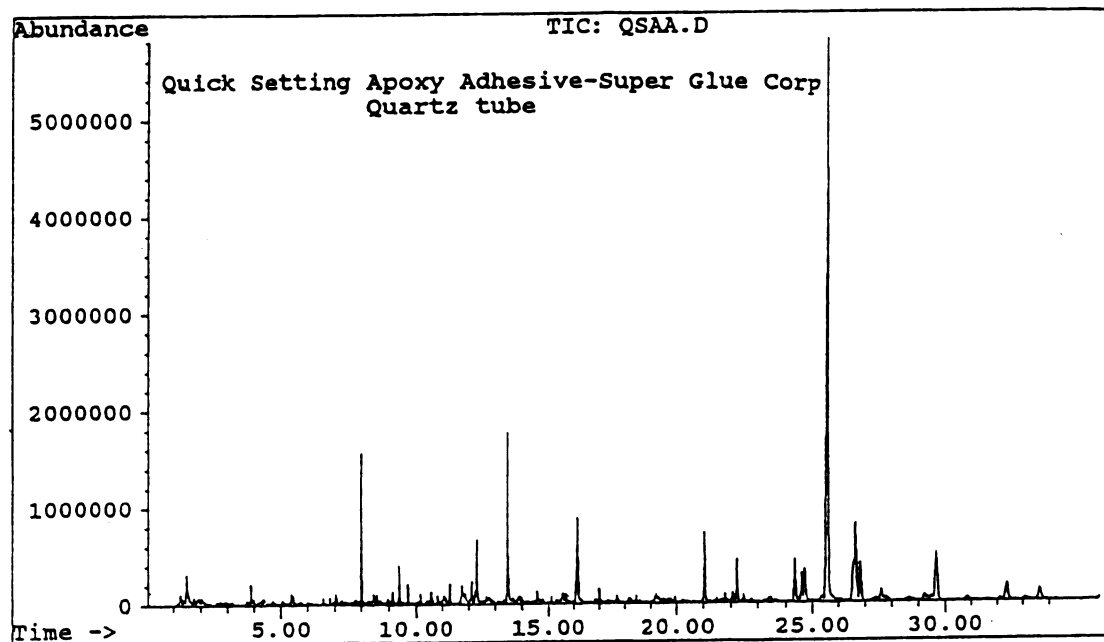
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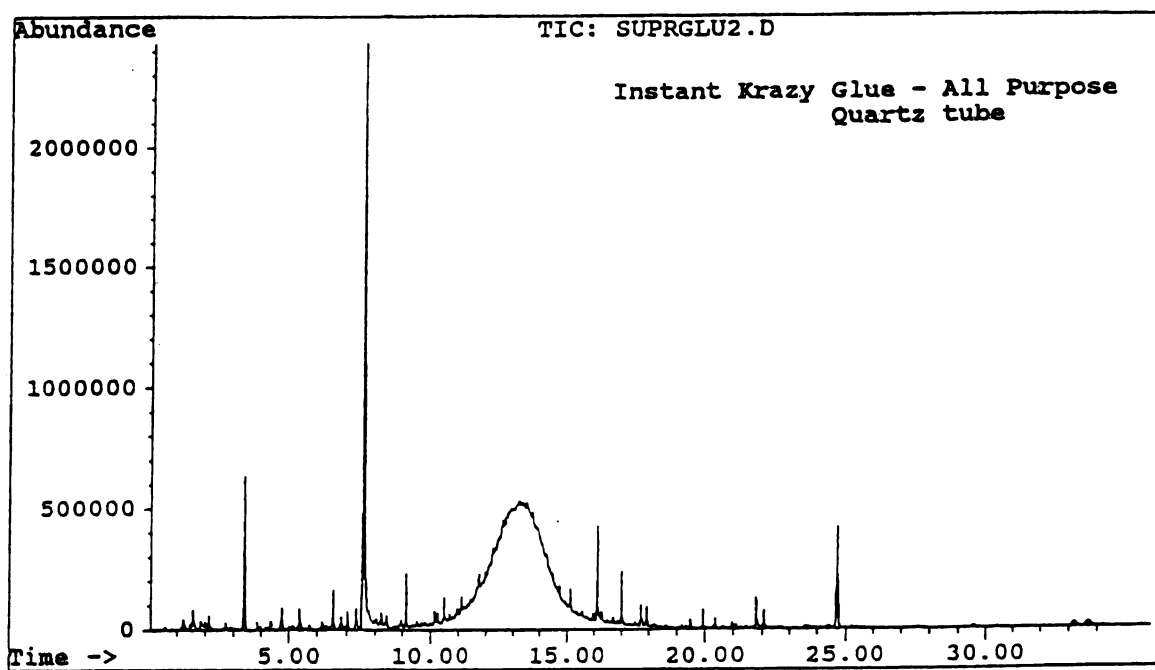
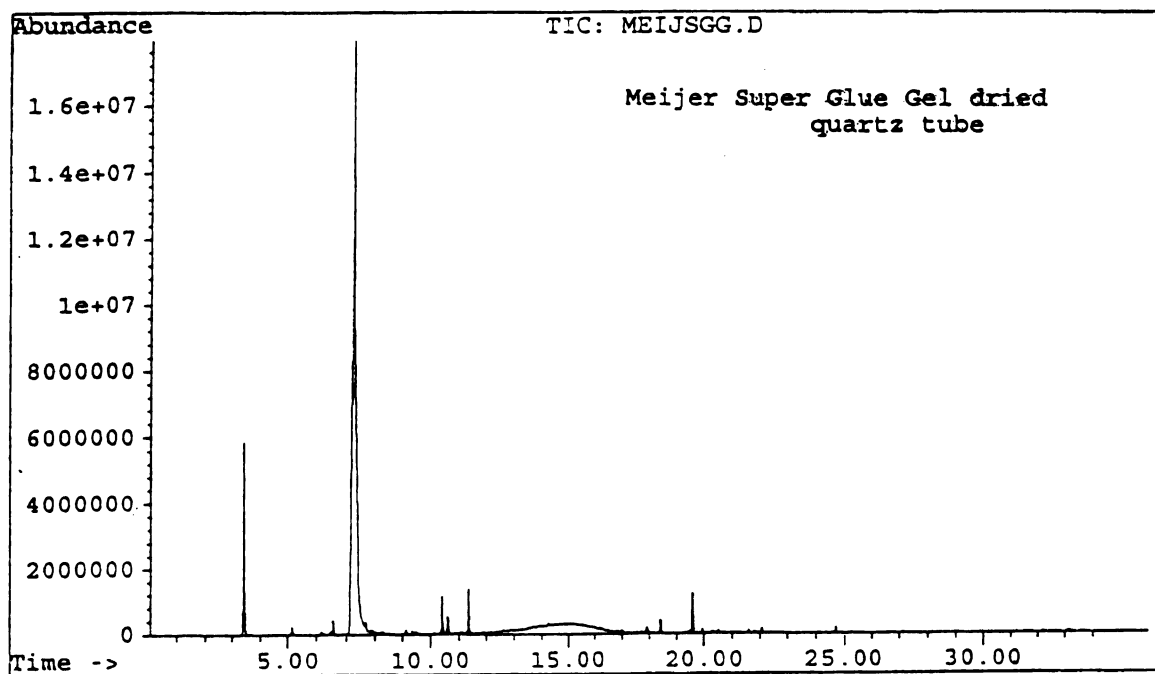


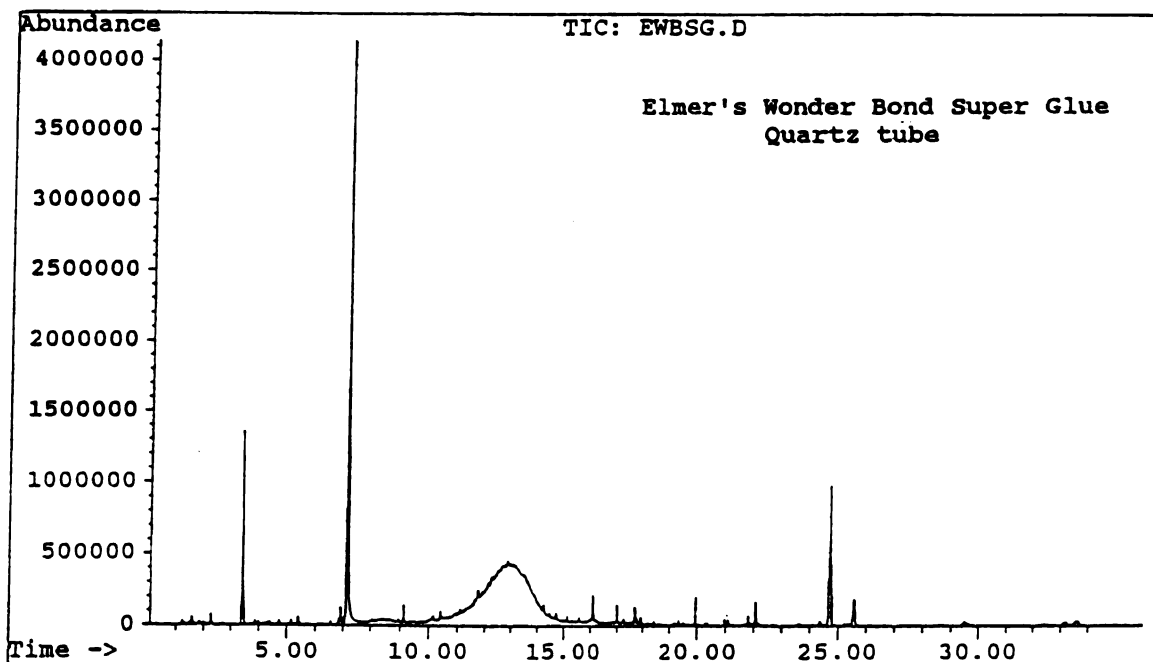
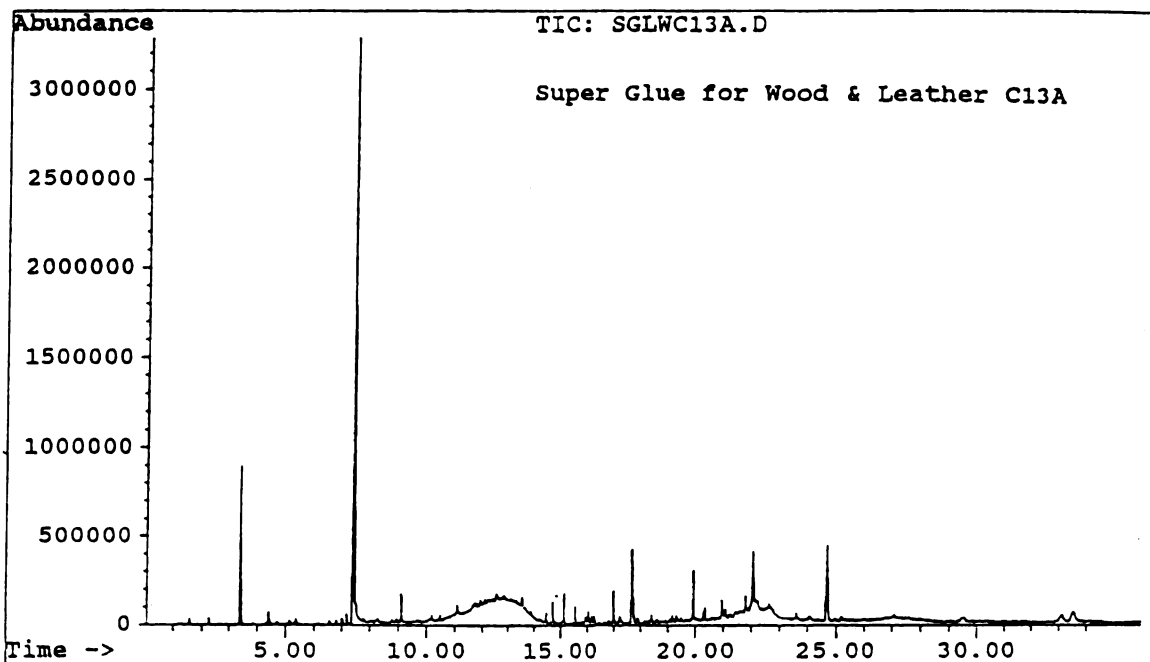
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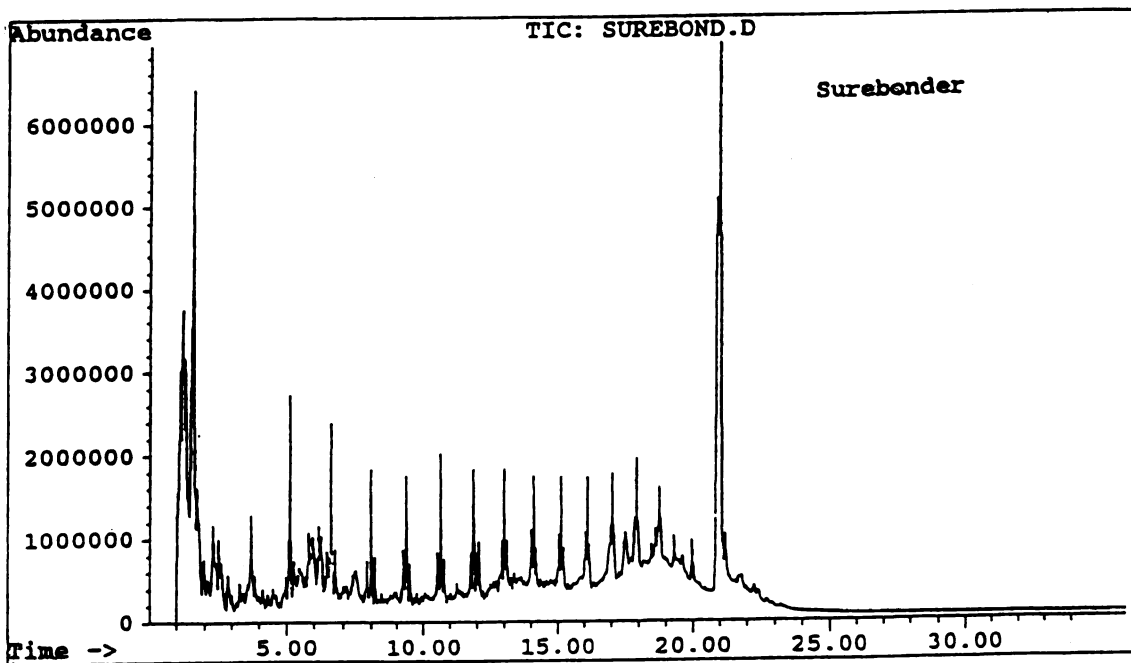
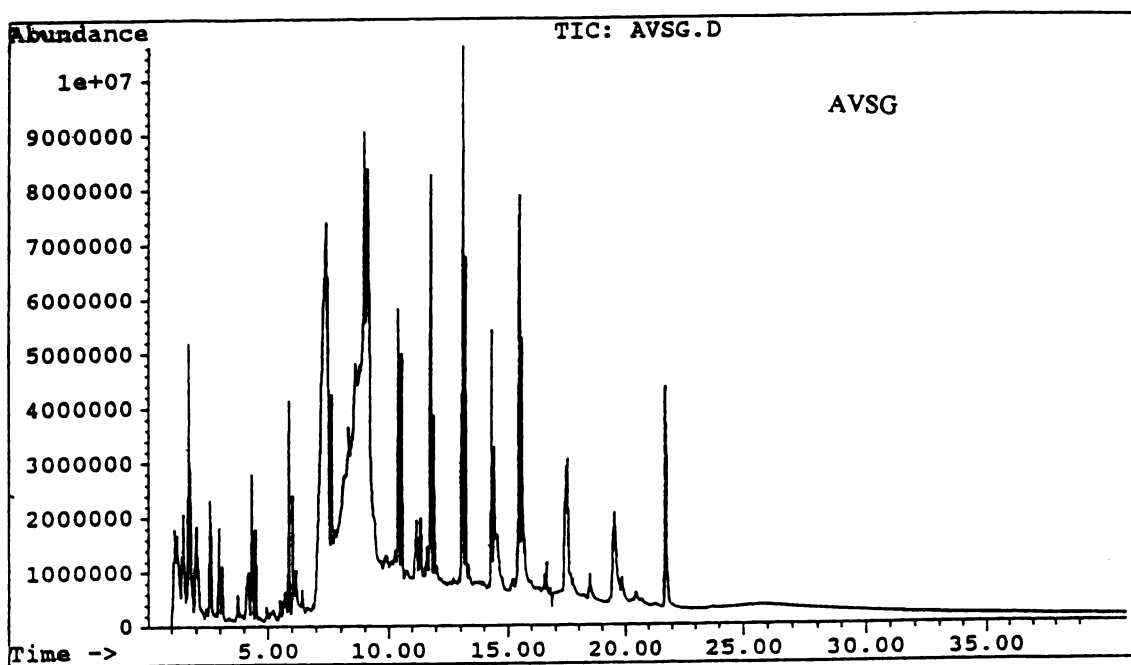




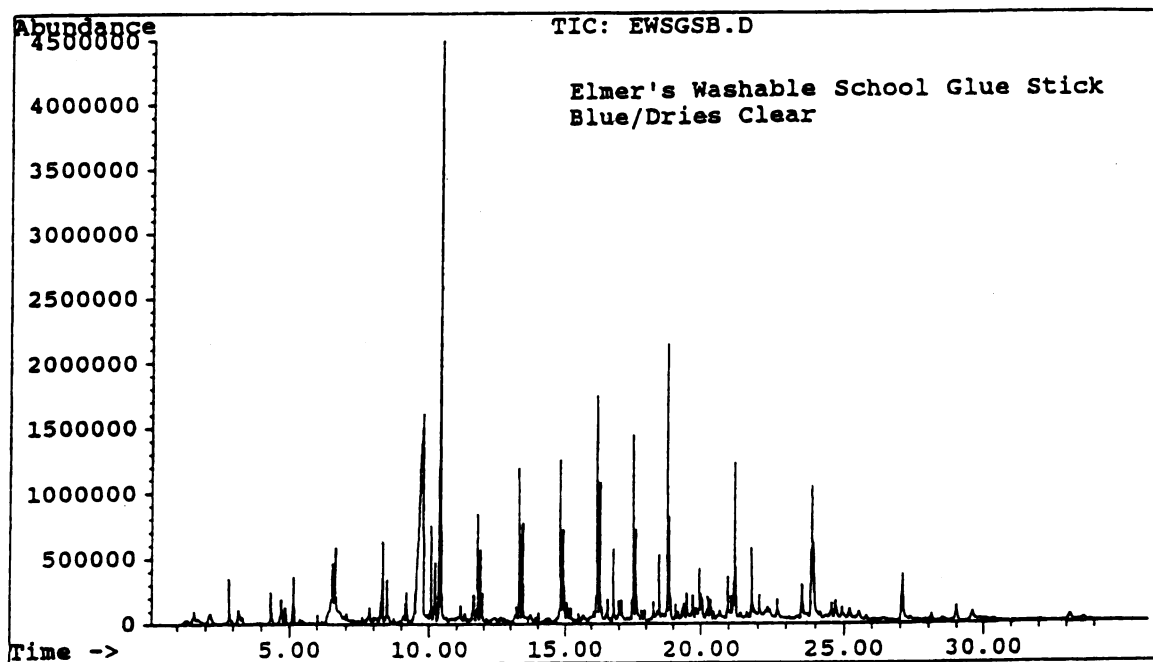
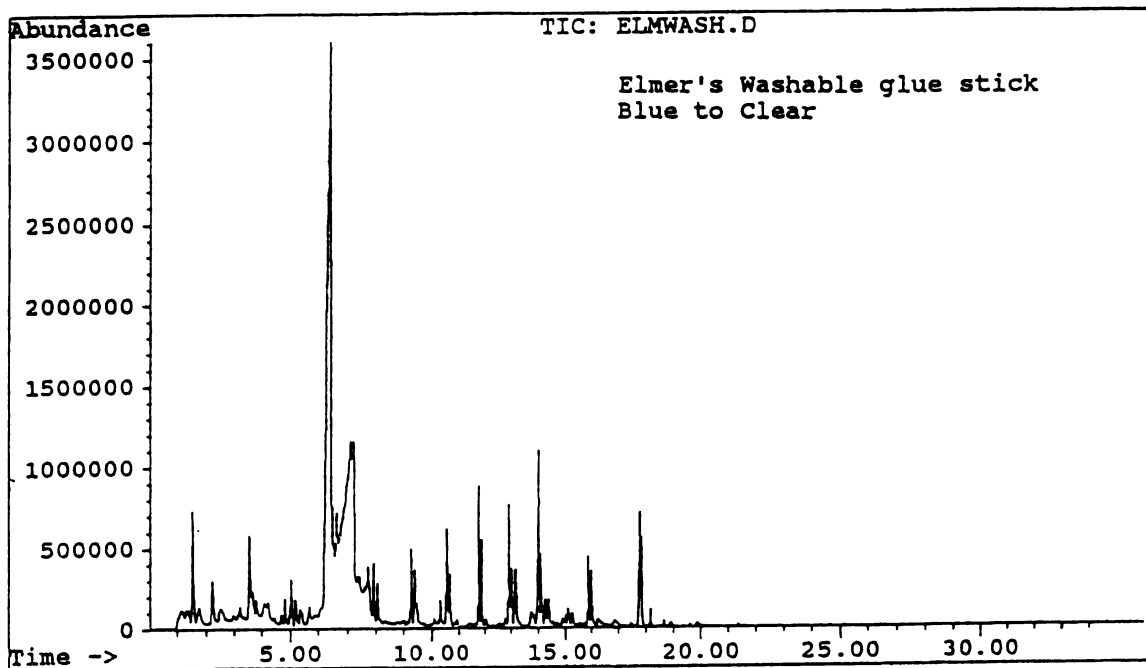


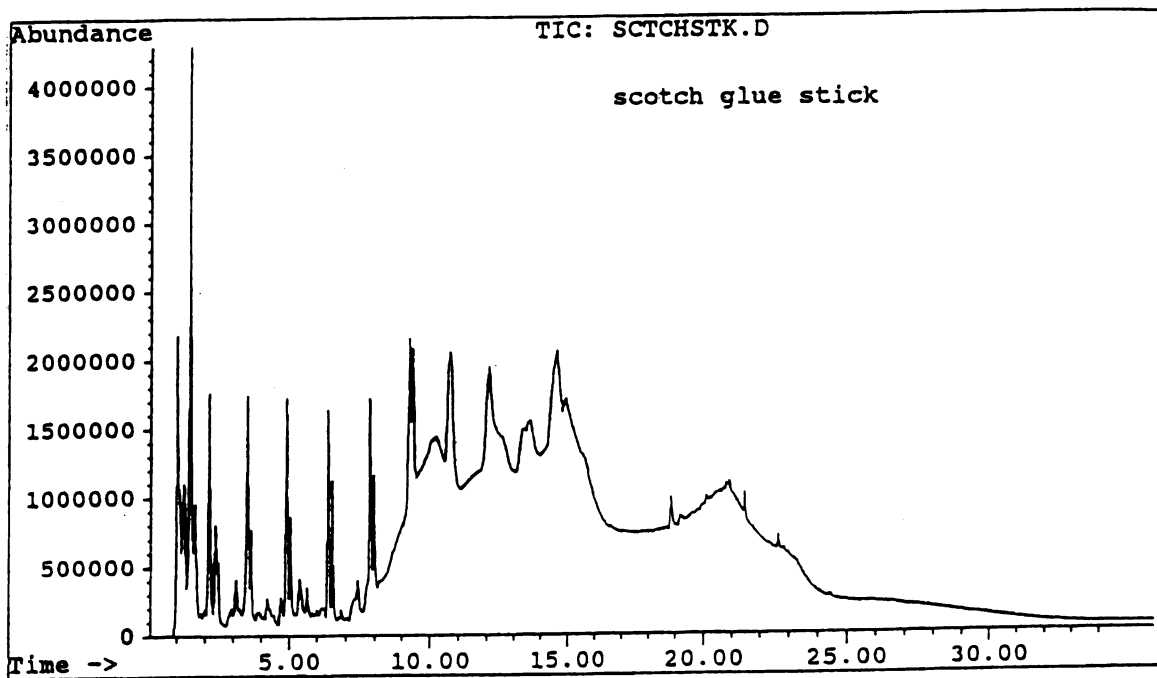
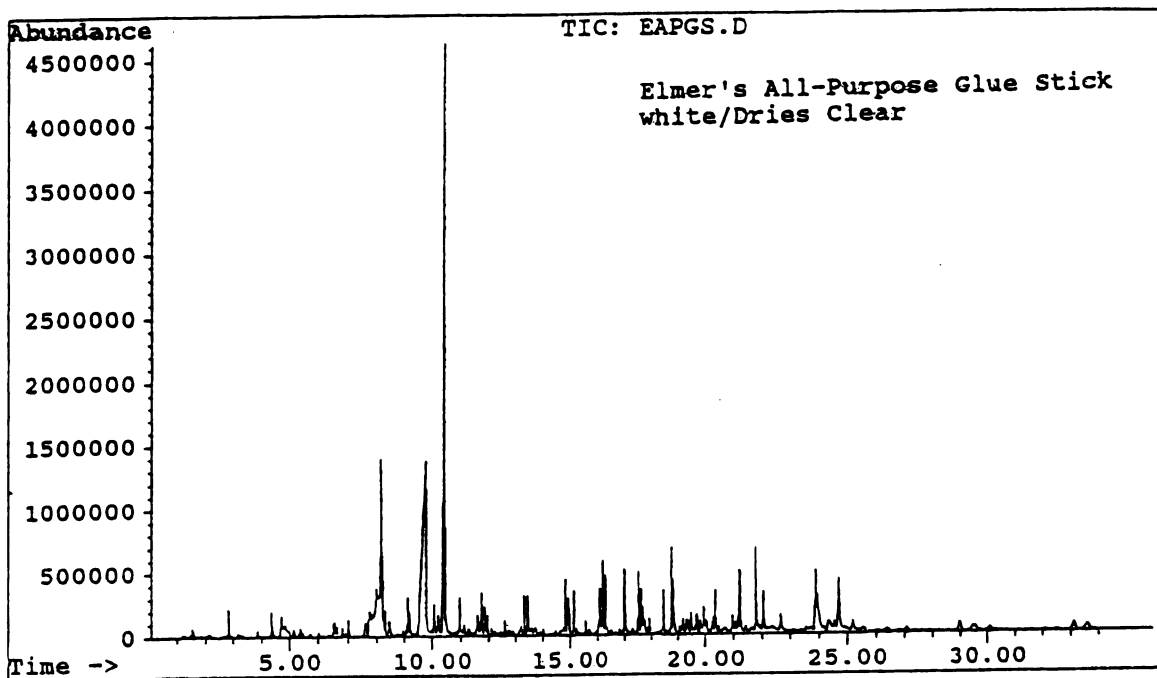




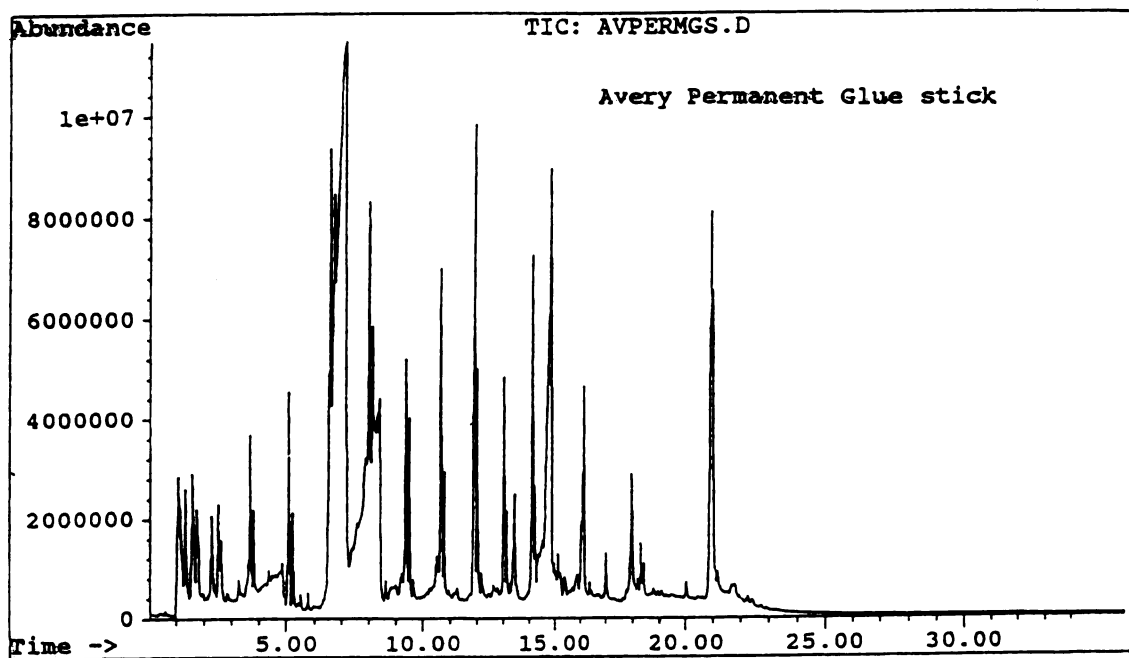


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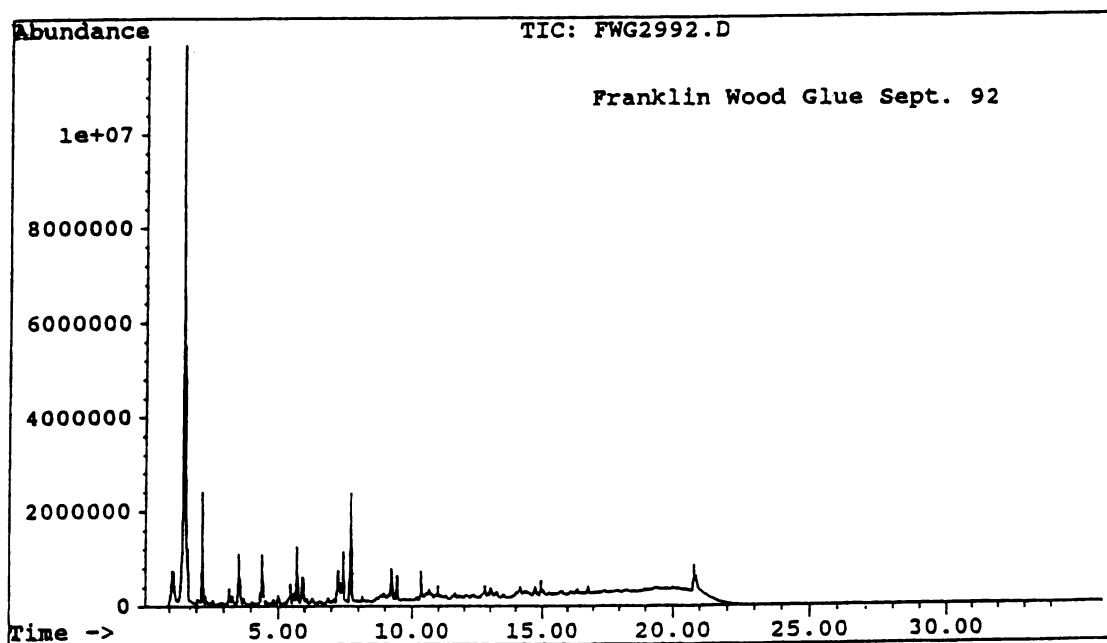
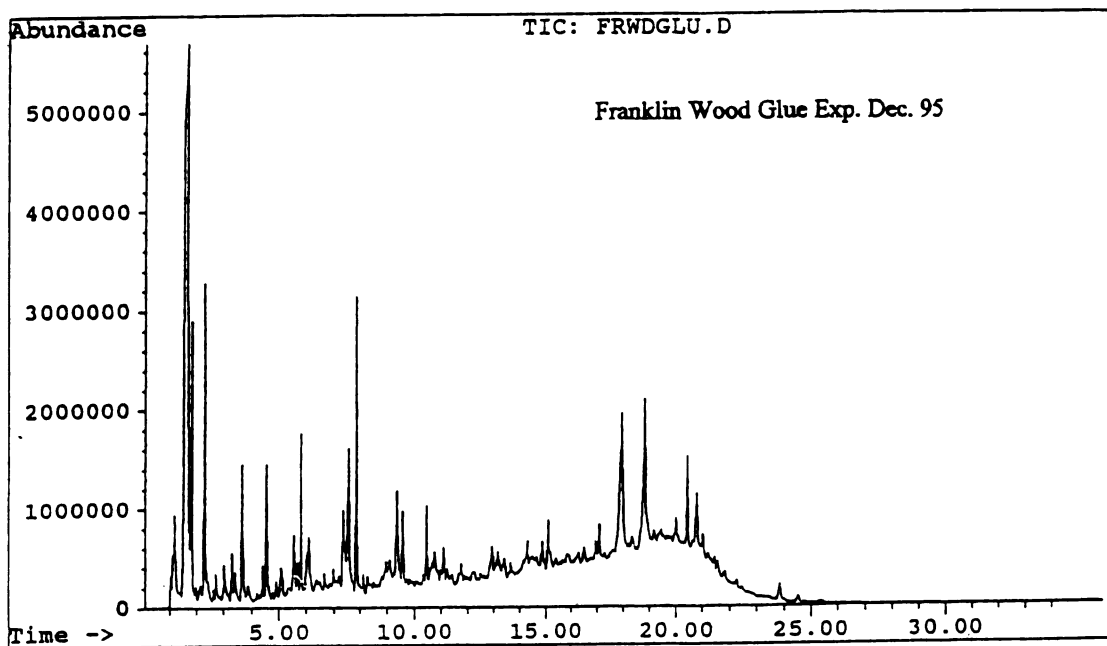


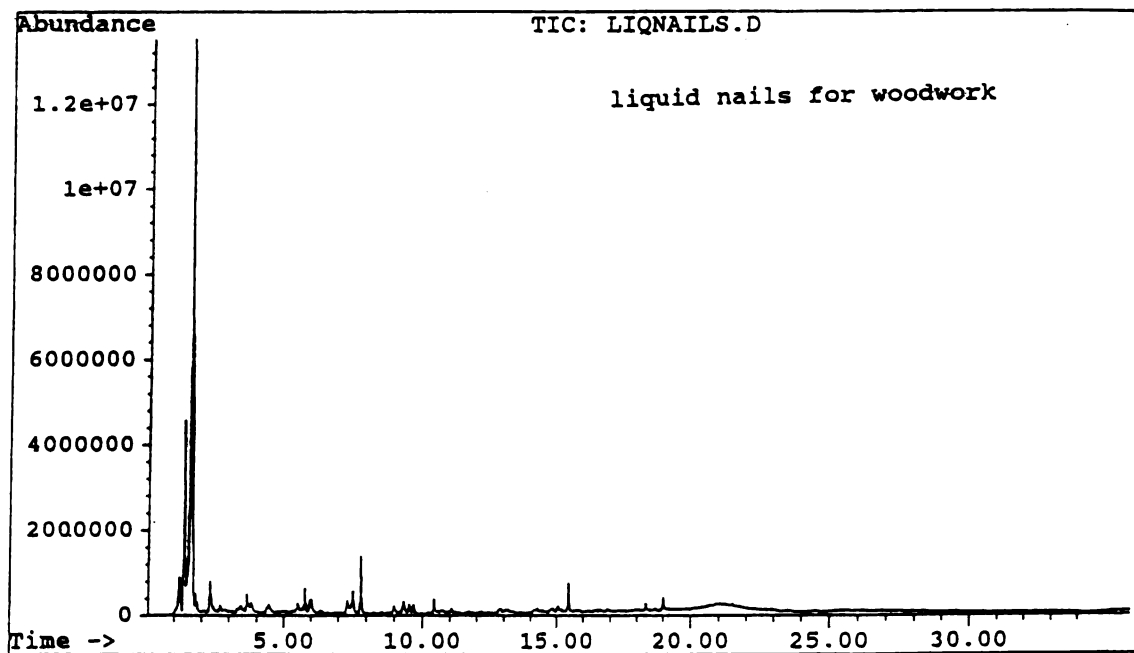
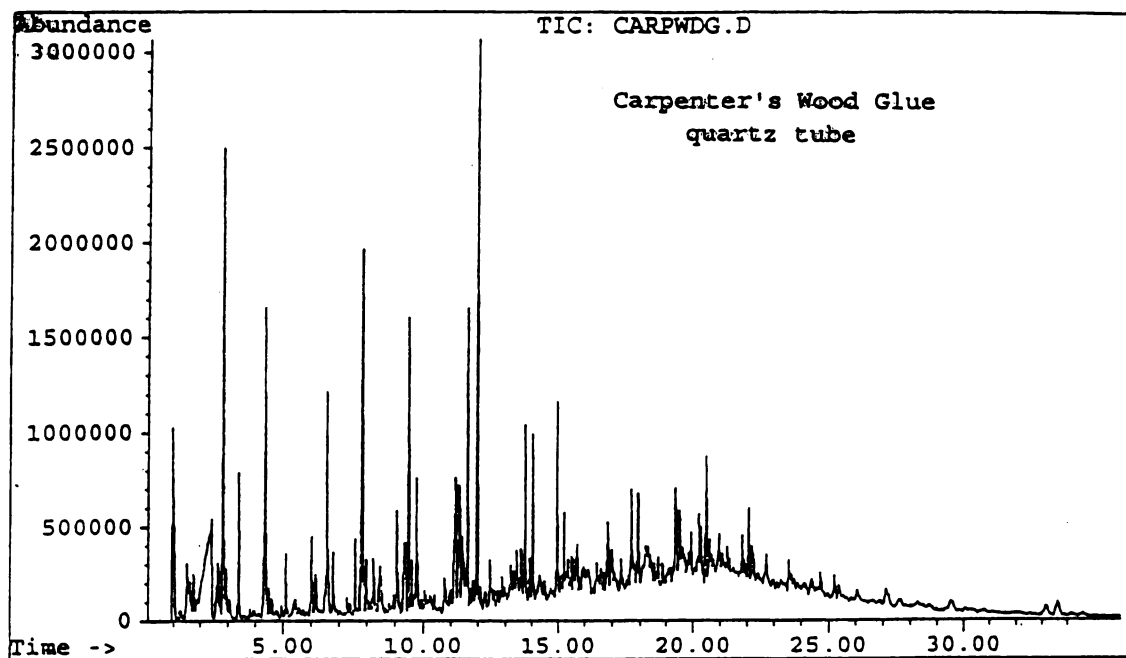






## Wood Glues





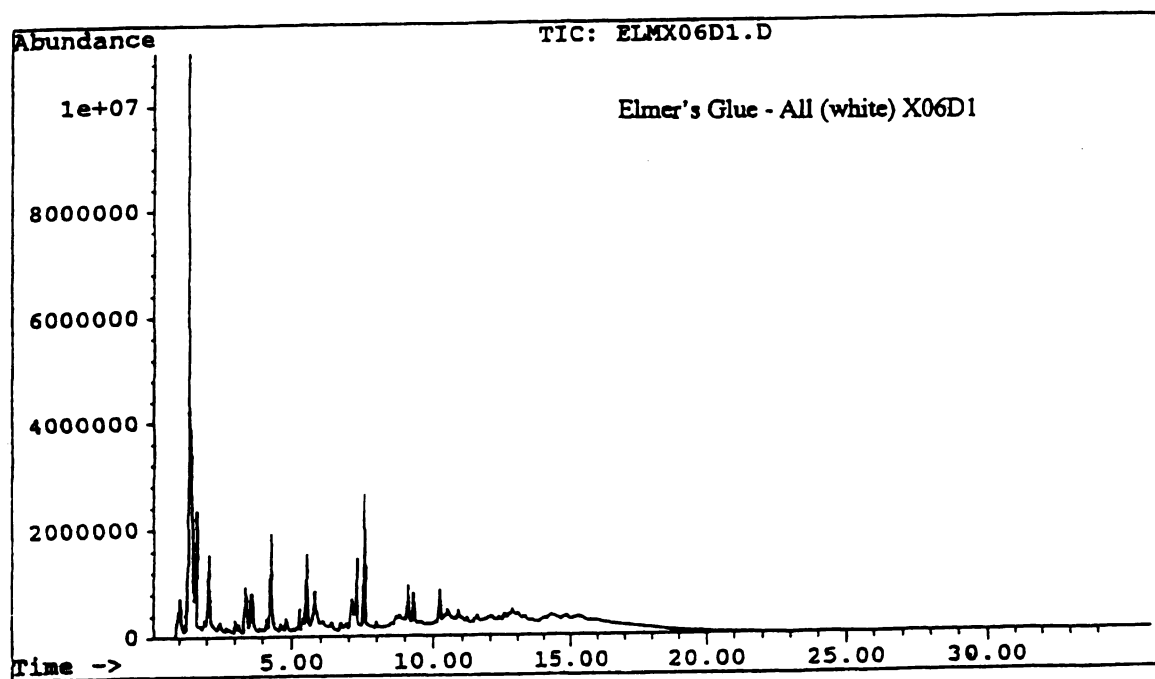
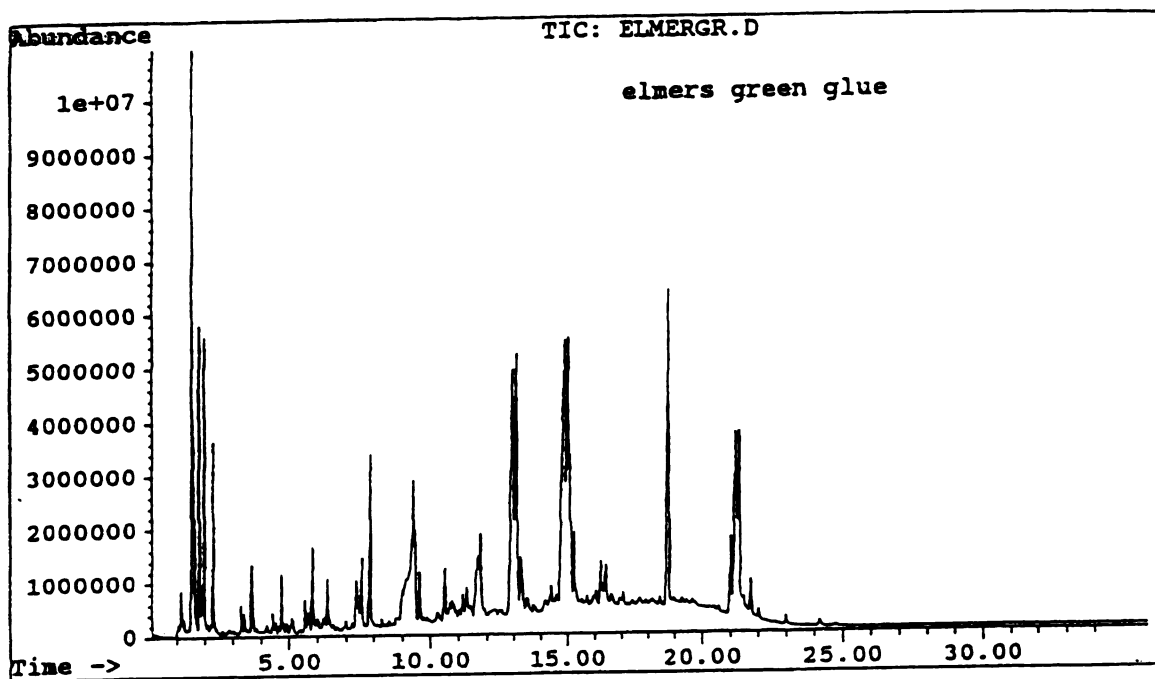
## APPENDIX B

### Three Sample Studies of Five Variables

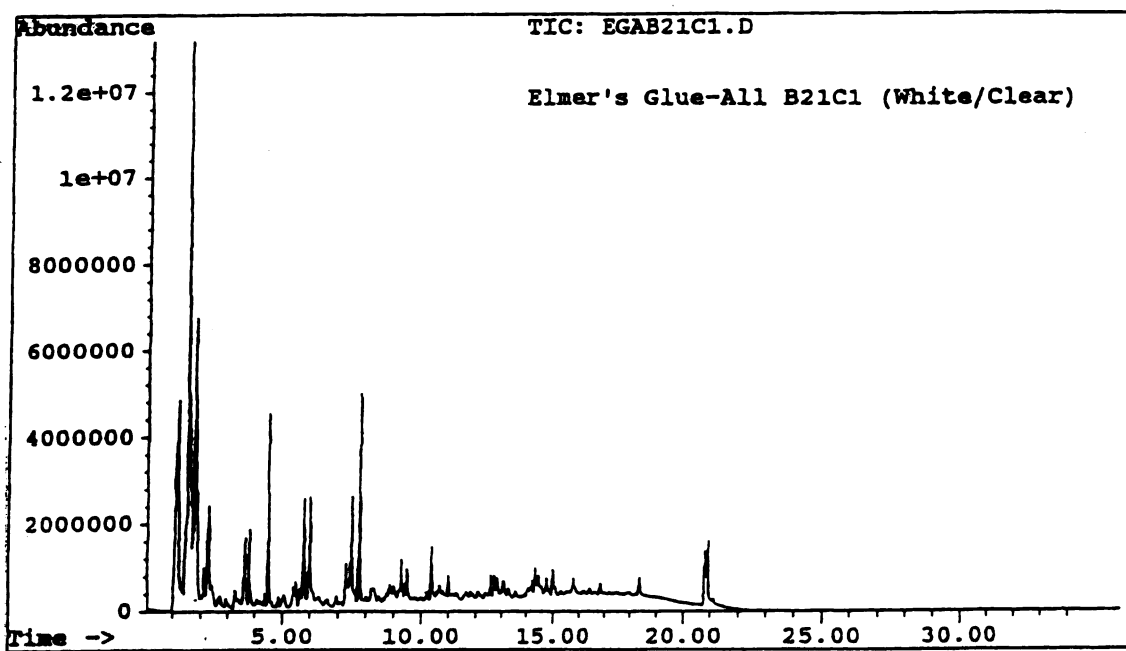
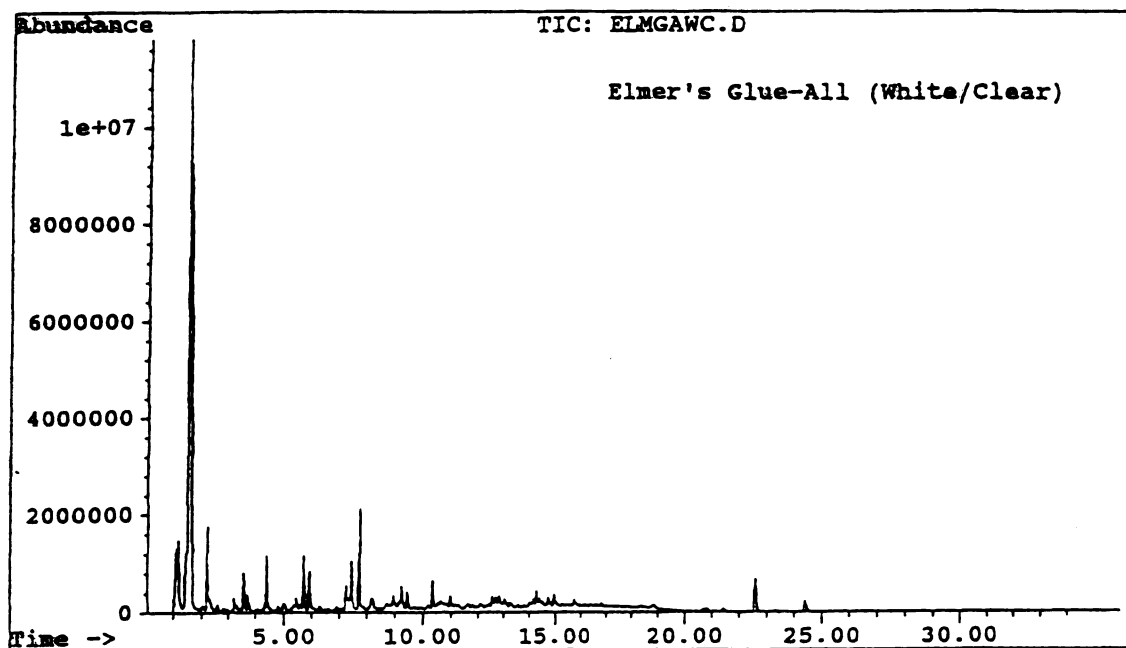
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2. Repeatability and the Affects of Drying Time
3. Sample Size

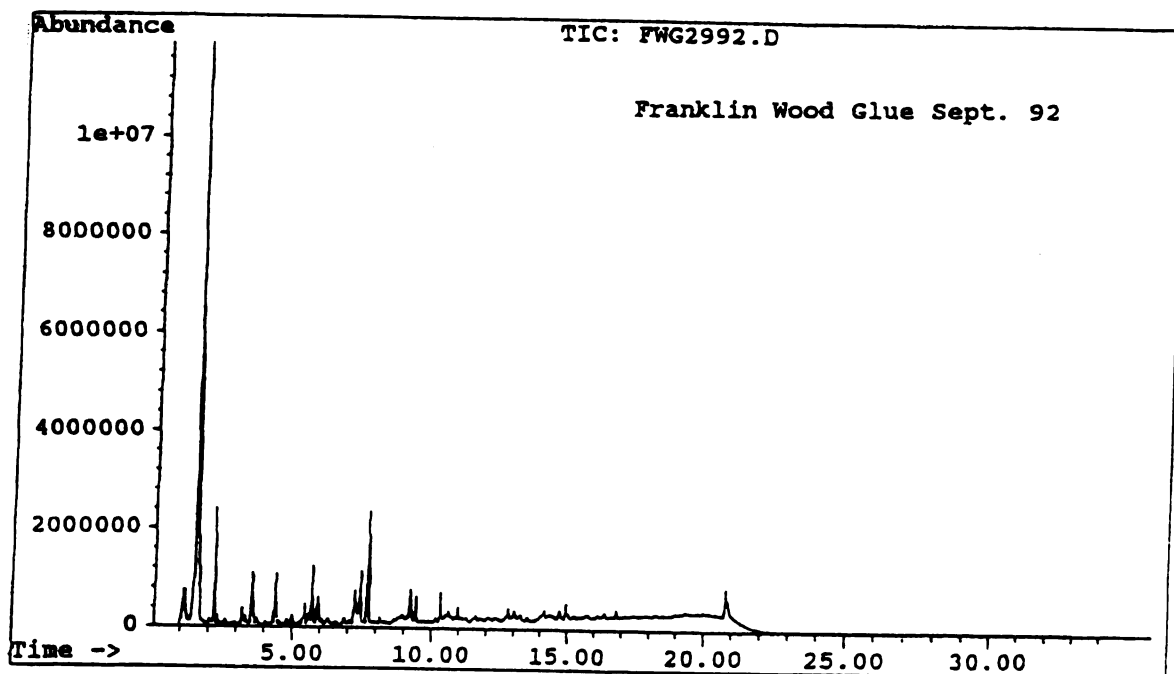
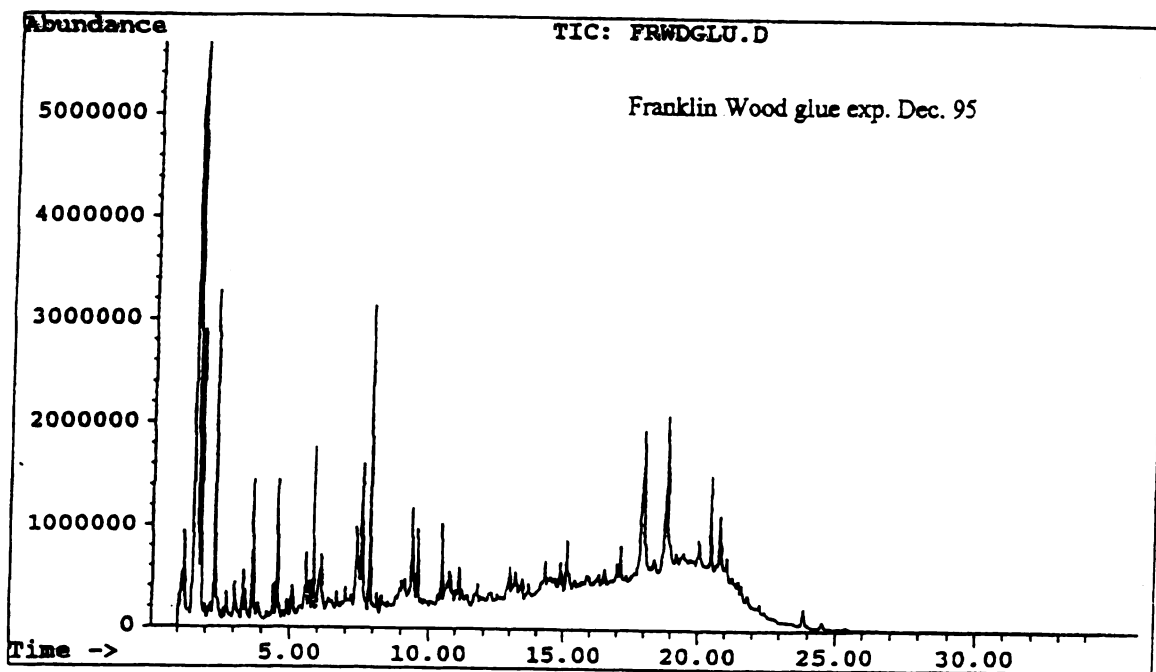


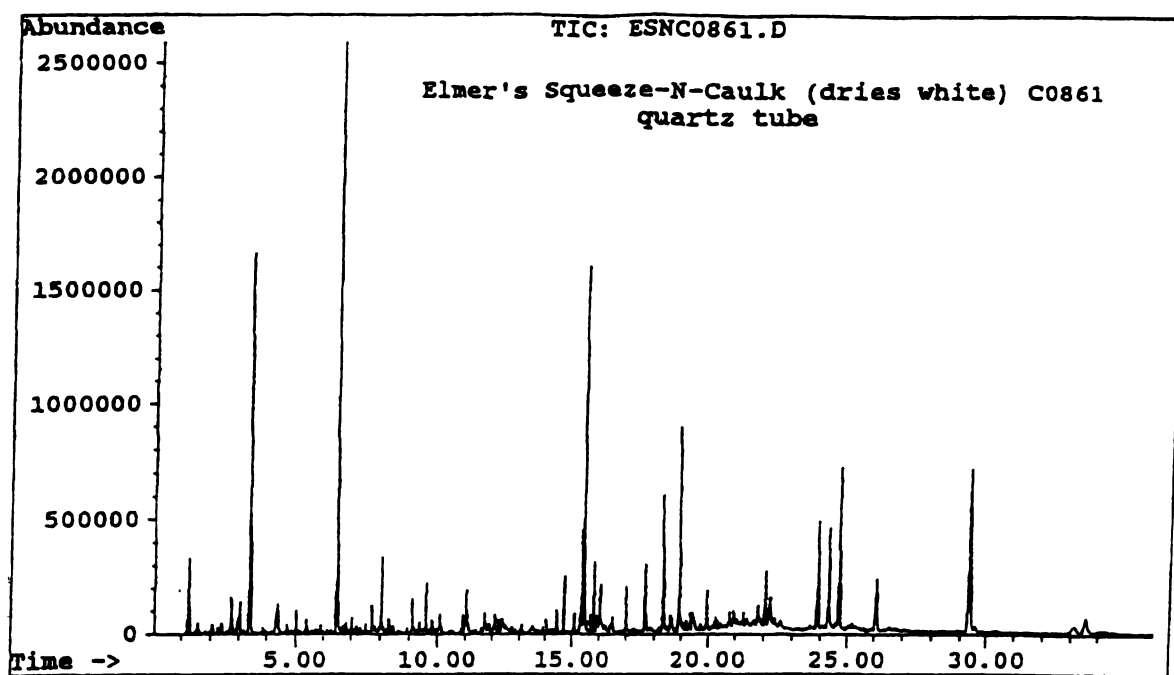
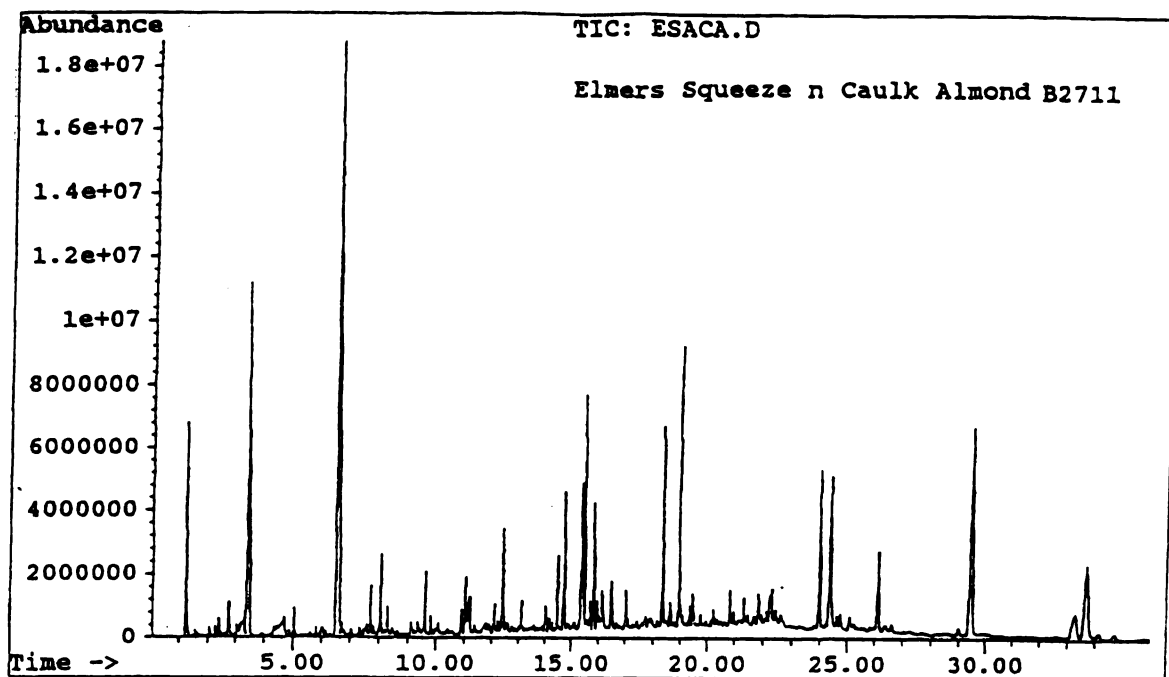
## Color and Batch Number Study

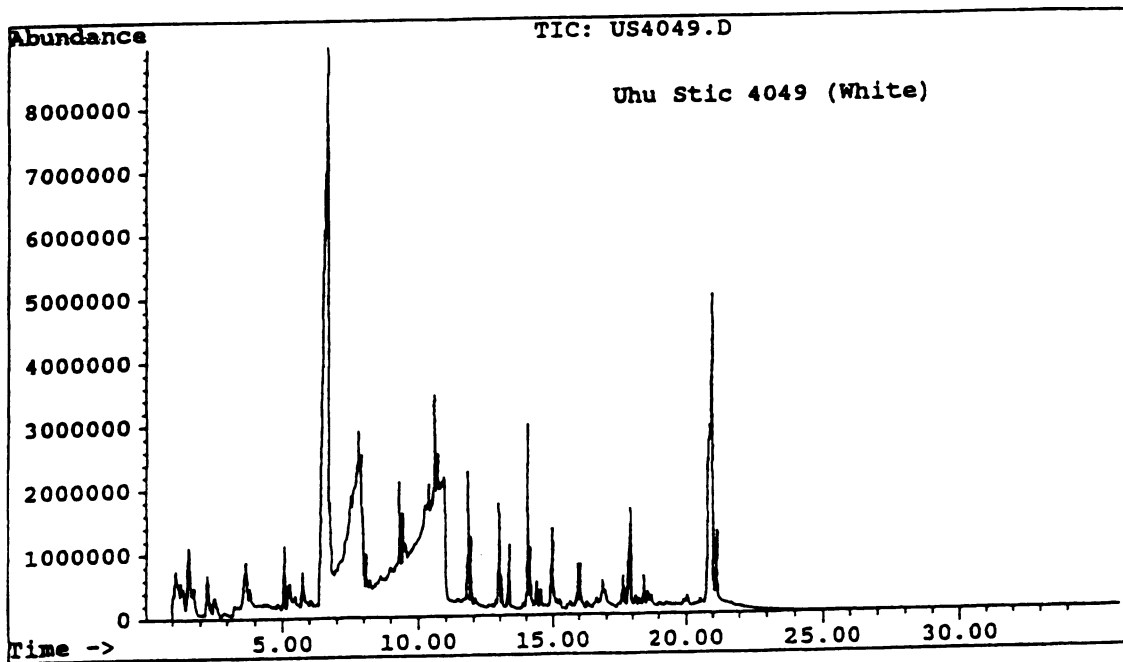
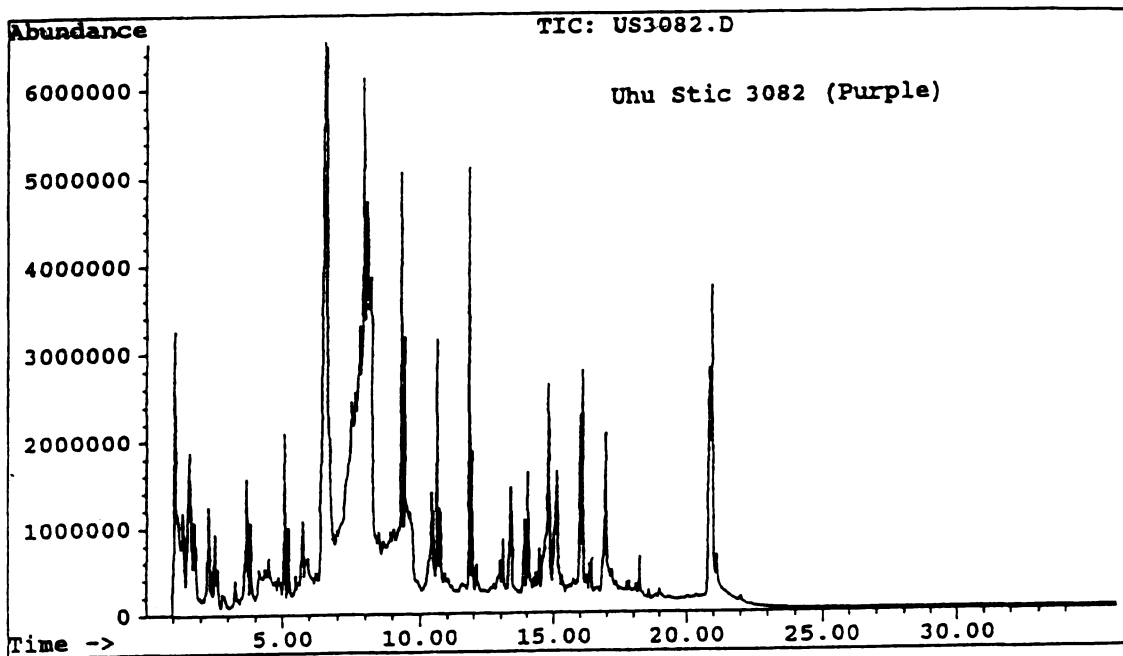




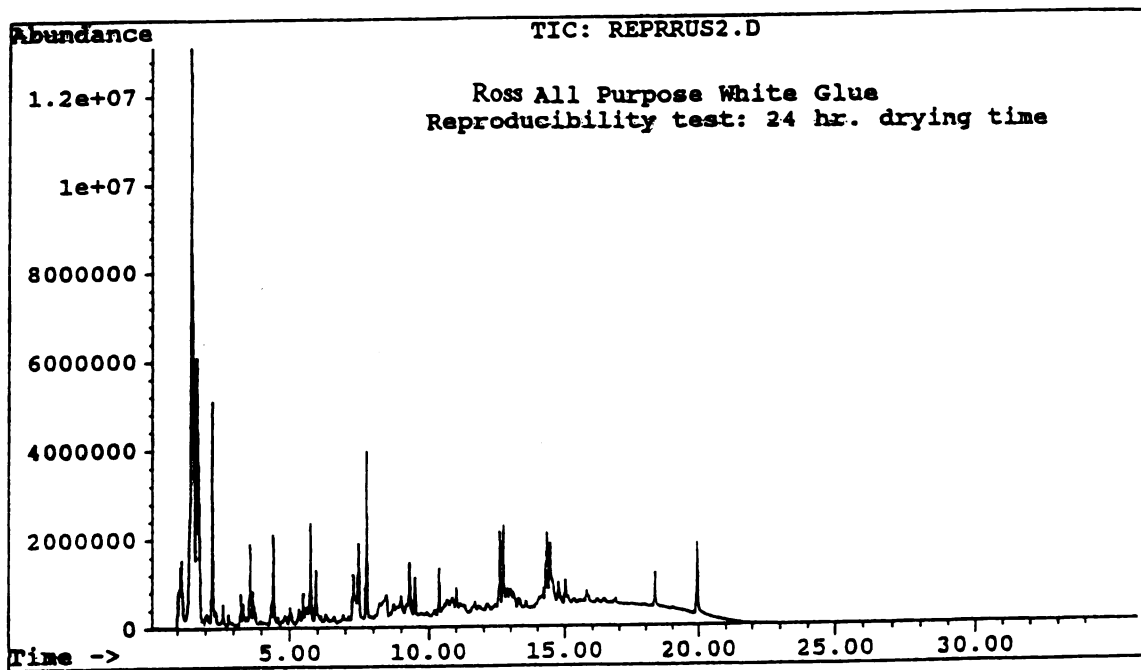
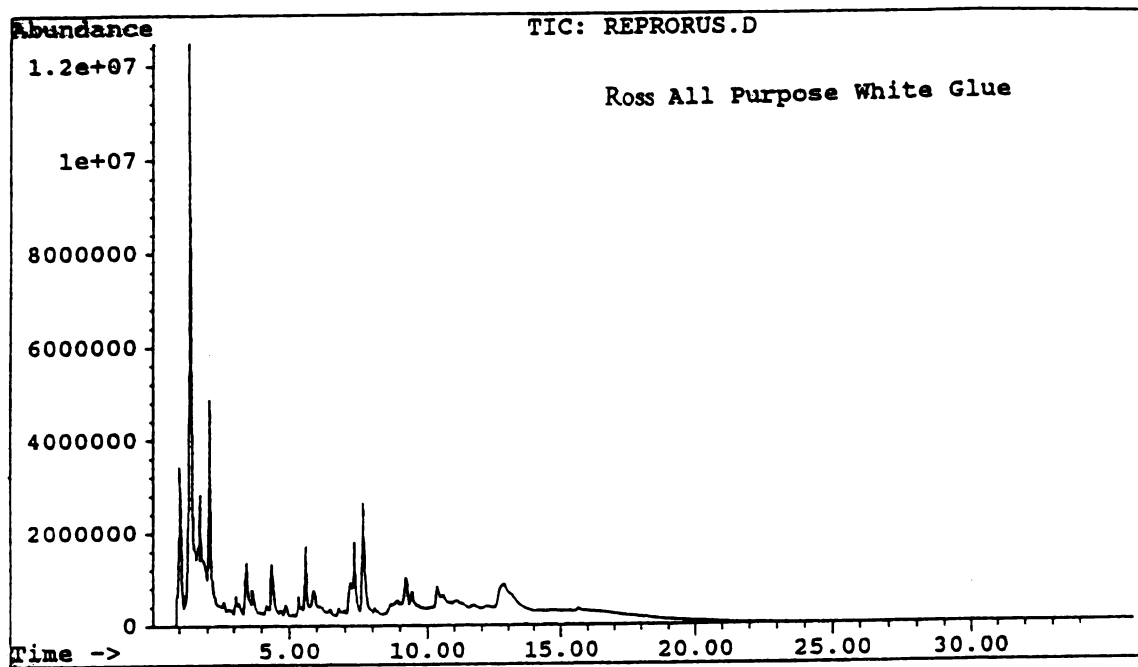


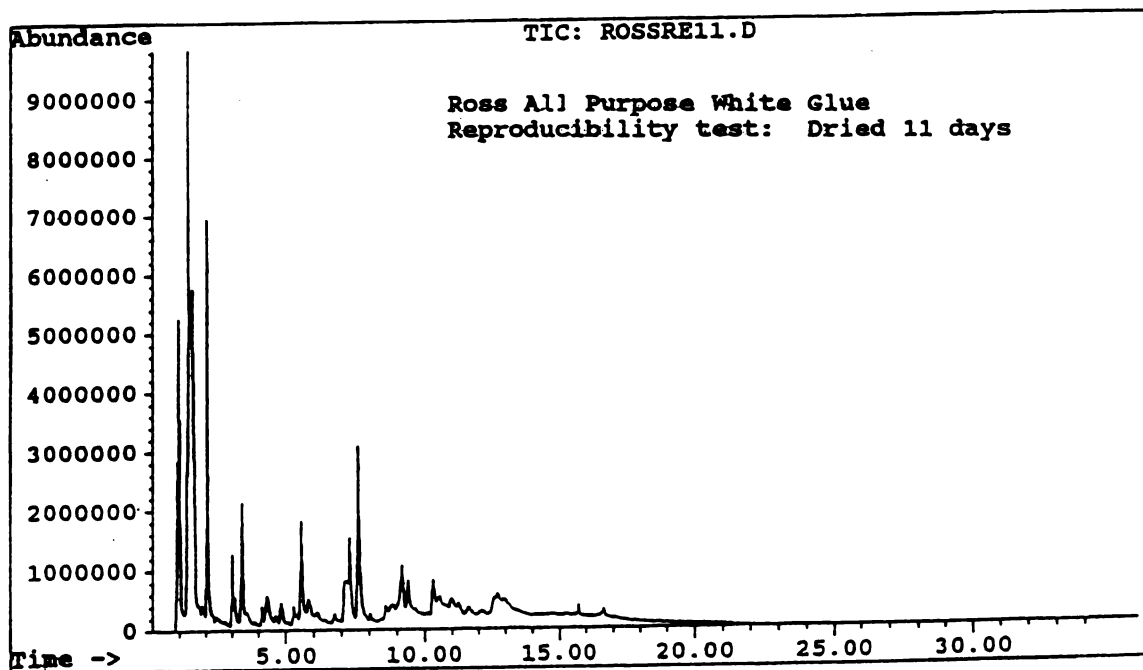
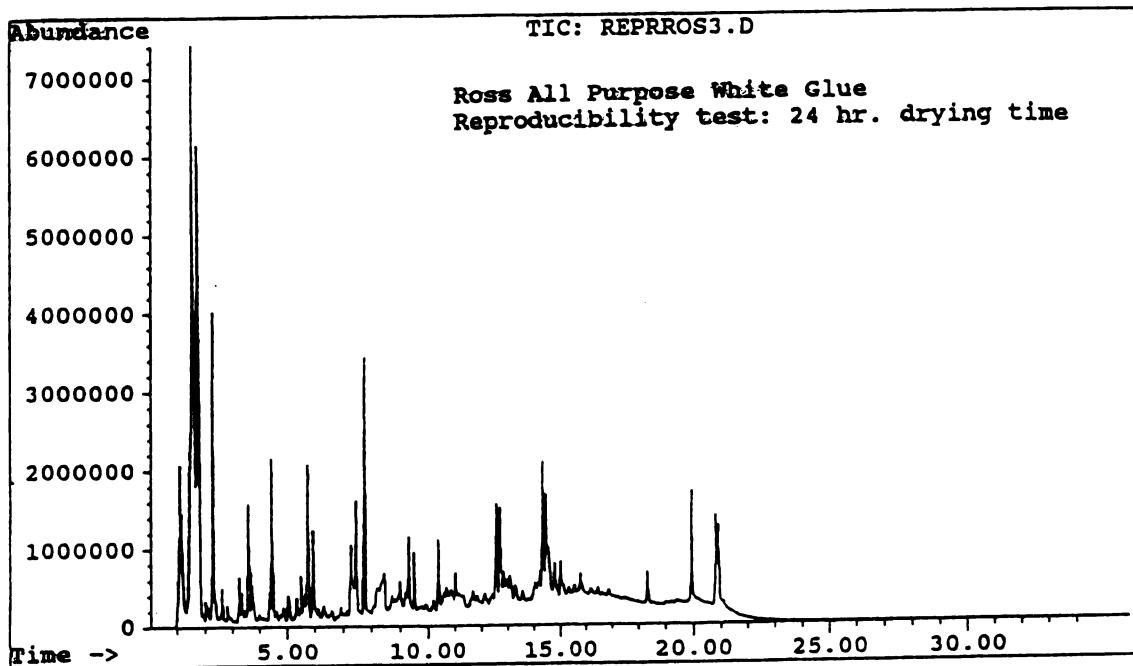


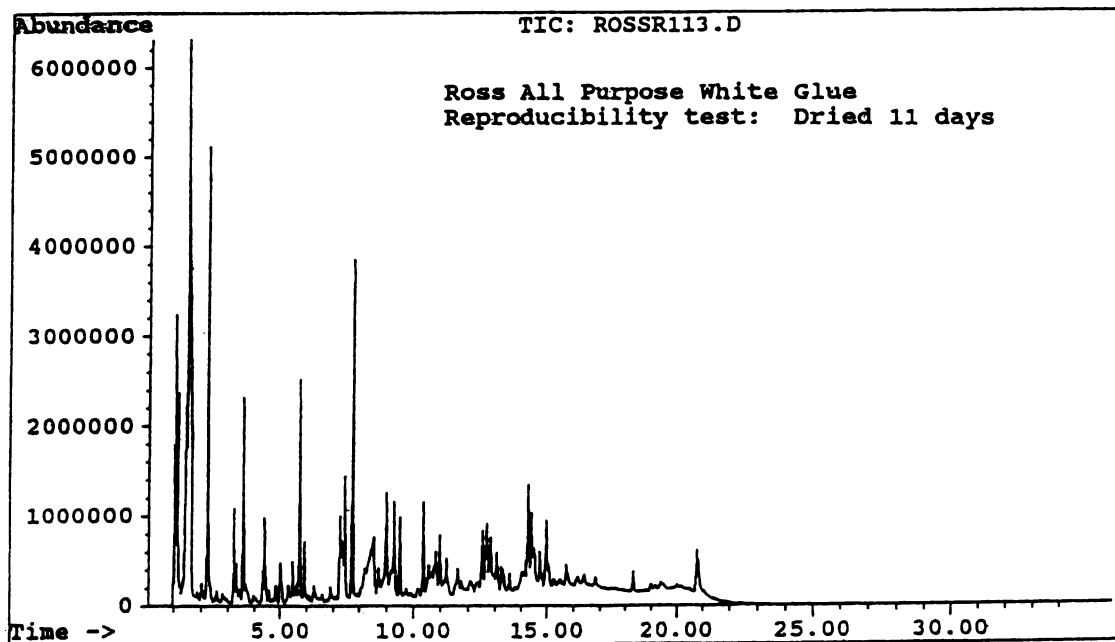
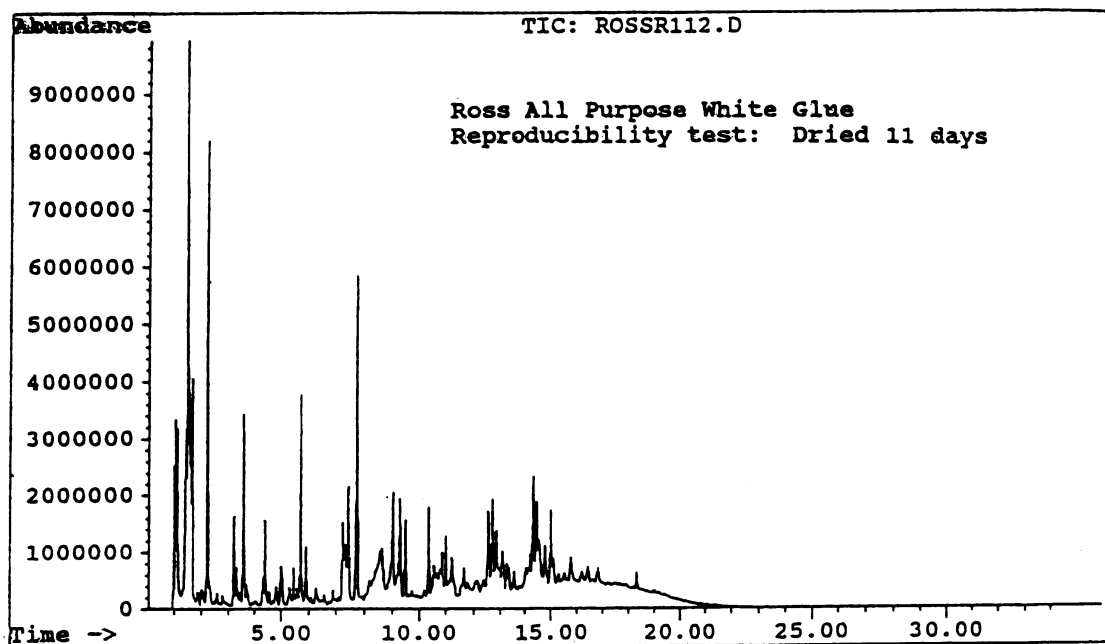




## Repeatability and Affects of Drying Time Study

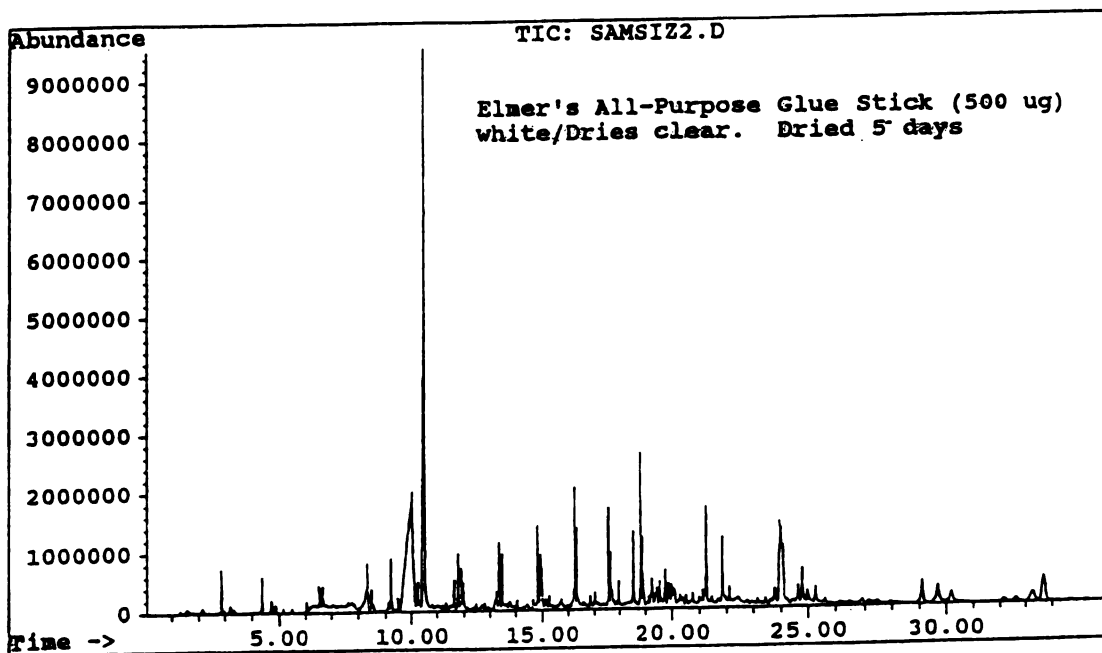
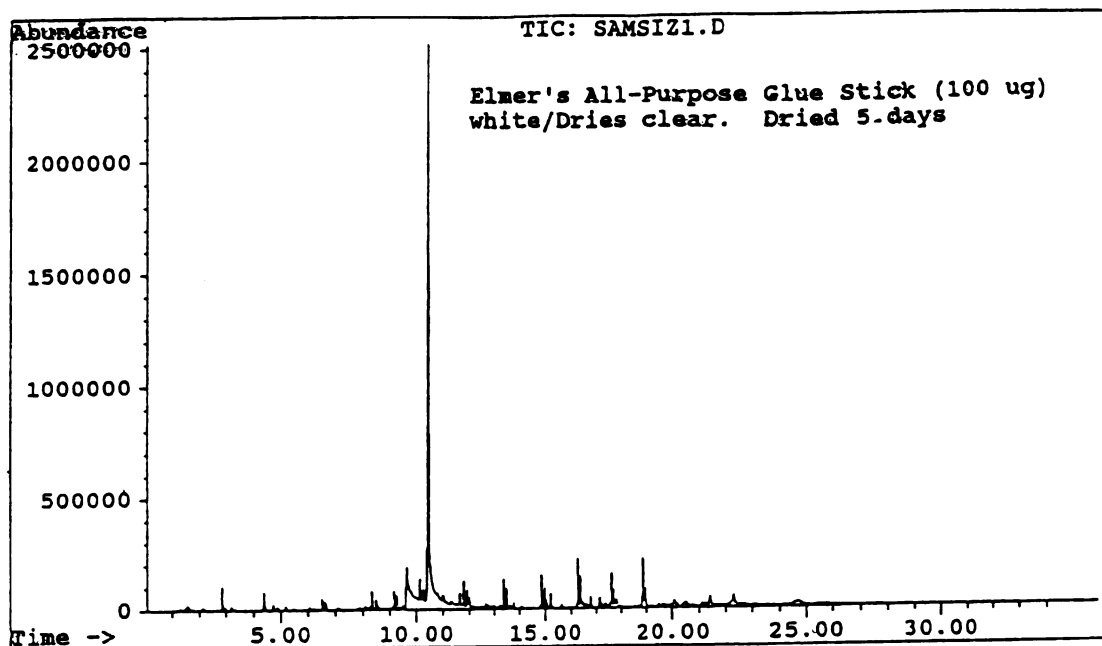


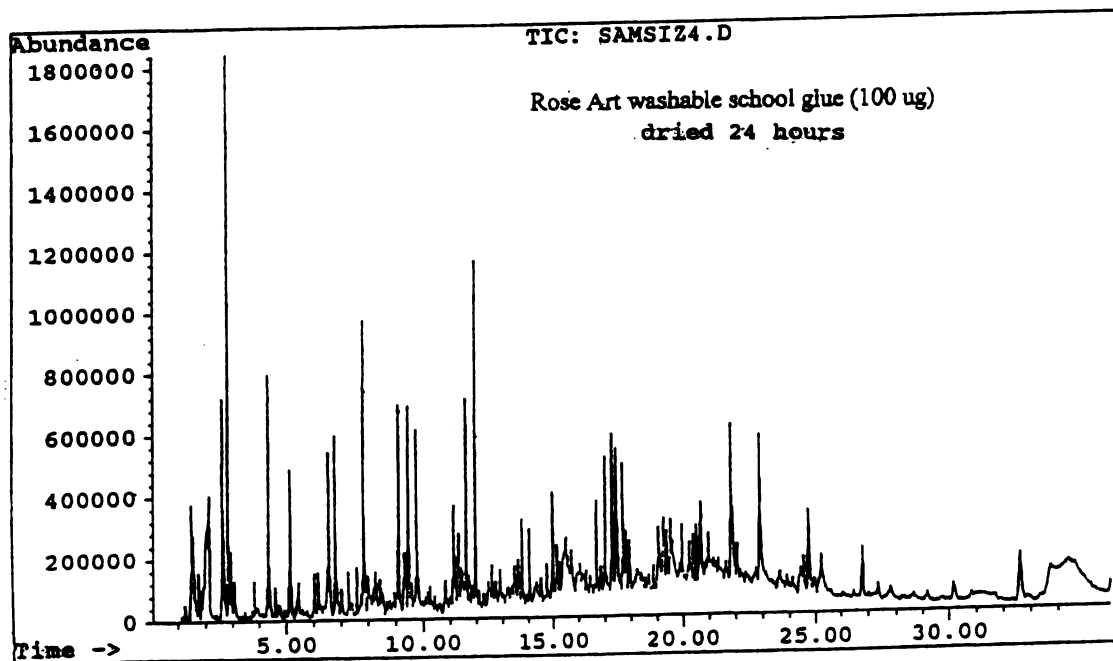
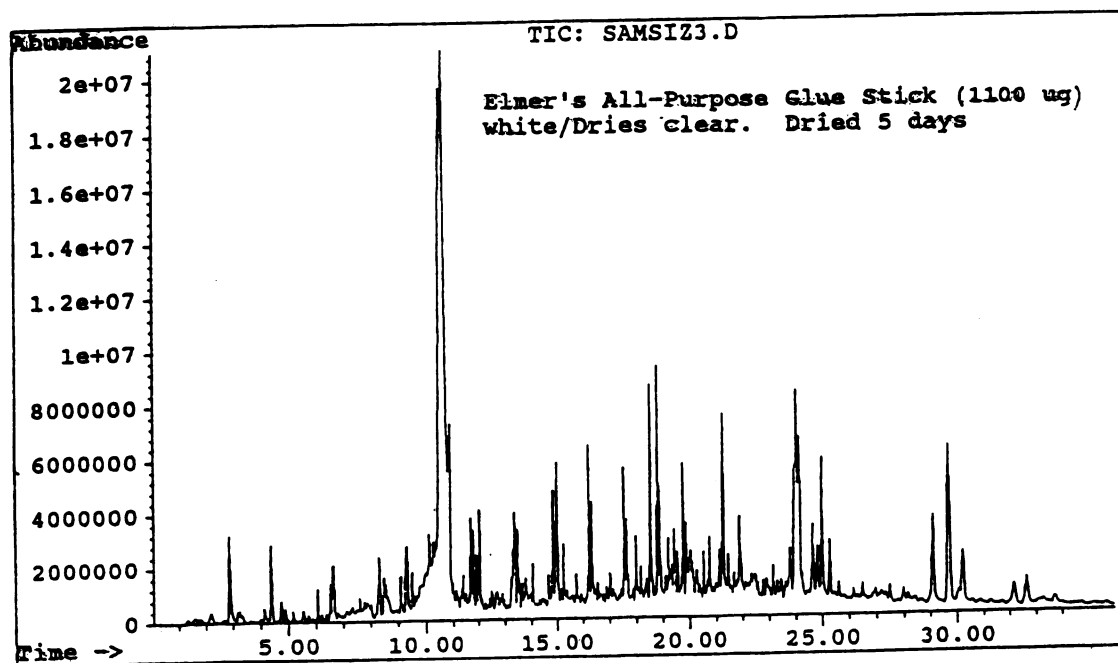


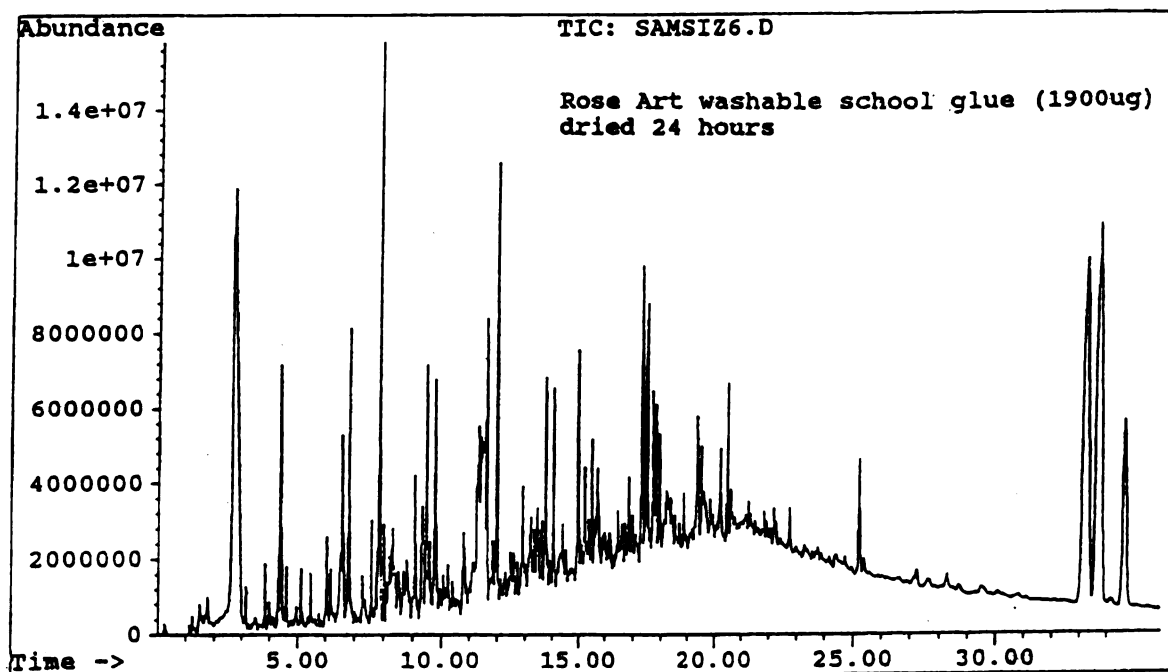
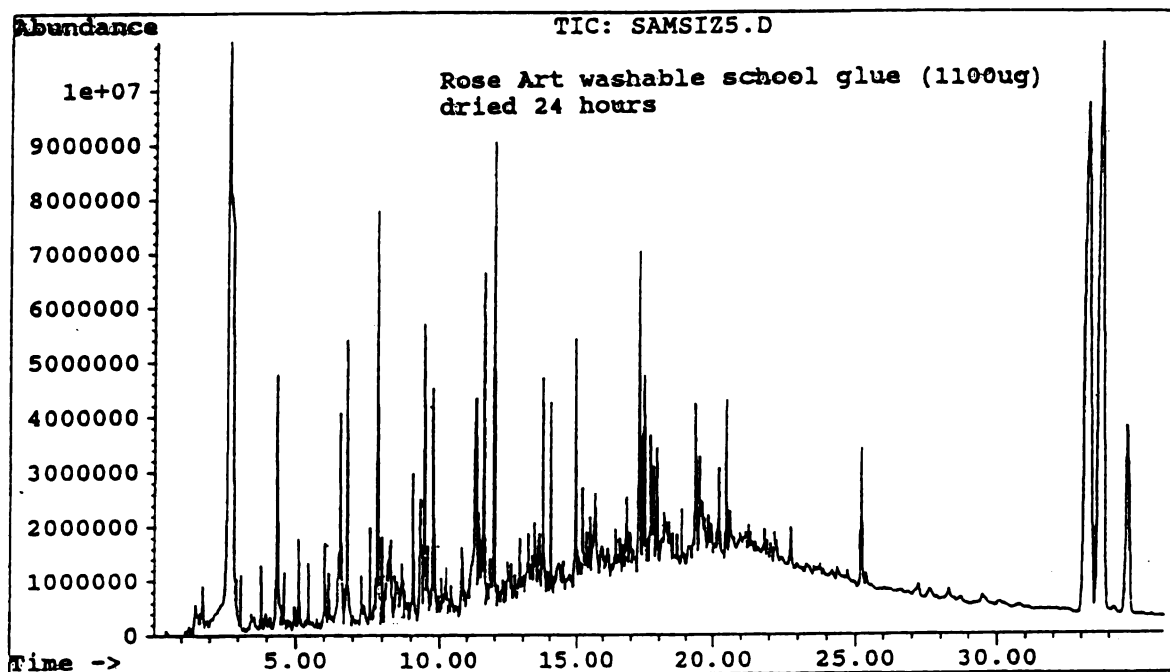


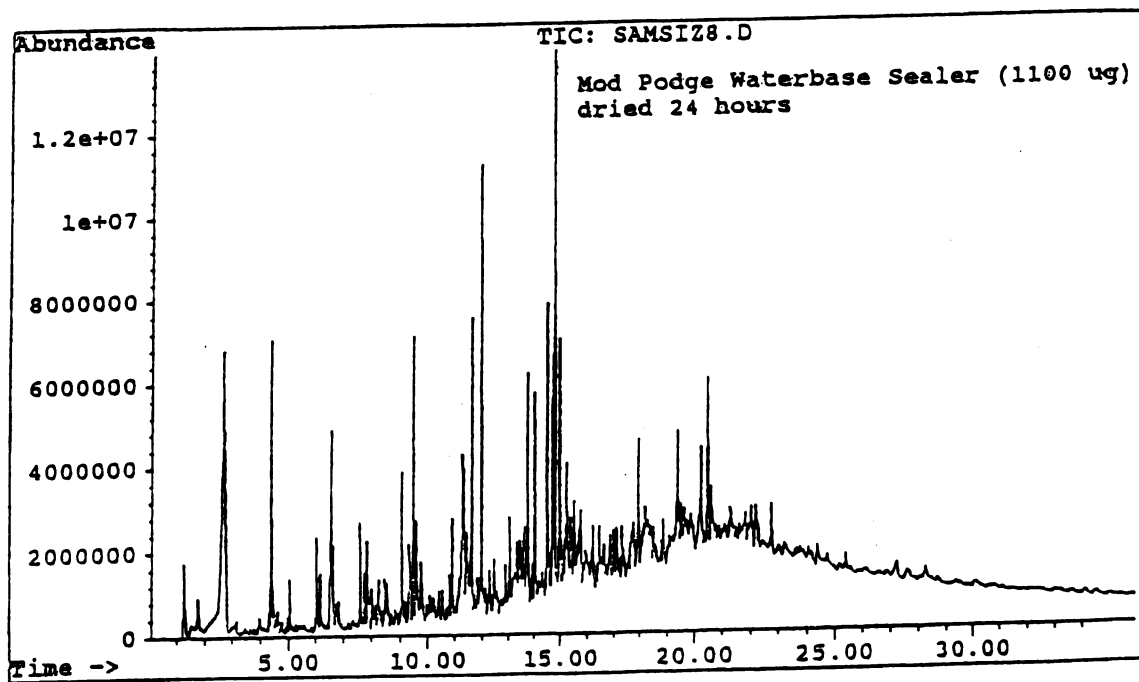
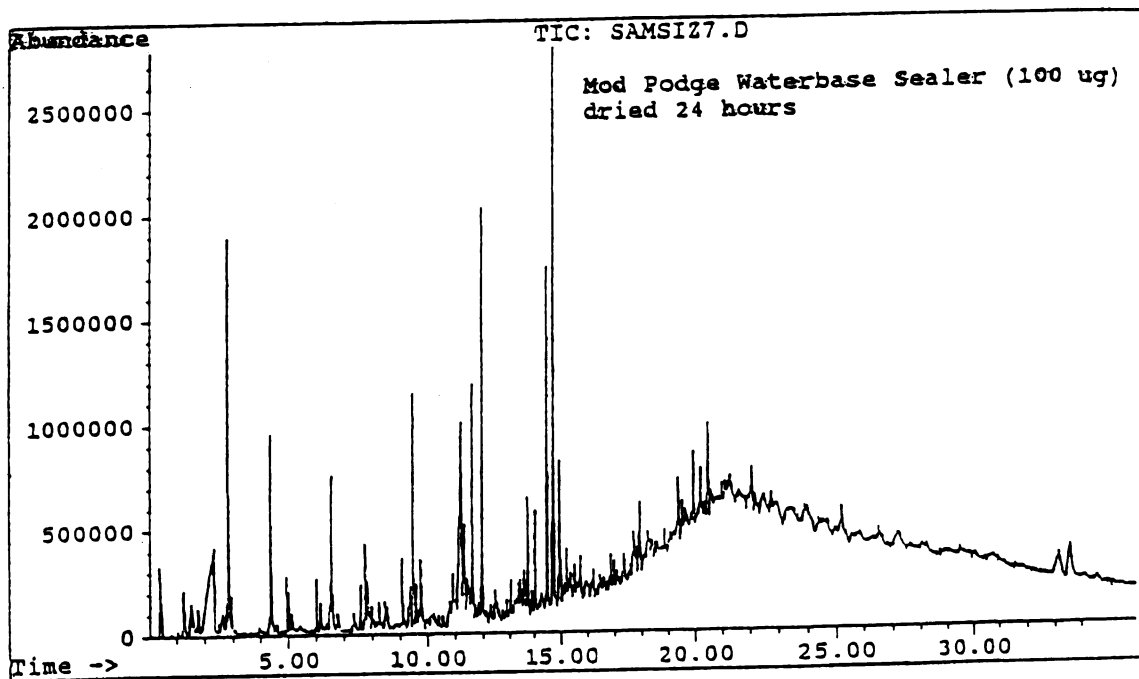


## Sample Size Study









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