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THE DEVELOPMENT OF A FTIR SPECTRAL

LIBRARY OF COMMERCIAL ADHESIVES

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THE DEVELOPMENT OF A FTIR SPECTRAL LIBRARY OF COMMERCIAL ADHESIVES

By

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ABSTRACT

THE DEVELOPMENT OF A FTIR SPECTRAL LIBRARY
OF COMMERCIAL ADHESIVES

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Adhesives can be an important class of evidence in the forensic science laboratory, particularly in the investigation of food or pharmaceutical product tamperings. However, the forensic significance of adhesive analysis using Fourier Transform Infrared (FTIR) spectroscopy has been hindered by the fact that no spectral library of general adhesives is commercially available. Therefore, the purpose of this research was to analyze samples of commercial adhesive products to compile into a FTIR spectral library. Based on spectral comparisons, the commercial adhesives were able to be categorized by similar type. A test of the spectral library was performed to demonstrate its validity. It was concluded that a comprehensive spectral library of commercial adhesives will assist in the classification and identification of unknown adhesives in forensic samples.

ACKNOWLEDGMENTS

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INTRODUCTION

Forensic science laboratories are responsible for analyzing many different types of evidence using a variety of analytical techniques. The techniques used by forensic scientists can be categorized as either "wet" chemistry or instrumental analysis. Examples of wet chemical tests are the spot tests that are routinely used in drug analysis. While this type of test is useful, it generally only provides "yes/no" information: either a spotting solution's color changes or it does not. In contrast to this, many of the scientific instruments used in instrumental analysis have the ability to be more informative by providing a chemical *profile* of the sample. Depending on the particular instrument being used, it may even be possible for the forensic scientist to determine the identity of the substance being analyzed.

One technique of instrumental analysis with the power to potentially identify a substance based on its chemical profile is Fourier Transform Infrared (FTIR) spectroscopy. The instrument used for FTIR spectroscopy is called a spectrometer, and it is operated using a computer. Inside the spectrometer, an infrared source gives off light which passes through a sample compartment and then reaches a detector. Many spectrometers are also equipped with an infrared microscope for the analysis of very small samples. The sample of evidence to be analyzed (or "measured") is placed in the sample compartment or under the microscope. When the analysis is performed, some of the infrared radiation from the source will be absorbed by the sample. This absorbance is registered by the detector and represents the characteristic chemical profile or "spectrum" of the sample being analyzed. The computer interfaced with the instrument records and displays the spectrum of the sample, allowing further data analysis to be performed. The importance of this is that it may be possible for the forensic scientist to identify the sample based on its spectrum. This is most commonly accomplished through the use of computerized "spectral libraries."

A spectral library is a searchable compilation of spectra, collected under carefully controlled, optimized conditions. Spectral libraries are commercially available for FTIR spectroscopy and other instrumental techniques, and may contain several thousand spectra of pure compounds. There are also spectral libraries available with specific forensic applications, such as those containing the spectra of drugs, fibers, arson accelerants, or explosives. Virtually all spectral libraries have been computerized, so that an unknown sample spectrum can be rapidly searched against the spectral libraries by the computer. Thus, a FTIR spectrum is analogous to a fingerprint: just as the Automated Fingerprint Identification System (AFIS) can be used to match an unknown print with one in the computer database, so can an unknown FTIR spectrum be matched with a spectrum in a spectral library.

One class of evidence for which no FTIR spectral library is currently commercially available is general adhesives. The term "adhesive" as used in this paper is to be interpreted broadly, and refers to any material used to fasten one thing to another. When considering the different types of evidence commonly processed by forensic science laboratories, adhesives may not immediately come to mind. However, there are a number of situations in which adhesive analysis could play an important role. In almost any offense involving the postal service, from mail fraud to letter bombs, adhesives may be valuable evidence. Stamps, envelopes, and packaging tapes all utilize adhesives, and laboratory analysis could demonstrate, for instance, that a stamp had been glued to an envelope with an adhesive other than the original one on the stamp backing. In another case, a questioned document analysis may involve a ransom note that was "written" by cutting out words from a magazine and gluing them to a piece of paper. Comparison of the adhesives from the ransom note and from a bottle of glue subsequently found in the possession of a suspect could provide important corroborative evidence. Finally, adhesive analysis can play an important role in cases involving food and pharmaceutical products.

Aside from fresh foods such as produce, the vast majority of food and pharmaceutical products are sold in some outer container, and most of these containers have adhesives present on them. Among other things, adhesives are used to hold paper labels to metal soup cans, to affix foil safety seals to the mouths of medicine bottles, and to seal the end flaps of cardboard cereal cartons. In a *counterfeiting* case, name-brand soup labels may be adhered to cans containing generic soup. In a *tampering* case, a sealed cereal carton may be opened, the cereal inside altered in some way, and the carton then resealed. These examples of counterfeiting and tampering cases both involve the adulteration of adhesives on product containers. In both instances, proper processing of the evidence by the forensic science laboratory would require a comparison of the counterfeit/tampered product adhesive with the adhesive on an unadulterated product of the same type (a "control" sample).

This comparison of the adhesives from the suspect and control samples can be readily accomplished using FTIR spectroscopy with an infrared microscope. This is an ideal technique for the analysis of adhesives due to the ease of sample preparation, the small amount of sample required for analysis, and the fact that FTIR spectroscopy is non-destructive to the sample. Assuming that the suspect and control samples are in fact different (i.e., the suspect sample has an <u>additional</u> adhesive), it would be desirable to identify the suspect adhesive's potential source. However, without a spectral library of adhesives, the classification and identification of samples is difficult to accomplish.

Therefore, the purpose of this research was to develop a FTIR spectral library of commercially available adhesives. FTIR spectra were collected of numerous adhesive samples, and the spectra were then compiled into a spectral library. This development should allow the classification and/or identification of suspect adhesives in the types of cases described above. Commercial adhesives were chosen for the spectral library due to their availability and their ease of use. Whereas product manufacturers typically use "hot-melt" type adhesives to heat-seal their packages, most commercial adhesives are designed to be applied as liquids and then solidify by drying in air. This makes most commercial adhesives more practical for use by offenders. Furthermore, if an offender applies an adhesive to a stamp, a piece of paper, or a product container, chances are good that the adhesive was one the offender had in his or her residence or office. Therefore, in all likelihood, the adhesive was purchased commercially rather than being obtained directly from a manufacturer.

REVIEW OF LITERATURE

A review of the literature reveals that many authors have discussed the topics of spectral libraries, adhesive analysis, FTIR spectroscopy, and forensic science in various combinations with one another. However, there have been very few papers that bring together all four of these subjects, as is being done in this research.

Some novel uses of spectral libraries in the context of forensic science have recently been described, though techniques other than FTIR spectroscopy were being utilized. In two papers (1,2), high-performance liquid chromatography with diode array detection (HPLC/DAD) was used to create spectral profiles of numerous drugs of abuse. Then, a library was used to identify drugs extracted from blood in forensic toxicology. Another paper described the use of a spectral library in conjunction with proton nuclear magnetic resonance spectroscopy (NMR) to identify "nitro-compounds" from explosives (3). In a fourth article, gas chromatography (GC) profiles of some common arson accelerants were matched against the profiles of suspect samples (4). These four papers demonstrate the potential utility of spectral libraries in the analysis of forensic samples.

Techniques besides FTIR have been used in the forensic analysis of adhesives. Two separate authors described the use of pyrolysis-gas chromatography (PGC) in forensic science analyses, with adhesives being among the samples discussed (5,6). In another paper (7), size-exclusion chromatography with electrochemical detection was used to detect the compound nitrocellulose. This compound may be found in trace amounts in many items, including some adhesives. While these three papers point out some forensic aspects of adhesive analysis, they do not focus on adhesives as their primary subject.

Several articles have described the use of FTIR spectroscopy in the analysis of specific adhesive types, including anaerobic sealants and adhesives (8) and the adhesives in multi-layer polymer laminates in packaging materials (9). In an analysis of water-based adhesives (10), a FTIR spectral library was used to identify specific components within the adhesive matrix. Among those papers that apply directly to forensic science using FTIR spectroscopy, two described the analysis of the adhesives on stamps (11,12). The materials used to contain illegal drugs, including adhesives, were also analyzed by FTIR (13). Finally, another paper described the use of both PGC and FTIR for adhesive analysis (14). All of these articles are important relative to this research because they demonstrate the practicality of using FTIR spectroscopy to analyze various adhesives.

Two previous papers described projects similar to the research presented here. In 1966, in one of the first attempts at the forensic identification of adhesives, researchers in Canada analyzed commercially available adhesives using a series of tests that included paper chromatography, spot tests, PGC, and IR spectroscopy (the precursor to FTIR). The authors were able to distinguish between different classes of adhesives (15). The second paper, in 1974, described the analysis of commercially available adhesives in Great Britain using PGC and IR spectroscopy. Once again, the researchers demonstrated the ability to differentiate among the products analyzed (16). In these two studies, the authors ended up with several infrared spectra of adhesives that could be considered spectral libraries. However, without the ability to do computer library searching, the researchers had to accomplish the comparison and identification of their adhesive samples by hand-searching hard copies of the spectra. Furthermore, because the authors were using conventional IR spectroscopy rather than FTIR, they could not achieve the greatly improved signal-to-noise ratio provided by Fourier transform instruments. Nevertheless, these two papers were the first examples of spectral libraries of adhesives for forensic science purposes.

MATERIALS AND METHODS

A total of 56 commercial adhesives were purchased to constitute the FTIR spectral library. An alphabetical list of the products is shown in Table 1. These products were purchased from six different locations (one hardware store, two department stores, and three office supply stores) and represent almost all of the adhesive products available at these six stores. An attempt was made to select adhesives designed for a wide variety of purposes, so that several different adhesive types would be represented in the spectral library. However, a premium was placed on those types of adhesives most likely to be used in offenses such as tampering with food or pharmaceutical products. Therefore, a number of "school" or "white" glues and "super" or "krazy" glues were selected because they were considered very common household adhesives. Also, most of the products purchased were name-brand adhesives (e.g., Elmer's, 3M, Instant Krazy Glue) because it was expected that these would be the most widely available at different stores throughout the country.

Prior to analysis, the adhesive samples were applied to glass microscope slides and allowed to dry in air. This was done for a number of reasons. First and foremost, the majority of adhesive evidence that is brought into the forensic science laboratory is likely to be in the dried form. However, even when this is not the case, it is easy enough to allow an adhesive to dry before analysis. The reverse is not true: in most instances it would be impossible to convert a dried adhesive back into its original, undried form. A second reason for drying the adhesives is that sample preparation is much less complicated with a dried solid than with a viscous, sticky

Table 1 - Commercial Adhesives

PRODUCT NAME	MANUFACTURER	DAYS DRIED
3M Counter Top Cement	3M	4
3M Plastic & Model Cement	3M	3
3M Super Glue Gel	3M	227
3M Super Strength Adhesive	3M	3
3M Water-Resistant Adhesive	3M	5
3M Wood Glue	3M	4
Avery Permanent Glue Stic	Avery Dennison	15
Avery Removable Glue Stic	Avery Dennison	17
DAP Weldwood Contact Cement	DAP	8
Devcon 2-Ton Crystal Clear Epoxy	ITW Brands	34
Duco Cement	ITW Brands	8
Duco Plastic & Model Cement	Devcon	2
Duro Clear Silicone Sealer	Loctite Corporation	16
Duro Fast Drying Contact Cement	Loctite Corporation	2
Duro Fixture Adhesive	Loctite Corporation	2
Duro Household Cement	Loctite Corporation	6
Duro Quick Gel	Loctite Corporation	1
Duro Stick With It Fix-All Adhesive	Loctite Corporation	7
Duro Super Glue	Loctite Corporation	15
Elmer's Carpenter's Wood Glue	Borden	9
Elmer's Glue-All	Borden	16
Elmer's Glue Stick	Borden	7
Elmer's Heavy Grip Cement	Borden	7
Elmer's School Glue	Borden	16
Elmer's School Glue Gel	Borden	17
Elmer's School Glue Stick	Borden	16
Elmer's Stix-All Hi-Tech Adhesive	Borden	7
Elmer's Washable School Glue	Borden	17
Elmer's Wonder Bond Plus Super Glue	Borden	15
Franklin Hide Glue	Franklin International	16
Franklin White Glue	Franklin International	14
GE Silicone II	General Electric	9
Glue Pen	Sirich International	18
Instant Krazy Glue - All-Purpose	Borden	3
Instant Krazy Glue - All-Purpose / Skin Guard Formula	Borden	1
Instant Krazy Glue - No Run Gel	Borden	17
Instant Krazy Glue - Wood Formula	Borden	15
Pliobond General Purpose Adhesive	Ashland Oil	2
Power Poxy One-N-Done Super Glue	Power Poxy Adhesives	19
Power Poxy One-N-Done Super Glue Gel	Power Poxy Adhesives	16
Quicktite High Performance Super Glue Pen	Loctite Corporation	15
Quicktite Super Glue Gel	Loctite Corporation	1
Richbond Super Glue Gel	Richbond Corporation	17
Ross Envelop Stik	Conros Corporation	18
Ross Office Glue Plus	Conros Corporation	18
Ross Rubber Cement	Conros Corporation	18
Ross Super Glue	Conros Corporation	17
Scotch Restickable Adhesive Glue Stick	3M	18
Seal-All	Allen Products	8
Super Duper Super Glue	ITW Brands	10
Titebond Home/School Glue	Franklin International	160
Titebond Liquid Hide Glue	Franklin International	7
Titebond Original Wood Glue	Franklin International	225
Titebond Wood Molding Glue	Franklin International	162
Titebond II Premium Wood Glue	Franklin International	15
UHU Stic	Eberhard Faber	18

liquid. Finally, the solvent(s) present in an undried product may dominate the FTIR spectrum and mask those spectral features due to the actual adhesive constituents. Therefore, drying the adhesive samples was considered the most practical procedure.

For the majority of the adhesives, the sample drying time ranged from 1 day to 19 days. This variation in drying time was mostly dependent upon how soon, after applying the sample to the glass slide to dry, an opportunity was found to conduct the analysis. However, five of the samples were re-measured at later dates and have drying times ranging from 34 days to 227 days. This occurred in the course of double-checking the spectra of the adhesive samples to ensure their accuracy before creating the spectral library.

The instrument used for the FTIR analysis of the adhesive samples was a Nicolet Magna-IR™ 550 spectrometer equipped with a Nic-Plan™ infrared microscope and a mercury-cadmium-telluride (MCT) detector. The samples were measured from 4000 cm^{-1} to 650 cm^{-1} at a resolution of 4 cm^{-1} using a minimum of 64 scans. The software used for data collection and analysis was OMNIC™ version 3.1a (the OMNIC software was upgraded twice--from version 2.1 to 3.0 to 3.1a--during the course of the project, but these upgrades did not affect the data in any way). The software was loaded with spectral libraries containing approximately 25,000 spectra. A list of these spectral libraries is in the appendix.

Each adhesive sample was prepared for FTIR analysis by transferring a small portion of the dried adhesive using a scalpel blade to one window of a miniature diamond anvil cell (High Pressure Diamond Optics, Inc.). The second window of the diamond anvil cell was placed on top and the screws tightened to compress the adhesive sample to a thin film. The diamond anvil cell was then dismantled and a single diamond window containing the thin film of sample was transferred to the infrared microscope. The infrared spectrum of the adhesive sample was measured in % transmittance using a blank portion of the diamond window as the background. Approximately four spectra were measured of each sample to ensure that a representative spectrum was collected, with the best spectrum being kept. The final spectrum of each adhesive was converted to absorbance and baseline corrected using the OMNIC software. Each adhesive spectrum was searched against the spectral libraries loaded onto the OMNIC software. This assisted in the classification of the adhesive samples by allowing comparison with the library spectra. Additionally, the major components of some of the adhesives were identified based on the library searches.

The preparation described above is also used for adhesives from actual case samples. The surface with the adhesive residue present is observed using a stereomicroscope, and a scalpel blade is used to remove a small portion of the adhesive. Care must be taken not to transfer any fibers from a paper or cardboard surface to the diamond window along with the adhesive sample. To demonstrate this sample preparation, and to test the spectral library of commercial adhesives upon its completion, 11 of the adhesive samples were applied to a cardboard pharmaceutical product carton and allowed to dry. These 11 "test" samples were arbitrarily selected from within each of the adhesive categories described in the "Results and Discussion," and they are listed in Table 2. The dried test adhesives were prepared and measured as described above.

Table 2 - Adhesives Used to Test the Spectral Library

Product Name	Adhesive Category*
Instant Krazy Glue - Wood Formula	Super Glue
Power Poxy One-N-Done Super Glue Gel	Super Glue Gel
Elmer's School Glue	Poly(Vinyl Acetate)
Glue Pen	Poly(Vinyl Acetate) Related
Elmer's Glue Stick	Glue Stick
3M Counter Top Cement	Poly(Alkyl Acrylate)
DAP Weldwood Contact Cement	Contact Cement
Titebond Liquid Hide Glue	Hide Glue
Duro Clear Silicone Sealer	Silicone
3M Plastic & Model Cement	Plastic and Model Cement
Duco Cement	Miscellaneous

* Adhesive categories described in the "RESULTS AND DISCUSSION" section.

RESULTS AND DISCUSSION

Once the FTIR spectra of all 56 samples were collected, analysis of the data revealed that many of the spectra could be categorized based on similarities to other spectra. Those that could not be grouped were placed in the last category, "miscellaneous." For the most part, the categories of spectra were highly characteristic, so that, in a forensic case, a suspect adhesive could at least be classified if not identified. The results are arranged and discussed by category.

Super Glues

Fifteen "super" glue type adhesives were analyzed, and all were observed to have similar spectral features. This was to be expected, as all fifteen products were labeled to contain a "cyanoacrylate" compound. The spectra of the nine regular super glues are shown in Figures 1 and 2. Among these nine spectra, the only one that differs substantially from the others is the spectrum of Instant Krazy Glue - All-Purpose / Skin Guard Formula. Since normal super glue rapidly bonds skin, the Skin Guard Formula must contain an additional ingredient that alters this behavior and gives rise to the additional spectral features observed. The spectra of the six super glue *gels* are shown in Figure 3. The spectrum of Instant Krazy Glue - No Run Gel appears very similar to the spectra of the regular super glues, with only variations in some band intensities. However, the spectra of the other super glue gels obviously exhibit additional strong bands. These spectral variations are due to the additional compound(s) that give the gels their different consistency.

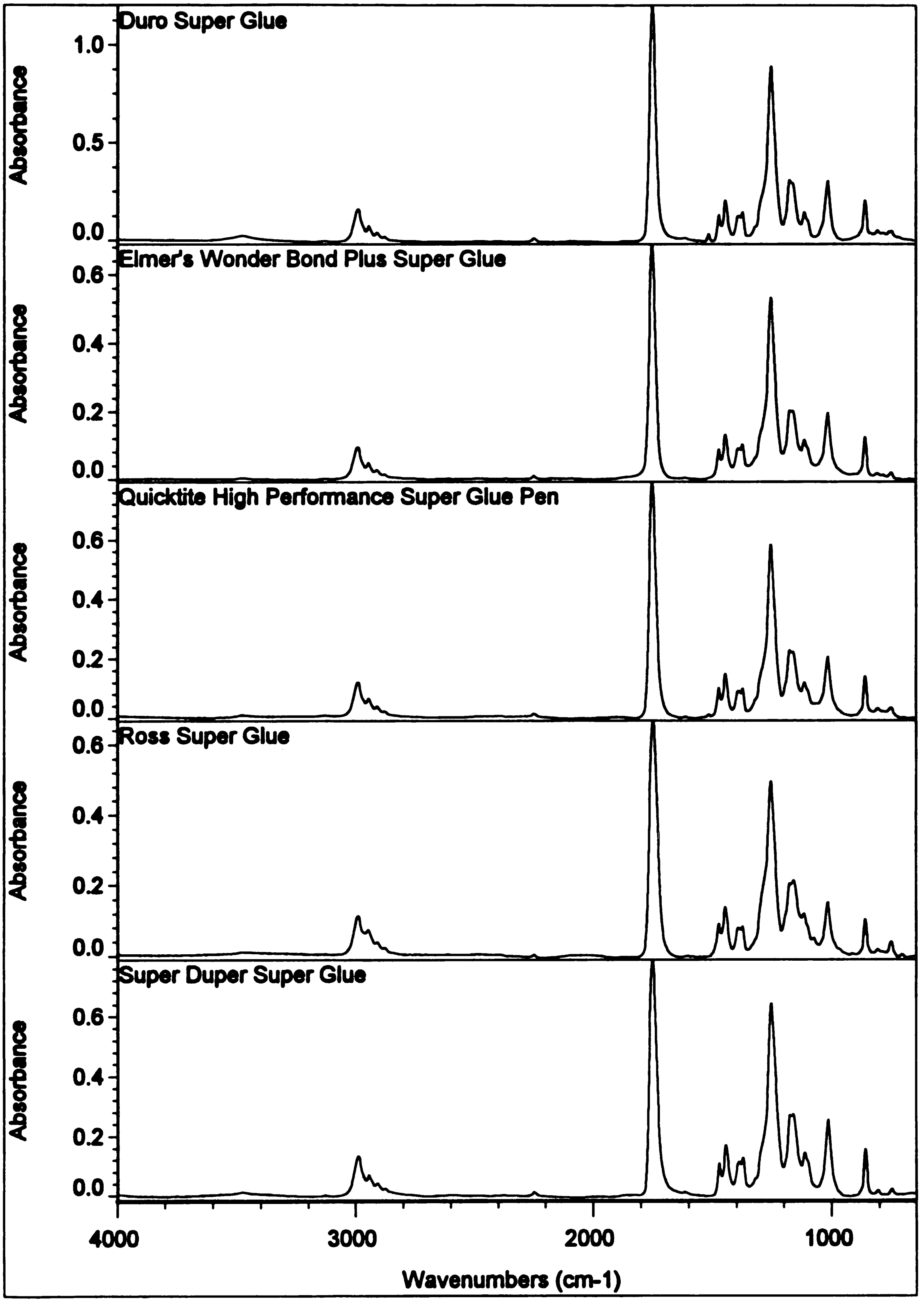

Figure 1 - Super Glue Type Adhesives (A)

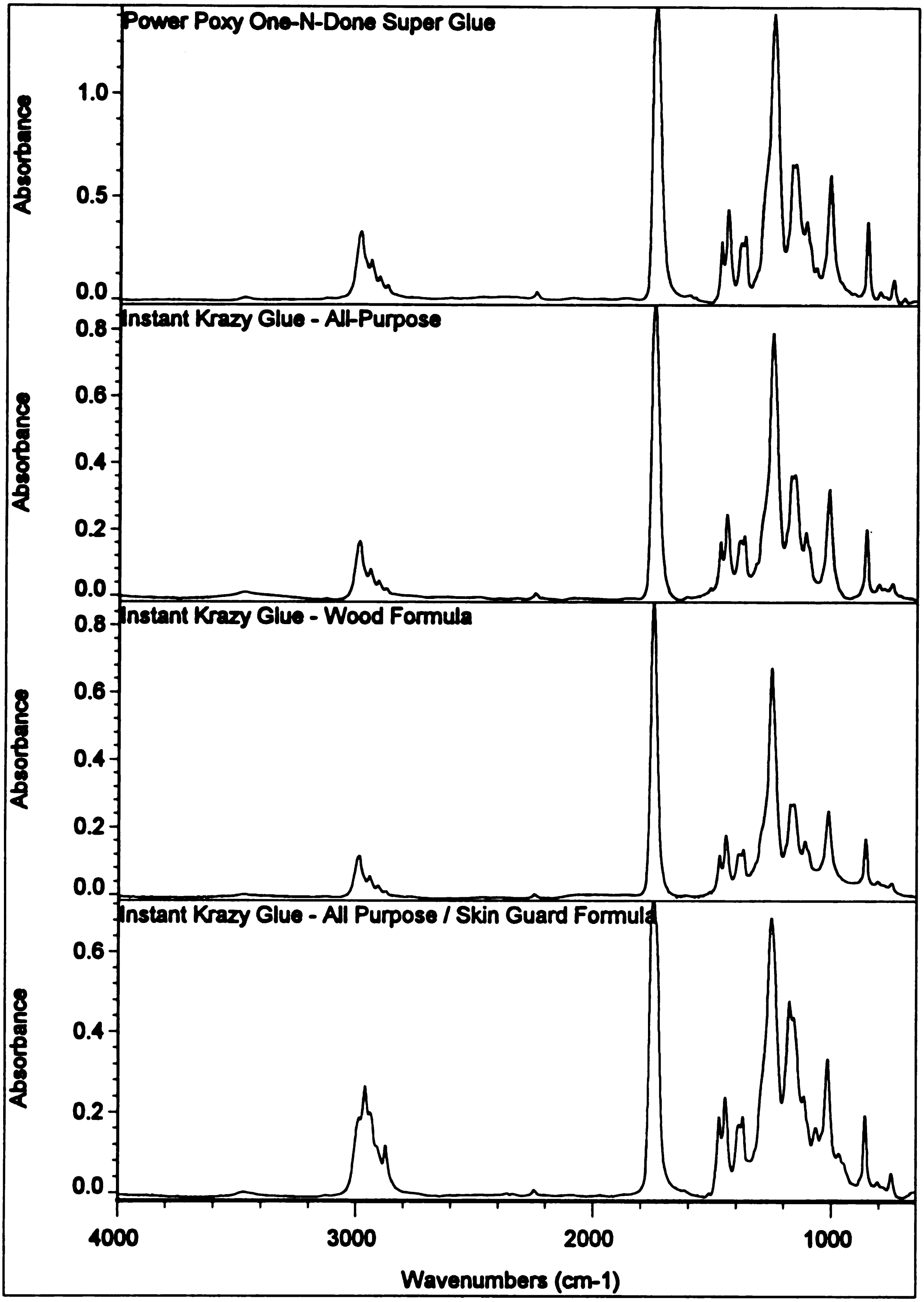

Figure 2 - Super Glue Type Adhesives (B)

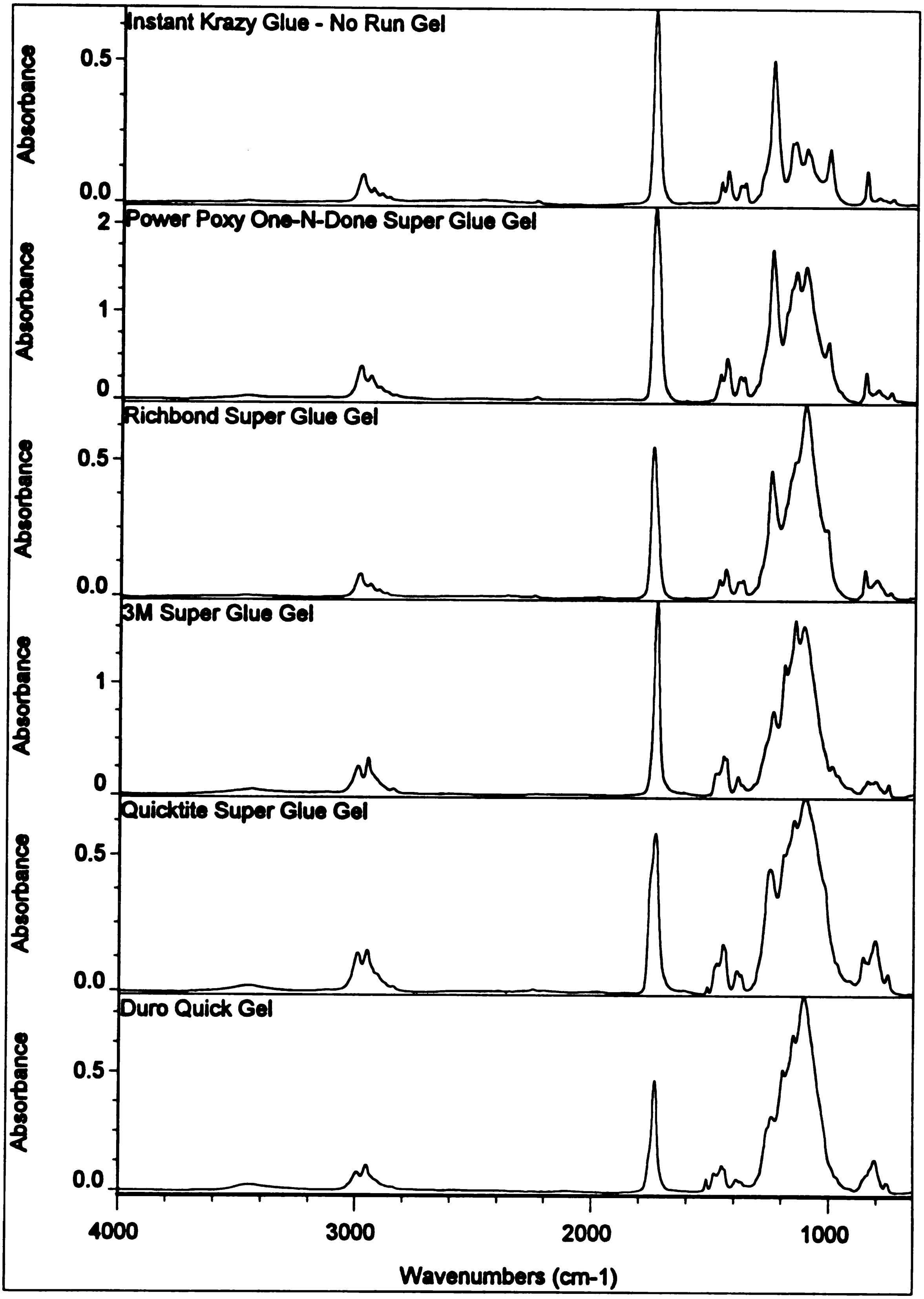

Figure 3 - Super Glue Gel Type Adhesives

Poly(Vinyl Acetate) and Related Adhesives

The common link between the various general purpose home, school, office, and wood glues in this category is their similar chemical composition. These sixteen products were all determined to contain poly(vinyl acetate), a poly(vinyl acetate) copolymer, or poly(vinyl alcohol). Because none of these compounds were listed on the product labels, the identifications were made based on searches of the OMNIC spectral libraries. Figure 4 displays the spectra of six adhesives that were determined to contain poly(vinyl acetate). The spectrum of Franklin White Glue differs somewhat in its band intensities, and the spectrum of Ross Office Glue Plus exhibits three additional weak bands. The spectra in Figure 5 are all of wood glues, and all five products also were determined to contain poly(vinyl acetate). Among these, the spectra of Titebond Wood Molding Glue and 3M Wood Glue exhibit additional weak bands at the same frequencies as the additional bands in the Ross Office Glue Plus spectrum. The spectrum of 3M Wood Glue also exhibits additional bands at 3000-2900 cm^{-1}. In all of the spectra in Figures 4 and 5, the slight fluctuation in intensity of the broad band centered at about 3350 cm^{-1} may be due to the degree of dryness of the sample.

The five spectra in Figure 6 represent compounds with structural similarity to poly(vinyl acetate). Because of this, each of these spectra has certain similarities to those in Figures 4 and 5. The spectrum of Seal-All, when searched against the OMNIC spectral libraries, was observed to have spectral features similar to those in a poly(vinyl chloride):poly(vinyl acetate) copolymer. It can be seen that the spectra of Duro Household Cement and 3M Super Strength Adhesive also have similar spectral

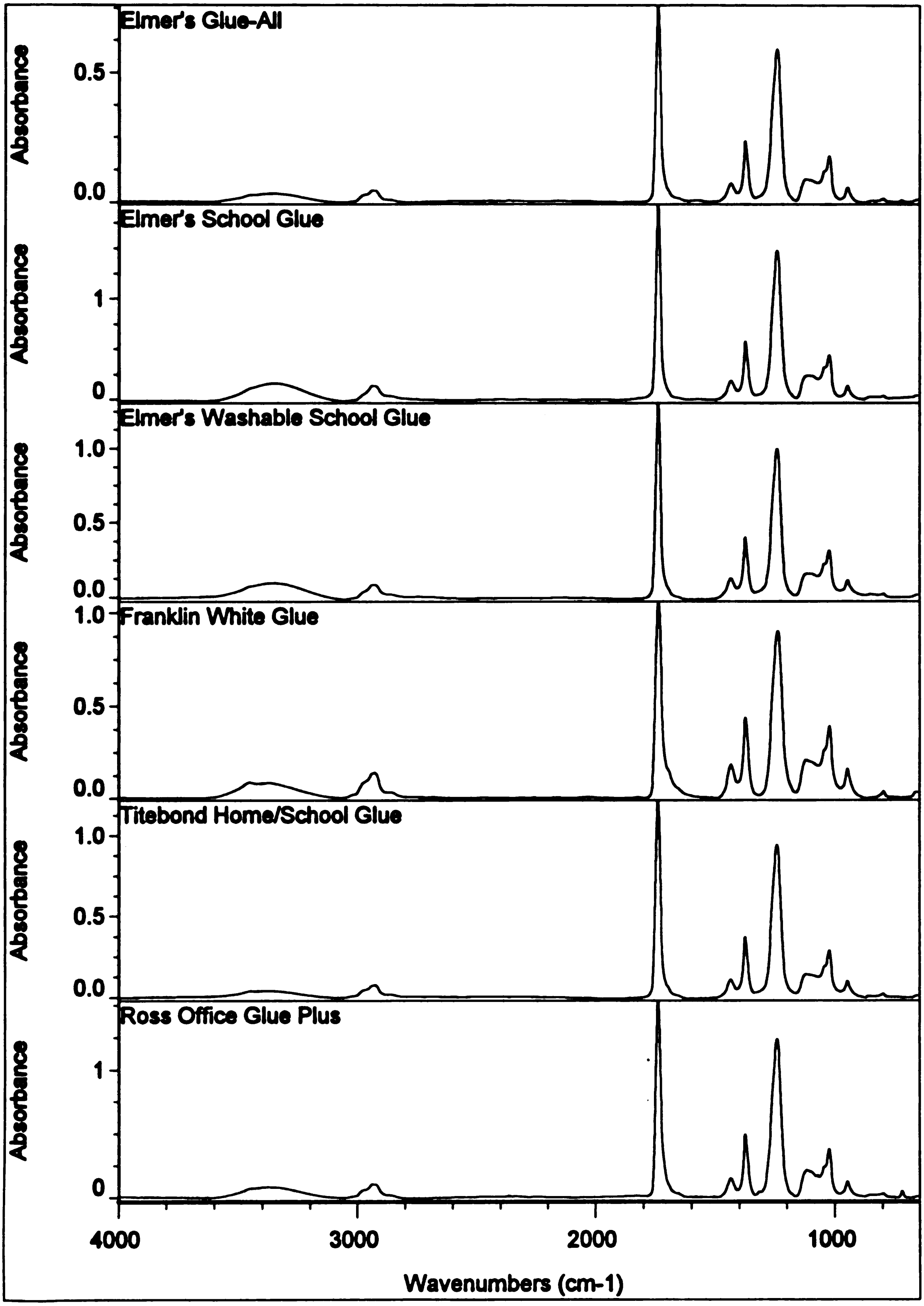

Figure 4 - Poly(Vinyl Acetate) Type Adhesives (A)

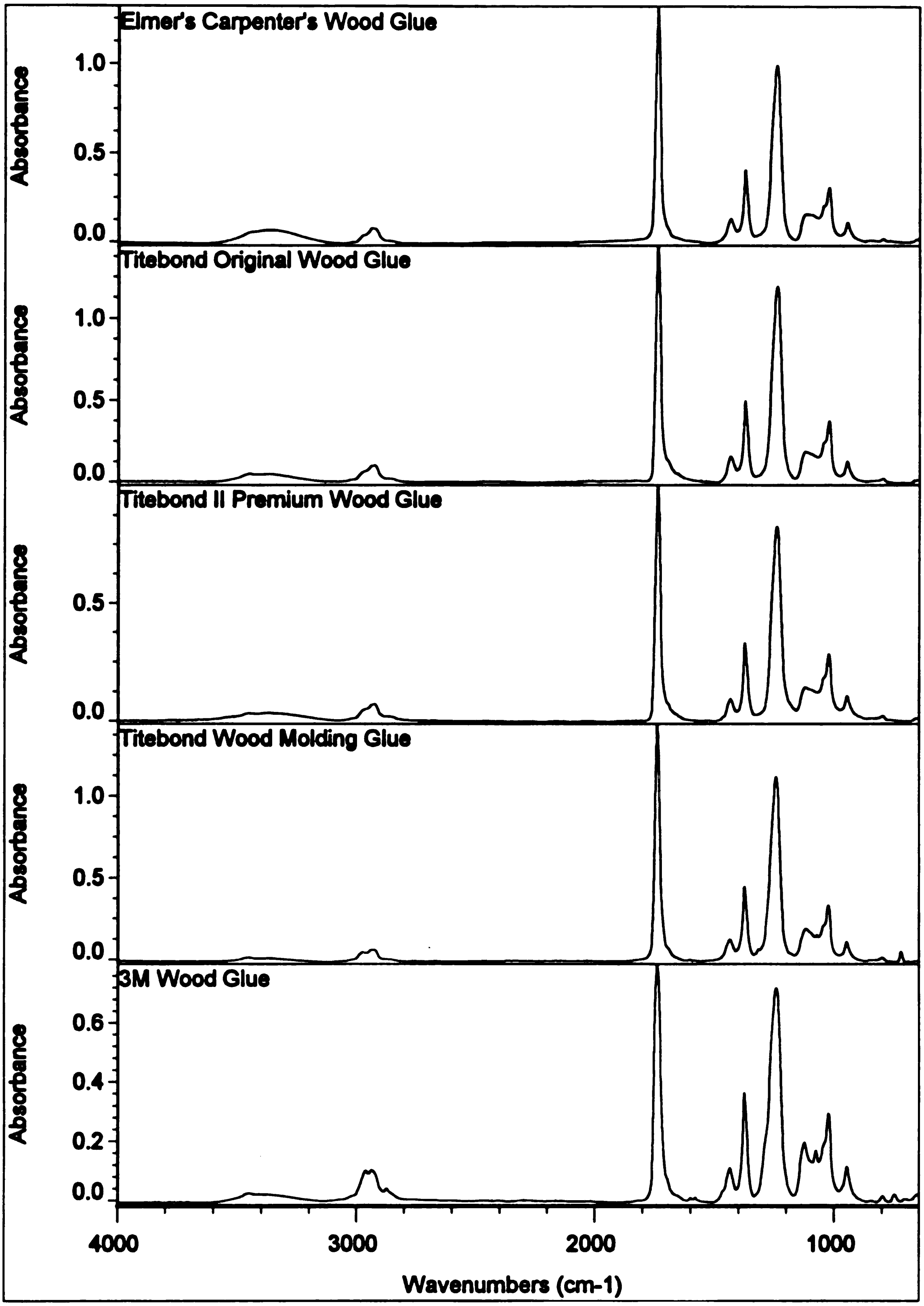

Figure 5 - Poly(Vinyl Acetate) Type Adhesives (B)

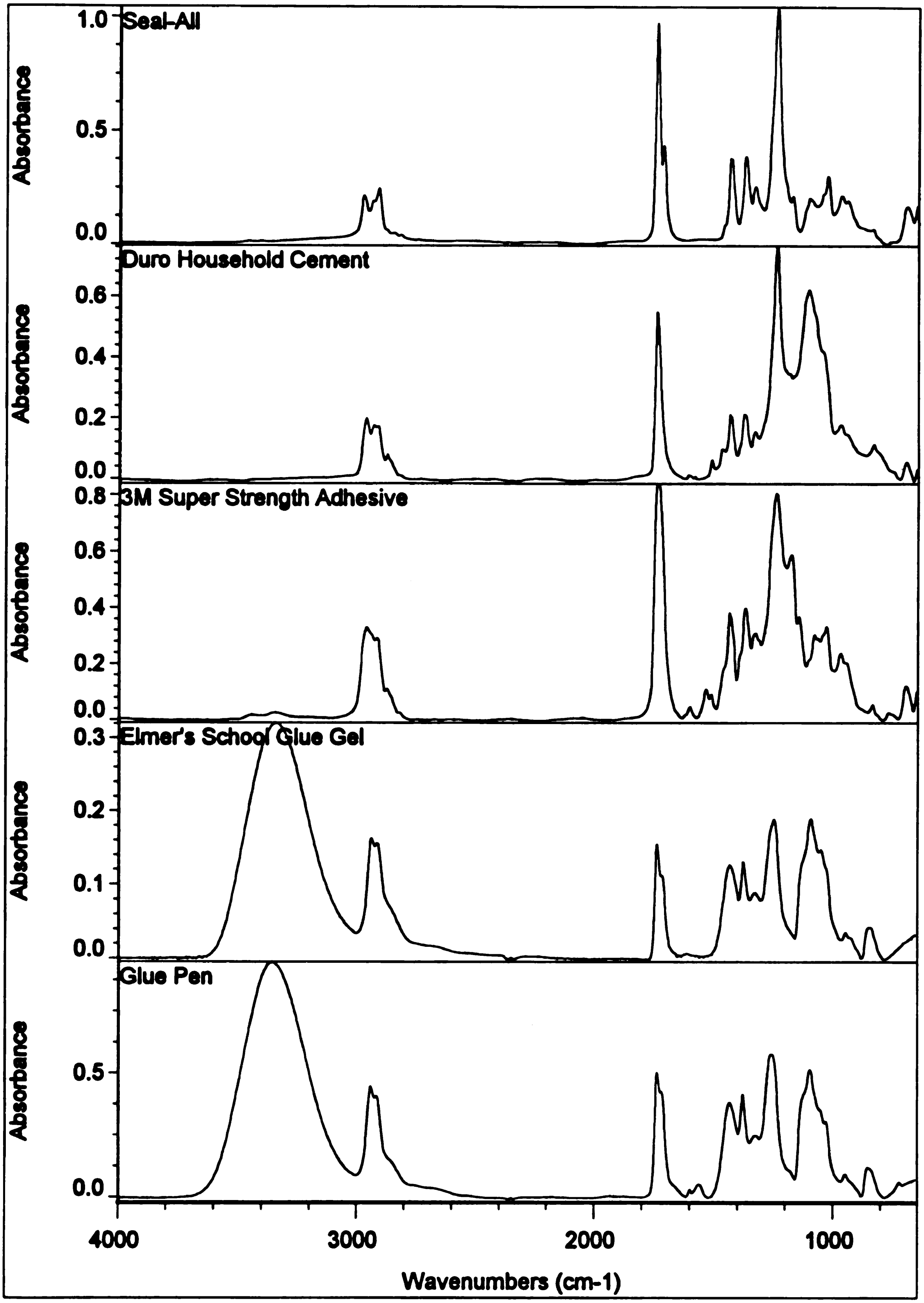

Figure 6 - Poly(Vinyl Acetate) Related Adhesives

features, but have additional bands present. Based on the library searches, the spectra of Elmer's School Glue Gel and the Glue Pen were found to be consistent with poly(vinyl alcohol). This compound is formed by the hydrolysis of poly(vinyl acetate) (17), and thus the two substances are structurally related.

Glue Sticks

The glue stick type adhesives analyzed were not labeled to contain any particular compound(s), and the library search of the six spectra shown in Figure 7 did not yield any spectral matches. Five of these glue stick spectra exhibit many similar spectral features, with some differences observed. The sixth spectrum, that of Avery Removable Glue Stic, is very different from the other glue stick spectra but was placed in this category for two reasons: to contrast it with the spectrum of Avery Permanent Glue Stic and because it did not fit into any of the other categories (except, of course, the miscellaneous category). The spectrum of Scotch Restickable Adhesive Glue Stick, though of a glue stick, fit into the next category.

Poly(Alkyl Acrylate) Adhesives

The spectra of Scotch Restickable Adhesive Glue Stick and 3M Counter Top Cement are not identical, but they exhibit many spectral similarities (see Figure 8). Both of these spectra, when searched against the spectral libraries, were observed to exhibit spectral features similar to those in the spectra of poly(2-ethylhexyl acrylate) and poly(butyl acrylate). However, neither adhesive spectrum exactly matched either library spectrum. Therefore, it was determined that either the adhesives contain one of the above compounds plus an additional ingredient(s), or else the adhesives contain some other poly(alkyl acrylate).

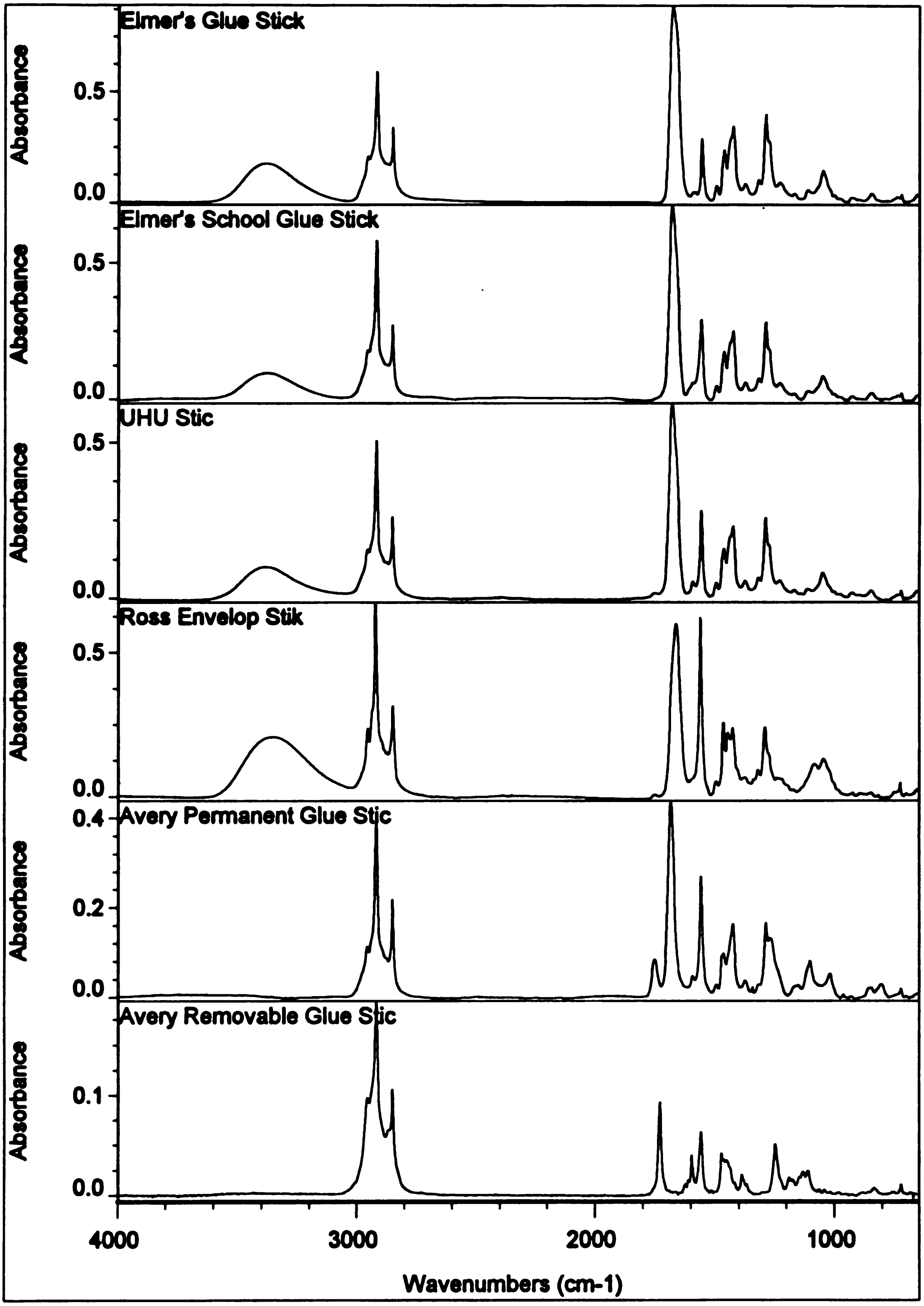

Figure 7 - Glue Stick Type Adhesives

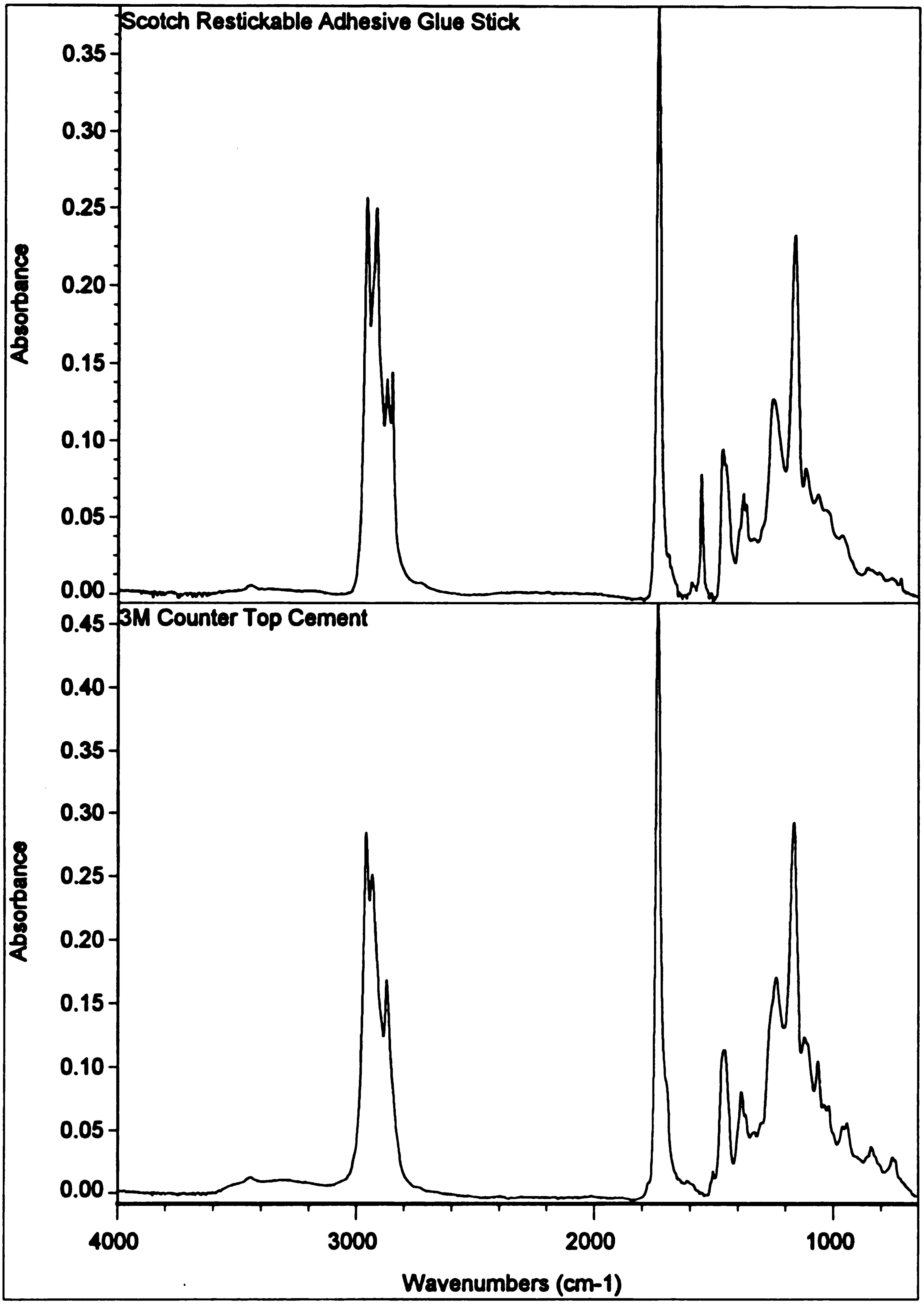

Figure 8 - Poly(Alkyl Acrylate) Type Adhesives

Contact Cements

The spectra of the three contact cement type adhesives in Figure 9 exhibit many similar spectral features. However, much like the glue stick type adhesives above, the compound(s) in the contact cements could not be identified from either the product containers or the library searches. Based on the complexity of the spectra in Figure 9 and the spectral variations observed from one to the next, it is likely that the contact cement adhesives are in fact mixtures of more than one compound, which would complicate identification. In any case, it is still clear that contact cements represent a characteristic class of adhesives.

Hide Glues

Like the contact cements above, the two "hide glues" in this category exhibit very characteristic, if not readily identifiable, spectra (see Figure 10). In this instance, the spectra are nearly identical. Titebond Liquid Hide Glue is labeled to contain the compounds ammonium rhodanate and dicyanodiamide, and, based on the spectra, Franklin Hide Glue (which is manufactured by the same company but has no ingredients listed) contains a similar formulation.

Silicones

The spectra of the silicones shown in Figure 11 represent another category of adhesives with highly characteristic spectra. One of the products, GE Silicone II, had ingredients listed on its label, which were polydimethylsiloxane and methoxypolydimethylsiloxane. All four of the silicones in this category exhibit very similar spectra, and all four spectra matched well with a spectrum of polydimethylsiloxane from the OMNIC spectral libraries.

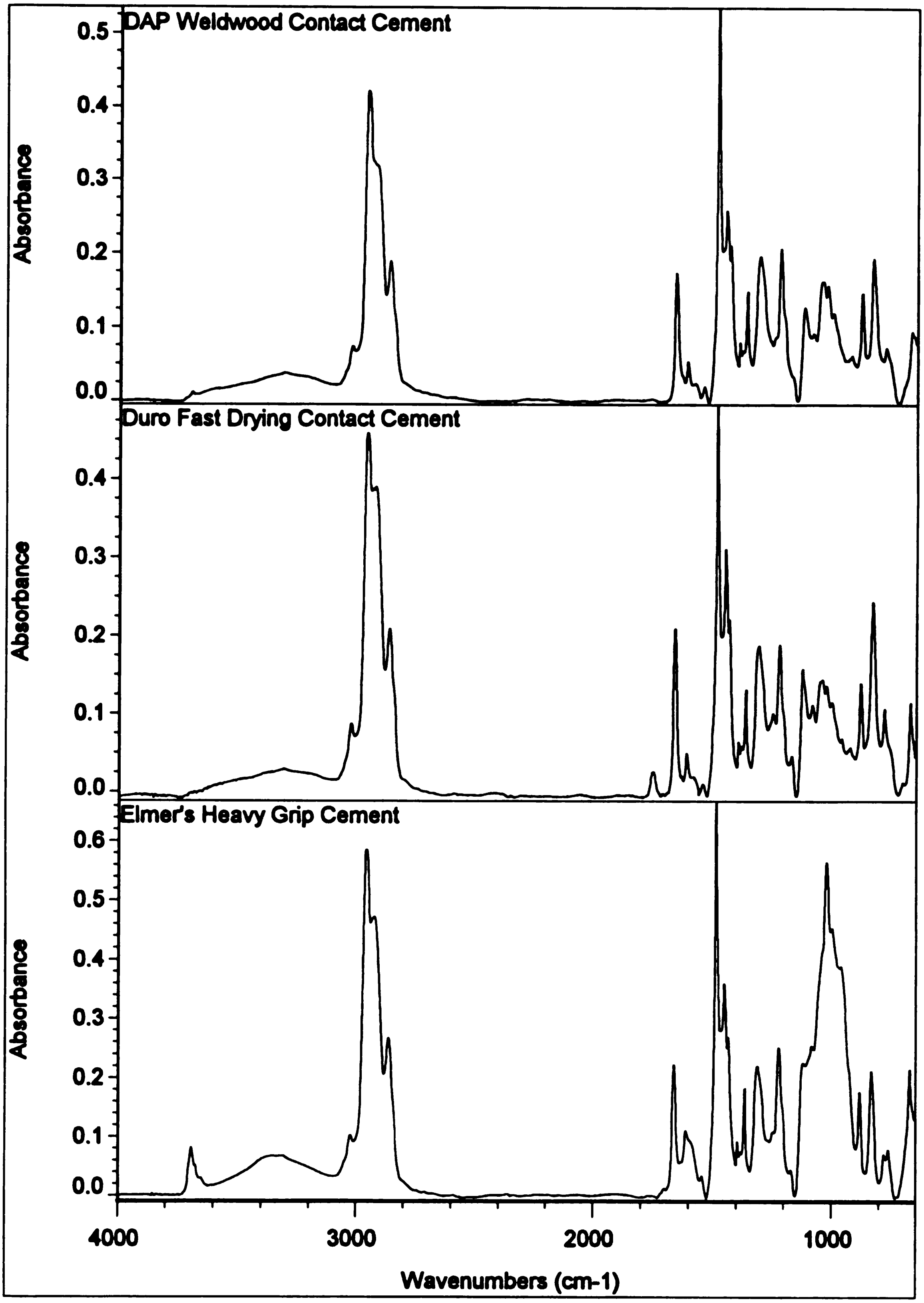

Figure 9 - Contact Cement Type Adhesives

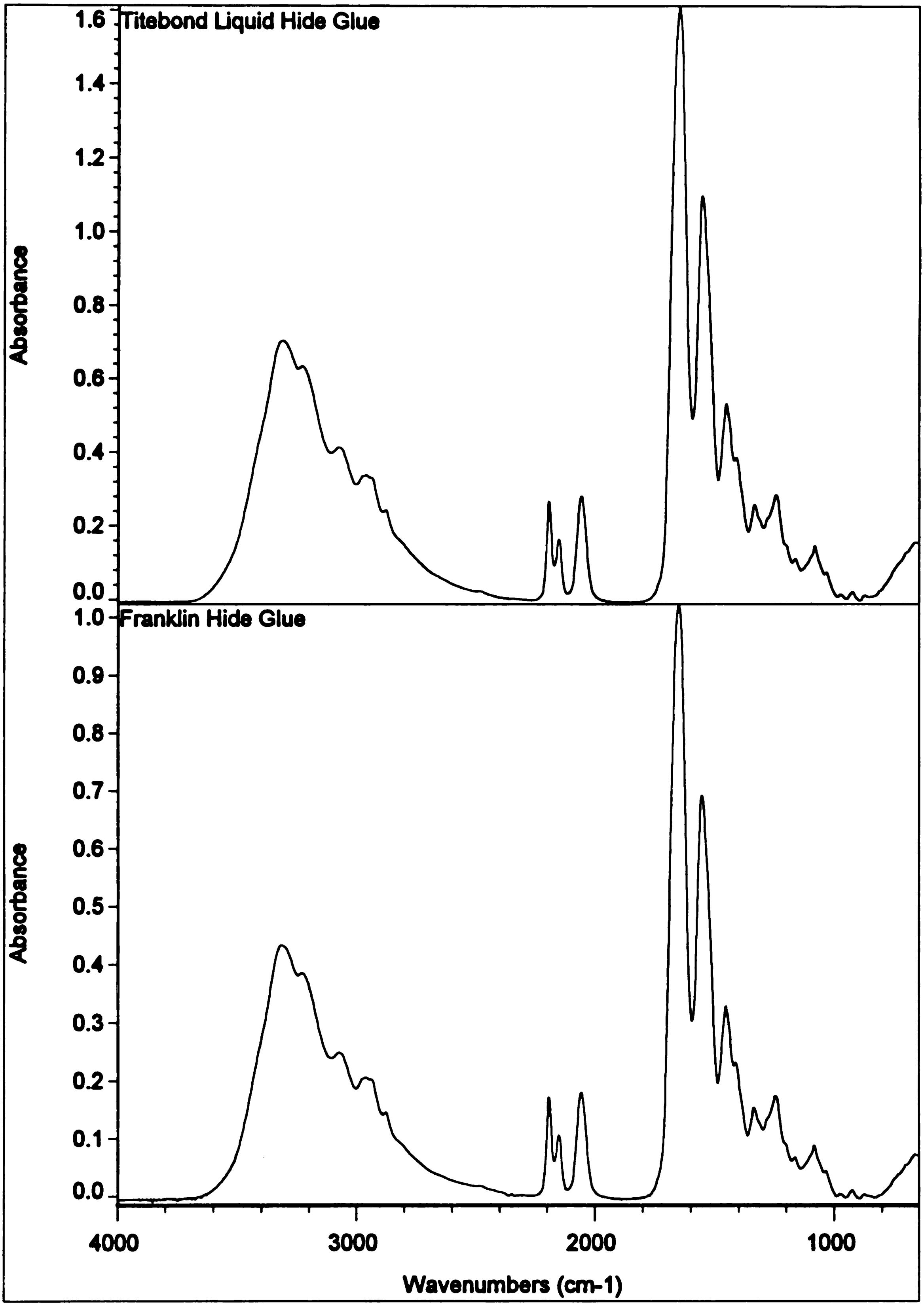

Figure 10 - Hide Glue Type Adhesives

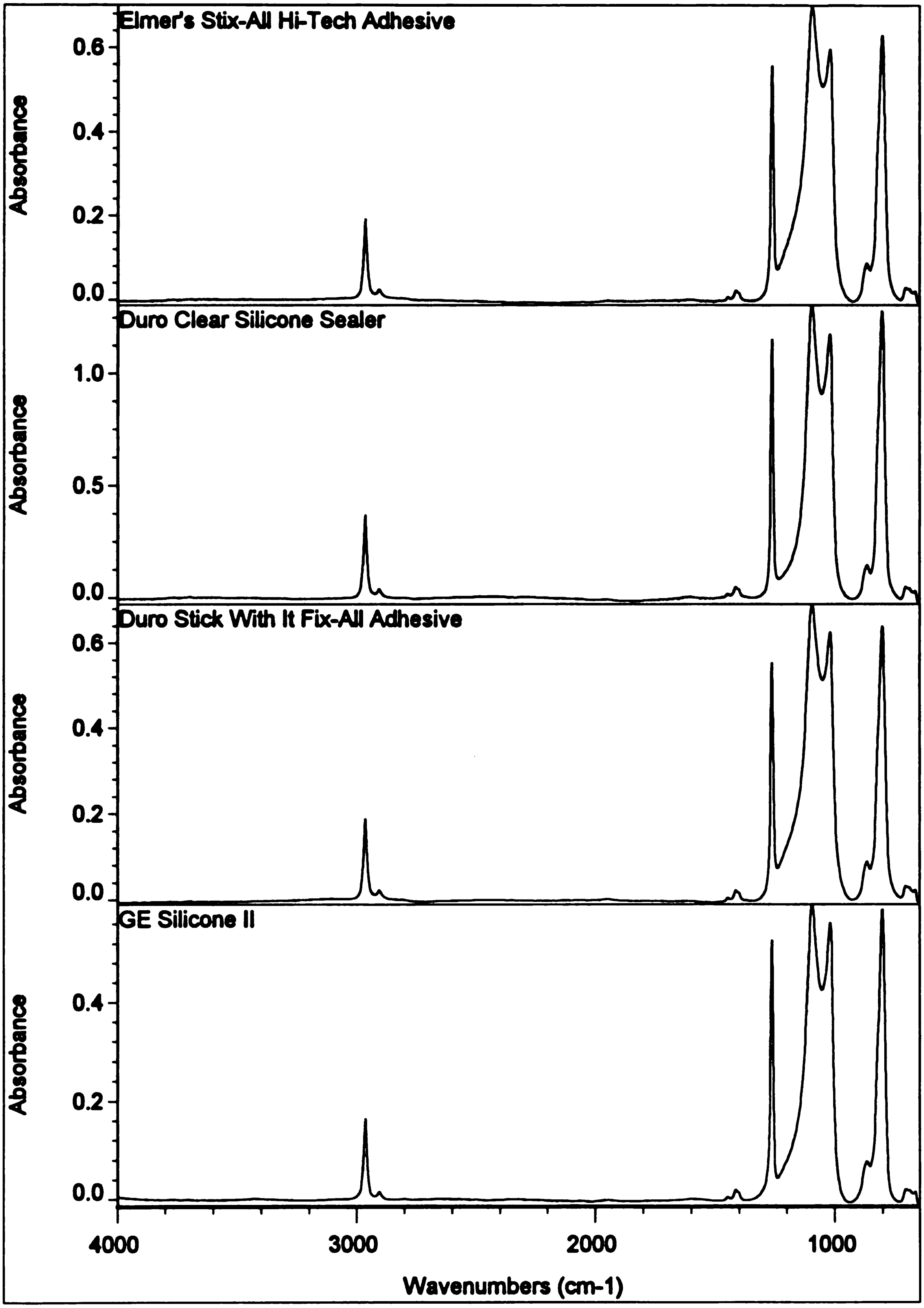

Figure 11 - Silicone Type Adhesives

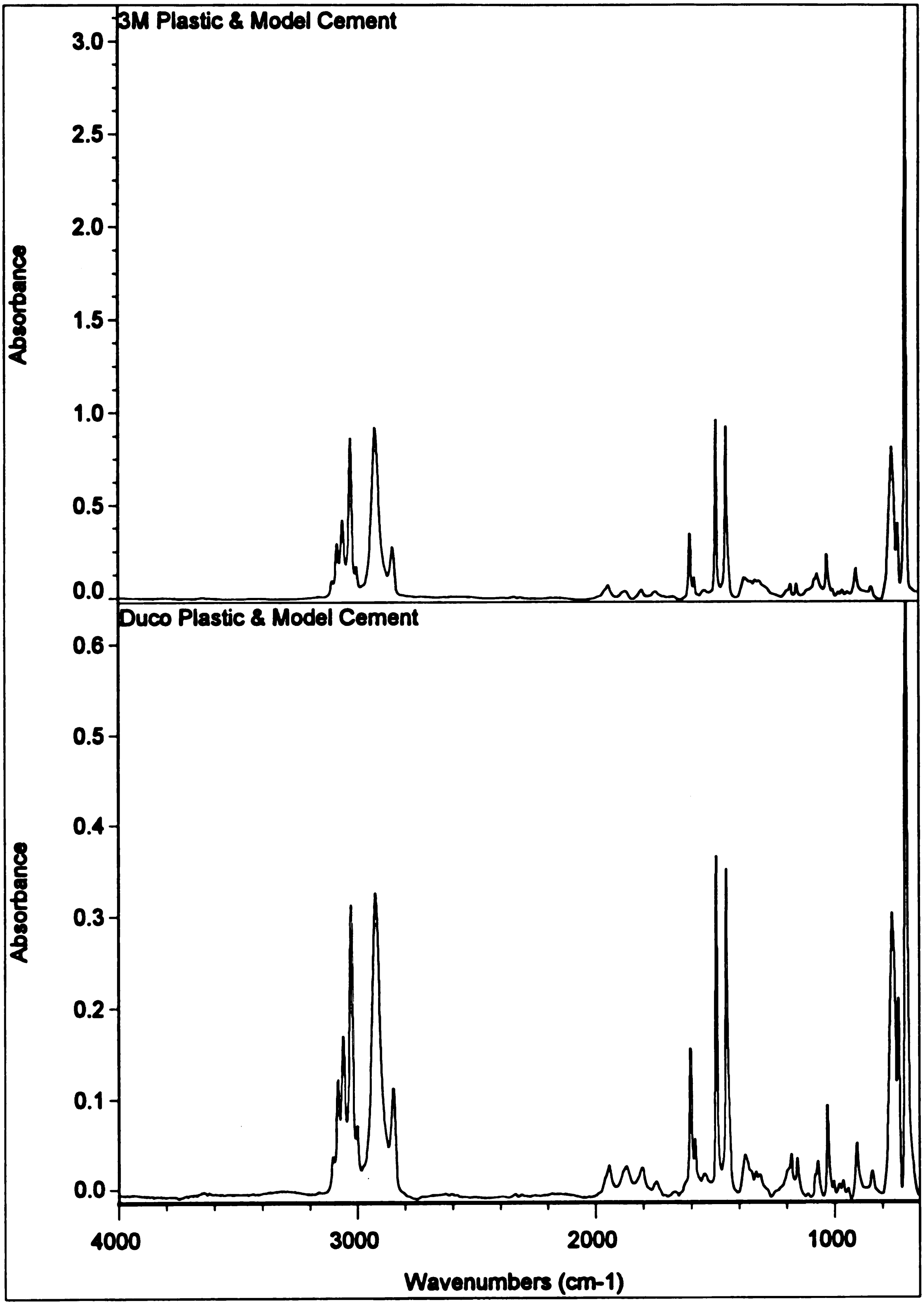

Figure 12 - Plastic and Model Cement Type Adhesives

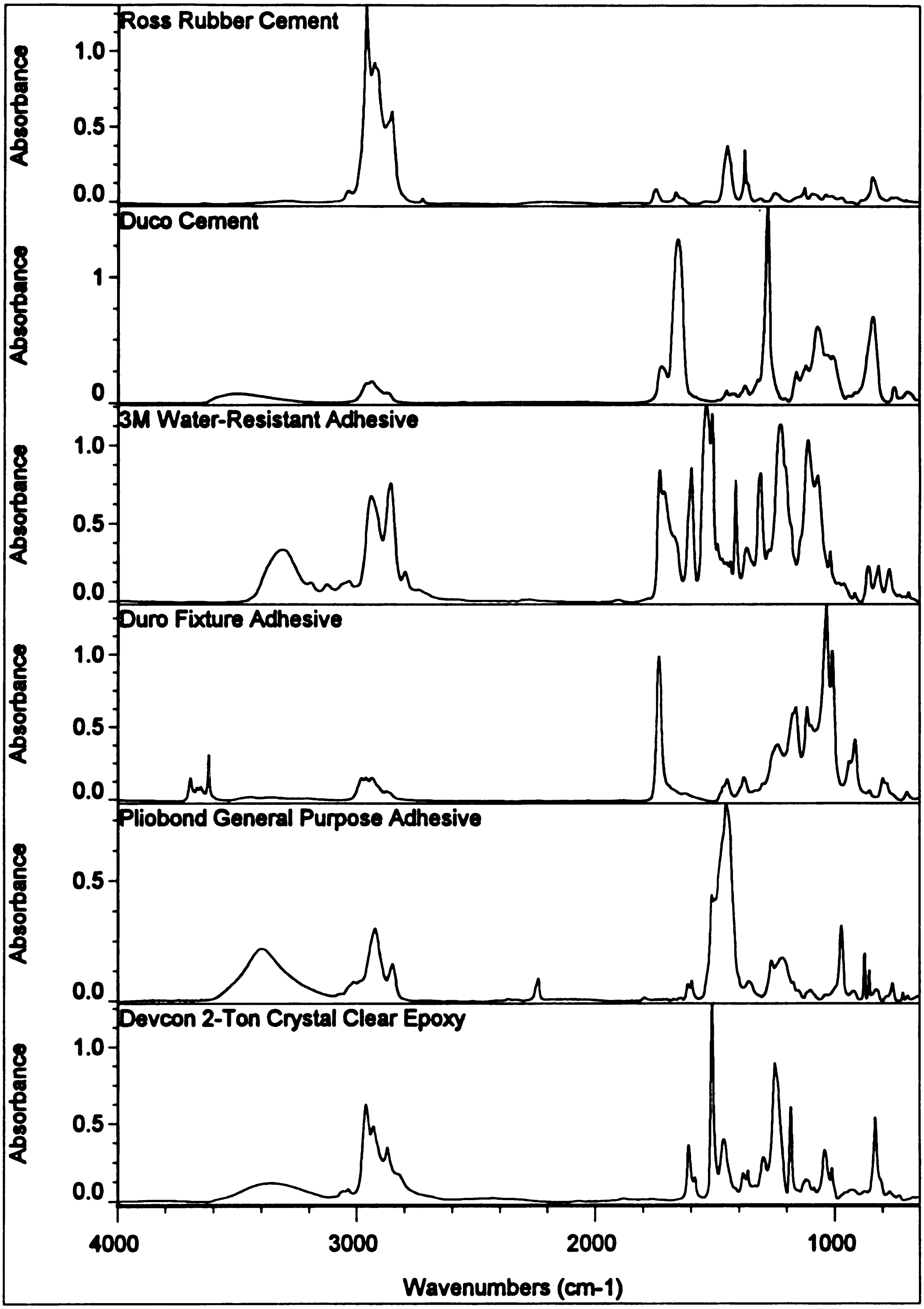

Figure 13 - Miscellaneous Adhesives

Plastic and Model Cements

Plastic and model cements are a final category of adhesives which are easily identifiable. The similar spectra of 3M Plastic & Model Cement and Duco Plastic & Model Cement are shown in Figure 12. Both of these products are labeled to contain polystyrene, and both spectra were identified as such based on the library searches.

Miscellaneous

The spectra of the six remaining adhesives were not similar to each other nor were they similar to any of the spectra in the other categories (see Figure 13). This fact would actually make them the most readily identifiable adhesives if present in a forensic sample. However, some of these products are also unusual and not very likely to appear in offenses like product tampering. The only spectrum in this category that matched reasonably well with any of the spectra in the OMNIC spectral libraries was that of Ross Rubber Cement, which showed some similarity to the spectrum of poly(isoprene).

The Spectral Library

The FTIR spectra of the 56 adhesives were finally compiled into a new "Commercial Adhesives" spectral library, created using the OMNIC software. When a spectral library is created, information regarding the spectra that will comprise the new library must be specified. This information includes the library frequency limits (in cm^{-1}), the spectral data format, and the data spacing. For the Commercial Adhesives spectral library, the specifications were set to match those of the baseline-corrected adhesive spectra: the frequency limits were 4000 cm^{-1} to 650 cm^{-1}, the spectral data format was designated as "Absorbance," and the data spacing was set to

2 cm^{-1} (which is equivalent to a resolution of 4 cm^{-1}). Additionally, the software provides for up to five "fields" of information to be entered with each spectrum when added to the library. The first field is required to be the compound name, which in this case was actually the product name. The second field was chosen to be the date of the data collection for each sample. This was done to facilitate retrieving the original data, if necessary, at a later time. Because the drying times of the adhesives varied from sample to sample, this information was entered into the third field. The fourth field was designated for the sampling technique used for data collection. In this project, all the samples were prepared using a diamond anvil cell. However, the spectral libraries are designed to be built upon, and it is possible that future commercial adhesives may be analyzed using a different sampling technique and their spectra added to the library. For this reason, a fifth field was also created for other additional information, if necessary. This field was left blank for the 56 adhesives sampled in this study, but future samples may require further details.

Test of the Spectral Library

The spectra of the 11 adhesive samples from the cardboard pharmaceutical product carton were searched against the OMNIC spectral libraries, including the new Commercial Adhesives library. This was a test of the new spectral library to determine if an adhesive from a general category could be distinguished from other adhesives with similar spectra.

When a search of the OMNIC spectral libraries is performed, the computer essentially compares every data point in the spectrum being searched (the unknown spectrum) with every data point in each of the library spectra. The computer assigns a "match quality" (a number from 0 to 100) to each library spectrum based on how closely it resembles the unknown spectrum. Then, a list of the best several matches is reported, with the top match being the library spectrum that has the highest match quality, and therefore is mathematically the most similar to the unknown spectrum. It should be noted that in identifying an unknown spectrum, the final determination of the "best" match is always made based on visual comparison with the library spectra.

When the 11 test adhesives were searched against the OMNIC spectral libraries, the Commercial Adhesives library produced very good results. The test adhesive was correctly identified by the top match in the library search in 9 of the 11 cases and was identified by the second match in the other two cases. For each of the test adhesives, the general adhesive category could easily be determined from the top several matches of the library search.

The 9 test adhesives identified by the top library match were: Power Poxy One-N-Done Super Glue Gel, Elmer's School Glue, Glue Pen, 3M Counter Top Cement, DAP Weldwood Contact Cement, Titebond Liquid Hide Glue, Duro Clear Silicone Sealer, 3M Plastic & Model Cement, and Duco Cement. Among these, some have very characteristic spectra and there was little doubt that they could be identified by the library. This was especially true for Duco Cement, since it is from the miscellaneous category, and thus has a unique spectrum in the library. Similarly, although Power Poxy One-N-Done Super Glue Gel, 3M Counter Top Cement, and DAP Weldwood Contact Cement fit into categories, their spectra have distinct differences from the other adhesives in their categories. The other five test adhesives identified by top matches were much more telling about the utility of the Commercial

Adhesives spectral library. In particular, Elmer's School Glue was distinguished from several very similar poly(vinyl acetate) type adhesives, and the spectrum of Titebond Liquid Hide Glue was differentiated from the nearly identical spectrum of the other hide glue.

The two adhesives identified by the second matches from the library searches were Instant Krazy Glue - Wood Formula and Elmer's Glue Stick. The top match for the Instant Krazy Glue - Wood Formula test sample was Quicktite High Performance Super Glue Pen, which is one of several super glue type adhesives with very similar spectra. The top match for the Elmer's Glue Stick test sample was UHU Stic; these two glue sticks and Elmer's School Glue Stick all have very similar spectra. Possible explanations for the "second-place finishes" of the two test adhesives are slight variations in the sample preparation (e.g., sample film thickness) or slight heterogeneity in the adhesives. Nevertheless, the general adhesive category was readily identifiable in both instances, which would still be important information in an actual forensic case.

CONCLUSION

The field of forensic science evolves constantly as new technology regularly becomes available. Each new development provides the forensic scientist with another tool in the evaluation of evidence. Along these lines, the development of the FTIR spectral library of commercial adhesives will be very beneficial in the forensic science laboratory. In all future cases, adhesives from forensic samples can be analyzed by FTIR and their spectra searched against all available spectral libraries, including the Commercial Adhesives library. If a commercially available adhesive has been used in a product tampering or other offense, the spectral library search may allow the suspect sample to be classified into a general adhesive category. If the suspect adhesive spectrum matches particularly well with a single adhesive spectrum from the library, then a preliminary identification of the suspect adhesive may be made. Either of these instances supplies the forensic scientist with important information.

The value of the scientific information obtained from adhesive evidence extends from the forensic science laboratory to the investigation process. In a particular case involving adhesives, the forensic scientist can potentially furnish the investigator with a specific product name to search for in the possession of a suspect. Additionally, the increased value of adhesive evidence provided by the Commercial Adhesives spectral library should encourage the investigator to collect adhesives for forensic analysis in all applicable cases.

The development of the FTIR spectral library of commercial adhesives also has the potential to save a great deal of analysis time in the forensic science laboratory. Before the library existed, attempting to classify or identify a suspect adhesive was a difficult task. Several different products might need to be analyzed before one was found that resembled or matched the suspect sample. However, with the Commercial Adhesives library, classification or identification of a suspect sample can potentially be accomplished by simply conducting a library search. The time saved in this process gives the forensic scientist the opportunity to pursue other analyses.

There are a number of areas of future research that could be pursued to build upon the work presented in this paper. First of all, it is acknowledged that there are many more products in the entire world of adhesives, and that the Commercial Adhesives library may never be totally complete. Therefore, as other commercially available adhesives are encountered in the future, their spectra should be added to the spectral library. Additionally, it may be desirable to obtain the adhesives used by product manufacturers for inclusion in a separate spectral library.

Another topic worthy of future study is the effect of drying time on adhesive samples. Dried adhesives could be studied to observe if significant spectral differences are noted over time. Most liquid adhesives utilize some solvent which suspends the adhesive components, and the adhesive dries as the solvent evaporates. Therefore, one way in which an adhesive's spectrum may change over time is by the disappearance of solvent bands. If the subject of drying time variations was thoroughly explored, it may theoretically be possible in the future to not only identify an adhesive based on its FTIR spectrum, but to determine approximately how long ago the adhesive was applied. Though this would require a great deal of future work, the ability to estimate the application time of an adhesive would be very valuable in the context of forensic science.

A final area of future research involves the use of different sampling techniques or instruments in the analysis of adhesives. In FTIR spectroscopy, a technique known as Attenuated Total Reflectance (ATR) could be used to measure the spectrum of an adhesive without removing it from the surface to which it is bound. This would have practical application to very thin adhesive films. Also, some past research used the instrumental technique of pyrolysis-gas chromatography (PGC) in adhesive analysis. Like FTIR, this technique has the ability to generate a characteristic profile of an adhesive sample, and therefore it also offers the potential to create a library of adhesives. Using both PGC and FTIR would provide two pieces of information about a sample, and may therefore allow similar samples to be more easily differentiated.

APPENDIX

APPENDIX

Table 3 - OMNIC Spectral Libraries

Library Name	No. of Spectra
Aldrich Condensed Phase	10,607
Aldrich Condensed Phase Supplement	5,075
Aldrich Vapor Phase Sample Library	112
*Black Plastic Tape Adhesive - 8 cm^{-1}	84
*Black Plastic Tape Plasticizers	90
*Black Plastic Tape-Back Side	94
*Extracted Inks (Limited)	88
*FBI Fibers (Version 3.1)	53
Georgia State Crime Lab Sample Library	200
†Glues and Adhesives	26
Hazardous Chemicals - Condensed Phase Spectra	411
Hummel Polymer Sample Library	53
*Photocopy Toners by R-A, 4 cm^{-1} Resolution	510
*Raw Inks in Pyridine (Limited)	89
Rubber Compounding Materials	350
Sigma Biological Sample Library	92
Sigma Steroids	3,011
Sprouse Polymer Additives	325
‡Standards	20
Synthetic Fibers by Microscope	376
Toronto Forensic	3,549
U.S. Geological Survey Minerals	78
	25,293

* User-created libraries obtained from the Federal Bureau of Investigation (FBI)
† User-created library of adhesives from casework samples
‡ User-created library of house standards
All other libraries purchased from Nicolet Instrument Corporation.

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