III-F

Tapes with Adhesive Backings: their Characterization in the Forensic Science Laboratory

R. D. Blackledge

United States Army Criminal Investigation Laboratory-Europe, Frankfurt, FRG
/Main D1

56LCAW

2-10-92 4-27-

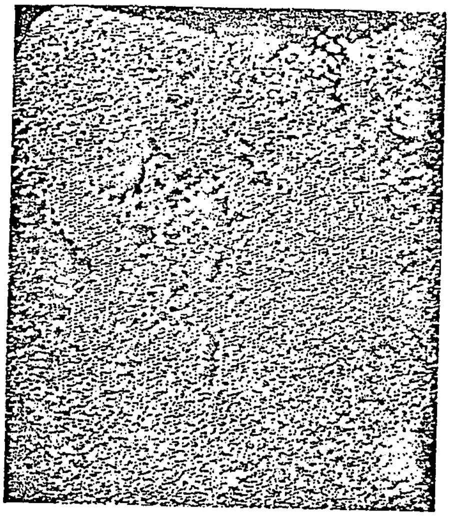
1. Introduction

Forensic science laboratories are frequently asked to characterize tapes having pressure-sensitive adhesive backings, since thay are often associated with criminal activity. Tape can be used to assemble improvised explosive devices, to bind and gag victims in kidnappings, robberies, homicides, and sex crimes, to package large quantities of marijuana, hashish, and other contraband, and to prevent doors from latching in burglaries. The amount of sample available for analysis may vary from an almost complete roll to minute fragments recovered after the detonation of an explosive device.

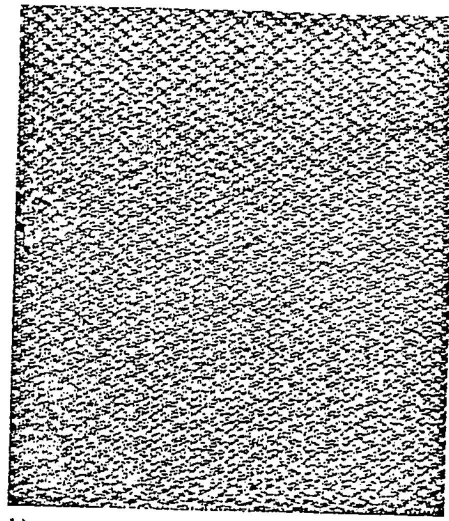
2. Preliminary Examinations

A positive association with the suspect can only be established through the development of fingerprints, or from a "jigsaw" fit of one end of the tape found at the crime scene with the end of a roll of tape found in the possession of the suspect, or from a physical match of the pattern of adhesive residues left on a surface with the missing adhesive backing on a piece of tape (Fig.-F-1). Therefore, these examinations are attempted first.

110089966 CA: 110(11)89966e CONFERENCE PROCEEDING
Tapes with adhesive backings: their characterization in the forensic science laboratory
AUTHOR(S): Blackledge, R. D.
LOCATION: United States Army Criminal Invest. Lab.-Europe, Frankfurt/Main, Fed. Rep. Ger.
JOURNAL: Appl. Polym. Anal. Charact. EDITOR: Mitchell, John, Jr (Ed),
DATE: 1987 PAGES: 413-21 CODEN: 56LCAW LANGUAGE: English PUBLISHER: Hanser, Munich, Fed. Rep. Ger



a)



b)

Fig.-F-1. (a) Pattern of adhesive residues remaining on an automobile speaker (found in suspect's possession);
(b) Pattern (negative reversed) from the back of a strip of "Velcro" (found in victim's automobile).

If the above examinations are unsuccessful, additional examinations may still provide useful information. If tape fragments found at the scenes of several similar crimes have the same characteristics, then this could suggest that the same individuals may be involved. Along with other evidence, a jury may consider a laboratory finding, such as: "the tape fragments found at the crime scene were microscopically and chemically examined and compared with the roll of tape found in the possession of the suspect, and they were found to be similar as far as type and brand. The tape fragments found at the crime scene could have originated from the roll of tape found in the possession of the suspect, or from some other source of the same type and brand of tape." And, of course, a positive nonassociation is possible; that is, that the tapes are different.

Some common types of tapes encountered include: black polyvinylchloride (PVC) electrical tape, beige masking tape, white adhesive type, silver-colored duct tape, black friction tape, and transparent tape. Although the type of tape involved will influence the analysis methods chosen, it is more convenient and useful to consider their analysis as a general class.

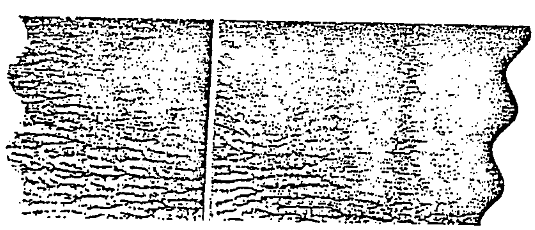


Fig.-F-2. Photograph of visualized primer pattern on the underside of the tape backing (Ref. 2).

First, examine the tape fragments visually. A low power stereobinocular microscope (7 to 30 X) is sufficient for this. Note features such as color, width, thickness, and surface texture. *Keto* (1984) (1) found that six brands of 19 mm (0.75 inch) wide by 0.18 mm (7 mils) thick black PVC electrical tape could all be distinguished by differences in the textures of their nonadhesive surfaces.

Kee (1984) (2) examined the undersides of black PVC electrical tapes after first removing the adhesive by soaking the tapes in hexane. He occasionally found wavy markings which he attributed to a pattern produced by the transfer roller during coating with a hexane insoluble primer (Fig.-F-2). These wavy markings may be used to show that two pieces were a continuous strip of tape. Using a scanning electron microscope, *Kee* also examined the nonadhesive surfaces and found varying features including ridges, irregular grooves, and small oval pits.

Benson (1984) (3) noted that the examination of tapes having cloth backings should include a comparison of the warp and weft and a determination of the number and composition of cloth backing fibers. Check the tapes for differences in fluorescent properties using short wave (254 nm) and long wavelength (366 nm) uv light. Differences in fluorescence at other wavelengths including infrared can be distinguished by those laboratories equipped with instrumentation such as the "Video Spectral Comparator" made by Foster & Freeman.

3. Instrumental Methods

a. Elemental Analysis

Black PVC electrical tapes have been examined by both *Keto* (1) and *Kee* (2) using energy dispersive X-ray spectrometry (EDX). *Keto* examined two rolls each from six different manufacturers, analyzing for ten different elements. He found no statistically significant differences either within a roll or between rolls from the same manufacturer, and the six brands all had clearly different elemental profiles (Figure-F-3). *Kee* examined tapes commercially available in Northern Ireland and found it useful to place tapes into four different categories based on the presence or absence of the elements lead and calcium. In 30.5% of the tapes lead was present and calcium was absent, in 5.3% both were absent, in 6.1% lead was absent and calcium was present, and in 58.1% both were present.

Duct tape was examined by *Benson* (3) using both emission spectroscopy and inductively-coupled plasma spectroscopy, while *Jenkins* (1984) (4) used EDX. *Jenkins* analyzed for chlorine, calcium, titanium, iron, copper, zinc, and lead. He found no significant variation between samples removed from the beginning, middle, and end of a roll of tape. In addition to differentiating among different brands, he also found differences between different batches of the same brand. He cited one case in which tape from eight holdups were linked to a roll of duct tape from the suspect's vehicle.

b. Infrared spectroscopy

Infrared (IR) methods are conveniently divided into those that are nondestructive and those that are destructive of the sample. Nondestructive methods include those involving attenuated total reflectance spectroscopy (ATR), the diamond anvil cell, and microspectrophotometry. *Keto* (1) used a KRS-5 ATR crystal and a Fourier transform infrared spectrophotometer (FTIR) to examine the adhesive side of six different brands of black PVC electrical tape and the resulting spectra were all easily distinguishable (Fig.-F-4). *Kee* (2) used ATR to look at the nonadhesive side of PVC electrical tapes and was able to identify different types of plasticizers. In a nonforensic application, *Pattacini* and *Anacreon* (1979) (5) used ATR

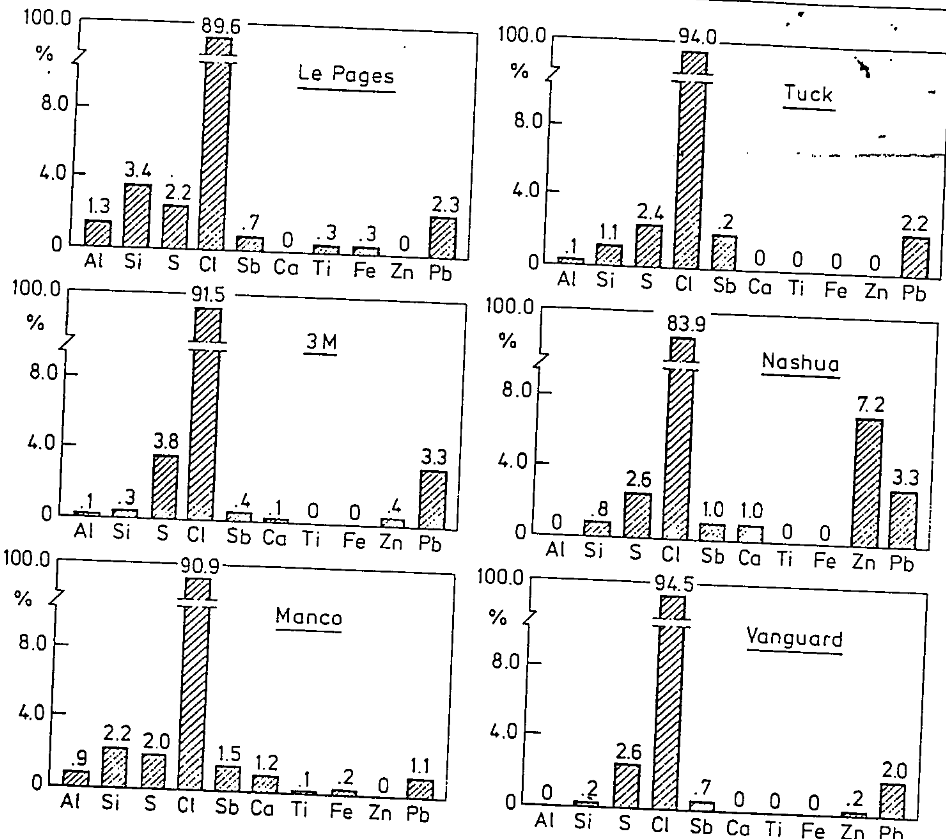


Fig.-F-3. Elemental profiles from EDX of six brands of black PVC electrical tape (Ref. 1).
Relative Abundances of Ten Elements in Tape Backings

and computer difference spectroscopy to study both sides of two samples of insulation adhesive tape, one exhibiting good and the other poor adhesive properties. Although the ATR spectra of the adhesive sides of the samples were quite similar, the computer difference spectrum revealed the presence of a "soap-like material" in the bad sample. Computer difference spectroscopy has the potential for identifying major components in adhesive formulations without having to resort to destructive and time-consuming chemical separations. *Tweed* and coworkers (1974) (6) used the diamond cell technique to examine a variety of polymeric materials, and *Lee* and coworkers (1984) (7) used a "NanoSpec"/20-IR microspectrophotometer to examine a wide range of adhesive materials. For forensic science applications the diamond cell and microspectrophotometry have an advantage over ATR in that they require only nanogram quantities of sample.

IR methods which are destructive of the sample include those involving pyrolysis and those in which the polymeric material is dissolved in a suitable solvent and then deposited as a cast film on a KBr plate. The pyrolysis procedure was developed by *Harms* (1953) (8) and applied to a variety of polymeric materials that were intractible by normal IR methods. The sample is placed in a borosilicate glass test tube and the tube is held nearly horizontal over the inner blue cone of a Bunsen burner flame. The sample is heated rapidly and the vaporous pyrolyzate condenses as a liquid on the cool portion of the tube. The condensed

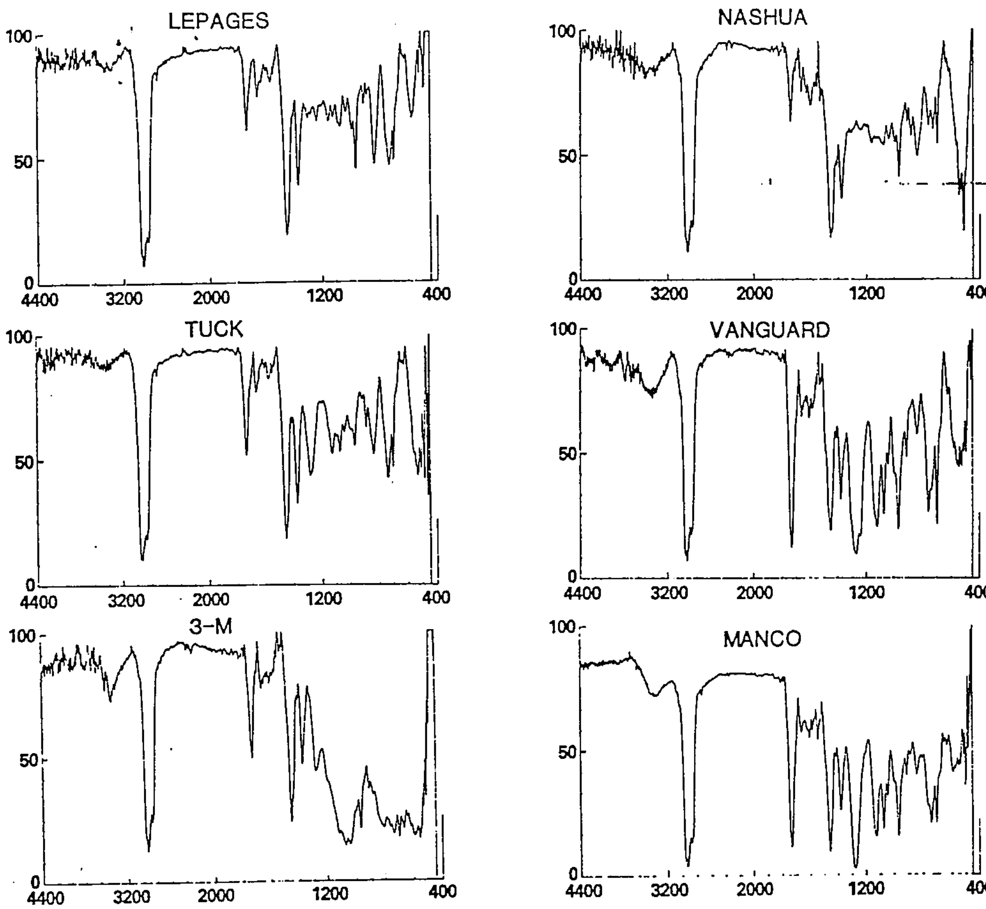


Fig.-F-4. ATR infrared spectra of adhesive side of six brands of black PVC electrical tape (Ref. 1).
Tape Adhesives by Internal Reflectance F.T.I.R.

material is then scraped off and examined as a smear on a KBr or NaCl plate. *Smalldon* (1969) (9) applied this method to a variety of forensically related polymeric materials. The pyrolyzate spectra were compared to spectra of known materials that were obtained under the same conditions. *Truett* (1977) (10, 11) described a pyrolysis chamber complete with power supply and the Wilks Model 40 "Pyro-Chem" pyrolysis unit. The chamber mounts in the sample compartment of the IR and requires around 10 to 20 mg of sample. Its advantage is that the volatile fraction is not lost. The pyrolysis chamber can either be mounted as a gas cell to record the vapor spectra, or as an ATR attachment to record the spectra of the condensed pyrolyzate. *Pattacini* (1974) (12) examined three adhesive formulations cast on KBr windows. Spectra of the entire adhesive formulations were first obtained by dissolving the adhesive in tetrahydrofuran and casting a film on a KBr window. Next, each adhesive was dissolved in toluene, the solutions filtered, and then methanol was added to the toluene solution to precipitate the polymer. The precipitated polymer was filtered, washed with methanol, dried, dissolved in tetrahydrofuran and then deposited as a cast film on a KBr window. The remaining solutions were extracted several more times with methanol to remove any remaining traces of polymer. Column chromatography was performed on the toluene solutions, the various fractions were evaporated, and the residues were examined, revealing additional major components such as resins in the adhesive formulations. *Noble* and coworkers (1974) (13) examined a collection of 179 different commercial adhesives using either cast films of the entire adhesive formulation or grinding the dried adhesive with KBr and making a pressed disc. *Blackledge* (1984) (14) examined three brands of beige masking tapes. Pieces of the tapes were soaked in dichloromethane, the solutions filtered, and then portions of the solutions evaporated onto KBr windows.

c. Pyrolysis-gas chromatography

In an early paper, *Groton* (1964) (15) described an apparatus for pyrolysis gas chromatography (PyGC) of the flash pyrolysis type which employed a platinum heating coil. He determined qualitative fingerprinting conditions so that over 150 polymers could be identified using essentially the same pyrolysis and chromatographic conditions. *May* and coworkers (1973) (16) described a system which was sufficiently reproducible as to permit interlaboratory comparisons. They used the Curie point method and recommended a "Poropack" Q column packing and a pyrolysis temperature of 610 °C. Examining adhesives as dried films, *Noble* and coworkers (13) examined a collection of 179 different commercial adhesives by IR and Curie point pyrolysis and were able to assign all but 14 to a particular class. *Andrasko* and coworkers (1984) (17) examined polymers by three different methods. The effluent from PyGC was split and routed to flame ionization and nitrogen/phosphorous detectors. Pyrolysis IR was also performed and the remaining ash was transferred to a scanning electron microscope for analysis by EDX. An excellent overall review of the PyGC of polymers is contained in the paper by *Wolf* and coworkers (1980) (18). Reviews of forensic applications which contain examples of the PyGC of adhesives may be found in the papers by *Wheals* and *Noble* (1972) (19), *Wheals* (1980/1981) (20), and *Challinor* (1983) (21).

Bakowski and coworkers (1984) (22) in the Forensic Science Research Group at the FBI Academy are in the process of examining a collection of more than 110 commercially available adhesives by pyrolysis capillary column gas chromatography/mass spectrometry. They find that the pyrograms are easily distinguishable from one another. Improvised explosive devices are being constructed using these adhesives and they are then detonated to simulate case samples.

Another method which would seem to offer great forensic science potential is pyrolysis capillary column-GC/FTIR. *Herres* and *Foelster* (1984) (23) have investigated a range of polymeric products with such a system.

d. Pyrolysis-mass spectrometry

Two of the principal disadvantages of PyGC are low sample throughput and lack of interlaboratory reproducibility. In pyrolysis-mass spectrometry (PyMS) the GC is eliminated and the pyrolyzate enters the mass spectrometer without separation. *Hughes* and coworkers (1977) (24) applied this method to a variety of paints, adhesives, putties and fibers using a Curie point pyrolyzer and a magnetic sector mass spectrometer in the electron impact mode. They found PyMS to be rapid, sensitive, usually reproducible and amenable to data storage and retrieval. *Saferstein* and *Manura* (1977) (25) examined various paints and fibers by PyMS. They used a flash pyrolysis apparatus employing a platinum heating coil (Chemical Data System Model 100) coupled to a magnetic sector mass spectrometer in the chemical ionization mode, employing isobutane as a reagent gas. Chemical ionization was selected in order to reduce the complexity of the mass pyrographs. *Curry* (1980, 1981) has reported on the PyMS of adhesives (26) and polymers (27).

e. Other methods

Blackledge (1984) (14) examined three brands of beige masking tapes by fluorescence spectroscopy using the technique of synchronous excitation. The nonadhesive sides were examined using the front surface accessory. Although the fluorescence intensity varied, the fluorescence patterns were reproducible within a tape roll and between rolls from the same sample lot. The different brands gave different patterns and two rolls that were different lots of the same brand also gave different patterns. Dusting the nonadhesive surface with black fingerprint powder merely reduced the fluorescence intensity. Pieces of tape were also soaked in dichloromethane, the solutions filtered through glass wool, and a few drops added to more dichloromethane in a cuvette and the solution examined. This also produced fluorescence spectra which showed differences between brands and between sample lots. Subsequently, the same solutions could be evaporated onto KBr windows for IR, or on to ribbon probes for PyGC.

Other methods may have promise, in fact they may be able to demonstrate differences where traditional IR and PyGC methods fail, but they are not yet in routine use in forensic science laboratories. *Brennan* and coworkers (1981) (28) have described a system for thermal analysis of polymers using a differential scanning calorimeter and a thermal analysis data station, and *Reffner* (1984) (29) has presented a paper on the thermal microscopy of polymers. *Alden* and *Dark* (1984) (30) have described the analysis of "such diverse commercial products as chewing gum, coatings, paints, adhesives, plastic components, smokeless gun powders, and many rubber and petroleum products" by gel permeation chromatography. Improvements in sample size requirements as well other improvements now make practical the use of nuclear magnetic resonance spectroscopy (NMR) in forensic laboratories, and its applications are being investigated by *Vordermaier* (1985) (31) at the Bundeskriminalamt in Wiesbaden, Federal Republic of Germany.

4. Summary

Forensic science laboratories characterize tapes with pressure-sensitive adhesive backings through a combination of visual and instrumental examinations. Nondestructive methods are preferred (due to evidence preservation requirements), as well as those methods requiring a minimum amount of sample and minimum preparation. The analysis methods chosen will depend on factors such as the type of tape, amount of sample, and available instrumentation. Most analyses involve at least two of the following: EDX, IR, and PyGC or PyMS.

Normally the objective is not to perform a detailed chemical analysis of the tape samples; forensic chemists are addressing the question of possible commonality of origin. It may be tempting to rely on pattern matching without identifying the various chemical components or understanding the processes involved, but this should be avoided. For example, two samples of polystyrene might give very similar patterns with IR and PyGC and yet gel permeation chromatography might show that they have different molecular weight ranges and are, therefore, different.

Increasingly, methods will be coupled with data stations capable of reducing the patterns to normalized, digitized form for storage, retrieval, and library searches. The display terminal will show the closest matches in the library, provide a number whose magnitude is an index of how closely two samples match, and indicate the previous frequency of occurrence of such samples. Each laboratory would not have to create its own data base; a large central laboratory can create and maintain a data base available to all, as already done in the United Kingdom.

5. References

1. *Keto, R. O.*, "Forensic Characterization of Black Poly(vinyl chloride) Electrical Tape," Crime Laboratory Digest, *11* (4), 71 (1984).
2. *Kee, T. G.* (Northern Ireland Forensic Science Lab., Belfast): "The Characterization of PVC Adhesive Tapes," presented at An International Symposium on the Analysis and Identification of Polymers, FBI Academy, Quantico, VA, July 1984. (See Ref. 3).
3. *Benson, J. D.* (Wyoming State Crime Lab., Cheyenne, WY 82002): "Forensic Examination of Duct Tape", presented at An International Symposium on the Analysis and Identification of Polymers, FBI Academy, Quantico, VA, July 30-Aug. 3, 1984, Abstract # 13. (Papers to be published by U.S. Government Printing Office, Washington, DC 20402.)
4. *Jenkins, T. L., Jr.*: "Elemental Analysis of Duct Tape," An International Symposium on the Analysis and Identification of Polymers, FBI Academy, Quantico, VA, July 1984, Abstract # 14. (See Ref. 3).
5. *Pattacini, S. C.* and *R. E. Anacreon*: "Applications of Computer Difference Spectroscopy in Polymer Analysis," Perkin-Elmer Infrared Bulletin 71, Dec. 1979.
6. *Tweed, F. T., R. Cameron, J. S. Deak* and *P. G. Rodgers*: "The Forensic Microanalysis of Paints, Plastics and Other Materials by an Infrared Diamond Cell Technique," Forens. Sci., *4*, 211 (1974).
7. *Lee, H. C., R. E. Gaensslen, D. Baughn, T. Carpenter, S. Lee* and *T. LoBello*, from the Connecticut State Police Forensic Laboratory and the University of New Haven: "Identification of Trace Adhesive Materials by Infrared Microspectrophotometry," presented in part at the 36th Annual Meeting of the American Academy of Forensic Sciences, Anaheim, CA, Feb. 1984, No. B20.
8. *Harms, D. L.*: "Identification of Complex Organic Materials by Infrared Spectra of Their Pyrolysis Products," Anal. Chem., *25*, 1140 (1953).
9. *Smalldon, K. W.*: "The Identification of Paint Resins and Other Polymeric Materials from the Infrared Spectra of Their Pyrolysis Products," J. Forens. Sci. Soc., *9*, 135 (1969).
10. *Truett, W. L.*: "Pyrolysis IR Analysis of Polymeric Materials," Amer. Lab., *9* (6) (1977).
11. *Truett, W. L.*: "Pyrolysis - Infrared Analysis of Polymeric Materials," Application Report No. 9, Wilks Scientific Corp., 1977.
12. *Pattacini, S. C.*: "Infrared Identification of Adhesive Formulations," Perkin-Elmer Infrared Bulletin 43, Jan. 1974. (See Ref. 5).
13. *Noble, W., B. B. Wheals* and *M. J. Whitehouse*: "The Characterization of Adhesives by Pyrolysis Gas Chromatography and Infrared Spectroscopy," Forens. Sci., *3*, 163 (1974).
14. *Blackledge, R. D.*: "Comparison of Masking Tapes by Fluorescence Spectroscopy," presented in part at An International Symposium on the Analysis and Identification of Polymers, FBI Academy, Quantico, VA, July 1984, Abstract # 11. (See Ref. 3).
15. *Groten, B.*: "Application of Pyrolysis-Gas Chromatography to Polymer Characterization," Anal. Chem., *36*, 1206 (1964).
16. *May, R. W., E. F. Pearson, J. Porter* and *M. D. Scothern*: "A Reproducible Pyrolysis Gas Chromatographic System for the Analysis of Paints and Plastics," Analyst, *98*, 364 (1973).
17. *Andrasko, J., L. Haeger, A. C. Maehly* and *L. Svensson*: "Comparative Analysis of Synthetic Polymers Using Combinations of Three Analytical Methods," Forens. Sci. Int. *25*, 57 (1984).
18. *Wolf, C. J., M. A. Grayson* and *D. L. Fanter*: "Pyrolysis Gas Chromatography of Polymers," Anal. Chem., *52*, 348 A (1980).
19. *Wheals, B. B.* and *W. Noble*: "Forensic Applications of Pyrolysis Gas Chromatography," Chromatographia, *5* (9), 554 (1972).
20. *Wheals, B. B.*: "Review - Analytical Pyrolysis Techniques in Forensic Science," J. Anal. Appl. Pyrol., *2*, 277 (1980/1981).
21. *Challinor, J. M.*: "Forensic Applications of Pyrolysis Capillary Gas Chromatography," Forens. Sci. Int., *21*, 269 (1983).
22. *Bakowski, N. L., E. C. Bender* and *T. O. Munson*, from Laboratory Division, Forensic Science Research Group, FBI Academy, Quantico, Virginia: "Comparison and Identification of Adhesives Used in Improvised Explosive Devices by Pyrolysis Capillary Column GC/MS," Abstracts, Sixth International Symposium on Analytical and Applied Pyrolysis, Wiesbaden, FRG, Sept. 1984.
23. *Herres, W.* and *U. Foelster*, from Bruker Analytische Messtechnik, Karlsruhe, FRG and ICI-Wiedehord GmbH, Hilden, FRG: "Analysis of Polymers using Pyrolysis-Capillary-GC/FTIR," Ab-