

Research Article

The usefulness of infrared spectroscopy in examinations of adhesive tapes for forensic purposes

Janina Zięba-Palus*

Institute of Forensic Research, Westerplatte 9, 31-033, Krakow, Poland

Abstract

Infrared spectroscopy was applied in examination and comparative analysis of adhesive tapes. By providing information about the polymer composition, it enables classification of both backings and adhesives into defined chemical classes. It was found that samples of the same type and similar infrared spectra can be differentiated sometimes based only on the presence of peaks of very low intensity originating from minor components. The results demonstrated that infrared spectroscopy appears to be a valuable analytical technique for discriminating between samples of adhesive tapes for forensic purposes.

Introduction

Tape fragments are found at various crime scenes. Electrical tapes can be used in the process of wiring electronic devices to bombs, duct tapes to bind victims of violent crimes, and other tapes to wrap packages containing drugs, explosives or other threatening materials. Frequently, forensic scientists are requested to compare fragments of a tape encountered at a crime scene with fragments originated from a suspect in order to establish whether they could come from the same roll (have a common origin). Visual investigations performed currently provide information about physical fit, tape width, colour and morphology [1]. Infrared spectroscopy (FT-IR) and pyrolysis gas chromatography (Py-GC-MS) enable characterisation of organic compounds in the backing layer and adhesive layer of the tape [2-4] and Inductively Coupled Plasma Mass Spectrometry (ICP/MS) points to their elemental composition [5,6] as well as X-ray fluorescence spectroscopy (XRF) [7].

The discriminating power of these methods is limited, however. FT-IR is used mainly to determine the class of adhesive and backing material used [8-10]. More information about organic compounds like polymers and additives can be obtained using Py-GC/MS [11,12].

A combination of FT-IR with visual comparison and elemental analysis enables discrimination between different brands of tapes but generally cannot be used for further discrimination between different batches of one brand of tape [10].

Some authors have found that application of High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS) enables determination of profiles of trace elements present in the tapes and could help in differentiation between different batches of the same type of tape [5,6].

As a non-destructive method, infrared spectroscopy is routinely applied in forensic examination of different polymer samples. Being sensitive to molecular structure, it provides valuable information about the chemical composition of such materials as paints, plastics and glues [13-16]. The information obtained is in many cases sufficient for classification of these materials. Some authors recommend application

of attenuated total reflection technique (ATR) in examination and comparison of polymer samples [8,9].

In this article, the focus will be on the potential of FT-IR in discrimination of adhesive types. Chemical functional group analysis of backing and adhesive, i.e. polymer components of tapes, carried out by infrared spectroscopy may help in distinguishing between different tapes. It will be demonstrated that this method offers a major step forward in forensic tape investigations by determining polymers and additives in both backings and adhesives of tapes.

Generally, tapes consist of a backing film and an adhesive layer. The backing film is primed with a primer layer for improved adherence of the adhesive layer to the backing film. A release coating is applied on the back side of the backing film. During unwinding of the tape roll, this coating assists in reducing unwind tension and preventing adhesives from the tape from sticking to the back side of the tape beneath it. So, the tape is usually structured as follows (starting at the back of the tape): release coating/backing film/primer layer/adhesive layer. In principle, all these separate layers can be investigated. In practice, however, it is difficult to isolate very thin primer layer as well as release coating. In this study, the tape was divided into two layers only, i.e. backing and adhesive (glue) and both layers were investigated separately.

Materials and methods

Both the glue and the backing of 50 adhesive tapes of various kinds (packaging tape, duct tape, insulation tape) (Table 1) were examined by the use of infrared spectrometry. All tapes were purchased from supermarkets and stores at different times.

Infrared measurements were performed using an FTS 40Pro Fourier-transform infrared spectrometer (BioRad/Digilab), which

Correspondence to: Janina Zięba-Palus, Institute of Forensic Research, Westerplatte 9, 31-033, Krakow, Poland, E-mail: jzieba@ies.krakow.pl

Key words: forensic identification, adhesive tapes, FTIR, discrimination

Received: February 08, 2017; **Accepted:** March 04, 2017; **Published:** March 07, 2017

Table 1. Examined tapes.

No.	Tape	Colour	No.	Tape	Colour
1	Prefecta	colourless	26	Tesaflex 53947	black
2	Painto	grey	27	Tesa perfect	green
3	Advance AT169	red	28	Grand	colourless
4	Advance AT175	green	29	Grand	white
5	Advance AT4	brown	30	Scotch 508	colourless
6	Advance AT6152	white	31	Scotch magic 810	white
7	Advance AT30	colourless	32	Scotch 550	colourless
8	Advance AT6102	black	33	Scotch Crystal 600	colourless
9	Advance AT272	silver	34	Scotch Removable 811	white
10	Advance AT202	yellow	35	Stick'n	white
11	Bizon	green	36	Scotch	colourless
12	Global System	colourless	37	Scley 914	black-yellow
13	Global System	grey	38	Goldtape	grey
14	Lobos	colourless	39	Goldtape	brown
15	Herlitz	colourless	40	Goldtape	yellow
16	Tesco	brown	41	Tape International	yellow
17	Tesco	colourless	42	Global point	yellow
18	Tesa- Fixing	white	43	Dalpo	grey
19	-	red-white	44	K2	grey
20	Blue dolphin tapes	yellow	45	Diall	colourless
21	Blue dolphin tapes	yellow	46	Tape International	yellow
22	Blue dolphin tapes	grey	47	Purs	black
23	Tesa signal	red-white	48	Euro-tape silent	colourless
24	Tesaflex 53947	blue	49	Euro-tape silent	brown
25	Tesco	colourless	50	Euro-tape	yellow

was equipped with a water-cooled high temperature ceramic source (MIR) and coupled with a UMA 500 microscope equipped with an MCT detector. IR spectra in the mid-infrared range were recorded at a resolution of 4 cm⁻¹. Each spectrum represented a collection of 512 scans. The samples were placed on the microscope stage of the spectrometer and measured by the transmission technique in the infrared beam. Glues were scraped from the backing and put directly on the KBr plate. Backings, after removing the glue and cleaning with appropriate solvent, were cut into thin slices using a scalpel. There were collected from each tape 3 samples of both backing and glue and then examined three times in the same conditions.

Results and discussion

On the basis of obtained IR spectra, tapes were divided into several groups that differed in terms of backing and adhesive content (Table 2). Each group was named on the basis of the main polymer present in the sample. Spectra were compared visually, taking into account the number, location and intensity of particular absorption bands.

Backing

Backing materials were divided into 4 groups – namely, polypropylene, polyethylene, cellulose and polyester backings. The backings of 3 of the studied tapes could not be classified into any of the above groups on the basis of the obtained IR spectra. However, these spectra differed significantly from each other and from the remaining spectra. Furthermore, in one of the tapes the backing was aluminium foil.

The largest number of samples were classified into the group of polypropylene backings. In the IR spectra of polypropylene backings,

Table 2. Grouping of examined samples on the basis of their infrared spectra.

	Type	Group	Number of samples	Differentiated samples
Backing	A	Polypropylene	20	0
	B	Polyethylene	17	6
	C	Polyester	6	4
	D	Acetylated cellulose	3	0
		Single spectra	3	3
		Aluminum	1	1
Glue	K	Rubber with styrene	15	6
	L	Polyester	4	2
	M	Butadiene-styrene	4	2
	N	Acryl	25	9
		Non identified	2	2

only absorption bands originating from vibrations of C-H, CH₂ and CH₃ groups in the polymer chain were visible (Figure 1a). That is why backings from tapes belonging to this group could not be differentiated from each other on the basis of their IR spectra (Table 3).

However, spectra of polyethylene backings differed from each other significantly. Some of the obtained spectra contained – apart from bands originating from vibrations of C-H and CH₂ functional groups in the polymer (Figure 1b) – bands originating from additives for improving the quality of the tape, such as carbonates, ionomers or vinyl acetate (Figure 2- labelled with arrows). On the basis of IR spectra, it was possible to distinguish 6 tapes with different spectra and thus (different) chemical composition from the remainder belonging to this group.

In the group of polyester backings, two subgroups were

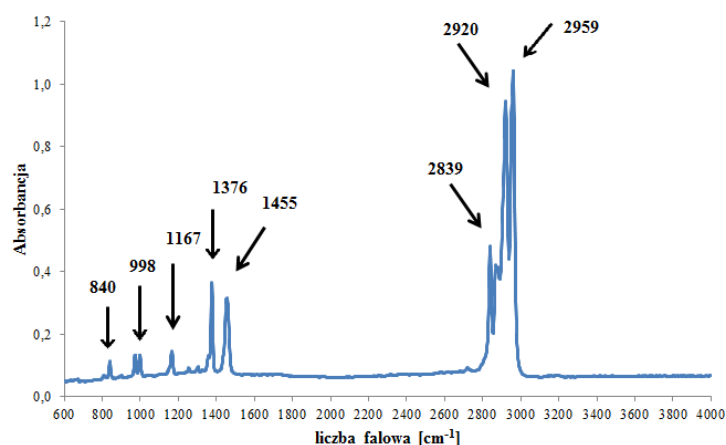


Figure 1a. Infrared spectrum of polypropylene backing.

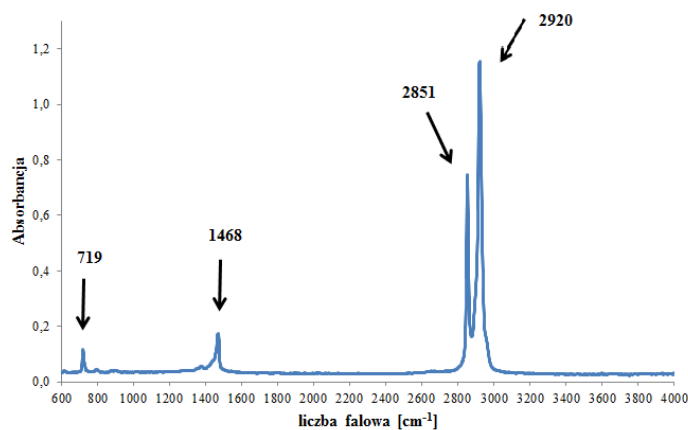


Figure 1b. Infrared spectrum of polyethylene backing.

Table 3. Characteristic absorption bands of polymers visible in IR spectra of backings.

Chemical compound	Absorption band	Assignment	Number of samples
polypropylene	842 cm ⁻¹ 998 cm ⁻¹ 1167 cm ⁻¹ }	vibrations characteristic for isotactic polypropylene	20
	1377 cm ⁻¹	C-H symmetric deformation vibrations	
	1460 cm ⁻¹	C-H asymmetric deformation vibrations	
polyethylene	720 cm ⁻¹	CH ₂ rocking vibration	17
	1460 cm ⁻¹	CH ₂ scissoring vibration	
	2850 cm ⁻¹	C-H symmetrical stretching vibration	
	2920 cm ⁻¹	C-H asymmetrical stretching vibration	
polyester type C1	845 cm ⁻¹	CH ₂ wagging vibrations	2
	970 cm ⁻¹	C-O stretching vibrations	
	1126 cm ⁻¹	C-O-C asymmetric stretching vibration	
	1252 cm ⁻¹	=C-O-C, Ar-O-C asymmetric stretching vibration	
	1340 cm ⁻¹	CH ₂ wagging vibrations	
polyester type C2	1718 cm ⁻¹	C=O stretching vibrations	4
	745 cm ⁻¹	stretching vibrations from the aromatic ring	
	1077 cm ⁻¹	stretching vibrations C-O in O-CH ₂	
	1125 cm ⁻¹ 1285 cm ⁻¹	stretching vibrations C-O-C	
	1726 cm ⁻¹	stretching vibrations C=O	
acetylcellulose	1050 cm ⁻¹	stretching vibrations C-O	3
	1237 cm ⁻¹	stretching vibrations C-O-C	
	1370 cm ⁻¹	deformation vibrations CH ₂	
	1744 cm ⁻¹	stretching vibrations C=O	
	~3400 cm ⁻¹	stretching vibrations O-H	

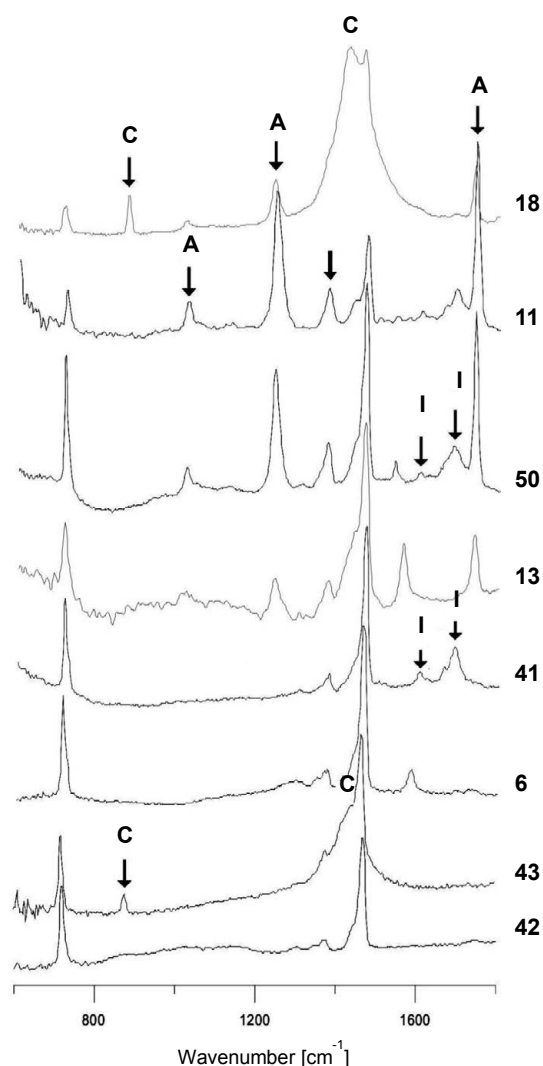


Figure 2. Comparison of infrared spectra of different polyethylene backings
C-carbonates, I-ionomers, A- polyvinyl acetate.

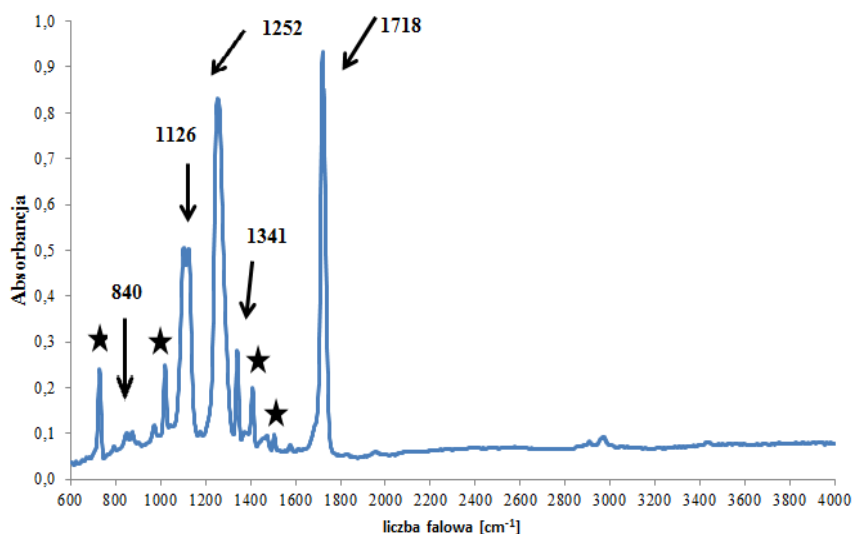


Figure 3a. Infrared spectrum of polyester backing type C1

★ - ring compounds

distinguished that differed in terms of the type of polyester forming the polymer network, i.e., a (sub)group of backings (C1) containing polyethylene terephthalate (Figure 3a), and a (sub)group of backings (C2) containing other esters (Figure 3b). In the spectra of backings in group C1 – apart from absorption bands originating from vibrations of C-O-C, C-O, C=O and C-H groups in esters – bands originating from vibrations of C-H groups in substituted aromatic rings were visible (Figure 3a), which were constituents of additives. Two tapes were classified into this group. Bands of the main polymer were visible in the spectra of the backings in group C2 (Figure 3b – indicated by arrows) as well as bands originating from carbonate type fillers: 875 and 1420 cm^{-1} . Small differences in obtained spectra were also observed, concerning the ratio of the intensity of band 875 (carbonates band) to band 1070 cm^{-1} (ester groups band). The observed differences in spectra allowed us to differentiate 4 out of the 6 samples belonging to this group.

Cellulose backings were characterised by very similar infrared spectra dominated by bands originating from vibrations of groups C-O, C-O-C, C=O and O-H of cellulose (Figure 4).

Additionally, weak bands originating from plasticizers (o-phthalates) were present on spectra, i.e., bands at 748, 1580 and 1601 cm^{-1} . Three tapes with infrared spectra that did not differ from each other were classified into this group.

Adhesives

Four main groups of adhesives were differentiated on the basis of the main polymer component – namely adhesives produced on the basis of natural isoprene rubber, styrene-butadiene rubber, esters and acrylates. Only IR spectra of two adhesives did not allow classification into the mentioned groups.

Most frequently, layers of adhesive present in studied tapes were produced on a base of isoprene rubber and acrylates (Table 4).

In the group of adhesives containing rubber on the basis of isoprene (Figure 5a), strong absorption bands originating from cis-1,4-isoprene were visible, as well as weak additional bands, i.e. indicating styrene, carbonates, titanium dioxide, kaolin and compounds containing a carbonyl group (Figure 5b). These differences in chemical composition

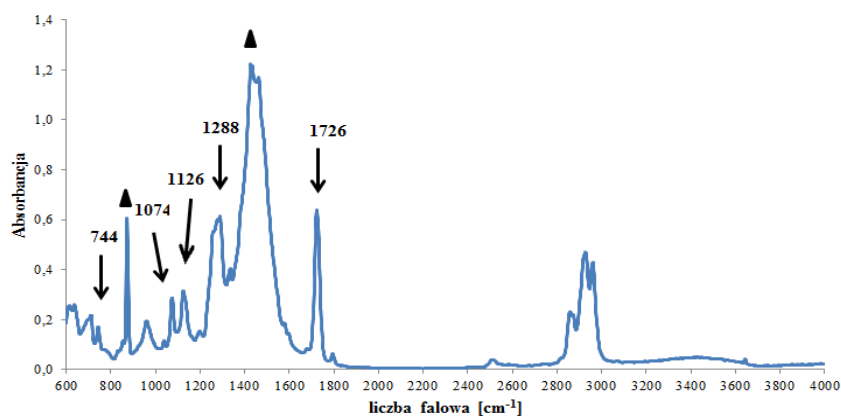


Figure 3b. Infrared spectrum of polyester backing type C2

▲ - carbonates.

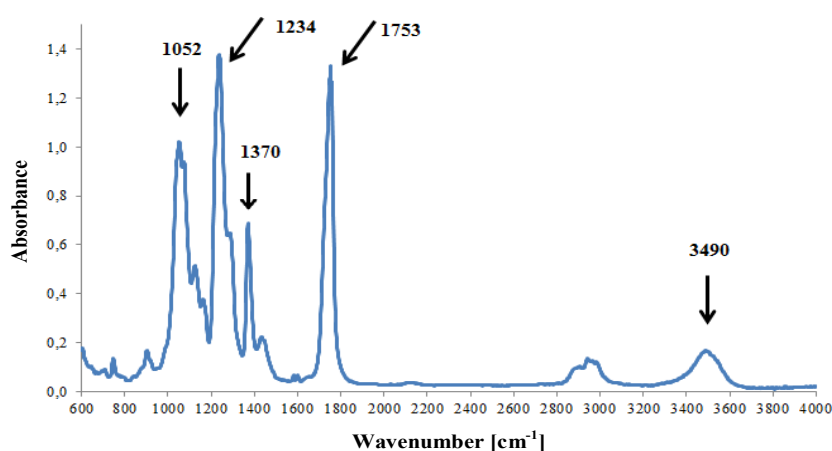


Figure 4. Infrared spectrum of acetocellulose backing.

Table 4. Characteristic absorption bands of polymers visible in IR spectra of glues.

Chemical compound	Absorption band	Assignment	Numer of samples		
polyacrylate	1165 cm ⁻¹	–C-O-C stretching symmetrical vibrations	25		
	1240-1265 cm ⁻¹	–C-O-C stretching asymmetrical vibrations			
	1380 cm ⁻¹	CH ₂ vibration			
	1450 cm ⁻¹	CH ₃ vibration			
	1730 cm ⁻¹	– C=O stretching vibration			
	2240 cm ⁻¹ very weak	– C≡N stretching vibration			
natural rubber	833 cm ⁻¹	=C-H deformation vibrations	15		
	1379 cm ⁻¹	CH ₃ deformation vibrations			
	1451 cm ⁻¹	CH ₂ deformation vibrations			
	1667 cm ⁻¹ weak	C=C stretching vibrations			
	2855 cm ⁻¹ 2926 cm ⁻¹ 2964 cm ⁻¹ }	C-H stretching vibrations			
	butadiene styrene rubber	700 cm ⁻¹ 760 cm ⁻¹ }		C H deformation vibrations in ring	4
912 cm ⁻¹ weak 968 cm ⁻¹ 995 cm ⁻¹ weak }		=C-H deformation vibrations in butadiene			
1380 cm ⁻¹ 1450 cm ⁻¹ }		CH ₃ deformation vibrations			
1495 cm ⁻¹ 1603 cm ⁻¹ weak		ring vibrations			
2854 cm ⁻¹ 2925 cm ⁻¹ }		drgania rozciągające C-H			
polyester		745 cm ⁻¹	stretching vibrations from the aromatic ring	4	
		1077 cm ⁻¹	stretching vibrations C-O in O-CH ₂		
	1125 cm ⁻¹	stretching vibrations C-O-C			
	1285 cm ⁻¹	stretching vibrations C-O in –O-C=O			
	1726 cm ⁻¹	stretching vibrations C=O			

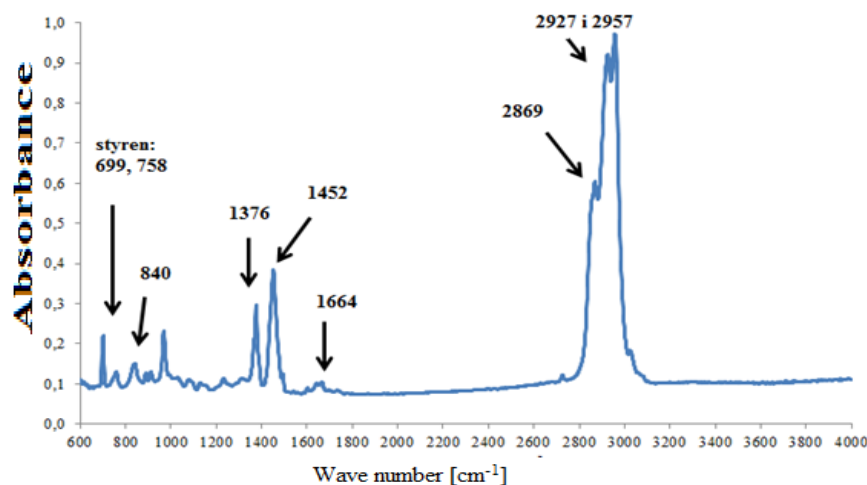


Figure 5a. Infrared spectrum of natural rubber glue modified with styrene.

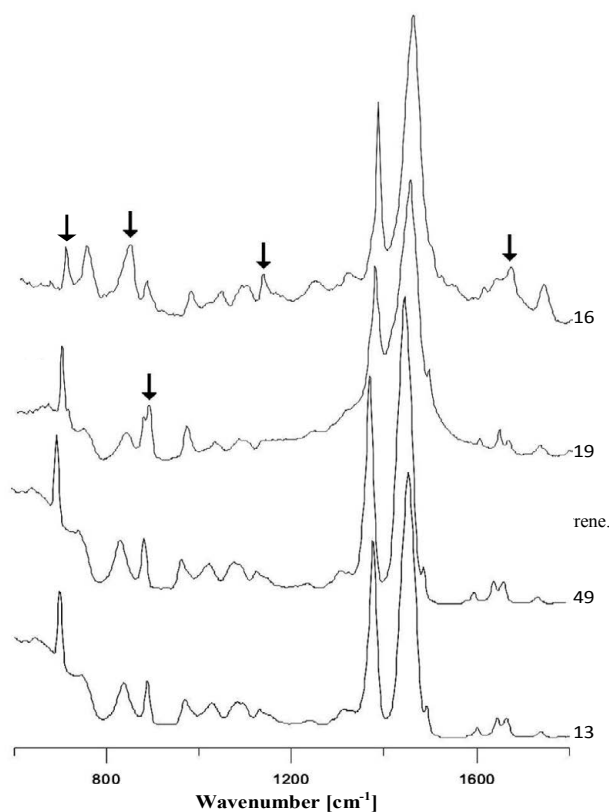


Figure 5b. Comparison of infrared spectra of different natural rubber glues (the main differences marked with arrows).

allowed four subgroups to be distinguished within this group of adhesives.

Acrylic adhesives (Figure 6a) most frequently contained methyl, ethyl, butyl or 2-ethylhexyl polyacrylates. The adhesives of 25 tapes that were classified into the group of acrylic adhesives were characterised by spectra that differed insignificantly in terms of location and intensity of bands, which may indicate their different chemical composition (Figure 6b).

However, in ester (Figure 7) and styrene-butadiene adhesives (Figure 8), only small differences were observed in the intensity of

absorption bands, which was probably the result of slight differences in their chemical composition. But it was not possible to identify such components of the adhesives that influenced the shape of the IR spectra.

Comparing spectra of tape samples visually within the distinguished chemical classes separately for adhesives and for backings, it was ascertained that in most cases, the observed difference between spectra was sufficient to distinguish them. Furthermore, it is probable that differentiation of samples of very similar spectra would be possible with the application of a more sensitive analytical technique, i.e., gas chromatography of pyrolysis products of samples. For this method allows identification of components of low content in a studied sample.

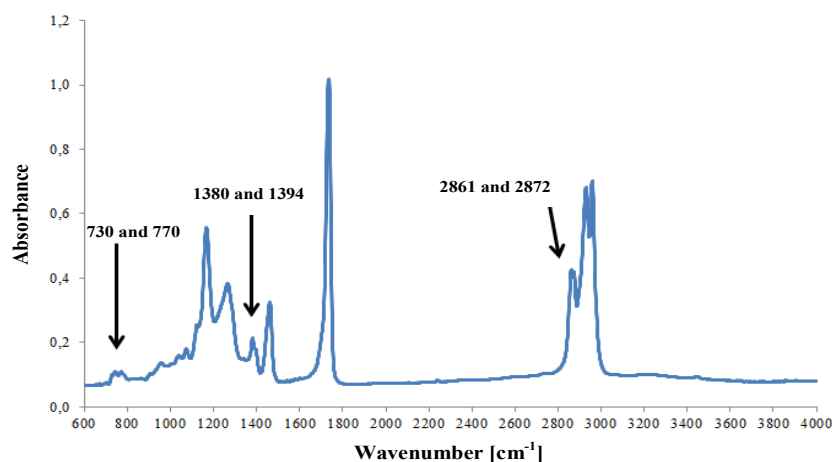


Figure 6a. Infrared spectrum of acrylic glue.

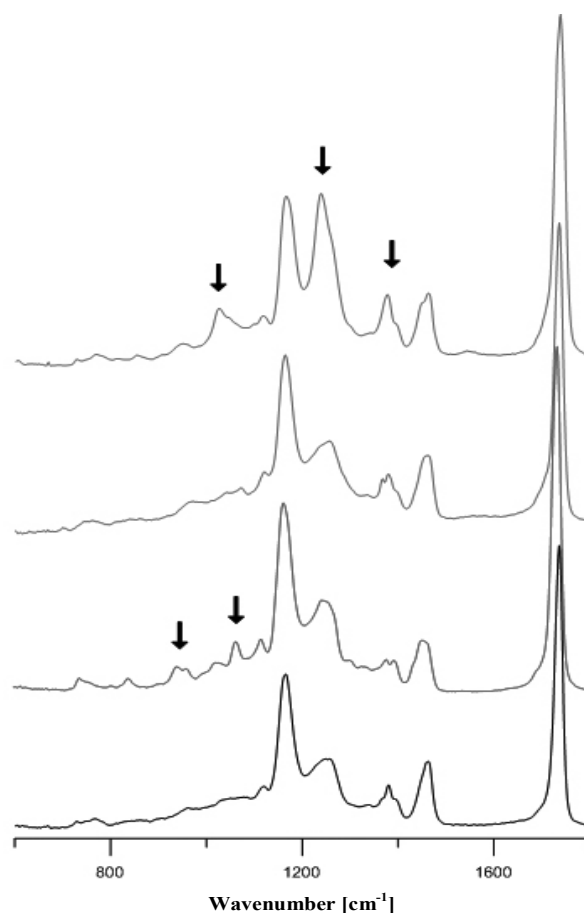


Figure 6b. Comparison of infrared spectra of different acrylic glues.

Conclusions

The results of the research show that infrared spectrometry is a valuable analytical technique in differentiating samples of adhesive tapes for forensic purposes. By providing information on polymer composition, IR spectrometry enables classification both of backings and adhesives into defined chemical classes. In the group of studied tapes, polyethylene and polypropylene backings and adhesives produced on

the basis of synthetic isoprene rubber and acrylates predominate. Small differences in the chemical composition observed within a given class are the result of the presence of additives, e.g., fillers (carbonates and silicates) or plasticizers (phthalates), and also the technological process. The influence of the thin separating layer and the primer present in the tape is negligible. As these layers were not visible under the microscope at a magnification of 150x, they were not initially separated from the backing and the adhesive but studied together with them. Due to their

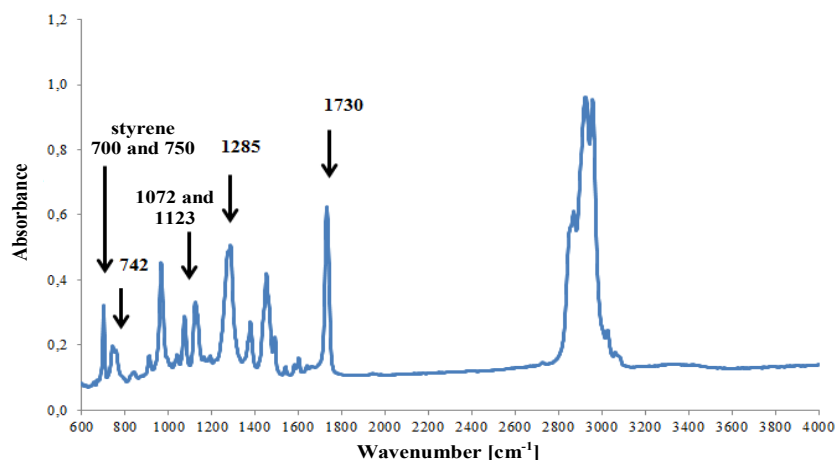


Figure 7. Infrared spectrum of polyester glue modified with styrene.

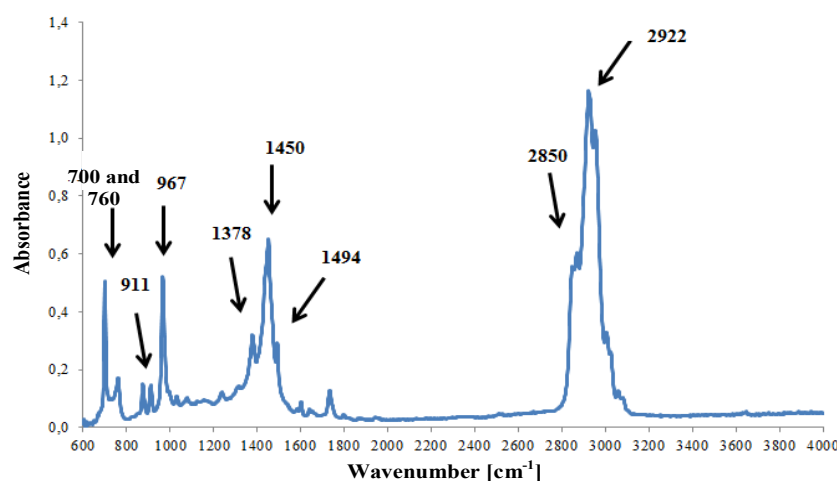


Figure 8. Infrared spectrum of synthetic rubber glue modified with styrene.

low content in the tape, the influence of these components is small. Taking into account the fact that a tape is composed both of a backing and an adhesive, it sometimes happens that compared tapes contain the same backing but different adhesives or the same adhesive, on different backings. Thus, there is greater possibility of differentiating tapes for forensic purposes. Additionally, application of another more sensitive analytical method, e.g., pyrolysis gas chromatography, enabling detections of subtle differences in chemical composition could help in further differentiation of adhesive tape samples belonging to the same chemical class of backings or glues.

The author declares that there is no conflict of interest regarding the publication of this paper.

Acknowledgement

The author would like to express her gratefulness to Mrs Sabina Nowińska for help with gathering a part of IR spectra of the studied material.

The research was financially supported by the Institute of Forensic Research, Poland, within the project no. II/K, 2009-2012.

References

1. Goodpaster JV, Sturdevant AB, Andrews KL, Briley EM, Brun-Conti L (2007)

Identification and comparison of electrical tapes using instrumental and statistical techniques: I Microscopic surface texture and elemental composition. *J Forensic Sci* 52: 610-629.

2. Blackledge RD (1992) Application of Pyrolysis Gas Chromatography in Forensic Science. *Forensic Sci Rev* 4: 1-16.[Crossref]

3. Kumooka Y (2006) Analysis of deteriorated rubber-based pressure sensitive adhesive by pyrolysis-gas chromatography/mass spectrometry and attenuated total reflectance Fourier transform infrared spectrometry. *Forensic Sci Int* 163: 132-137.

4. Williams ER, Munson TO (1988) The comparison of black polyvinylchloride (PCV) tapes by pyrolysis gas chromatography. *Journal of Forensic Sciences* 33: 1163-1170.

5. Dobney AM, Wiarda W, de Joode P, van der Peijl GJ (2001) Elemental comparison of packing tapes using HR ICP/MS. *Problems of Forensic Sciences XVII* 275-287.

6. Dobney AM, Wiarda W, de Joode P, van der Peijl GJ (2002) Sector field ICP-MS applied to the forensic analysis of commercially available adhesive packaging tapes. *Journal of Analytical Atomic Spectrometry* 17: 478-484.

7. Ninomiya T, Nomura S, Taniguchi K, Ikeda S (1995) Applications of a glazing incidence X-ray fluorescence analysis to forensic samples. *Analytical Sciences* 11: 489-494.

8. Kumooka Y (2009) Hierarchical cluster analysis as tool for preliminary discrimination of ATR-FT-IR spectra of OPP acrylic and rubber-based adhesives. *Forensic Sci Int* 189: 104-110.

9. Merrill RA, Bartick EG (2000) Analysis of pressure sensitive adhesive tape: I. Evaluation of infrared ATR accessory advances. *J Forensic Sci* 45: 93-98.[Crossref]

10. Zieba-Palus J, Augustynek A (2011) Effective differentiation of adhesive tapes by

- the use of infrared spectroscopy and pyrolytic-gas chromatography for criminalistic purposes, *Problems of Forensic Sciences* 86: 103-113.
11. Nakamura S, Takino M, Daishima S (2000) Analysis of pressure sensitive adhesives by GC/MS and GC/AED with temperature and programmable pyrolyser, *Analytical Sciences* 16: 627-631.
 12. Kumooka Y (2010) Classification of OPP adhesive tapes according to MALDI mass spectra of adhesives. *Forensic Sci Int* 197: 75-79. [\[Crossref\]](#)
 13. Sakayanagi M, Konda Y, Watanabe K, Harigaya Y (2003) Identification of pressure-sensitive adhesive polypropylene tape. *J Forensic Sci* 48: 68-76. [\[Crossref\]](#)
 14. Zięba-Palus J, Kowalski R, Nowinska S (2016) Application of infrared spectroscopy and pyrolysis gas chromatography for characterisation of adhesive tapes. *J Molecular Struct* 1126: 232-239.
 15. Pahl A (1996) Identification of adhesives in adhesive tapes. *Kleben Dichten* 41: 28-31.
 16. Mehlretter AH, Bradley MJ, Wright DM (2011) Analysis and discrimination of electrical tapes: Part I. Adhesives. *J Forensic Sci* 56: 82-94. [\[Crossref\]](#)