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Identification of Pressure-Sensitive Adhesive Polypropylene Tape

ABSTRACT: Identification of colorless, transparent, pressure-sensitive adhesive polypropylene tape (PP tape) was performed using infrared absorption spectrometry (IR) and pyrolysis gas chromatography mass spectrometry (Py-GC/MS) to determine the pressure-sensitive adhesive. Twenty different products of colorless, transparent PP tapes were examined in this study, and the results of analysis of IR spectra and Py-GC/MS were classified into twelve groups. In addition, the tapes were classified into 14 groups on the basis of IR measurement of release agent present in the backside. The results indicate that colorless, transparent PP tapes can be distinguished in terms of manufacturer, thereby demonstrating that this method of identifying colorless, transparent PP tape is effective. Moreover, the method was applied to the analysis of an actual forensic sample.

KEYWORDS: forensic science, pressure-sensitive adhesive, polypropylene tape, infrared spectroscopy, pyrolysis, gas chromatography, mass spectrometry

In homicide, assault, and rape cases, victims are often immobilized by pressure-sensitive adhesive tape. Such tapes used in crimes are frequently entrusted to a forensic laboratory as evidence, and the goal in examining such tapes is to specify the product and its manufacturer. General methods of examining such tapes used in a crime are color examination of backside and adhesive face, physical examination of the backing (cloth, paper, resin, and etc.), pyrolysis gas chromatography (Py-GC) or pyrolysis gas chromatography mass spectrometry (Py-GC/MS) (1–4), and infrared spectroscopy (IR) (3–5) of pressure-sensitive adhesive. Measurement by ATR (attenuated total reflection) has also been recently reported as a new method for measuring IR (4–6). Additionally, ash content analysis of pressure-sensitive adhesive cloth tape has been reported (7).

Meanwhile, use of pressure-sensitive plastic tapes such as pressure-sensitive adhesive polypropylene tapes (PP tape) in crimes has increased in recent years. PP tape has been used as a packing tape and is composed of polypropylene backing and pressure-sensitive adhesive. The pressure-sensitive adhesive is composed of rubber, which is often used as a main component, and additives such as tackifiers, fillers, crosslinking agents, and antioxidants. The rubber constituent (elastomer), which is a main constituent material, is broadly divided into rubber, silicone, acrylic, and others. Almost all colorless, transparent PP tapes employ rubber-based pressure-sensitive adhesive or acrylic-based pressure-sensitive adhesive.

The results of visual examination and color examination are important indices of colored pressure-sensitive adhesive tape such as cloth tape, etc. However, examination of colorless, transparent, pressure-sensitive adhesive plastic tape does not include color examination and visual examination of the backing.

Nowadays, colorless, transparent, pressure-sensitive adhesive tape has been used more and more frequently in crimes. Few studies have been published on examined discrimination of colorless, transparent, pressure-sensitive adhesive tape, although the investigative field demands discrimination of such tape. In the present study, such tapes having polypropylene backings were examined. Then, the pressure-sensitive adhesive that serves as the major component of the PP tape was used as an analyte, and discrimination by use of IR and Py-GC/MS was investigated, along with the possibility of determining the manufacturer.

Materials and Methods

Materials

Twenty colorless, transparent PP tape products made by eleven manufacturers were collected. Such tapes are prevalent in Japan. All products measured 5 cm in width and were identical in appearance.

Methods

IR Analysis—In each sample, IR of the backing material, the pressure-sensitive adhesive, and the release agent were measured. Analysis was carried out using a Nicolet (Madison, WI) Magna 550 FT-IR (fourier transform infrared) spectrometer and a Nic-Plan FT-IR microscope. The backing material and pressure-sensitive adhesive were analyzed using the FT-IR microscope, which is equipped with a MCT-A (mercury cadmium telluride-A) detector. Samples were put on the potassium bromide disk above the microscope slide. The spectra were measured with the transmission mode. The release agent on the surface of the backing material was analyzed using the ATR accessory (Thunderdome), equipped with

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a TGS (triglycine sulfate) detector. The spectra were collected over 64 scans spanning the range of 4000 to 650 cm^{-1}.

Py-GC/MS Analysis—Py-GC/MS analysis was performed using a Hewlett-Packard HP-5890II gas chromatograph (GC) equipped with a Hewlett-Packard HP-5972 mass spectrometer. The GC is equipped with a HP-1MS fused silica capillary column, 30 m by 0.25 mm inside diameter, 0.25-μm film thickness. Temperature was programmed from 50°C (5-min hold) to 300°C at 4°C/min. Helium was used as a carrier gas for the capillary column at a flow rate of 1.0 mL/min. The injection port was operated in split mode; the split ratio was set at 50:1. The GC injection port temperature and transfer line temperature were 300°C. The mass spectrometer was operated in the electron impact (EI) ionization mode at 70eV ionization energy. The scan range was m/z 35 to 500. Pyrolysis was performed at 590°C for 5 s by use of a Japan Analytical Industry (Tokyo, Japan) JHP-3S model curie point pyrolyzer.

Results and Discussion

IR Analysis of Backing Materials

The results of IR spectra clearly show that all backing materials consist of polypropylene, and all show similar spectra. Characteristic absorptions of the polypropylene of methyl asymmetric deformation vibration appear at 1457 cm^{-1} and methyl symmetrical deformation vibration at 1377 cm^{-1}. And all backing materials have absorption at 1168, 998, 973, 879, 841, and 809 cm^{-1}, especially absorptions at 1168, 998, and 809, which are characteristic absorptions of isotactic polypropylene (8,9). The above results show that the polypropylene of backing materials is the isotactic polypropylene and not the atactic and syndiotactic polypropylene. Therefore, these spectra could not be discriminated from each other by visual comparison of spectra.

IR Analysis of Pressure-Sensitive Adhesives

Figure 1 shows the IR results of pressure-sensitive adhesives. By the IR measurement of the pressure-sensitive adhesives, Tapes A1, A2, D3, and H1 were classified into Group 1, and Tapes B1, F1, H2, and J1 were classified into Group 2. Absorption at 1740 cm^{-1} indicates the stretching vibration of C═O, and absorption at 1250 cm^{-1} and that at 1160 cm^{-1} indicate the stretching vibration of C—O—C. Therefore, all adhesive of Groups 1 and 2 were identified as acrylic-based pressure-sensitive adhesive. The pressure-sensitive adhesives of the other tapes were isoprene rubber-based pressure-sensitive adhesive. Tape C1 in Group 3 does not contain polystyrene; unlike the cases of tapes in Groups 4 to 8, no absorption was detected at 700 cm^{-1}. The isoprene rubber is mainly cis −1,4-polyisoprene, which has main absorption peaks at 1450, 1376, and 840 cm^{-1}. Absorption at 700 cm^{-1} is characteristic of monosubstituted benzene, which appears in the presence of polystyrene. Tapes that do not contain polystyrene were classified into Group 3. Other isoprene rubber-based pressure-sensitive adhesives were classified into Groups 4 to 8, according to the fine structure of each spectrum. Groups 4 to 8 are styrene-isoprene block copolymer-based pressure-sensitive adhesives. Table 1 summarizes the IR result of pressure-sensitive adhesives. In accordance with IR results of pressure-sensitive adhesives, four products of three manufacturers are classified into Group 1, four products of four manufacturers are classified into Group 2, one product of one manufacturer is classified into Group 3, two products of one manufacturer are classified into Group 4, four products of two manufacturers are classified into Group 5, two products of one manufacturer are classified into Group 6, one product of one manufacturer is classified into Group 7, and two products of one manufacturer are classified into Group 8. In total, 20 colorless, transparent PP tape products of eleven manufacturers were classified into Groups 1 to 8; that is, eight types of products were discriminated.

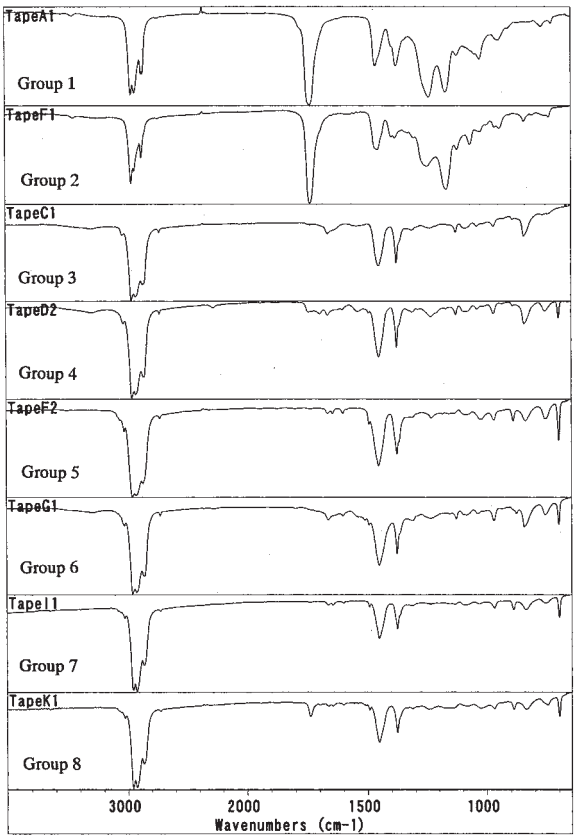

FIG. 1—*IR spectra of pressure-sensitive adhesives from PP tapes.*

TABLE 1—*IR results of pressure-sensitive adhesives.*

Sample	Manufacturing Company	Classified	Pressure-Sensitive Adhesive Type
Tape A1	A	Group 1	*
Tape A2	A	Group 1	*
Tape B1	B	Group 2	*
Tape C1	C	Group 3	†
Tape D1	D	Group 4	†
Tape D2	D	Group 4	†
Tape D3	D	Group 1	*
Tape E1	E	Group 5	†
Tape E2	E	Group 5	†
Tape E3	E	Group 5	†
Tape F1	F	Group 2	*
Tape F2	F	Group 5	†
Tape G1	G	Group 6	†
Tape G2	G	Group 6	†
Tape H1	H	Group 1	*
Tape H2	H	Group 2	*
Tape I1	I	Group 7	†
Tape J1	J	Group 2	*
Tape K1	K	Group 8	†
Tape K2	K	Group 8	†

* Acrylic-based pressure-sensitive adhesive.
† Rubber-based pressure-sensitive adhesive.

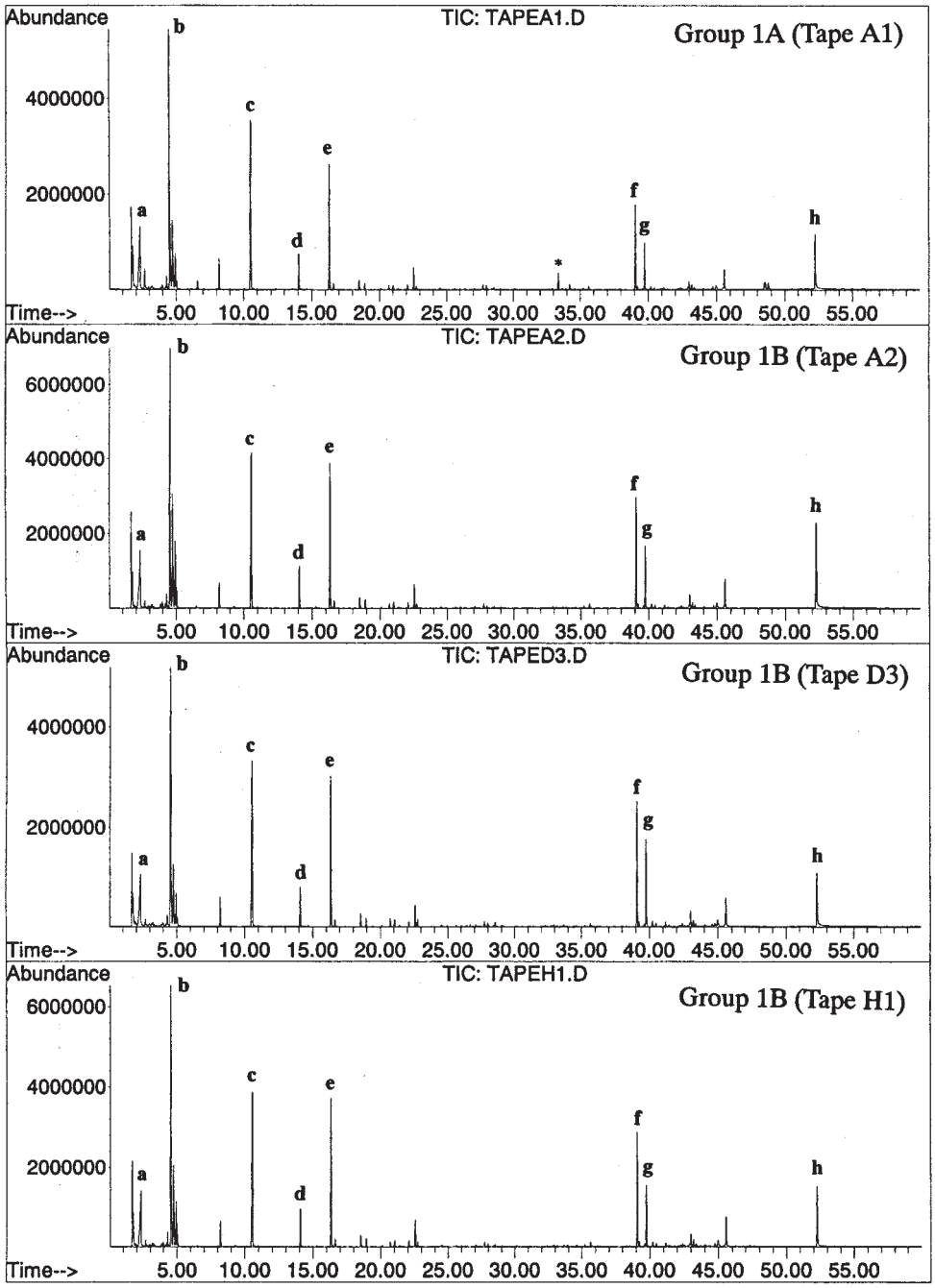

FIG. 2—*Pyrogram of pressure-sensitive adhesives on Group 1. a: Acetic acid, b: 2-Ethylhexene, c: 2-Ethylhexanol, d: 2-Ethylhexyl acetate, e: 2-Ethylhexyl acrylate, f: $C(COOC_8)CCCOOC_8$, g: Dimer of 2-ethylhexyl acrylate, h: Trimer of 2-ethylhexyl acrylate, *: unknown*

Py-GC/MS Analysis of Pressure-Sensitive Adhesives

As shown in Fig. 2, pyrograms of Group 1, which include Tape A1, A2, D3, and H1, are classified by IR. The reference characters given in the figure indicate the compounds specified in the footnotes. In each pyrogram shown in Fig. 2, 2-Ethylhexyl acrylate, which seems to be a main monomer, is detected, along with dimers and trimers. A peak of an unknown compound, denoted by * in Fig. 2, was detected in Tape A1, and this peak was not detected in other tapes. Therefore, this peak distinguished Tape A1, classified into Group 1A, from Tapes A2, D1, and H1, classified into Group 1B. Tapes B1, F1, H2, and J1 were classified into Group 2 by IR analysis of the pressure-sensitive adhesives, and their pyrograms are shown in Fig. 3. In this case as well, the tapes differed in pyrogram pattern. Therefore, Tapes B1, F1, H2, and J1 were classified into Groups 2A, 2B, 2C, and 2D, respectively. These results show that Py-GC/MS can further classify Group 2 into four subgroups. In Group 2, butyl acrylate was detected as a main monomer of each tape. Tapes B1 and H2 contain butyl acrylate and 2-ethylhexyl acrylate as main monomer; therefore, hybrid dimer was also detected. Tapes classified by IR into Groups 3, 4, and 6 are as follows. Unlike the other isoprene rubber-based

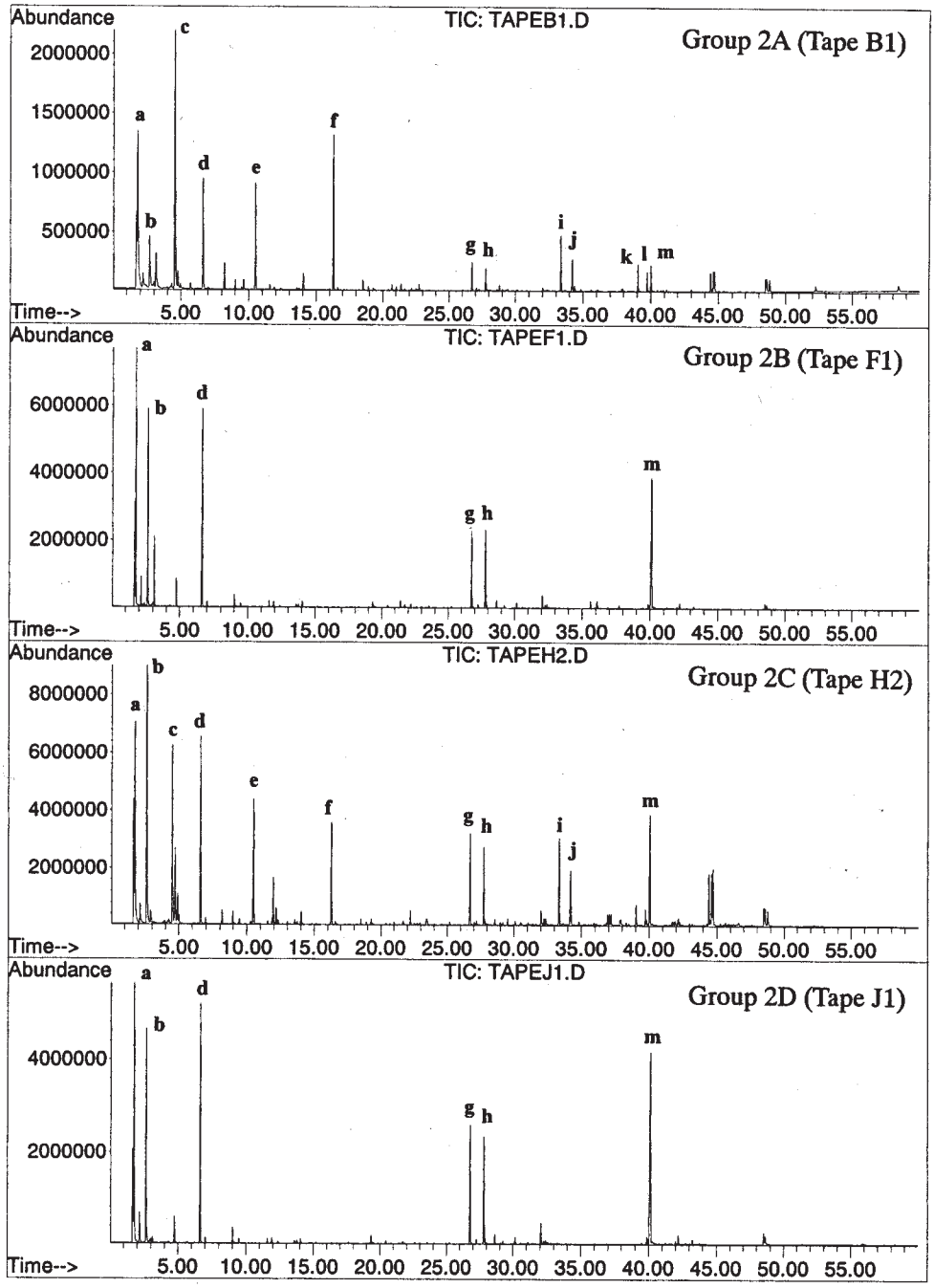

FIG. 3—*Pyrogram of pressure-sensitive adhesives on Group 2. a: Buten, b: Butanol, c: 2-Ethylhexene, d: Butyl acrylate, e: 2-Ethylhexanol, f: 2-Ethylhexyl acrylate, g: C(COOC$_4$)CCCOOC$_4$, h: Dimer of butyl acrylate, i: C(COOC$_4$)CCCOOC$_8$, j: Hybrid dimer of butyl acrylate and 2-ethylhexyl acrylate, k: C(COOC$_8$)CCCOOC$_8$, l: Dimer of 2-ethylhexyl acrylate, m: trimer of butylacrylate*

pressure-sensitive adhesives, IR shows that Tape C1 does not contain polystyrene, nor is the peak of styrene detected in pyrograms. Similar pyrograms were obtained in Tapes D1 and D2 of Group 4, as shown in Fig. 4, and further classification was impossible. Therefore, they are classified into Group 4, according to IR result. Similarly, pyrograms for Tapes G1 and G2 of Group 6 failed to enable further classification, as shown in Fig. 4. Therefore, they were classified into Group 6 in accordance with the IR result. Tapes E1, E2, E3, and F2 of Group 5 were not classified further because similar pyrograms were obtained, as shown in Fig. 5. Therefore, they were classified into Group 5 on the basis of IR result. Figure 6 shows the pyrogram of Tape I1 of Group 7. As shown in Fig. 6, Tapes K1 and Tape K2 of Group 8 show similar pyrograms. Therefore, they were classified into Group 8 on the basis of IR result.

Table 2 summarizes the results of Py-GC/MS analysis of pressure-sensitive adhesive. Twenty colorless, transparent PP tape products made by eleven manufacturers were classified into eight groups by IR analysis. In addition, the tape products could be classified into twelve groups by Py-GC/MS analysis.

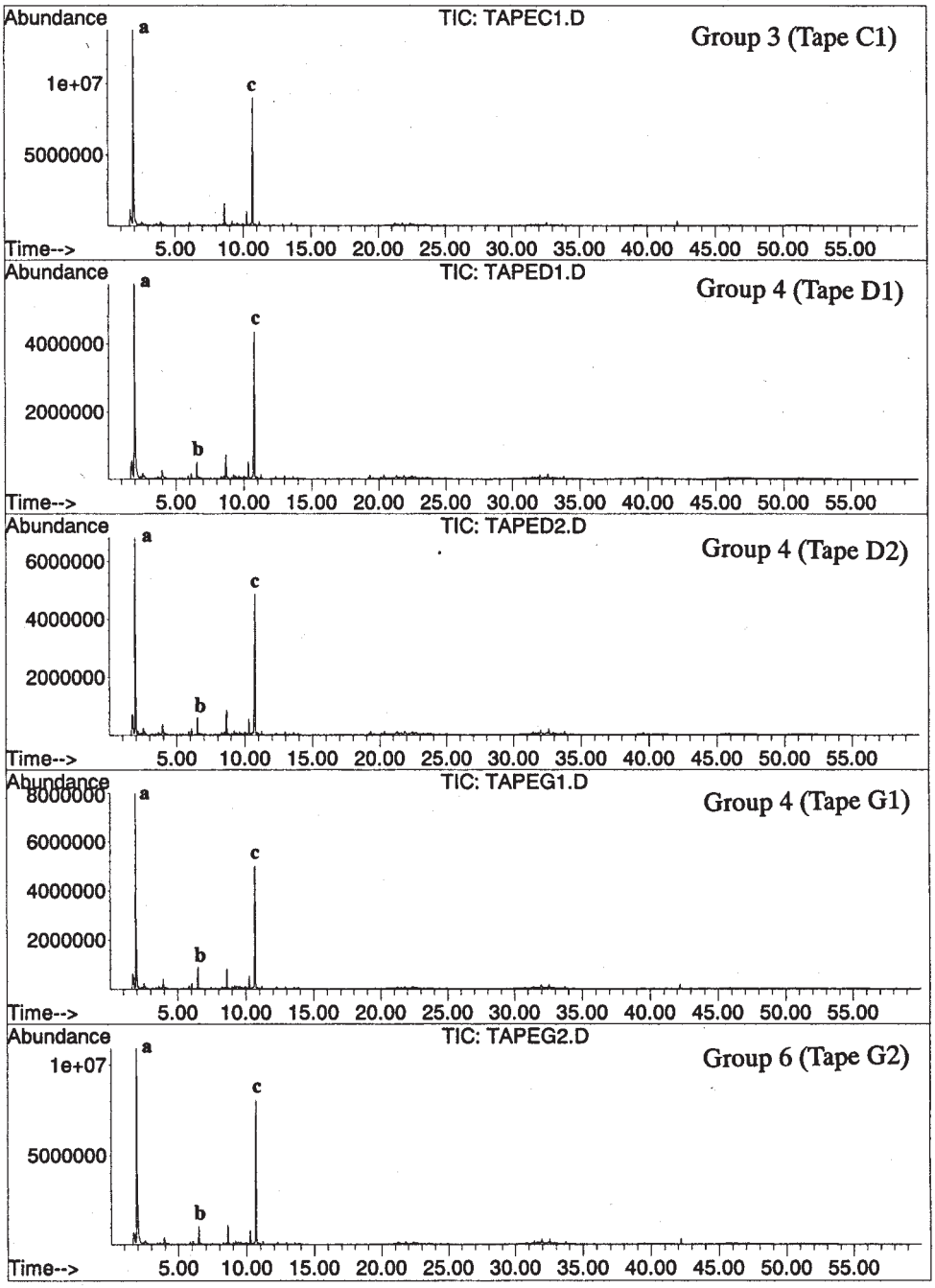

FIG. 4—*Pyrogram of pressure-sensitive adhesives on Groups 3, 4, and 6. a: Isoprene, b: Styrene, c: Limonene*

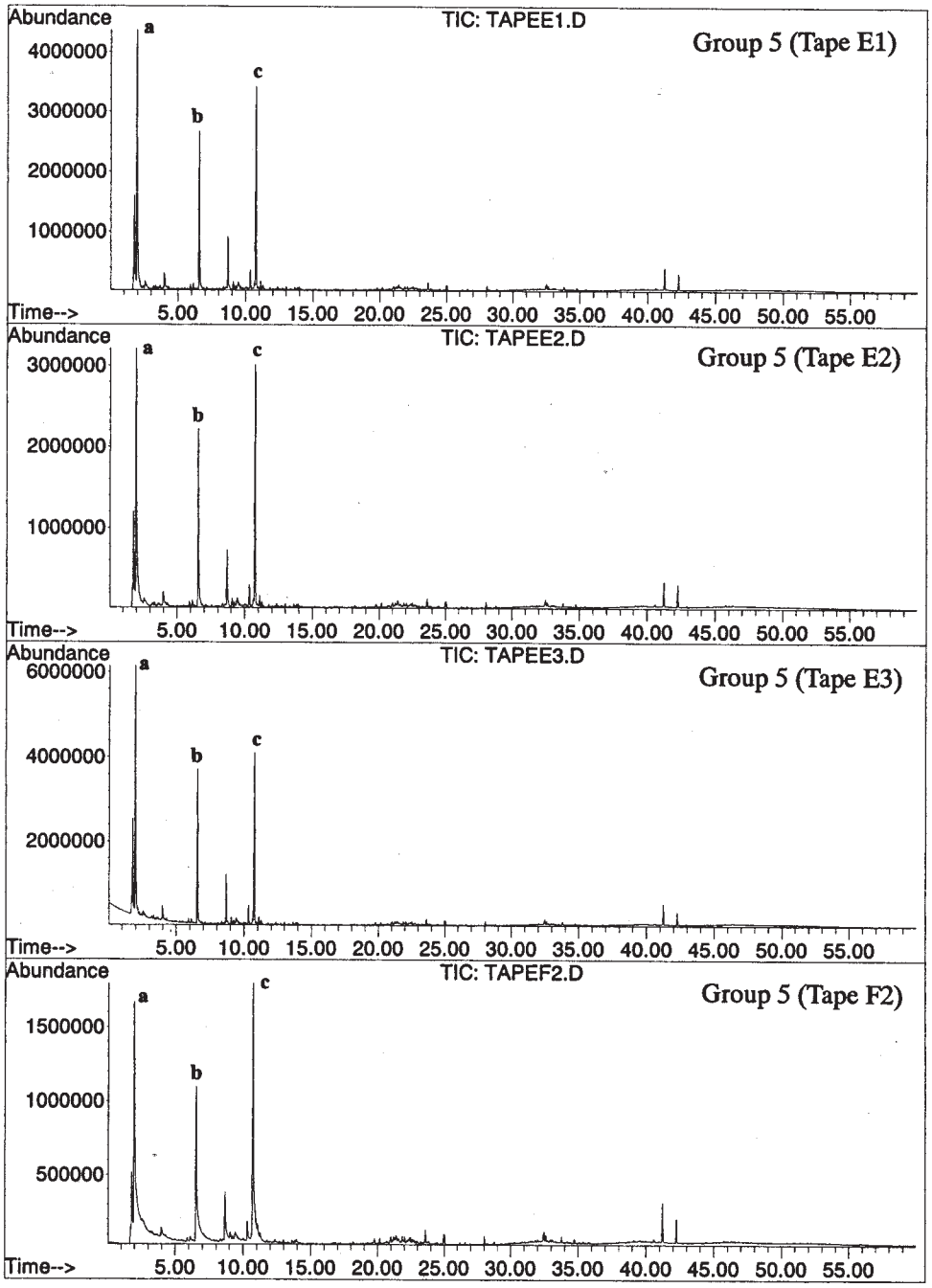

FIG. 5—*Pyrogram of pressure-sensitive adhesives on Group 5. a: Isoprene, b: Styrene, c: Limonene*

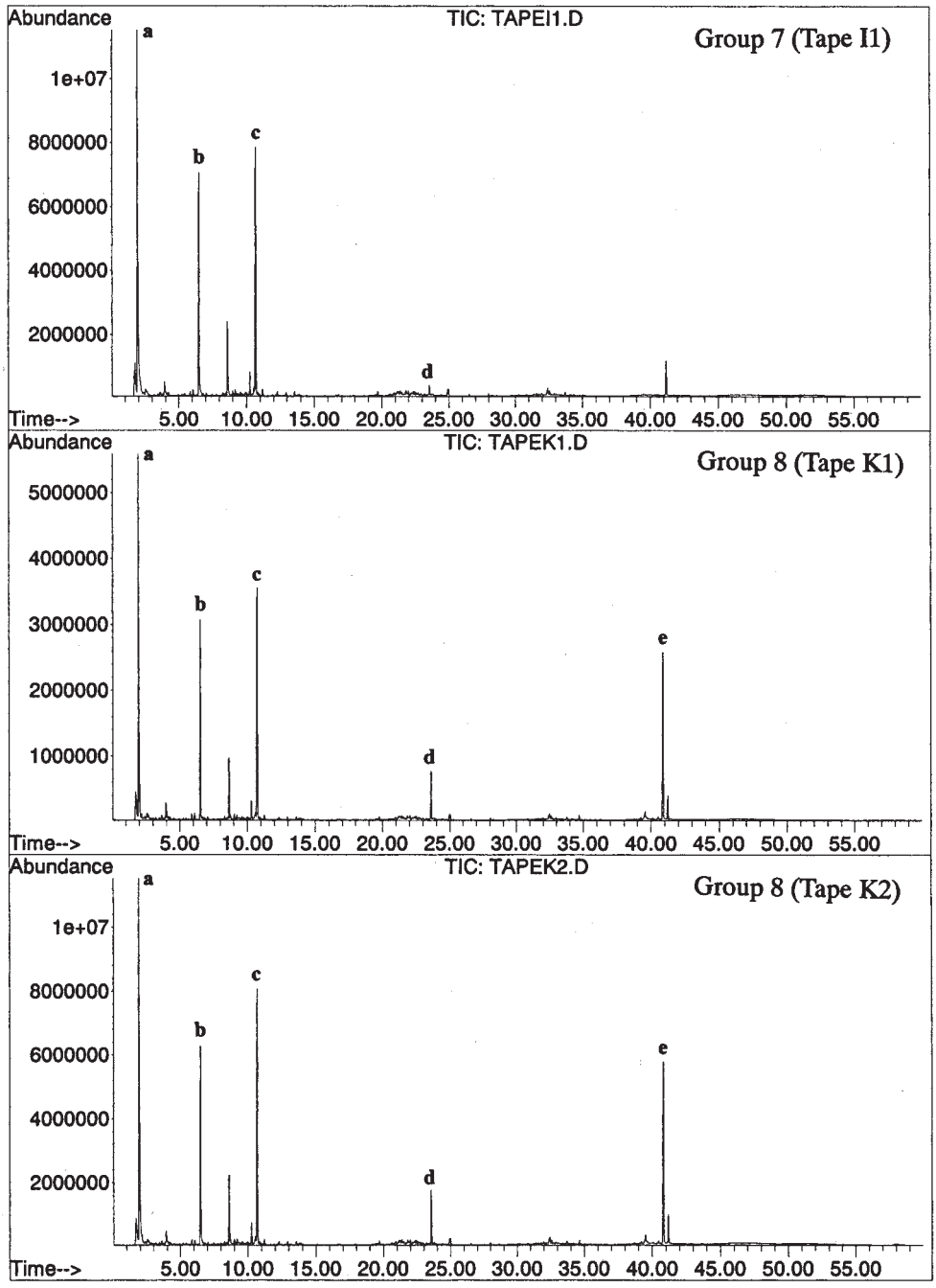

FIG. 6—*Pyrogram of pressure-sensitive adhesives on Groups 7 and 8. a: Isoprene, b: Styrene, c: Limonene, d: Butyl hydroxy toluene, e: Bis (2-ethylhexyl) adipate*

TABLE 2—*Py-GC/MS results of pressure-sensitive adhesives.*

Sample	Manufacturing Company	Classified
Tape A1	A	Group 1A
Tape A2	A	Group 1B
Tape D3	D	Group 1B
Tape H1	H	Group 1B
Tape B1	B	Group 2A
Tape F1	F	Group 2B
Tape H2	H	Group 2C
Tape J1	J	Group 2D
Tape C1	C	Group 3
Tape D1	D	Group 4
Tape D2	D	Group 4
Tape E1	E	Group 5
Tape E2	E	Group 5
Tape E3	E	Group 5
Tape F2	F	Group 5
Tape G1	G	Group 6
Tape G2	G	Group 6
Tape I1	I	Group 7
Tape K1	K	Group 8
Tape K2	K	Group 8

IR Analysis of Release Agent

Release agents present in the backsides of tape products were analyzed by IR with ATR. Silicon was detected as a release agent in Tapes D2 and E2 (as shown in Fig. 7). Therefore, the 20 products made by eleven manufacturers could be classified into 14 types by IR analysis of release agent with ATR, in contrast to classification into twelve groups by Py-GC/MS analysis and IR analysis of pressure-sensitive adhesives (Table 3).

Analysis of Forensic Sample

An actual forensic sample was analyzed by the method employed in the present study. The sample had been used for binding a victim tight. Prior to analysis, the sample was subjected to fingerprint inspection by the cyanoacrylate method. No effect of the fingerprint inspection was observed in the analysis of pressure-sensitive adhesives by this method. Figures 8 and 9 show the results of IR and Py-GC/MS measurement of pressure-sensitive adhesive of the forensic sample, respectively, and show that this sample is identical with the tapes of Group 1B. Thus, this method enables discrimination of the manufacturer. The examination result was actually utilized in the crime investigation.

Conclusions

Although the PP tape used in the present study, being colorless and transparent, has no apparent characteristics, measuring IR spectra of pressure-sensitive adhesive could classify 20 products made by eleven manufacturers into eight groups, called Groups 1 to 8.

Py-GC/MS analysis of pressure-sensitive adhesives enabled further classification of Group 1 in two subgroups (Tapes 1A and 1B) and Group 2 into four subgroups (Tapes 2A to 2D). Py-GC/MS analysis was effective for analysis of the above acrylic rubber-based pressure-sensitive adhesive. Py-GC/MS could not further classify isoprene rubber-based pressure-sensitive adhesive (Groups 3 to 8); however, IR spectrum was proven to be effective for the discrimination of the isoprene rubber-based pressure-sensitive adhesives. Moreover, analysis of pressure-sensitive adhesive was proven to be effective for the discrimination of the color-

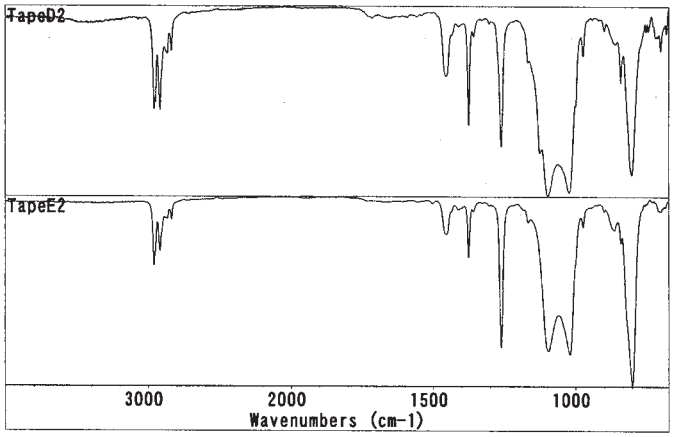

FIG. 7—*IR spectra of release agent from backside of PP tapes.*

TABLE 3—*IR results of release agent.*

Sample	Manufacturing Company	Classified
Tape A1	A	Group 1A
Tape A2	A	Group 1B
Tape D3	D	Group 1B
Tape H1	H	Group 1B
Tape B1	B	Group 2A
Tape F1	F	Group 2B
Tape H2	H	Group 2B
Tape J1	J	Group 2B
Tape C1	C	Group 3
Tape D1	D	Group 4A
Tape D2	D	Group 4B*
Tape E1	E	Group 5A
Tape E3	E	Group 5A
Tape F2	F	Group 5A
Tape E2	E	Group 5B*
Tape G1	G	Group 6
Tape G2	G	Group 6
Tape I1	I	Group 7
Tape K1	K	Group 8
Tape K2	K	Group 8

* Release agent detected.

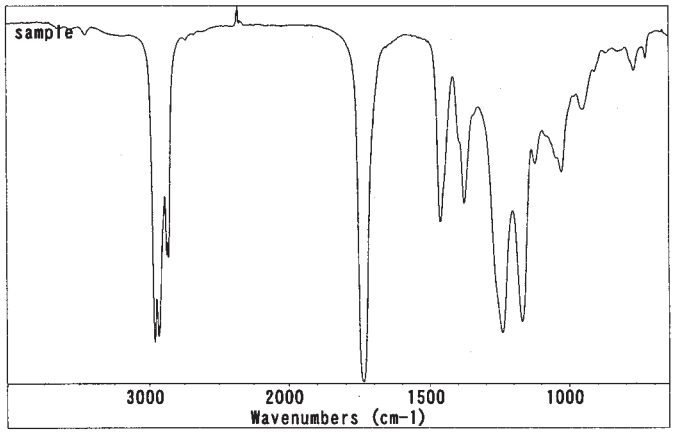

FIG. 8—*IR spectrum of pressure-sensitive adhesive from forensic sample.*

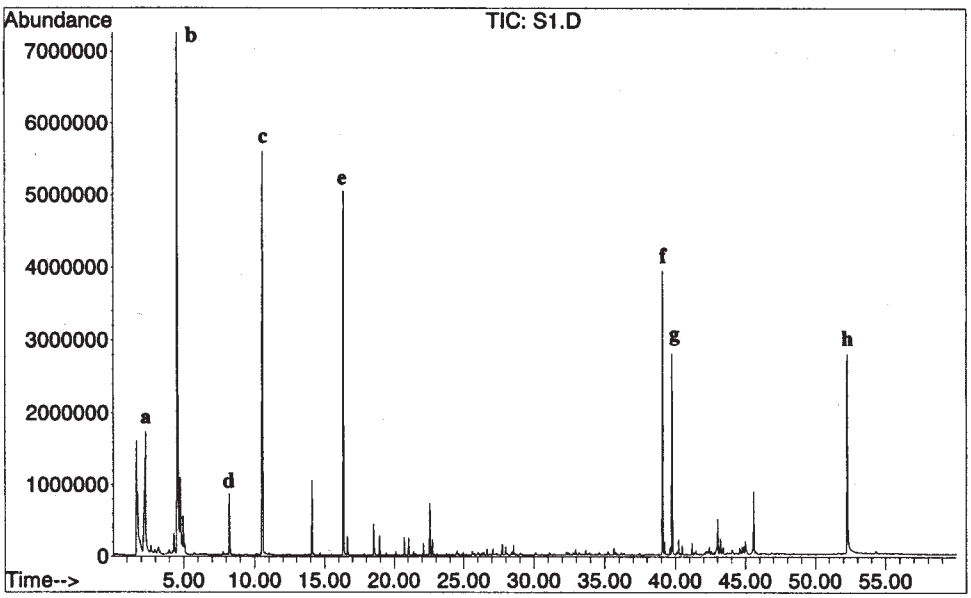

FIG. 9—*Pyrogram of pressure-sensitive adhesive from forensic sample. a: Acetic acid, b: 2-Ethylhexene, c: 2-Ethylhexanol, d: 2-Ethylhexyl acetate, e: 2-Ethylhexyl acrylate, f: $C(COOC_8)CCCOOC_8$, g: Dimer of 2-ethylhexyl acrylate, h: Trimer of 2-ethylhexyl acrylate*

less, transparent PP tape. The combination of IR and Py-GC/MS analysis could classify 20 products made by eleven manufacturers into twelve groups. In addition, the tapes were classified into 14 groups by IR with ATR measurement of the release agent present in the backside.

Large differences between products of PP tape made by the same manufacturer are not recognized. However, the results of the present study indicate the possibility of discrimination between manufacturers.

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