TECHNICAL NOTE

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Chemical Fingerprinting of Adhesive Tapes by GCMS Detection of Petroleum Hydrocarbon Products

ABSTRACT: Pressure-sensitive adhesive tapes often represent key evidence of crimes such as assault, rape or homicide; thus, the development of analytical techniques able to contribute to a detailed characterization of these materials is of forensic importance. The gas chromatography-mass spectrometry (GCMS) analysis of the solvent extractable fractions of a suite of electrical and gaffer adhesive tapes spanning a range of colors and manufacturers identified a number of petroleum-derived hydrocarbons. Molecular and isotopic analyses of hydrocarbon constituents of complex materials have found wide analytical utility including the forensic investigation of oil spills and arson. Here, we investigate the utility of these techniques for characterizing the hydrocarbon composition of pressure-sensitive adhesive tapes for forensic correlation purposes. Subtle distinction of tape samples was evident in the GCMS distribution of several hydrocarbon groups including alkyl-naphthalenes, hopane and sterane biomarkers. Linear discriminant analysis of the abundances of these products provided high level differentiation of tape manufacturer. The distinction of different adhesive tape samples was further extended by measurement of their stable carbon isotopic values. The molecular and isotopic differences of the petroleum content of tapes are consistent with the use of different petroleum materials used in the manufacturing process and demonstrate the benefits of the combined use of complementary oil hydrocarbon characterization approaches. This study reveals the forensic potential of using established petroleum characterization methods for characterizing materials with a petroleum-derived hydrocarbon element.

KEYWORDS: forensic science, adhesive tapes, gas chromatography mass spectrometry, stable isotopes, petroleum hydrocarbons, biomarkers, chemical fingerprinting, linear discriminant analysis

Pressure-sensitive adhesive tapes have the potential to represent important forensic evidence. They are often used to restrain victims of assault, robbery, rape, or homicide, and to seal drug packages and improvised explosive devices. Rigorous analytical characterization may help specify the tape product and its manufacturer, and provide a convincing forensic link between a suspect and a criminal activity.

Here, the potential of molecular and stable carbon isotopic analyses of petroleum-derived hydrocarbons consistently detected in a broad suite of adhesive tape samples is investigated for forensic cross-correlation purposes. Petroleum or terpene-based tackifying resins and plasticisers are common additives used in the manufacture of adhesive tapes (1,2). The large array of hydrocarbon constituents within crude oils and many of the materials made from them provide a powerful forensic cross-correlation capacity.

Many different analytical techniques have previously been used to assist the forensic characterization of adhesive tape samples. The microstructural appearance of adhesive tapes may be optically assessed for morphological characteristics or for evidence of physical aberrations such as tape pieces separated by cuts or tears (3), but these analyses are now limited by the generally high morphological uniformity of current day tapes (4).

Several chemical methods have been used to characterize adhesive tapes, ranging from simple ash content (5) and elemental (5,6) analyses to more sophisticated spectroscopic methods such as X-ray fluorescence spectroscopy (7) and infrared spectroscopy (IR) (8–10). Chemical functional group analysis of the backing, adhesive or polymer elements of tapes provided by Fourier transform (FT)-IR analysis has helped distinguish different tape manufacturers (9,10). Complementary IR measurement by attenuated total reflectance (10–12) and Laser Raman spectroscopy (13) have also assisted the differentiation of adhesive tape samples. Inductively coupled plasma mass spectrometry detection of the trace inorganic components of adhesive tapes has also been used to help distinguish both different brands and different rolls of a brand, although the generally low metal concentration of adhesive tapes can limit the sensitivity of this approach (14).

Analytical pyrolysis (Py), another frequently used method in forensic investigations, has also been applied to the characterization of adhesive tapes (9,15,16) and was reported to provide greater discrimination of adhesive tapes than FT-IR (9). With this approach, low molecular weight (MW) Py fragments of organic materials can be detected by gas chromatography (GC) (17,18). GC combined with mass spectrometric (MS) detection can measure very small differences in molecular composition. Each of the tens to hundreds of pyrolysates typically detected by PyGCMS analysis of complex organic materials such as adhesive tape samples represents a potentially distinguishing aspect of a chemical fingerprint.

GCMS analysis has proved extremely important for the characterization of crude oils and oil-based samples (19,20), hence also has the potential to characterize and discriminate materials containing hydrocarbon products of oil. The distribution and abundance of petroleum biomarker compounds, the preserved and recognizable

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molecular evidence of formerly living organisms (e.g., algae, bacteria, plants) from which oils and organic matter rich sediments were formed, are the fundamental strategy of oil–oil and oil-source rock correlations important to oil exploration endeavors (20). Oil-derived hydrocarbon signatures detected by GCMS have previously provided important forensic evidence for oil spill identifications as well as incidents involving arson or explosives (21–28).

Another common hydrocarbon characterization technique that could extend the forensic characterization of adhesive tapes, and other petroleum-based materials, is bulk stable isotopic analysis. The stable isotopic composition of oils and their discrete hydrocarbons can be highly variable, dependant on the inherited value of their organic precursor and the degree of fractionation associated with any subsequent transformation processes (20). The forensic usefulness of stable isotope ratios has been on the rise, specifically helping determine the origin of illegal drugs (e.g., heroin, cocaine, and methylamphetamines), the identification of synthetic testosterone found in athletes (29,30), foodstuff authenticity, and ignitable liquids. Stable carbon, deuterium, and oxygen isotopic measurements of both whole tapes and their isolated polymer backing were found to readily distinguish different types of packaging tapes (31).

In this study, GCMS and elemental analysis isotope ratio mass spectrometry (EA-irMS) has been used to characterize and discriminate 32 adhesive tapes comprising eight colors sourced from eight manufacturers.

Experimental

Samples

The 32 adhesive tape samples (22 electrical, two duct, and eight gaffer tapes) analyzed in this study are listed in Table 1 together with their manufacturer and country of origin as determined from packaging details.

Extraction and Fractionation of Tape Samples

The adhesive tape samples (c. 2 g) were extracted with a dichloromethane (DCM):methanol (8:2; 100 mL) solvent mixture in an ultrasonic bath for 2 h. The total extract was separated into polarity-based fractions by small-scale column chromatography using a silica gel stationary phase. Saturate, aromatic, and polar fractions were successively eluted with 2 mL each of hexane, hexane:DCM (7:3), and DCM:methanol (1:1), respectively. The adhesive "sticky" moiety was scraped from the backing to provide a solid phase sample for EA-irMS.

GCMS

GCMS analysis of the saturate and aromatic fractions was performed using an Agilent (6890/5973) GCMS fitted with a 60 m × 0.25 mm i.d. fused silica capillary column coated with a 0.25 µm 5% phenyl–methyl–silicone stationary phase (DB5, J&W Scientific, Folsom, CA). Samples were injected using an autosampler into a vaporization injector at 280°C operated in pulsed splitless mode with helium carrier gas at a constant head pressure of 17.5 psi. The GC oven was programmed from an initial temperature of 40°C held isothermal for 1 min to increase at 3°C/min to 310°C held isothermal for a final 30–40 min. Full scan (m/z 50–550) and selected ion data were separately acquired with an ionization energy of 70 eV, a constant source temperature of 230°C, and a GC transfer line temperature of 300°C were used. Selected ions used to analyze the aromatic fraction included the m/z 128, 142, 156, 170 parent ions of naphthalene and the C_1–C_3 alkylnaphthalenes. Selected ions used to analyze the aliphatic fractions included m/z 191 and m/z 217, the diagnostic fragment ions of hopanes and steranes, respectively. Peak identification was based on GC elution order and full scan mass spectral interpretation. AGSO Standard Oil 2 was used as an instrument calibration and chromatogram peak reference standard. This sample is a mixture of five oils which collectively comprise the full suite of hopane and sterane biomarkers typically found in oils (32). Alkylnaphthalene isomers were identified through correlation with the alkylnaphthalene distribution of aromatic oil fractions analyzed extensively in our laboratory (e.g., 33). GCMS peak areas were integrated to report product abundances and biomarker ratios with a conservatively estimated error of ±5%.

Statistical Treatment of GCMS Data

The semi-quantitative GCMS data were treated with the XLSTAT (Addinsoft, Brooklyn, NY) linear discriminant analysis (LDA) statistical package. LDA is a classical statistical approach used to classify data sets of unknown sample classes, based on training data from samples of known classes.

EA-irMS

The bulk stable carbon isotopic composition of the adhesive moiety of the tapes was measured using a Micromass IsoPrime isotope ratio mass spectrometer interfaced to a EuroVector Euro-EA3000 elemental analyzer. A small aliquot (c. 0.3 mg, representing 50–120 µg carbon) of isolated adhesive moiety was weighed into a small tin capsule, folded, and compressed into a pellet to remove atmospheric gases, and then dropped into a combustion reactor held at 1025°C. The isotopic compositions were calculated by integration of the masses 44, 45, and 46 ion currents of the CO_2 peak. The $^{13}C/^{12}C$ composition is reported relative to that of a reference gas pulse produced by allowing carbon dioxide of known $^{13}C/^{12}C$ content into the mass spectrometer. Average values of at least two runs and standard deviations are reported. Isotopic compositions are given in the δ-notation relative to the Vienna-Pee-Dee Belemnite standard.

TABLE 1—List of adhesive tape samples.

Color	Scotch (U.S.A.)	RS (U.K.)	SM (China)	6X (France)	Anticor (China)	Cling (Indonesia)	Eurocel (S. Africa)	Norton (Australia)
Green	Electrical	Electrical	Electrical	Electrical	-	-	-	-
Red	Electrical	Electrical	Electrical	Electrical	-	Gaffer	-	-
Blue	Electrical	Electrical	Electrical	Electrical	-	-	Gaffer	-
Yellow	Electrical	Electrical	Electrical	-	-	Gaffer	-	-
White	Electrical	Electrical	Electrical	Electrical	-	-	Gaffer	-
Black	-	Gaffer	-	Electrical	-	Gaffer	Gaffer	-
Brown	-	-	-	-	Electrical	-	-	-
Gray/Silver	-	Gaffer	-	-	Electrical	Duct	-	Duct

Results and Discussion

Solvent Extraction of Tapes

The extractable proportion of the tapes ranged from 20% to 64% but showed no obvious trend with manufacturer. Visual examination indicated the adhesive component to be much more soluble than the backing material.

GCMS Analysis

GCMS of the aliphatic and aromatic fractions of the tapes yielded a large range of products and large qualitative differences between tapes. For example, the very different product profiles of the black gaffer and gray duct tapes are obvious from their total ion chromatogram data shown in Fig. 1. The saturate fraction of the black gaffer tape comprises several homologous series of $> C_{20}$ branched and cyclic aliphatic hydrocarbons in high abundance, whereas the duct tape (and also many of the electrical tapes) showed only trace amounts of resolvable aliphatic hydrocarbons. The major aromatic products detected from the tapes comprised parent and alkylated phenols and polycyclic aromatic hydrocarbons. A large hump was observed in the total ion chromatogram (TIC) baseline of the aliphatic and aromatic fractions of all tapes studied (e.g., Figs. 1a–d), indicative of a high degree of complexity and the co-elution of many unresolved products.

Such distinct TIC product profiles are useful for forensically distinguishing different materials. However, the analytical significance of the variation in product abundances needs to be better understood and discrete constituents within complex data reliably measured.

Lower abundances of hydrocarbon products typical of a petroleum source were also detected in the saturate and aromatic fractions of most of the tapes studied. The aromatic fractions of all the tapes contained alkylnaphthalenes in low concentration. Trace levels of hopanes and steranes, important petroleum biomarkers, were also detected in the aliphatic fraction of several of the tapes. Alkylnaphthalene, terpane, and sterane hydrocarbon distributions have proved particularly valuable for oil characterization studies (20)

including forensic investigations of petroleum accelerants (23–26). Given the low tape concentrations of these products, selected ion monitoring acquisition was used to target their detection.

C_0–C_3 Alkylnaphthalene Distributions

Selected ion chromatograms showing the C_0–C_3 alkylnaphthalenes of the aromatic fraction of the red 6X electrical tape are shown in Fig. 2. The isomeric identity of these products and the relative abundances with which they were detected in all tapes studied is typically based on visual comparison of mass chromatograms or on product ratios. The peak area ratio of related products is by their nature more precise than absolute concentrations, provided analytical conditions remain identical.

Several features of the alkylnaphthalene distribution of the tapes (Table 2) reveal a nominal correlation with the manufacturer. For example, the Cling (CL) gaffer tapes all show a relatively high abundance of naphthalene (>74% of C_{0-3} naphthalenes; Table 2) and the Scotch (SC) tapes have generally lower total abundances of C_3 naphthalenes (all but blue <30%) compared to the RS electrical and gaffer tapes (all but white electrical >30%). Greater distinction of tape samples on the basis of their alkylnapthalene profiles was sought by multivariate LDA of the relative concentrations (i.e., peak areas) of each of the C_0–C_3 alkylnaphthalene products.

LDA of Alkylnaphthalene Peak Abundances

LDA can significantly increase the quantitative interpretation of GCMS data and frequently provides an unbiased and defensible means to differentiate quantitatively similar data with high resolution (19). The powerful correlation capacity of chemometric assessment of GCMS fingerprints of oil hydrocarbons has been recently demonstrated (23–28).

Sample discrimination increases with the number of variables of LDA classification, but a larger number of variables also increase the complexity of the analysis. Hence, the amount of variance accounted for by the most abundant C_0–C_3 alkylnaphthalene (Table 2) constituents in relation to classification of the 22
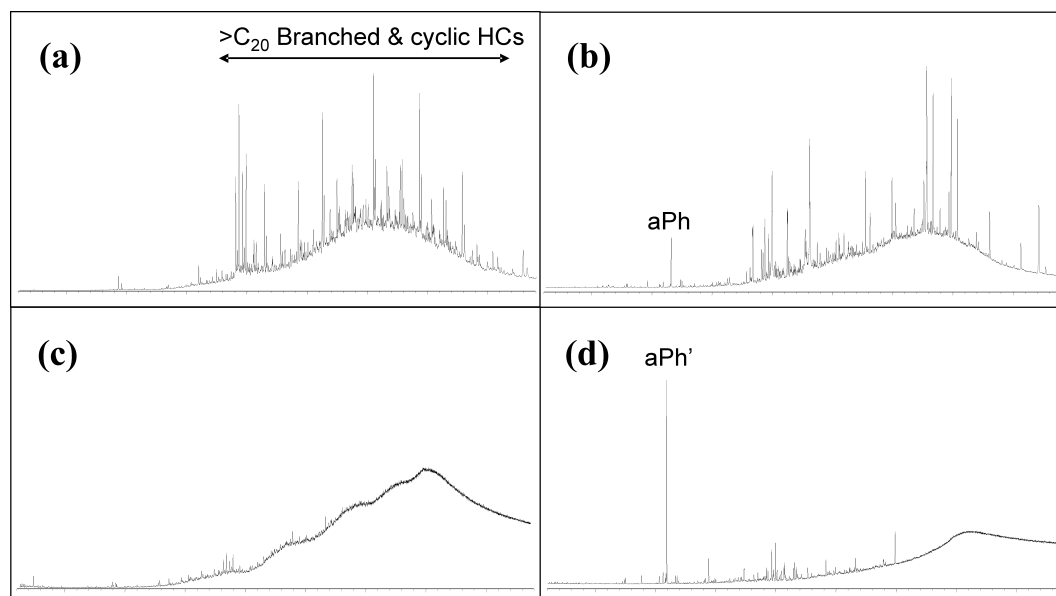

FIG. 1—TIC of the (a) saturate and (b) aromatic fractions of the Cling black gaffer tape, and (c) saturate and (d) aromatic fractions of the Norton Silver duct tape. Each of a–d reflect a retention time window of 20–110 min. aPh, alkylated phenol product.
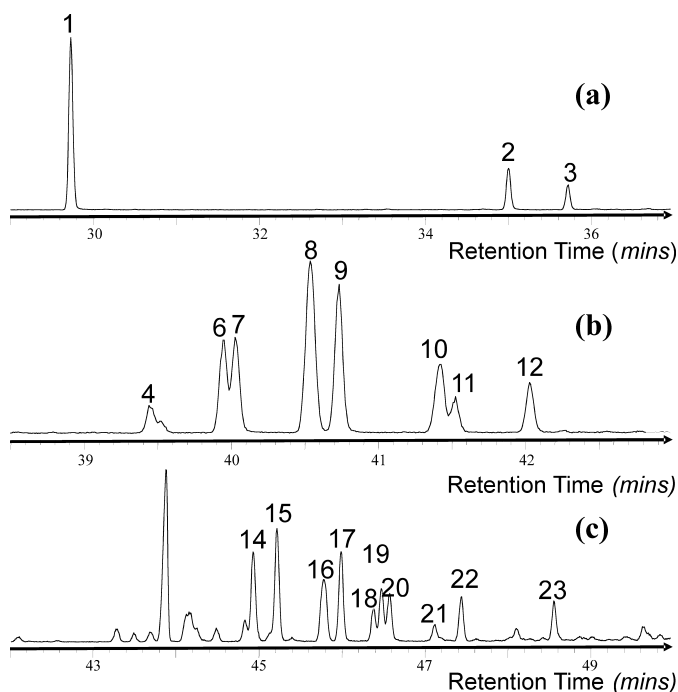
FIG. 2—*Partial selected ion chromatograms of (a) m/z 128 + m/z 142, (b) m/z 156, and (c) m/z 170 displaying C_0–C_3 alkylnaphthalenes detected by GCMS analysis of the aromatic fraction of the red 6X tape. Peak assignments correspond to products listed in Table 2.*

electrical and eight gaffer tapes were correlated with their known manufacturer to construct a training set for the LDA model. Products which were consistently <2% (i.e., 18DMN and 124TMN) limited the accuracy of the principal component analysis (PCA) and discriminant analysis (DA), and hence were excluded from these assessments.

Covariance-based PCA of the data showed that the first three principal components (PCs) accounted for 97% of the variance in the data (PC1 90.6%, PC2 5.1%, and PC3 1.3%) and was successfully able to distinguish the CL and Eurocel (EC) from the remaining tape groups as shown in Fig. 3. CL tapes are readily identified on the first PC (Fig. 3a) and EC tapes are distinguishable on the first and third PCs (Fig. 3b). Correlation-based PCA was less successful in distinguishing tape groups, probably due to the increased weighting given to small components and the amplification of noise. Analysis of the contributions to the covariance-based PCs showed that the CL tapes are most distinguishable on the basis of their very high naphthalene content (Table 2c), although the separation of the EC tapes was not readily attributed to a single compound or group of compounds. The ability of an unsupervised classification method, such as PCA, to at least partially discriminate between the tapes suggested that a supervised classification method, such as DA, would fare better.

Discriminant analysis (DA) of the data showed that four Factors (F) were required to account for the 97% equivalent variance of the first three PCs (F1 82.5%, F2 8.0%, F3 3.9%, and F4 2.9%). The first two factors readily discriminate between Anticor (AN), CL, EC, RS electrical and SM tapes but not between 6X, RS gaffer and SC tapes (Fig. 3c). Separation of the latter three tapes required inclusion of F3 and F4 (Fig. 3d).

Two tapes extraneous to the training set (the CL and Norton Duct tapes) were plotted to assess the robustness of the classification (Figs. 3c and 3d). The alkylnaphthalene distribution of both duct tapes is clearly distinguished from the other tapes. The DA

process attempts to classify the data of the unknown tapes with one of trained groupings. The Norton duct tape, for example, most closely aligns with the RS and SC electrical tape groupings of the trained data, but it does not cluster nearly as tightly as the other tapes of these groupings, correctly indicating its exotic character. The precision of LDA classifications can be inferred from the distance between the data points within a particular group, with smaller distances giving rise to more confident correlation.

While successfully demonstrating the feasibility of the chemometric treatment of oil-derived alkylnaphthalene abundances for distinguishing different types of pressure-sensitive adhesive tapes, the present assessment was limited by the small data set and trace levels of some alkylnaphthalene products. Larger samples sets (more samples and replicate analysis) and higher concentrations of extractable hydrocarbons are recommended with this approach.

Hopane and Sterane Distributions

Only trace amounts of hopane and sterane hydrocarbons were detected in the tape samples, with highest abundances generally detected in the SC and gaffer tapes. These ubiquitous high MW cyclic hydrocarbons are often highly specific of oil type, which combined with a recalcitrance to early biodegradation make them particularly useful oil diagnostic markers. However, they are typically present in oils in much lower concentration than normal alkanes, alkylnaphthalenes, and most other hydrocarbon constituents.

The m/z 191 and m/z 217 chromatogram from selected ion analysis of the black EC gaffer tape is shown in Fig. 4, with a list of the major hopane and sterane products shown in Table 3. The C_{30} hopane ($C_{30}H$) was typically the major hopane detected and the two extended hopane ($\geq C_{31}$) stereoisomers (S and R), arising from the chiral centre at C_{22}, were also often prominent (Fig. 4a). The steranes profile showed both C_{27} and C_{29} steranes (Fig. 4b) indicative of oil comprising both terrestrial and marine organic matter inputs (20).

Many biomarker-based parameters have been developed over the last 30 years largely by empirical association of hydrocarbon biomarker features with particular geological settings. These rules have also been increasingly underpinned by proven links among hydrocarbon compounds, their biological precursors, and the types of environment in which the parent organisms lived (20).

Where measurable, the relative concentration of the major hopane and sterane products of the gaffer, duct, and several electrical tapes were used to calculate the value of source and maturity parameters (Table 4) defined from organic geochemistry studies (20). This small data set reflects several quite distinct differences among tape manufacturers including the relatively high T_s/T_m value of the CL and SM tapes, high $C_{29}H/C_{30}H$ value of the RS and EC gaffer tapes and the two duct tapes, and high C_{27} $\beta\alpha S/C_{27}\alpha\alpha\alpha S$ value of the duct and EC gaffer tapes.

Despite the low hopane and sterane concentrations reported here, which could be easily increased by extraction of more of the tape material, the limited data set shown in Table 4 demonstrates the oil diagnostic utility of these biomarker products.

Stable Carbon Isotope Analysis

The $\delta^{13}C$ results from EA-irMS analysis of the adhesive layer of the electrical tape samples are listed in Table 5. The $\delta^{13}C$ values of the electrical tapes range from −26.5 to −29.4‰. The SM and 6X electrical tapes are the most ^{13}C depleted with values ranging between −28.9 and −30‰. The SC tapes are the least depleted with $\delta^{13}C$ values ranging between −26.5 and −27.0 ‰, apart from

TABLE 2—*Relative abundances of the C_0–C_3 alkylnaphthalenes detected in the aromatic fraction of (a) Scotch and SM electrical tapes (b) 6X, RS, and Anticor electrical tapes, and (c) RS, Eurocel, and Cling gaffer tapes and Cling and Norton Silver Duct tapes.*

				SCOTCH					SM				
Peak	Product	Abbrev	MW	Green	Red	Blue	Yellow	White	Green	Red	Blue	Yellow	White
(a)													
1	naphthalene	N	128	31.9	34.9	25.3	27.8	24.3	11.9	21.5	19.1	36.2	11.7
2	2-methylnaphthalene	2MN	142	11.7	17.1	8.8	11.4	9.3	9.6	11.6	8.0	13.2	6.7
3	1-methylnaphthalene	1MN	142	6.2	13.1	5.3	8.2	6.0	6.3	6.0	4.9	9.8	4.1
4	2-ethylnaphthalene	2EN	156	0.6	1.1	1.0	1.1	1.4	2.7	2.7	1.4	1.0	1.4
5	1-ethylnaphthalene	1EN	156	0.6	0.3	0.0	0.3	0.3	0.2	0.3	0.2	0.5	0.1
6	2,6-dimethylnaphthalene	26DMN	156	2.1	1.9	2.9	2.5	3.3	4.5	4.0	3.2	3.2	3.4
7	2,7-dimethylnaphthalene	27DMN	156	2.6	2.8	2.9	2.0	3.5	4.6	3.7	3.0	3.2	3.4
8	1,3- & 1,7-dimethylnaphthalene	13&17DMN	156	5.7	5.6	6.6	6.9	8.2	11.0	10.2	8.4	8.3	9.1
9	1,6-dimethylnaphthalene	16DMN	156	4.3	3.7	5.3	4.6	6.6	6.2	5.9	5.0	5.1	4.7
10	1,4- & 2,3-dimethylnaphthalene	14&23DMN	156	2.1	2.6	2.6	2.6	3.3	4.2	3.9	3.3	1.7	3.7
11	1,5-dimethylnaphthalene	15DMN	156	1.3	0.7	1.3	1.3	1.4	1.3	0.4	1.0	2.0	1.0
12	1,2-dimethylnaphthalene	12DMN	156	1.0	1.2	1.7	1.6	2.3	2.0	2.8	1.9	1.5	1.8
13	1,8-dimethylnaphthalene	18DMN	156	0.2	0.3	0.1	0.5	0.1	0.3	0.5	0.1	0.2	0.3
14	1,3,7-trimethylnaphthalene	137TMN	170	4.0	1.8	4.1	3.7	3.8	6.9	4.8	6.7	1.7	7.9
15	1,3,6-trimethylnaphthalene	136TMN	170	4.8	2.4	5.0	4.5	5.5	6.9	5.5	7.8	3.1	9.7
16	1,4,6- & 1,3,5-trimethylnaphthalene	146&135TIW	170	5.6	2.0	4.7	4.2	5.0	5.8	4.0	6.2	3.2	7.0
17	2,3,6-trimethylnaphthalene	236TMN	170	3.5	1.4	3.8	3.3	4.1	6.3	3.8	7.9	1.7	9.6
18	1,2,7-trimethylnaphthalene	127TMN	170	1.5	0.6	0.3	1.6	1.7	1.7	1.6	2.0	0.6	2.5
19	1,6,7-trimethylnaphthalene	167TMN	170	2.3	1.2	1.7	2.5	2.7	2.4	2.3	3.2	1.2	4.4
20	1,2,6-trimethylnaphthalene	126TMN	170	1.7	0.8	12.2	2.3	2.1	1.4	1.7	2.0	0.6	3.1
21	1,2,4-trimethylnaphthalene	124TMN	170	0.9	0.6	0.9	0.9	0.9	1.6	0.6	1.6	0.3	1.3
22	1,2,5-trimethylnaphthalene	125TMN	170	3.6	1.8	3.0	3.0	3.5	1.9	1.7	2.3	0.9	2.2
23	1,4,5-trimethylnaphthalene	145TMN	170	1.7	2.3	0.5	3.1	0.5	0.3	0.6	1.0	0.6	0.9
		Total C2N	156	20.5	20.1	24.3	23.5	30.4	37.1	34.2	27.5	26.7	29.0
		Total C3N	170	29.7	14.8	36.3	29.1	30.0	35.1	26.6	40.5	14.1	48.5

	6X					RS—Electrical					Anticor	
Peak	Red	Green	Blue	Black	White	Green	Red	Blue	Yellow	White	Brown	Gray
(b)												
1	31.5	15.4	6.5	23.9	16.6	25.1	17.9	22.5	18.4	38.3	31.2	4.7
2	8.2	10.3	5.8	12.0	7.9	7.8	7.0	9.7	7.8	8.3	11.8	17.7
3	4.8	6.6	4.3	7.0	4.5	4.9	4.4	5.4	5.3	5.2	6.3	13.6
4	0.9	0.6	0.9	1.3	1.4	1.3	1.9	1.6	1.6	0.2	0.9	1.6
5	0.6	1.2	2.9	3.7	0.3	0.1	1.9	0.1	0.0	0.1	0.0	0.0
6	3.0	5.4	2.9	3.7	2.6	3.3	3.6	2.1	3.1	2.7	2.7	5.4
7	3.0	6.7	2.9	3.5	2.6	3.0	3.5	2.4	3.0	2.5	2.7	5.9
8	6.7	13.8	7.6	7.9	7.4	7.3	7.4	6.5	8.3	6.5	6.4	13.8
9	4.8	8.4	5.1	5.3	5.0	5.9	6.0	4.2	6.0	5.4	5.0	7.5
10	2.7	3.1	3.4	3.1	3.1	3.0	3.3	2.4	3.2	2.3	2.5	4.5
11	1.0	1.1	0.9	1.0	1.3	1.3	1.5	1.0	1.6	1.0	1.1	1.5
12	1.6	1.1	2.4	1.6	2.0	1.9	2.2	1.7	2.4	1.7	1.4	2.7
13	0.0	0.8	0.2	0.0	1.0	0.0	0.7	0.5	0.2	0.3	0.0	0.1
14	4.2	3.1	7.5	3.9	6.8	4.9	6.6	1.3	5.8	4.8	5.2	3.8
15	5.5	5.2	10.5	5.2	7.8	6.0	7.0	6.9	6.9	4.1	5.3	4.4
16	4.0	4.5	8.0	3.7	7.5	5.7	6.7	7.1	6.8	3.7	4.3	3.4
17	4.2	3.6	7.7	3.7	6.0	4.8	4.9	5.5	5.0	3.2	3.9	3.1
18	1.5	1.1	2.5	1.3	2.3	2.1	2.0	2.9	2.4	1.3	1.5	1.2
19	2.5	1.1	4.8	3.6	4.2	2.9	2.9	4.1	3.4	1.8	2.4	1.7
20	2.3	2.0	4.3	2.0	3.4	2.5	2.9	3.7	3.1	1.9	2.2	1.4
21	1.0	1.4	1.5	0.7	1.6	1.1	1.1	1.7	1.4	1.1	0.9	1.0
22	2.0	2.4	3.7	1.7	4.1	4.8	4.1	5.9	3.9	3.5	1.9	0.8
23	1.7	1.2	3.9	0.4	0.6	0.2	0.3	0.6	0.4	0.1	0.3	0.1
Total C2N	24.3	42.1	29.2	31.1	26.8	27.1	32.0	22.6	29.5	22.6	22.8	42.9
Total C3N	28.9	25.6	54.3	26.1	44.2	35.1	38.6	39.8	39.0	25.5	27.9	21.0

	RS—Gaffer		Eurocel			Cling				Norton Silver
Peak	Black	Gray	Black	Blue	White	Black	Red	Yellow	Duct	Duct
(c)										
1	35.8	32.2	12.9	9.1	5.7	85.8	74.2	75.1	6.9	19.2
2	4.9	6.2	13.1	9.3	22.9	5.8	4.6	9.5	2.8	3.6
3	3.3	4.0	4.0	4.3	4.8	3.5	3.0	4.5	2.3	2.6
4	4.0	0.9	6.2	5.8	2.5	0.1	0.0	0.2	1.0	1.1
5	0.3	0.0	0.5	0.4	0.2	0.0	0.0	0.6	0.0	0.2
6	2.1	3.3	4.5	4.5	3.8	0.3	0.8	0.6	3.1	2.1

TABLE 2—Continued.

Peak	RS—Gaffer Black	RS—Gaffer Gray	Eurocel Black	Eurocel Blue	Eurocel White	Cling Black	Cling Red	Cling Yellow	Cling Duct	Norton Silver Duct
7	2.2	3.2	3.2	3.1	3.5	0.2	0.8	0.5	2.8	2.1
8	4.3	6.7	7.7	8.7	8.2	0.6	1.9	1.2	7.0	5.5
9	3.6	5.9	5.0	6.2	5.4	0.4	1.6	1.0	6.0	4.6
10	1.6	2.8	3.6	3.6	3.8	0.3	0.9	0.5	3.9	2.6
11	1.8	1.2	3.4	2.2	1.6	0.2	0.5	0.2	1.4	1.7
12	1.0	1.3	0.1	2.2	2.3	0.1	0.6	0.3	1.5	1.7
13	0.8	0.0	0.1	0.2	0.1	0.4	0.6	0.0	0.0	0.1
14	5.4	4.7	4.9	5.3	4.8	0.3	1.6	0.8	7.6	6.1
15	6.2	5.9	7.7	9.0	6.8	0.4	2.0	1.1	9.7	8.6
16	5.3	5.2	6.5	7.7	5.9	0.4	1.8	0.9	9.9	10.0
17	4.1	4.6	4.8	4.8	4.7	0.3	1.4	0.8	8.5	7.0
18	1.9	1.9	1.5	1.9	2.1	0.2	0.5	0.3	3.9	2.8
19	2.6	3.3	2.4	3.0	3.1	0.3	1.0	0.5	7.5	4.9
20	2.8	2.3	2.3	3.4	2.9	0.2	0.7	0.4	4.6	4.3
21	1.4	0.9	1.4	1.4	1.4	0.0	0.2	0.2	1.9	1.5
22	4.2	3.1	2.4	3.4	3.1	0.2	1.1	0.5	6.8	6.6
23	0.4	0.3	1.7	0.5	0.5	0.1	0.1	0.1	0.7	1.1
Total C2N	21.7	25.4	34.5	36.9	31.3	2.6	7.8	5.2	26.8	21.6
Total C3N	34.3	32.2	35.5	40.4	35.3	2.4	10.4	5.6	61.2	53.0

Peak numbers in (a)–(c) correspond to products indicated in (a). Abundances are calculated from peak areas and expressed as a percentage of the total C_0–C_3 alkylnaphthalene signal. The summed abundances of C_2 and C_3 naphthalenes are also indicated.
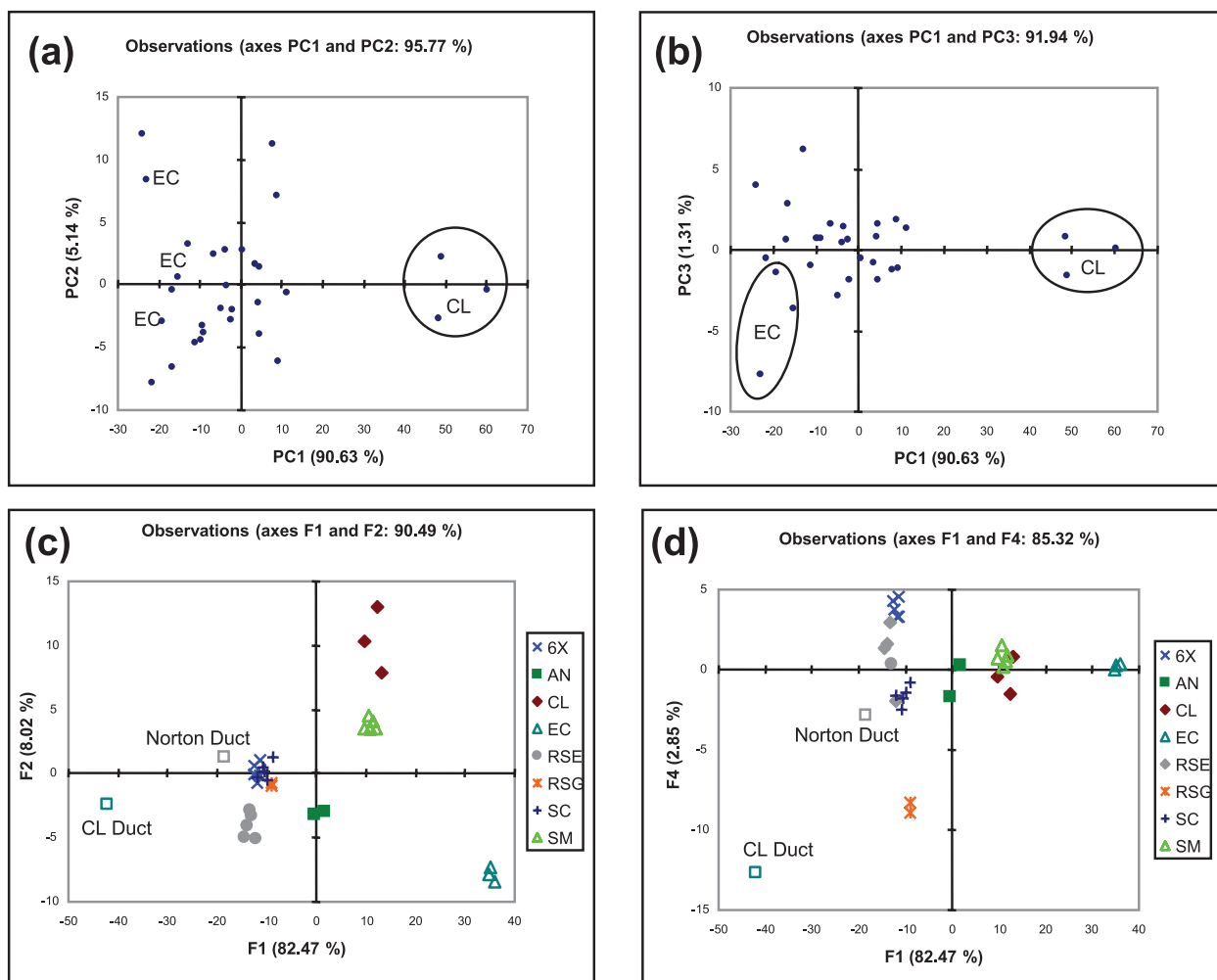

FIG. 3—LDA classification plots of the relative GCMS abundances of the C_0–C_3 alkylnaphthalene products of the electrical and gaffer adhesive tapes showing covariance PCA discrimination of (a) Cling tapes on PC, (b) Cling and Eurocel tapes on PC1 and PC3, discriminant analysis differentiation of (c) AN, CL, EC, SM, and RSE tapes on F1 and F2, and (d) 6X, RSG, and SC tapes on F4. The additional untrained data from the Norton and Cling Duct tapes are also shown in (c) and (d).
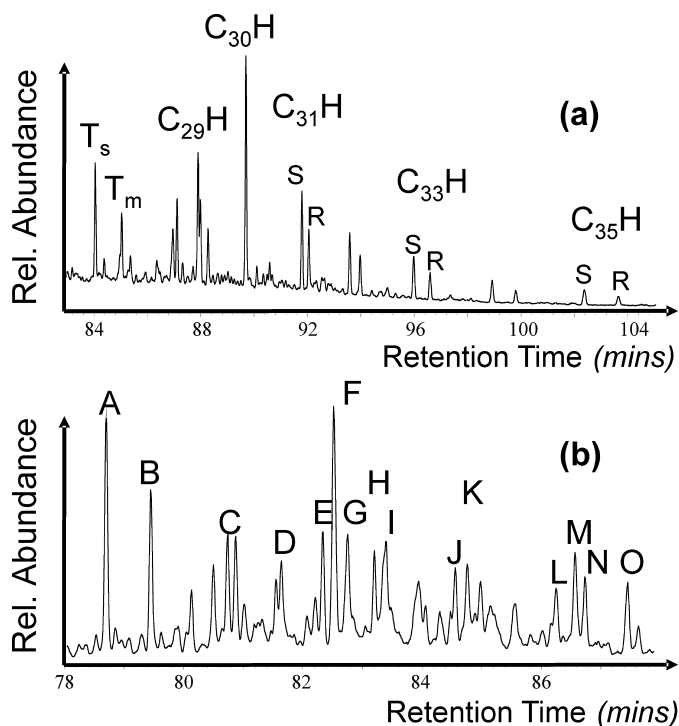
FIG. 4—*Partial selected ion chromatograms of (a)* m/z 191 *(hopane profile) and (b)* m/z 217 *(sterane profile) detected by GCMS analysis of the Eurocel black gaffer tape. Peak assignments correspond to products listed in Table 3.*

TABLE 3—*Hopane and sterane biomarkers detected by GCMS analysis of the aliphatic fraction of the tape extracts.*

Abbreviation	MW	Hopane Identity
T_s	372	$18\alpha,21\beta$-22,29,30-trisnorneohopane
T_m	372	$17\alpha,21\beta$-22,29,30-trisnorhopane
$C_{29}H$	398	$17\alpha,21\beta$-30-norhopane
$C_{30}H$	412	$17\alpha,21\beta$ hopane
$C_{31}HS$	426	$17\alpha,21\beta$-30-homohopane (22S)
$C_{31}HR$	426	$17\alpha,21\beta$-30-homohopane (22R)
$C_{32}HS$	440	$17\alpha,21\beta$-30-bishomohopane (22S)
$C_{32}HR$	440	$17\alpha,21\beta$-30-bishomohopane (22R)
$C_{33}HS$	454	$17\alpha,21\beta$-30-trishomohopane (22S)
$C_{33}HR$	454	$17\alpha,21\beta$-30-trishomohopane (22R)
A (C_{27} $\beta\alpha20S$)	386	$13\beta,17\alpha$-diacholestane 20S
B (C_{27} $\beta\alpha20I$)	386	$13\beta,17\alpha$-diacholestane 20R
C (C_{28} $\beta\alpha20S$)	400	$13\beta,17\alpha$-diaergostane 20S (24S + R)
D ($C_{28}\beta\alpha20R$)	400	$13\beta,17\alpha$-diaergostane 20R (24S + R)
E ($C_{27}\alpha\alpha\alpha20S$)	386	$5\alpha,14a,17\alpha$-cholestane 20S
F ($C_{29}\beta\alpha20S$/ $C_{27}\alpha\beta\beta20R$)	414/386	$13\beta,17\alpha$-diastigmastane 20S/ $5\alpha,14\beta,17\beta$-cholestane 20R
G ($C_{27}\alpha\beta\beta20S$)	386	$5\alpha,14\beta,17\beta$-cholestane 20S
H ($C_{27}\alpha\alpha\alpha20R$)	386	$5\alpha,14a,17\alpha$-cholestane 20R
I ($C_{29}\beta\alpha20R$)	414	$13\beta,17\alpha$-diastigmastane 20R
J $C_{28}\alpha\beta\beta20R$)	400	$5\alpha,14\beta,17\beta$-ergostane 20R
K ($C_{28}\alpha\beta\beta20S$/ Bicad.)	400/412	$5\alpha,14\beta,17\beta$-ergostane 20S/ Bicadinane T1
L ($C_{29}\alpha\alpha\alpha20S$)	414	$5\alpha,14a,17\alpha$-stigmastane 20S
M ($C_{29}\alpha\beta\beta20R$)	414	$5\alpha,14\beta,17\beta$-stigmastane 20R
N ($C_{29}\alpha\beta\beta20S$)	414	$5\alpha,14\beta,17\beta$-stigmastane 20S
O ($C_{29}\alpha\alpha\alpha20R$)	414	$5\alpha,14a,17\alpha$-stigmastane 20R

TABLE 4—*Oil source dependent hopane and sterane biomarker ratios detected by GCMS analysis of the aliphatic fraction of tape extracts.*

Sample	T_s/T_m	$C_{29}H/$ $C_{30}H$	$C31R/$ $C30H$	$C_{27}\beta\alpha S/$ $C_{27}\alpha\alpha\alpha R$
Scotch White	0.99	0.64	0.15	-
Scotch Red	0.95	0.64	0.21	-
SM Red	2.24	0.71	0.05	-
SM Green	2.16	0.47	0.20	-
SM Black	2.16	0.78	0.09	-
RS Black Gaffer	1.10	0.93	0.27	0.65
RS Gray Gaffer	1.20	1.06	0.31	0.82
RS Black Elec.	1.38	0.74	0.32	11.92
Cling Black Gaffer	2.48	0.54	0.23	7.36
Cling Red Gaffer	2.37	0.52	0.24	6.90
Cling Yellow Gaffer	2.52	0.54	0.23	6.90
Cling Black Duct	2.26	1.03	0.24	15.99
Eurocel black	1.14	0.61	0.33	28.18
Eurocel blue	0.93	0.91	0.61	42.13
Eurocel white	1.03	0.90	0.35	22.86
Norton Silver Duct	1.47	0.86	0.19	27.50

TABLE 5—*The $\delta^{13}C$ data from the EA-irMS analysis of the adhesive layer of the electrical tape samples.*

Sample	$\delta^{13}C$ (‰) Average	Standard Deviation
Scotch Green	−26.8	0.01
Scotch Red	−26.9	0.16
Scotch Blue	−26.9	0.17
Scotch Yellow	−27.9	0.09
Scotch White	−26.5	0.26
SM Green	−28.9	0.16
SM Red	−28.9	0.11
SM Blue	−29.0	0.05
SM Yellow	−28.9	0.05
SM White	−29.0	0.01
6X Red	−29.4	0.08
6X Green	−29.3	0.17
6X Blue	−29.1	0.14
6X Black	−28.9	0.02
6X White	−29.3	0.34
RS Green	−27.7	0.14
RS Red	−27.7	0.04
RS Blue	−27.2	–
RS White	−27.2	–
RS Yellow (1)	−27.6	0.10
RS Yellow (2)	−27.7	0.11
RS Yellow (3/1)	−27.8	0.12
RS Yellow (3/2)	−27.5	0.08
RS Yellow (3/3)	−27.3	0.01

Three batches and three rolls (of batch 3) of the RS Yellow tapes were separately analyzed.

Three batches and three rolls (of batch 3) of the RS Yellow tapes were separately analyzed. Consistent $\delta^{13}C$ values were obtained from these analyses with all values within 0.5‰.

The variance in the $\delta^{13}C$ data of different tapes likely reflects the small variances in the stable carbon isotopic composition of the oils used by the different manufactures in their production. While not reflecting the same level of distinction as the molecular distributions (e.g., alkylnaphthalene), the stable carbon isotopic data do support the sample distinctions indicated by the molecular profiles.

Interestingly, the stable carbon isotopic value measured for the backing (i.e., excluding the oil element of the adhesive fraction of interest here) of a selection of brown packaging pressure-sensitive adhesive tapes was shown to span a similar range from −25 to −29‰ (31). The similarity of the $\delta^{13}C$ values of the backing

the blue tape which has the significantly more depleted value of −27.8‰. The RS tapes are more tightly constrained with values between −27.2 and −27.7‰. A 0.5‰ $\delta^{13}C$ variance was typical for tapes of a given manufacturer with the reproducibility or random error associated with bulk EA-irMS analysis typically 0.1‰.

moiety (usually made of polypropylene or some other polymer) measured by Carter et al. (31) and the adhesive moiety measured here probably reflect the common use of petroleum products in the preparation of both materials.

Conclusions

GCMS analysis of the solvent extractable fractions of adhesive tapes detected low concentration of alkylnaphthalene, hopane, and sterane hydrocarbon products. Tapes from different adhesive tape manufacturers were distinguished by small variances in the distributions of these oil-derived hydrocarbons. LDA assessment of the relative abundances of alkylnapthalene products provided conclusive discrimination of the tape manufacturer identity, with the LDA classification able to correctly correlate data from foreign tape samples not used in the trained model. Stable carbon isotope ($\delta^{13}C$) signatures of the adhesive layer of the tapes also showed a small, but measurable difference between tapes from different manufacturers.

The molecular hydrocarbon and isotopic analyses of the pressure-sensitive adhesive tapes contributes to a detailed chemical fingerprint from which different manufacturers could be distinguished. Characterization of the tapes could be further extended by incorporation of additional petroleum hydrocarbon products or other stable isotopic values (e.g., δD, $\delta^{15}N$, $\delta^{34}S$), as well as by extraction of larger sample amounts to allow measurement of more of the biomarkers of low concentration. This study demonstrates the forensic potential of established petroleum analytical methods for characterizing adhesive tape samples. This strategy will be broadly applicable to many common materials comprising petroleum products (e.g., polymers, lubricants, condoms, etc.).

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