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The Analysis of Forensic Samples Using Laser Micro-Pyrolysis Gas Chromatography Mass Spectrometry

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ABSTRACT: Laser micro-pyrolysis gas chromatography-mass spectrometry is used for the analysis of paint, photocopier toner, and synthetic fiber materials to test the forensic potential of this emerging technology. It uses a laser microprobe to selectively target very small parts of the materials for GC-MS analysis. Whereas the paint and the toner samples were amenable to direct laser pyrolysis, the synthetic fibers proved transparent to the 1064 nm laser radiation. The difficulty with the fibers demonstrates that a specific laser wavelength may not be appropriate for all types of materials. Nevertheless, the fibers were able to be indirectly pyrolyzed by impregnation in a strongly absorbing graphite matrix. A vast array of hydrocarbon pyrolysates was detected from the different materials studied. Unique product distributions were detected from each sample and in sufficient detail to facilitate individual molecular characterization (i.e., molecular fingerprinting). The integrity of the laser data were confirmed by comparison to data obtained from the same samples by the more conventional pyroprobe pyrolysis GC-MS method. The high spatial resolution and selectivity of the laser method may be advantageous for specific forensic applications, however, further work may be required to improve the reproducibility of the data.

KEYWORDS: forensic science, paint, synthetic fibers, photocopier toner, pyrolysis, laser, gas chromatography, mass spectrometry

The molecular analysis of the trace amounts of organic material left at the scene of a crime may make an important contribution towards linking a suspect to the scene (1). Gas chromatography mass spectrometry (GC-MS) combines the separating abilities of GC with the identification powers of MS and is an important forensic tool of molecular analysis. It is commonly used to analyze for such volatile materials as fire and explosive debris, blood alcohol, and many drugs of abuse (2). However, many other materials of forensic interest are involatile and not directly amenable to these gaseous analyt-

ical methods (e.g., paint, fibers, soils, rubbers, plastics, and adhesives). Chemically intractable substances must first be pyrolyzed or extracted with solvents prior to GC-MS analysis. Pyrolysis (Py) GC and PyGC-MS are well-established techniques for the characterization of complex, involatile samples of forensic interest (2).

Pyrolysis can generally be regarded as a minimally destructive technique since the sample amounts consumed are typically very small (~mg's). This is important since forensic evidence is often limited to trace quantities and it is useful to preserve as much of it as possible for further examination. However, traditional bulk pyrolysis methods do not account for the physical and chemical heterogeneity often inherent in very small and complex organic materials. Micro analytical techniques (e.g., micro-FTIR spectrometry, micro-spectrophotometry) that facilitate the separate analysis of distinct moieties within complex materials have an increasing application in forensic science. The recently developed laser-micro-pyrolysis GC-MS (3–8) is another such technique, and here its potential for forensic analysis is examined.

Laser micro-pyrolysis GC-MS offers several advantages over traditional methods of analytical pyrolysis. Foremost, these include: 1) the pyrolysis of very small samples or very small parts of samples—by focusing the laser output to very localized areas; and 2) relatively high detection sensitivity—due to optimum transfer of pyrolysates to the GC via a purpose built inlet system.

The representative forensic samples used in this study were automobile paints, synthetic fibers, and photocopy toners. The former two represent typical types of trace evidence while the latter may be directly linked to the source of questioned documents. The wide variety of presently used paints (automotive and industrial), synthetic fibers and photocopier toners (black and colored) can usually be distinguished on the basis of their molecular composition as determined by pyrolysis GC-MS (1). The limited sensitivity of PyGC (MS) has at times attracted criticism, however, sufficient molecular detail for identification purposes has been obtained from single fibers with the use of contemporary pyrolyzers and GC systems (1,9). The potential for detailed molecular characterization of photocopy toners (10–14) and inks (15) to assist in the investigation of crimes such as counterfeiting, fraud and forgery has also been previously demonstrated.

The samples were also analyzed by pyroprobe (filament) pyrolysis GC-MS to provide more traditional data for comparative purposes. The discriminative capabilities of the two pyrolysis methods was particularly scrutinized. Sensitivity, reproducibility, degree of destructivity, and associated sample preparation were briefly evaluated for laser micro-pyrolysis GC-MS analysis.

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Experimental

Materials

Five automotive paints, 11 photocopier toners, and 16 different fiber types were examined. Details regarding the source and physical characteristics of these samples are given in Table 1. The same paints were recently examined by conventional optical and solubility tests, FT-IR spectrometry and micro-spectrophotometry (16). They constitute a range of colors (white, blue, yellow green, and red), type (metallic and nonmetallic) and degrees of lamination (i.e., numbers of layers).

The toners were obtained directly from several manufacturers. Black toners were obtained from Mita ($\times 3$) and four other manu-

TABLE 1—Forensic materials studied by pyrolysis GC-MS.

Automotive Paint Samples				
Topcoat Color	Model	Layers	Topcoat Composition	Metallic?
White	1990 Ford Laser	3	Refinished acrylic/methyl methacrylate	no
Blue	1991 Ford Falcon	8	Refinished acrylic urethane plus styrene	yes
Yellow	1985 Toyota Corona	3	Acrylic with inorganic pigments and extenders	no
Green	1993 Daihatsus Charade	4	Original acrylic urethane plus styrene	yes
Red	1985 Holden Gemini	6	Original acrylic urethane plus styrene	no

Photocopier Toner Samples		
Color	Manufacturer	Type
Black	Fujitsu	Print Partner 10/14
Black	Lanier	M6745/35
Black	Mita	DC1860
Black	Mita	DC3060
Black	Mita	DR3020
Black	Sanyo	SFT/50
Black	Toshiba	7550
Yellow	Canon	Color laser copier 800
Blue	Canon	Color laser copier 800
Magenta	Canon	Color laser copier 800
Black	Canon	Color laser copier 800

Synthetic Fiber Samples		
Fiber Type	Trade Name	CTS ID No.
Acetate	Estron	A0066
Acrylic	Orlon	A0011
Aramid	Kevlar	H0009
Modacrylic	Verel	A0068
Nylon	Nylon 6	A0163
Olefin	Polypropylene	A0034
Olefin	Polyethylene	A0407
Polyester	Dacron (PET)	A0001
Rayon	Avril	A0088
Saran	—	A0153
Spandex	Lycra	A0015
Vinyon	—	A0098
Fluorocarbon	Teflon	A0023
Polycarbonate	Monobaste	A0154
Sulfar	Ryton	A0327

facturers. Blue, magenta, yellow, and black colored toners were all obtained from Canon. The paints and toners were analyzed by laser microprobe directly from their respective paper supports, whereas for pyroprobe analysis, small quantities of toner had to be etched first from the substrate.

The synthetic fiber samples were obtained from the Collaborative Testing Services (CTS-PO Box 1049, Herndon, VA) Reference Collection of Synthetic Fibers. The fiber samples proved transparent to the 1064 nm radiation and were unable to be directly pyrolyzed by the Nd:YAG laser used in the present study. They were able to be indirectly pyrolyzed, however, by impregnation (physically by hand) in a strongly absorbing graphite substrate.

Laser Microprobe Pyrolysis

The laser microprobe GC-MS apparatus has been described in detail elsewhere (7,8). The main components of the instrument are a laser, microscope, and GC-MS. A schematic of the overall instrument is shown in Fig. 1.

The laser microprobe facilitates sample viewing and selection of the part of the sample to be pyrolyzed. The fundamental beam (1064 nm, near infrared) from a Laser Applications (9500) continuous wave Nd:YAG laser was used. The maximum energy available from this laser was measured to be 30 W/s, but pyrolysis of the forensic samples was typically achieved with lower energies (13 to 23 W/s) by regulation of the output energy from the laser power console. An Olympus (BH2) microscope was used for visual observation of the sample and the focusing of the laser beam.

The laser microprobe is interfaced to the gas chromatograph via a purpose built sample chamber and gas inlet system. Small portions of sample were loaded into the 7 mm diameter sample chamber port with no special preparation procedures necessary. All lines downstream of the chamber were kept at elevated temperatures ($>250^{\circ}\text{C}$) to minimize product losses due to pyrolysate condensation. Two separate inlet flow routines were assessed: i) a single flow routine in which pyrolysates were transferred directly from the sample chamber to the GC column; and ii) a more elaborate two-flow routine utilizing an initial fast flow ($>100\text{ mL/min}$) to efficiently transfer the pyrolysates from the chamber to an external cold trap combined with a second slower flow (1.5 mL/min) more suitable for GC chromatography. A 6-port switching valve allows selection between the two flows and on switching to the second flow the trap is heated to remobilize pyrolysates and allow their transfer onto the GC column. The more simplistic single flow routine proved suffi-

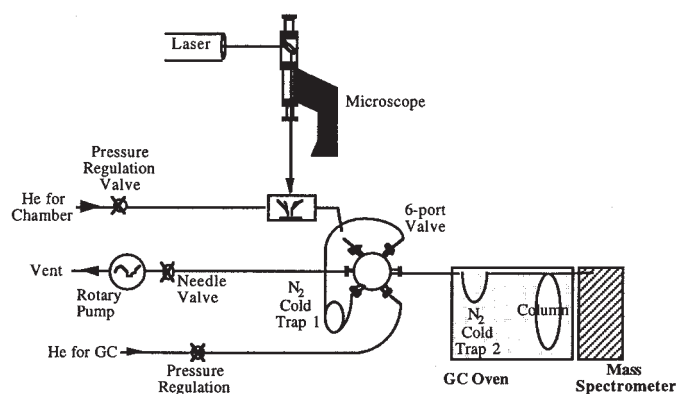


FIG. 1—Instrumental schematic of the laser microprobe pyrolysis GC-MS apparatus.

cient for samples yielding predominantly low MW components (established from prior pyroprobe analysis), whereas the dual flow routine was markedly better for higher MW pyrolysates.

All samples were typically pyrolyzed with a 2 s output of 19 W/s, focused through the 20× objective. These optimal parameters were selected after repeat analysis of the white paint sample with varied laser parameters (power: 6.5 to 23 W/s; irradiation times: 1 to 30 s), and different degrees of focusing (via 10×, 20× or 50× microscope objectives). The intensity of the pyrolysate distributions were strongly influenced by the power and time of the laser event. The power threshold for pyrolysis of the paints was observed to be 13 W/s with no pyrolysates nor visually evident disturbance (i.e., ablation) of the paint surfaces detected with lesser energies. Higher laser energies typically yielded higher pyrolysate concentrations and increased crater sizes. Excessive laser energies (>19 W/s) were generally avoided to prevent GC column overload.

An initial brief assessment of the reproducibility capabilities of laser pyrolysis GC-MS was conducted with five repeat analyses of the white paint and four repeat analysis of the Mita DC3060 black photocopier toner using identical laser conditions (19 W/s, 2s, 20× obj).

Pyroprobe Pyrolysis

Conventional pyrolysis was performed using a Chemical Data Systems pyroprobe (CDS-160) which was ballistically heated to 850°C and held for 10 s (7). Small portions of the samples (0.3 to 1.4 mg of paint and toner; ~1 to 10 mm of fiber strands) were weighed into a quartz tube which was then inserted into the platinum coil of the pyroprobe. The pyroprobe, in turn, locates into the probe interface (~250°C) which is mounted on the split/splitless injector of the GC. An optimal pyrolysis temperature of 850°C was identified from repeat analyses of the white paint sample at several pyrolysis temperatures over the range 500°C to 1000°C. At 850°C a range of predominant products were produced across a wide retention window providing detailed sample characterization.

GC-MS Analysis

Pyrolysates from the paint and fibers were detected with a Hewlett Packard (HP) 5890 series gas chromatograph (SGE BPX5 fused silica capillary column; 25 m × 0.22 mm i.d × 0.25 μm film thickness) interfaced to a HP 5970 series mass selective detector. An Agilent 6890/5973 GC-MS (HP-5MS fused silica capillary column; 30 m × 0.25 mm × 0.25 μm) was used in the analysis of the photocopier toners.

For all analysis, the pyrolysates were cryogenically focused onto the GC column by immersing a short section of column in a liquid nitrogen bath. The GC-MS analysis was started on removal of the column from the cold trap. Typical GC oven programs included: 1) initial 30°C held for 2 min then increased at 4°C/min to final 300°C for 25 min (paint and fiber analyses); and 2) 30°C for 4 min then 2°C/min to 100°C, then 10°C/min to final 300°C for 25 min (toner analyses; NB: slower temperature ramp used because of lower MW nature of pyrolysates from toner). Relatively standard MS detection parameters were used (70 eV; 250°C source temperature) to acquire full scan analysis (i.e., m/z 50 to 550). Several individual ions were selectively monitored for some applications requiring greater sensitivity (e.g., fiber analyses).

Results and Discussion

Automotive Paints

The low MW region (retention times <30 min) of the pyrograms from laser and pyroprobe GC-MS analysis of the blue and red paints are shown in Fig. 2.

Tentative product assignments based on comparison to MS libraries are listed in Table 2. No isomeric assignments were attempted. The major products from the paints include benzene (1), methyl-,methylesterpropenoic acid (3), toluene (4), C₂-benzene (7), and styrene (8). Several distinct qualitative and quantitative differences in molecular composition distinguish the blue and red paints. A slightly larger number of pyrolysates were detected from the blue paint. C₃-benzene (13), naphthalene (19), and ethyl-,hexylesterpropenoic acid (28) were detected in much higher abundances from the blue paint, whereas methyl-butylesterpropenoic acid (12) was significantly more pronounced in the analysis of the red paint. These observations were consistent for both laser and pyroprobe GC-MS analysis.

The abundance of the higher MW products (retention times >30 min) detected by laser and pyroprobe analysis showed greater deviation. The macromolecular bond cleavages induced by all fast pyrolysis methods are generally thought to be quite similar. However, the two pyrolysis methods used here employ very different temperature regimes (650°C of pyroprobe compared with ≥1000°C of laser) so some minor differences in product distributions might be anticipated.

Sufficient complexity (i.e., qualitative and quantitative data) was similarly evident in the chromatograms from the white, yellow, and

TABLE 2—Pyrolysates detected from laser and pyroprobe pyrolysis GC-MS analysis of the paint and photocopier toner samples shown in Figs. 2 and 3. (NB: Products are tentatively assigned based solely on mass spectral data, hence isomeric assignments are not attempted).

Peak Nos.	Product
1	Benzene
2	Cyclopentadiene
3	Methyl-,methylester-propenoic acid
4	Toluene
5	Furfural
6	Cyclopentenone
7	C ₂ -benzene
8	Styrene
9	Methyl-cyclopentenone
10	Methyl-furan-carboxaldehyde
11	Methyl-styrene
12	Methyl-,butylester-,propenoic acid
13	C ₃ -benzene
14	Phenol
15	Indene
16	Methylene-,propenyl-benzene
17	Cresol
18	Butoxymethylacetate
19	Naphthalene
20	C ₂ -styrene
21	Butyl-phenol
22	C ₄ -benzene
23	Dimethyl-,ethylphenol
24	Propandyl-benzene
25	Decyl-benzene
26	Stilbene
27	Diphenyl-cyclopropane
28	Ethyl-,hexylester-propenoic acid
29	Phenyl-naphthalene
30	Phenyl-terphenyl

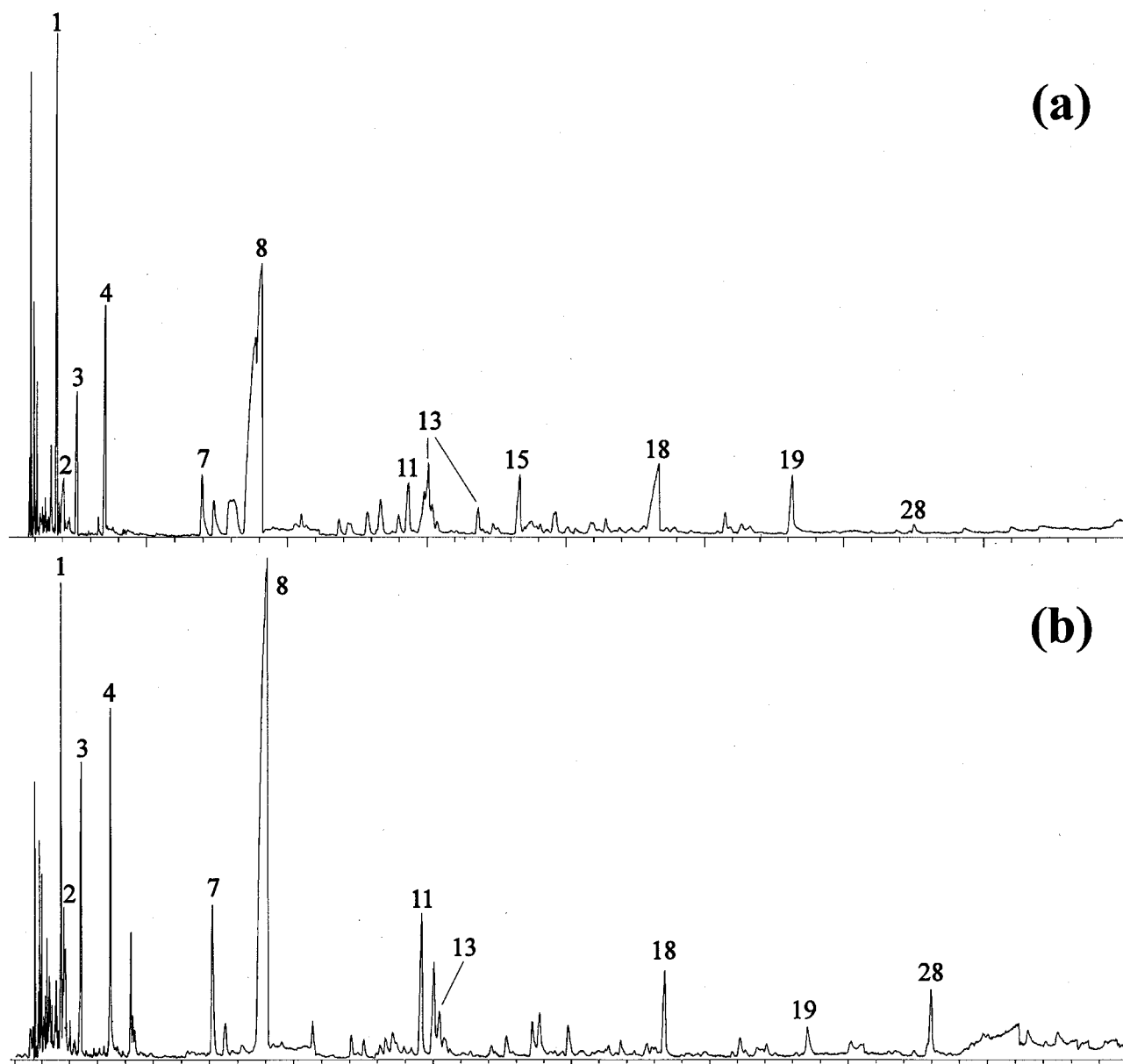


FIG. 2—Partial (Low MW) pyrograms from the laser microprobe pyrolysis GC-MS of (a) blue paint; and (c) red paint; and pyroprobe pyrolysis GC-MS of (b) blue; and (d) red paint. Numbered peaks correspond to the products listed in Table 2.

green paints, such that all of the paints could be uniquely characterized for molecular fingerprinting purposes.

Photocopier Toners

The laser and pyroprobe pyrograms from the Mita DR3020 black toner and the laser pyrogram from the magenta colored Canon toner are shown in Fig. 3. The abundance of the TICs from the black toner (Fig. 3a and b) have been enlarged by a factor of 2 to more readily observe product detail (otherwise overwhelmed by the large abundance of styrene—hence now off scale). The tentatively assigned products are included in Table 2. The major pyrolysates include various alkylbenzenes (4,7,22,24), furans (5,10), unsaturated cyclic hydrocarbons (2,6,9), phenols (14,17,21,23,26), and polycyclic aromatics (19,28,29) as well as several unidentified products of relatively high abundance (A-F). Not all products could

be unequivocally identified, however, this does not preclude their contribution to the molecular fingerprint signature of the samples. The respective toner signatures show sufficient differences to allow them to be distinguished from each other.

The pyrolysis data provided ready distinction between black and colored toners. Whereas styrene, for example, was a major product of the black toners, it was detected in only minimal abundance from the colored toners. The colored toners were characterized by a much higher proportion of phenolic compounds and a distinctive cluster of unidentified relatively high MW peaks at retention time 48 to 53 min.

Compositional differences within the respective sets of black and colored toners were more subtle. Overall, a large number of pyrolysates (>100) were detected from the 11 toners studied. Some products were unique to particular toners or small toner subsets while a quantitative assessment of the relative concentrations of

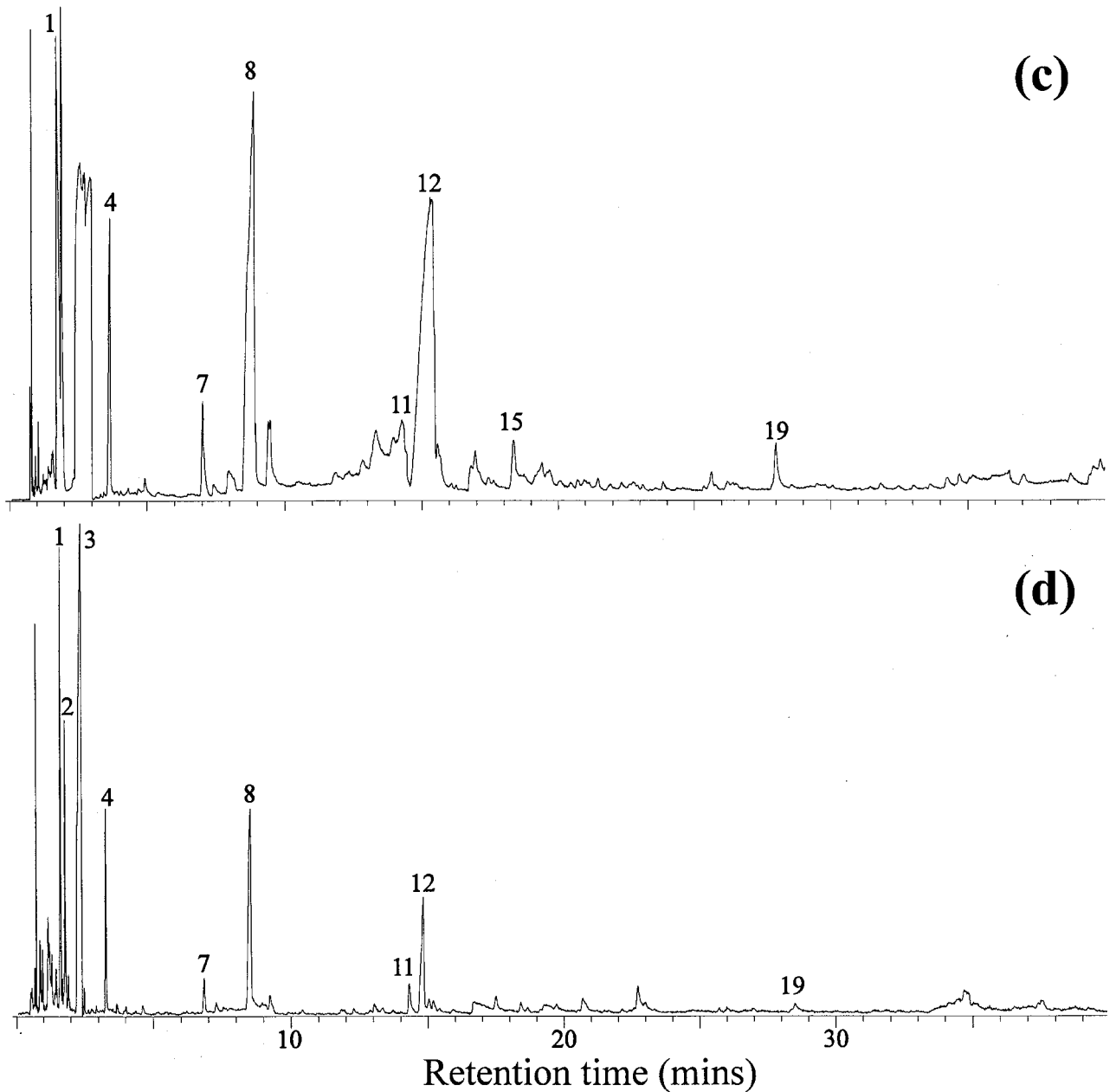


FIG. 2 (continued)

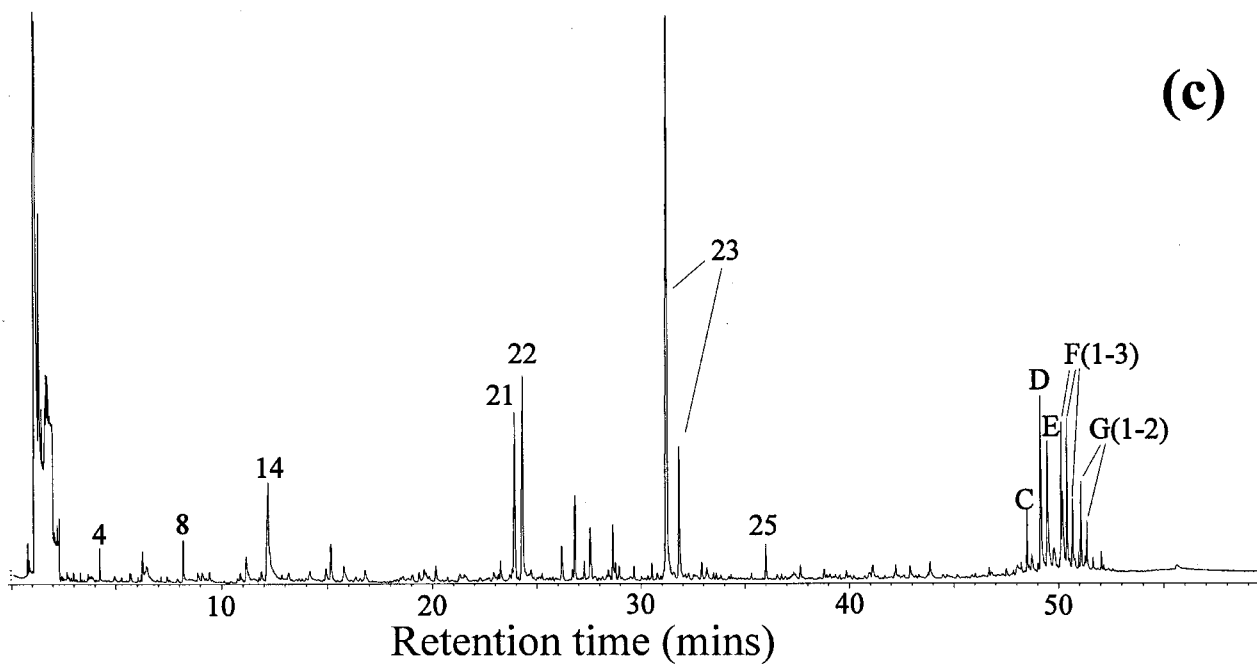
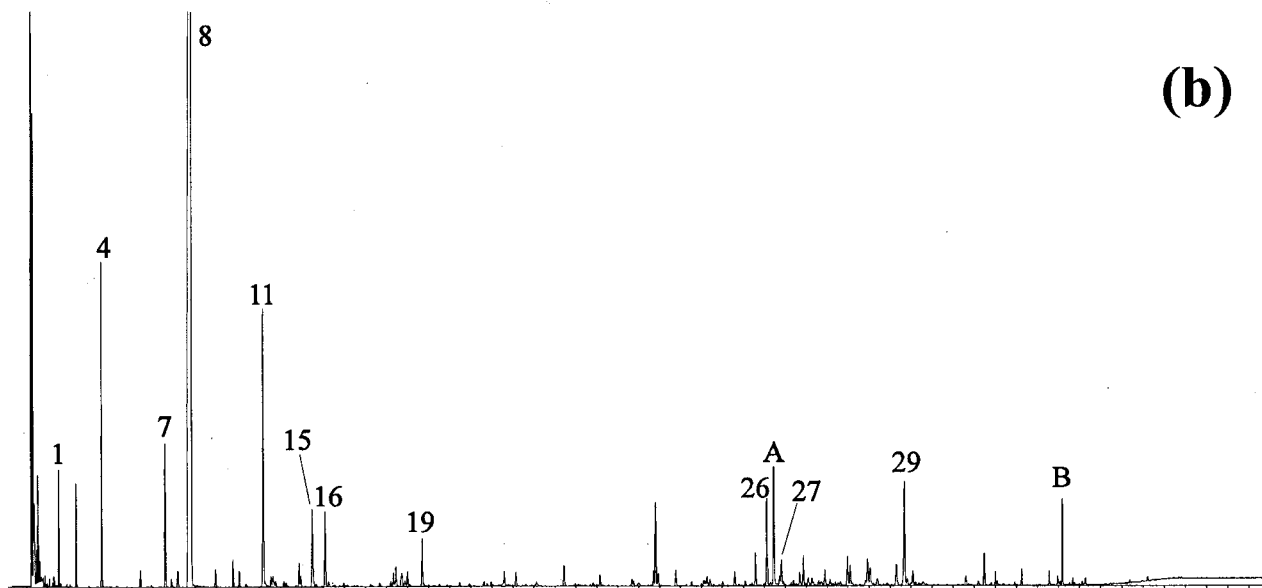
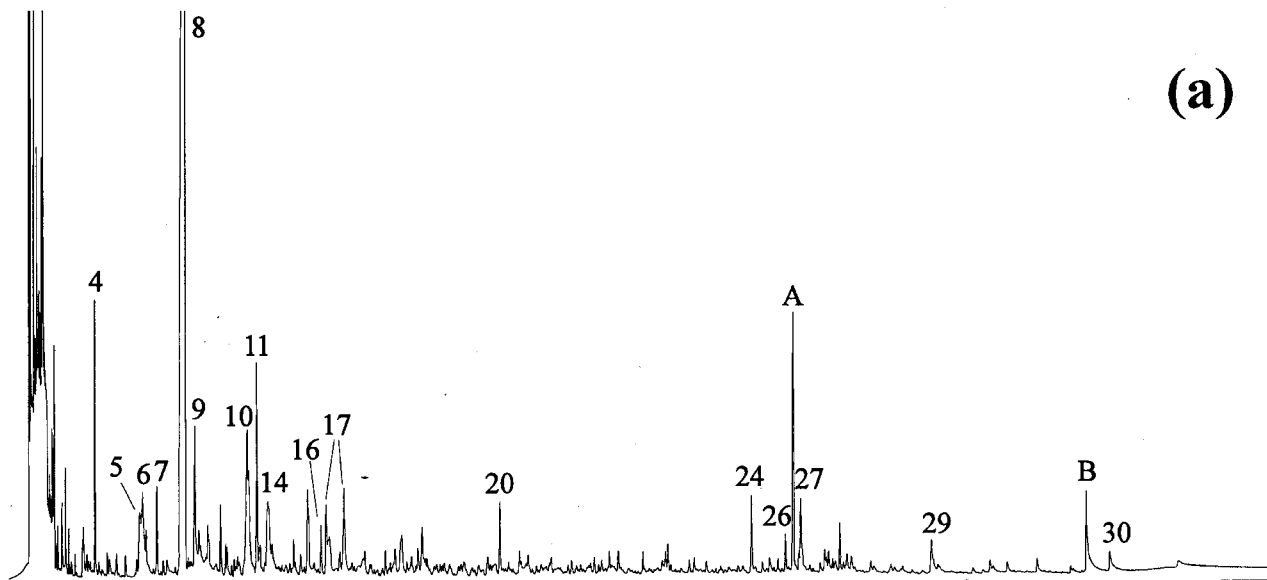
other products allowed even further differentiation. For example, the magenta toner was the only colored toner from which decylbenzene (25; Fig. 3c) was detected. From a quantitative viewpoint, the relative abundance of peak B (Figs. 3 a and b) was very high from five of the black toners (Mita DC1860, Mita DC3060, Sanyo, Fujitsu, and Toshiba 7550), but this unknown product was in significantly lower concentrations in the other two black toners (Mita DR3020—Fig. 5a and b, Lanier).

The capacity of the laser method to selectively pyrolyze the fused toner directly from the paper matrix represents a significant advantage over other pyrolysis methods. Several separate experiments in which blank (toner free) portions of the paper supporting the Lanier black toner were directly laser pyrolyzed produced no pyrolysates and showed no visible damage to the paper surface (even with maximum laser energy) indicating a lack of absorption

at 1064 nm. Chlorobenzene was occasionally detected in low concentrations in the analysis of some of the fused toners (probably due to conductive heat transfer between the pyrolyzed toner and paper), but this was the only product attributable to the paper supports. It is easily recognized so proves no great hindrance to the detailed characterization of the toners. Because of the minimal interference from the paper supports, laser pyrolysis may be a convenient method for determining the common origin of toner samples on different supports.

Synthetic Fibers

The synthetic fibers were generally well characterized by their pyroprobe pyrolysate distributions. The nylon and polyolefinic fibers, in particular, were highly susceptible to thermal pyrolysis



producing large numbers of products in high abundance over a wide molecular weight range. Several of the other fibers (e.g., teflon), however, proved more thermally stable yielding only a few pyrolysates of low abundance.

Initial attempts at laser pyrolysis of the fibers proved unsuccessful due to poor absorbance at 1064 nm. Similar difficulty with the attempted laser pyrolysis of polybutylstyrene and polyethylene granules using a pulsed ruby laser (694 nm) had been previously encountered by Stout and Hall (3). To overcome the transparency of these materials to the incident laser irradiation, the granular polymers were mixed with graphite particles (~1:1 ratio) (3). Heat transfer from the more strongly absorbing graphite matrix then induced indirect pyrolysis of the polymers.

Without alternative laser sources to test the absorbance of the fibers at different wavelengths (e.g., UV), a similar procedure to the one used by Stout and Hall was also adopted here (NB., graphite absorbance across the electromagnetic spectrum is relatively uniform). Several sections of the fibers (~5 mm in length) were pressed (by protected hand) into the surface of a graphite disk of approximately 4 mm diameter. Successful pyrolysis of the fibers was then achieved by irradiating the graphite matrix immediately surrounding the embedded fiber. Conveniently, the absence of any pyrolysates from the laser microprobe GC-MS of pure graphite established that the graphite matrix does not contribute any interfering peaks to the analysis.

The polyolefinic fibers in particular yielded a large distribution of pyrolysates. The summed *m/z* 57 (saturated aliphatics) and *m/z* 69 (unsaturated, branched, and cyclic aliphatics) chromatogram from the laser microprobe GC-MS (selected ion) analysis of polypropylene fibers are shown together with the corresponding pyroprobe pyrograms in Fig. 4. Note: the high detection sensitivity of selected ion monitoring was used in the laser experiment (Fig. 4c). The pyroprobe data shows that the *m/z* 57 + 69 summed chromatogram (Fig. 4b) is very representative of the total pyrolysate distribution measured by full scan analysis (Fig. 4a).

The pyrolysate distributions from the laser and pyroprobe analyses were almost identical as indicated by the common detection of products labeled *a* to *w* (Fig. 4). Dimethylheptene was consistently detected in high abundance and a predominant distribution of branched chain oligomers over a wide MW range was also observed. The data also closely match the product profile of a previous pyrolysis study of polypropylene (9).

Further, the laser and pyroprobe pyrolysate distribution from the polyethylene fibers (results not shown) were both dominated by homologous series of the normal alkanes and associated unsaturates (i.e., *n*-alkadiene and *n*-alk-1-enes) and similarly reflected almost identical distributions to those previously detected from polyethylene by conventional pyrolysis methods (3,9).

Forensic Qualification of Laser Microprobe Pyrolysis

Destructivity

The laser microprobe can be used to selectively pyrolyze very small portions of sample. While traditional pyrolysis has been re-

ferred to as a minimally destructive technique, even smaller amounts of sample may be analyzed by the laser method. With the standard laser parameters used in this study (i.e., 19W/s, 2s, 20× objective) the average size of the surface craters ablated in the paint and toner samples was ~100 μm² in diameter. Even if the crater penetrates to significant depth (e.g., ~100 μm) this still corresponds to a significant reduction to the sample amounts required for conventional methods of analytical pyrolysis (which can approach mg quantities for some materials). The laser method may be beneficial in situations where only very minute sample quantities are available and/or where preservation of the sample for subsequent analysis is important. Furthermore, the directional character of the laser microprobe allows small parts of heterogeneous samples to be selectively pyrolyzed and analyzed.

Molecular Discrimination and Reproducibility

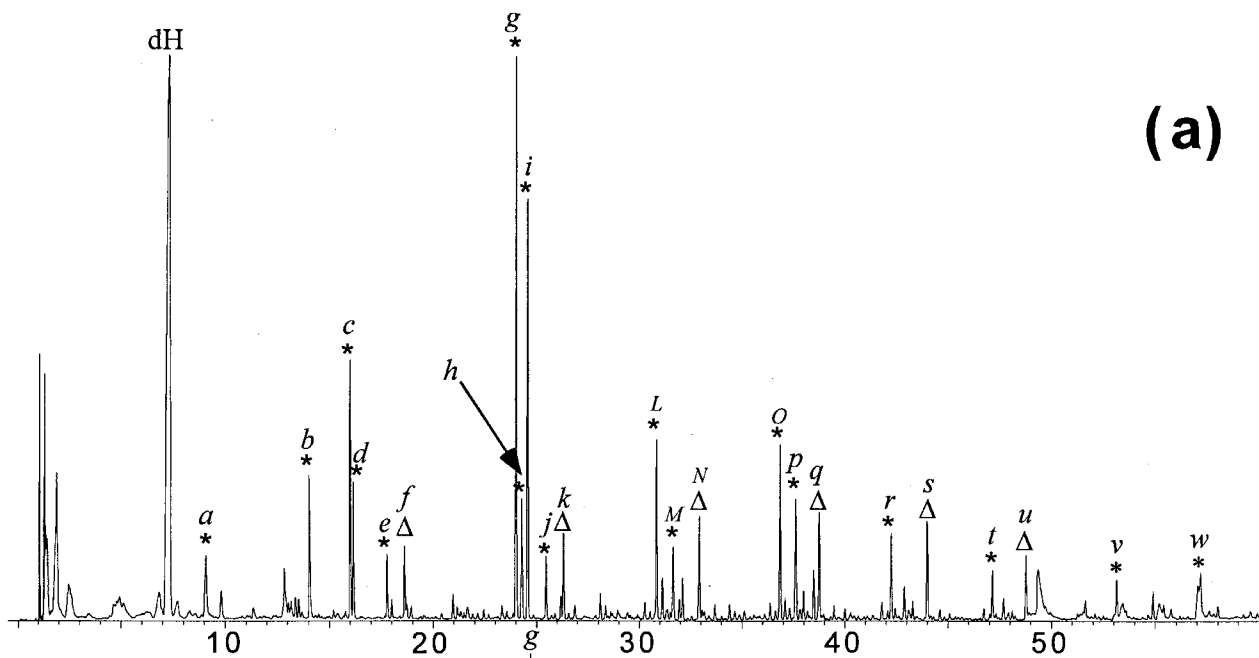
The laser pyrograms reflected sufficient detail to molecularly distinguish all of the samples studied here. Consistent with most previous laser pyrolysis studies (4–8), the laser data were in good agreement with conventional pyrolysis data and showed a similar degree of molecular discrimination. Laser pyrolysate data had the potential, therefore, to uniquely characterize individual samples at the molecular level.

Conventional forms of pyrolysis have been reported to have very good qualitative reproducibility (14,17), although they have proved to be quantitatively less reliable. Pyrolysate abundances are very sensitive to a variety of experimental parameters including pyrolysis temperature, sample quantity, and sample composition (2,17). Nevertheless, by careful replication of experimental conditions, quantitative data with standard deviations of between 0.5 to 3% have been achieved (2).

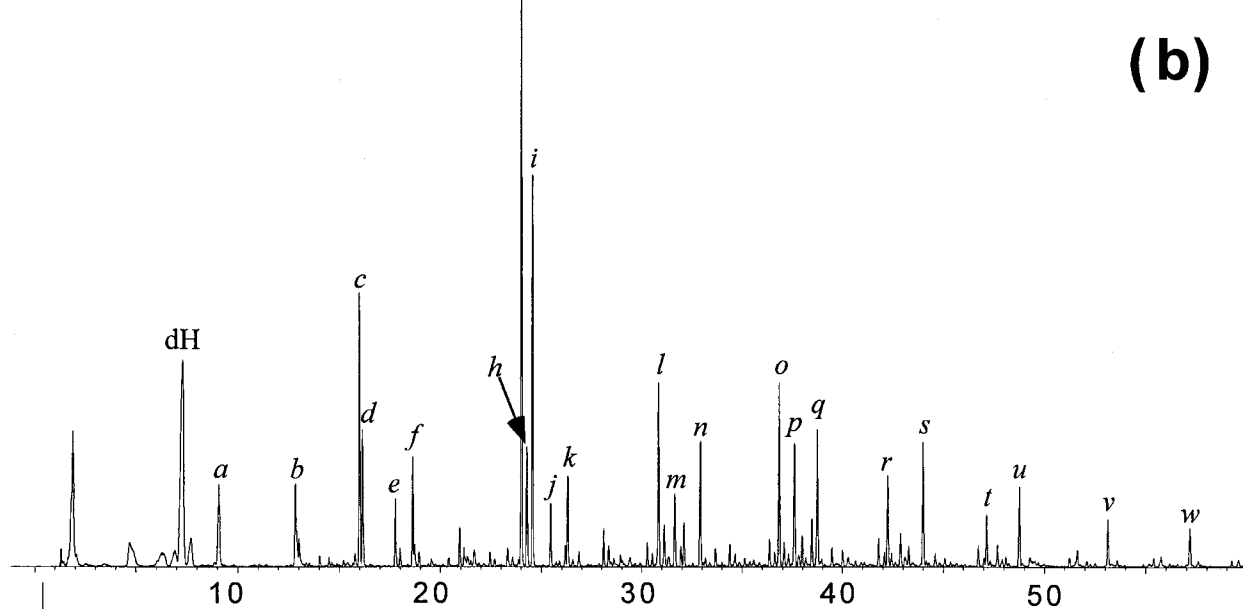
Here, the analytical reproducibility of the laser microprobe GC-MS method was briefly investigated by five repeat analysis of the white paint and four repeat analysis of the Mita DR1860 black toner with standard laser conditions. For each repeat analysis, fresh parts of the toner surfaces were selected by (hand) adjustment of the sample chamber under the microscope. The relative abundances (% cf. styrene) of several of the major products from these analyses are shown in Tables 3 and 4, respectively. The statistical mean and relative standard deviations of the data were calculated. These statistical values reflect quite variable product abundances and this level of reliability may limit the usefulness of the technique for involved forensic applications, although it is not often that PyGC is used in a quantitative way in forensic science. Further, a much larger data set should be considered for a robust estimation of reproducibility.

While most of the observed variability in product abundances may be due to random fluctuations of instrumental parameters (e.g., laser output/sample temperature), it may also reflect a small degree of molecular heterogeneity inherent within the paint and toner samples. Whereas the chemical nonuniformity of some samples may not be evident from the analysis of large sample amounts, it may become apparent when subjected to micro-analytical techniques.

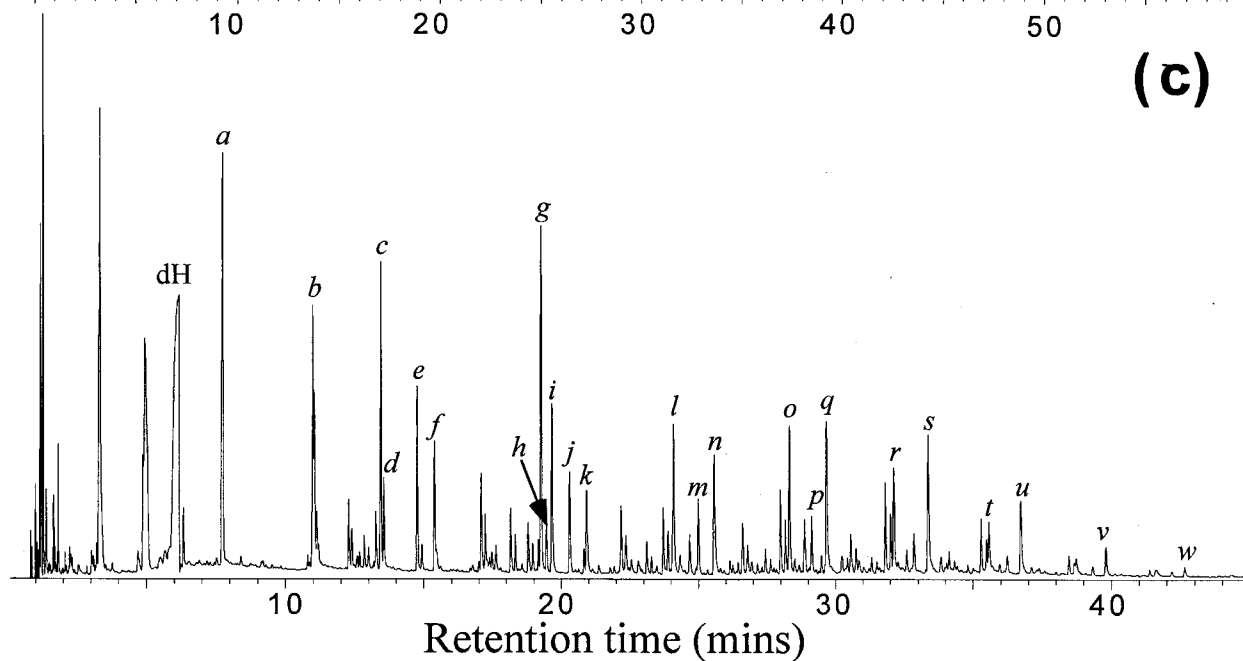
FIG. 3—(a) TIC from the laser microprobe GC-MS analysis of Mita DR3020 fused black photocopier toner; (b) TIC from the pyroprobe pyrolysis GC-MS analysis of Mita DR3020 fused black photocopier toner; and (c) pyrogram from laser microprobe GC-MS analysis of the Canon magenta colored photocopier toner. NB. The chromatogram abundances of a and b were ×2 to enhance pyrolysates otherwise overwhelmed by the large styrene peak (8). Nos. peaks correspond to the products listed in Table 2. A–G = unidentified pyrolysates of high abundance. [5 pt mass spectra: A: 91(100%), 208(33%), 104(28%), 130(26%), 115(19%); B: 91(100), 117(35), 202(20), 194(17), 312(5); C: 219(100), 234(80), 204(31), 189(17), 102(8); D: 253(100), 268(22), 232(20), 119(7), 202(4); E: 251(100), 266(25), 119(12), 157(4), 128(3); F: 293(100), 308(23), 119(7), 253(4), 165(4); and G: 291(100), 306(25), 119(5), 149(4), 219(4)].



(a)



(b)



(c)

Retention time (mins)

TABLE 3—Relative abundances of major pyrolysates from replicate laser micropyrolysis GC-MS analysis of the white paint.

Product (Ret Time/min)	Relative Abundance (% Cf. to Styrene)					Statistics	
	1	2	3	4	5	Mean	%RSD
Benzene (1.8 min)	26.0	27.2	29.7	17.3	17.0	23.4	24.8
Methyl-,methylesterpropenoic acid (2.5 min)	149.1	166.1	159.0	84.7	82.6	128.3	32.1
Toluene (3.5)	29.2	29.1	37.3	27.3	19.2	28.4	22.5
3,methylene heptane (4.2)	13.4	16.8	13.4	10.8	10.1	12.9	20.2
C ₂ -benzene (7.1)	4.9	11.2	10.4	5.5	6.1	7.6	38.2
Styrene (8.9)	100.0	100.0	100.0	100.0	100.0	100	—
Benzaldehyde (14.5)	8.7	12.6	9.0	6.1	10.6	9.4	25.5
Methyl butyl ester propenoic acid (14.9)	51.5	53.6	48.7	40.4	28.1	44.4	23.4
Cyclododecane (30.1)	5.3	9.9	5.5	3.3	4.1	5.6	44.6
Unknown aliphatic (33.0)	18.7	22.9	20.1	13.5	16.3	18.3	19.1
<i>m/z</i> 55(100%),70(53),57(30),56(18),83(14)							

TABLE 4—Relative abundances of major pyrolysates from replicate laser micropyrolysis GC-MS analysis of Mita DC1860 black fused black photocopier toner.

Product (Ret Time/min)	Relative Abundance (% Cf. to Styrene)				Statistics	
	1	2	3	4	Mean	%RSD
Toluene (4.2 min)	4.69	3.90	3.24	4.63	4.1	17.1
Furfural (6.2)	3.34	1.51	5.27	2.70	3.2	50.0
Styrene (8.1)	100	100	100	100	100	—
Methyl-styrene (11.9)	5.25	3.22	2.26	5.72	4.1	39.0
Stilbene (37.0)	1.43	22.6	16.9	2.61	10.9	96.3
Unknown peak A (37.3) (see Fig. 3)	8.54	65.5	24.5	8.71	26.8	100
Unknown peak B (51.2) (see Fig. 3)	50.5	47.2	31.9	32.4	40.5	24.0
Phenyl terphenyl	6.29	8.04	6.14	17.15	9.4	55.3

Conclusions

The very high spatial resolution and selectivity of a laser microprobe was combined with GC-MS detection to provide in situ molecular characterization of common forensic materials. Paint and photocopier toner materials proved particularly susceptible to the near IR output of a Nd: YAG laser. Fused toners were directly analyzed from their paper support with minimal contamination, eliminating the traditional need for extraction of the toner from documents prior to analytical pyrolysis.

The laser method may not be suitable for all types of analysis, as exemplified by the transparency of the synthetic fibers to the IR radiation. Additional laser sources (e.g., UV or visible lasers) may enhance the analytical scope of this methodology and even given the one wavelength available here, the fibers were able to be indirectly pyrolyzed by embedding them in a graphite matrix.

The laser micropyrolysis GC-MS technique maintains both the molecular integrity and the discriminating capacities of conventional pyrolysis methods. Well over 100 pyrolysates were detected from the forensic samples studied here with generally similar product profiles from a given sample obtained with both laser and pyroprobe analysis. The samples were readily distinguished from each other by the unique occurrence of some products and the disparate concentrations of others. Such distinctions were clearly observed even within the reproducibility limitations of the technique

that needs to be more rigorously assessed by a much larger data base than the $\times 4$ and $\times 5$ data sets considered here.

Overall, the laser micropyrolysis GC-MS results are particularly promising and suggest that this technique may assist forensic scientists in specific analytical applications, particularly where samples are either physically heterogeneous or available in very limited quantities.

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FIG. 4—Polypropylene fiber pyrograms showing (a) total ion chromatogram from 600°C pyroprobe pyrolysis with full scan analysis; (b) *m/z* 57 + 69 extracted ion chromatogram from a; and (c) *m/z* 57 + 69 selected ion chromatograms from laser micropyrolysis. dH = dimethylheptene; a-w = aliphatic products common to both laser and pyroprobe analyses distinguished by * = distinctive *m/z* 55 & 57; Δ = distinctive *m/z* 55 only.

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