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Pyrolysis Capillary Gas Chromatography/ Mass Spectrometry for Analysis of Automotive Paints

ABSTRACT: Pyrolysis capillary gas chromatography/mass spectrometry was used to analyze automotive paints. The mass spectral data from the entire chromatogram of a given paint was combined using an INCOS 2000 data system. This composite spectrum, after subtraction of background, was then stored in a library. Tentative identification of an unknown was effected by using the pattern recognition algorithm of the data system to search the library for the best comparison to the composite mass spectrum of the unknown. Although only a small portion of the samples from the FBI National Automotive Paint File was used, results showed good discrimination when a combination of the mass spectral and chromatographic data was utilized. Preparation of a searchable data base with the potential for widespread use is demonstrated.

KEYWORDS: forensic science, paints, pyrolysis, pyrogram, chemical analysis, capillary gas chromatography, mass spectrometry, automotive paints, data base, GC/MS

The analysis of automotive paints by pyrolysis gas chromatography (PGC) is a well-established method which is routinely used in forensic science laboratories [1,2]. The usual procedure is to compare an unknown paint to known samples which have similar physical characteristics, notably solubility properties and color.

The breakdown of the paint components during pyrolysis results in relatively small fragments and the resulting gas chromatogram (pyrogram) is quite reproducible. The comparison of chromatograms of known and unknown samples is left up to the individual investigator. Although the need for a comprehensive paint pyrogram data base has been recognized for nearly a decade [3,4], to date no standardized method has been adopted. This lack of standardization, coupled with the realization that a large data base would be needed in order to be of use for routine investigations, has thus far prevented serious attempts at such a compilation.

Recently, Martz et al [5] reported on a library building procedure which was useful for identification of smokeless powders after separation of extracts via capillary gas chromatography. By using a gas chromatograph/mass spectrometer (GC/MS) equipped with a computer data system, library entries were formed by combining the mass spectra of the total gas chromatographic profile into a single composite spectrum. Tentative identification was then effected by computer-searching the library with the composite spectrum of the questioned material. Verification of this identification was accomplished by visual comparison of the capillary GC traces, which were still available in the data system, or by comparison of other physical and chemical properties of the known and questioned samples. A data base of 80 smokeless powders has been compiled and is being used successfully.

In some cases pyrolysis-mass spectrometry (PMS) is used as an alternate method [2,6–9]. In this technique, the total mass spectrum of the pyrolyzate is recorded and compared to that of known material. Analysis time is significantly shorter than for PGC, and most mass spectrometer systems can be equipped with computerized data systems which allow library storage, retrieval, and comparison of the mass pyrograms. A major drawback to PMS, however, is that the mass pyrogram is often so complex that the types of pyrolysis products formed during the thermal degradation step cannot always be deduced [2].

In the present work, a combination of pyrolysis, capillary gas chromatography, and mass spectrometry was employed with subsequent data handling as cited above. The goal was to utilize the information available in both PGC and PMS while not requiring unduly long analysis times. Use of fused silica capillary columns with a fairly rapid temperature program allowed peaks of interest to be eluted in a reasonable length of time. Incorporating the mass spectral information in a data system provided a system which could be searched on color, presence or absence of metallic particles, paint type, or model year. Information about the first three characteristics is available from microscopic or chemical tests and the fourth may be useful if a known sample were available or if the search were to be limited to certain model years.

This method was applied to paint chips available from the FBI National Automotive Paint File (NAPF). A total of 39 paints were examined, including several which were known to be difficult to differentiate by techniques currently employed in the FBI Laboratory. In some cases, paints of the same composition but of different colors were used; in others, paints of the same formulation including color, but made by different manufacturers, were used.

Experimental Procedure

Equipment

Pyrolysis—A CDS-100 Pyroprobe unit (Chemical Data System, Oxford, PA) with a coil probe was used. A quartz tube was used to hold the paint chip. The pyrolysis products were swept into the inlet of the gas chromatograph through a needle assembly (CDS) which held a small plug of glass wool. Pyrolysis conditions are shown in Table 1a.

Gas Chromatograph—A Perkin-Elmer Sigma 3B gas chromatograph equipped with a split/splitless capillary inlet system as supplied with the Finnigan mass spectrometer (see below) was used. The column was a SE-30 fused silica column, 30 m by 0.25 mm. GC conditions utilizing two different starting temperatures are given in Table 1b.

Mass Spectrometer—A Finnigan-MAT 1020 gas chromatograph-mass spectrometer was used to acquire mass spectral data (electron impact mode). Mass spectral conditions are given in Table 1c. The calibration of the mass spectrometer was checked each day by using a reference sample of decafluorotriphenylphosphine (DFTPP) [10].

Data System—After acquisition, data was stored on disk and manipulated using an INCOS 2000 data system (Finnigan-MAT Corp., San Jose, CA) equipped with a Control Data Corp. 96 Mbyte disk drive.

TABLE 1—*Experimental conditions.*

a Pyrolysis	Experimental	Cleaning
Ramp	off	off
Temperature	750°C	1000°C
Time	5 s	20 s
Interface temp.	175°C	(in air)
He flow rate	15 mL/min	(in air)

b Gas chromatography	Slow Run	Fast Run
Injector temp.	165°C	165°C
Separator oven temp.	165°C	165°C
He flow rate	0.76 mL/min	0.76 mL/min
Split ratio	20/1	20/1
Initial oven temp.	40°C	65°C
Time at initial temp.	3 min	4 min
Rate of temp. increase	25 deg/min	25 deg/min
Final temp.	250°C	250°C
Time at final temp.	2 min	2 min

c Typical mass spectrometer conditions	
Electron multiplier voltage	1800 V
Scan parameters: low mass	45 amu
high mass	360 amu
scan time	0.5 s
Filament off time	45 s

Samples

Paint panels (from the NAPF) from model years 1971-1981 were used. They consisted of both metallic and nonmetallic paints of several types, as shown in Table 2.

Procedure

A small chip of paint (about 30 μg) was placed in the quartz tube which had been cleaned by heating in the Pyroprobe for 20 s at 1000°C (in air). The tube was positioned so that the paint chip was near the center of the coil probe and the probe inserted to a constant depth into a

TABLE 2—*Types and numbers of paints used.*

	Metallic			Nonmetallic				
	Blue	Brown	Tan	Yellow	White	Black	Green	Red
Acrylic enamel	4				4	2		
Urethane enamel	1				1			
NAD acrylic enamel[a]	1	6			6			
Base coat (acrylic enamel clear coat)		1	2					
Acrylic lacquer	1			1	3		2	2
NAD acrylic lacquer[b]				1				
Miscellaneous lacquer					1			
Totals	7	7	2	2	15	2	2	2

[a]Nonaqueous dispersion acrylic enamel.
[b]Nonaqueous dispersion acrylic lacquer.

heated interface. Carrier gas was allowed to flow through the interface for 3 min after insertion of the probe. Then, simultaneously, data acquisition was begun and the "run" button depressed on the Pyroprobe unit, initiating the heating of the probe coil to 750°C for 5 s to pyrolyze the sample.

Duplicate samples of each paint were analyzed and the chromatograms inspected to insure that no spurious peaks were present. One chromatogram was then chosen to be processed for placement into the library.

To create a library entry from a pyrogram, the "ADD" program on the INCOS data system was used to create a background-subtracted composite spectrum. The spectra from approximately Scan 180 (just before the first peak was eluted) through Scan 1200 (somewhat after all peaks had eluted) were specified to be composed, and a few spectra from before Scan 180 and after Scan 1200 were specified for the background subtraction. This composite spectrum was then condensed by editing out ion intensities which were less than 0.5% of the base peak. The resultant spectrum was stored in the library, along with a variety of parameters which could be used for later directing the computer search (see Results and Discussion).

After the library was built, the remaining pyrograms, as well as several others prepared in the same manner, were used as "unknowns." The mass spectra for the total pyrogram (Scans 180–1200, less background) were composed into a single spectrum which was then compared to the assembled library via the INCOS search program. In some cases the "unknown" composite spectrum was condensed by removing small ions before the search. This adjustment had the effect of improving the purity value (defined in the following section) reported by the search program but did not affect the order of the potential matches.

Results and Discussion

It is now generally agreed that reproducibility in PGC is not a major problem if careful attention is paid to the various parameters involved in the pyrolysis and the chromatography [1]. In our work, the replicate pyrograms were qualitatively alike, although peak areas varied somewhat. No attempt was made to document carefully the variation in peak area because somewhat different GC conditions were used periodically. Because we increased the beginning oven temperature, peak shape in later chromatographic runs was relatively poor. The search feature, however, does not require good chromatography, and starting at a higher temperature allowed faster accumulation of data without the need for cryogenic cooling of the GC oven. In careful work where the chromatograms are to be compared, conditions such as those in Table 2b (slow run) are suggested. Peak shape is much more acceptable under these conditions (see Fig. 1a and b). In either case, the pyrogram is completed in 1200 scans (11 min), and the oven can be cooled while another sample is being prepared. A run can be completed every 20 min, and most of the data processing can be accomplished during the time the data for the next run is being accumulated.

A total of 102 "unknowns" were run and the resultant composite mass spectra compared to the 39 library entries. The results are summarized in Table 3. A pattern recognition algorithm of the computer library search program was used to provide a measure (PURITY) of how similar the measured composite spectrum is to that of a spectrum stored in the library. A PURITY of 0 indicates that the two spectra have no mass peaks in common, and a PURITY of 1000 indicates that the two spectra have identical mass peaks with peak intensities that are exactly proportional [11]. The results in Table 3 are based upon RELATIVE PURITY—the PURITY of the sample spectrum compared to a particular library entry, divided by the PURITY of the sample spectrum when compared to the "best" computer match (the match the computer found to have the highest PURITY) expressed as a percent. When the sample spectrum is compared to the computer best match, the RELATIVE PURITY is 100%.

When searched against the library, 89 of the 102 samples gave RELATIVE PURITY values ≥ 95% of the top value as determined by the search algorithm when compared to their correct
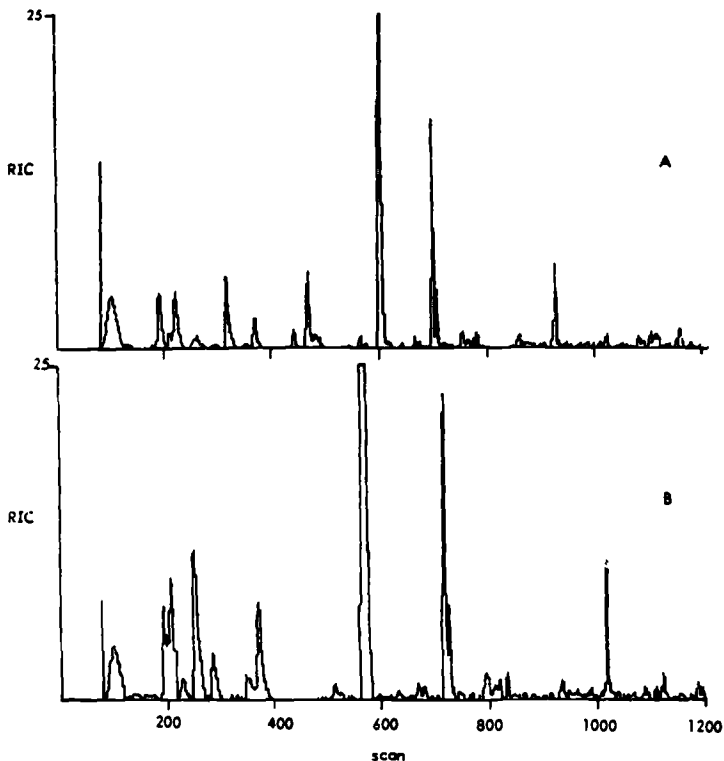
Fig. 1—*Comparison of peak shape for pyrogram of a white paint under different GC conditions:* (a) *conditions as in Table 2b, slow run;* (b) *conditions as in Table 2b, fast run.*

match. This includes 57 which were picked by the computer as the "best" match. Only in three cases were the RELATIVE PURITY values less than 90%. In two of these, the pyrogram had a poor signal to noise ratio, presumably because of small sample size or improper placement in the probe coil. We are therefore proposing that those paints which have a RELATIVE PURITY of >95% (or perhaps >90%) be considered as potential matches and subjected to further examination. Table 4 shows the results of typical searches using the composite spectrum from a sample of a blue acrylic enamel. In Part *a* the full library was searched. Three entries (1, 13 and 16) had PURITY values of ≥95% of the top ranked entry. In Part *b*, the search was limited to blue paints by using the Code C7 to direct the search. In this case no other blue paint was within 5% of the correct choice (Entry 1) although Entry 7 is within 10% and could perhaps be considered. Verification would come easily by looking at the pyrograms of the two under consideration (see Fig. 2).

In our current work, we used the molecular formula position to code for color (as C number), paint type (as 0 number), and metallic or nonmetallic nature (as N number). The molecular weight position was used to enter model year. It would be easy to include other coded information which might help to restrict the search using the algorithm supplied by the manufacturer or to implement other algorithms to include a variety of other information.

For comparison of similar paints, the technique required both the computer search to suggest the most likely candidates and a visual comparison of the chromatograms. Use of capillary columns, while not a prerequisite for the library building and searching, does give the added differentiation associated with increased resolution when compared to packed columns. Storing the data allows easy manipulation to expand the reconstructed ion chromatograms should

TABLE 3—*Comparison of paint samples to their composite library spectra.*

Library Entries	Color	Number of Pyrograms[a]	Relative Purity Rankings[b]			
			100%	95-99%	90-94%	90%
1-7	blue	25	15	5	3	2
8-9	yellow	4	2	1	1	...
10-16	brown	19	11	4	3	1
17-31	white	36	17	16	3	...
32-33	tan	4	1	3	...	...
34-35	black	4	3	1	...	...
36-37	green	5	4	1	...	...
38-39	red	5	4	1	...	...
Totals		102	57	32	10	3

[a]Excludes those values used to build the library.
[b]RELATIVE PURITY rankings: these numbers are the number of sample runs in each color category which lead to RELATIVE PURITY values of the indicated magnitude (for example, 100%, 95-99%). See the discussion of Table 3 in the text for the definition of RELATIVE PURITY.

TABLE 4—*Library search using blue acrylic paint (library Entry 1).*

a Sample searched against full library

Rank[a]	Entry Number[b]	Name[c]	Formula[d]	Molecular Weight[e]	Base Peak[f]	Purity[g]
1	1	BLUE 1G73BA0259	C7.O.N	73	104	976
2	13	BROWN 1E78HG0698	C5.O7.N	78	104	962
3	16	BROWN 1E78JG0698	C5.O7.N	78	104	932
4	7	BLUE 1G71GA0148	C7.O.N	71	104	907
5	26	WHITE 2A76DA0172	C.O.N2	76	104	904
6	12	BROWN 1E78BG0698	C5.O7.N	78	104	897
7	20	WHITE 2A76GG0172	C.O7.N2	76	104	893
8	15	BROWN 1E78AG0698	C5.O7.N	78	104	892
9	14	BROWN 1E78DG0698	C5.O7.N	78	104	882

b Sample searched against only blue paints (C7 specifier)

Rank	Entry Number	Name	Formula	Molecular Weight	Base Peak	Purity
1	1	BLUE 1G73BA0259	C7.O.N	73	104	976
2	7	BLUE 1G71GA0148	C7.O.N	71	104	907
3	2	BLUE 1G77GG0741	C7.O7.N	77	104	871
4	5	BLUE 1G72GA0148	C7.O.N	72	104	859
5	4	BLUE 1G72GA0259	C7.O.N	72	104	760
6	3	BLUE 1G77GC0741	C7.O3.N	77	56	361
7	6	BLUE 1G75FM0397	C7.O10.N	75	69	161

[a]The comparisons are ranked from highest PURITY to lowest.
[b]The entry number is the numerical order in which the entries were added to the library (for example, Number 2 was added second).
[c]The name is made up of the paint color followed by the National Automotive Paint File number.
[d]The molecular formula position is used to code for color, paint type, and metallic or nonmetallic (C, O, N numbers, respectively).
[e]The molecular weight position is used to code for model year.
[f]The base peak entry is the strongest ion in the composite mass spectrum.
[g]The PURITY value generated by comparing the library spectrum to the sample spectrum (see text for definition of PURITY).
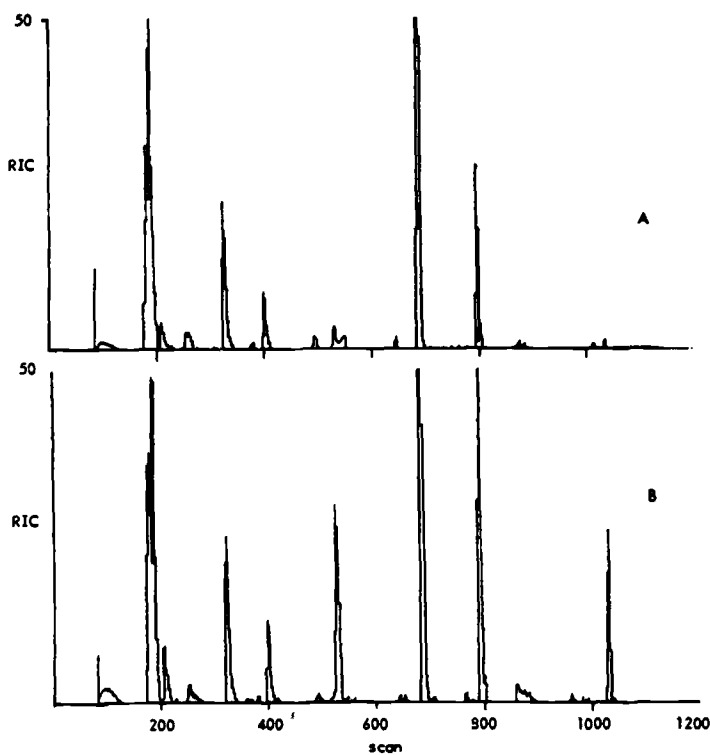
FIG. 2—*Pyrograms of two blue paints:* (a) *library Entry 1;* (b) *library Entry 4. GC conditions as in Table* 2b, *fast run.*

it be necessary to examine smaller peaks during the comparison of pyrograms. Since the computer search of the library is based on composite mass spectra, it will not be much affected by changes in GC conditions so that the difficulty in achieving GC standardization among forensic science laboratories will not hamper the use of such a data base. Substantial differences in pyrolysis conditions, however, might be expected to lead to major differences in the composite spectra.

Occasionally, a low PURITY value is obtained. Although the search algorithm still gives fairly good selections, prudence would suggest the sample be rerun. This problem occurred infrequently and was evidenced by extraneous peaks in the pyrogram. We speculate that some impurity was on the paint chip or in the pyrolysis interface.

Several of the samples used in this study were chosen because of their similarities. For example, nine groups of paints differing only in the manufacturer (and in two instances the model year) were compared using the library search program. In Table 5 are presented the RELATIVE PURITY values obtained when composite spectra for replicate runs of a paint were compared to the library entry for that paint, and the RELATIVE PURITY values obtained when those composite spectra were compared to the library entries for other paints of the same type. For instance, in Part *a* of the table, data are presented from the comparisons of two blue paints (library Entries 1 and 4). The blue paint which had been used for library Entry 1 was pyrolyzed twice again and the composite spectra searched against the library. In both cases, Entry 1 (the correct identity of the paint used) was the best match (100% RELATIVE PURITY). Entry 4 was discriminated against quite well, giving 78 and 74% RELATIVE PURITY values when the computer compared the composite spectra from the replicate runs of paint Entry 1 to library Entry 4. Conversely, paint entry 4 was run three times and RELATIVE PURITY values of 99, 100, and

TABLE 5—*Computer library comparison of paints differing only in manufacturer.*

a   RELATIVE PURITY for replicate runs of blue paints[a]

Library entry	1		4		
1	100	100	92	76	82
4	78	74	99	100	100

b   RELATIVE PURITY for replicate runs of brown paints[a]

Library entry	12			14		15			16		
12	100	98	94	89	95	85	96	89	90	90	90
14	83	87	93	100	100	87	91	85	89	96	96
15	88	96	90	91	99	96	98	100	83	95	93
16	84	87	97	99	90	93	86	82	100	100	100

c   RELATIVE PURITY for replicate runs of white paint[a]

Library entry	19		22		29				31		
19	95	95	87	94	87	89	86	98	82	89	93
22	91	90	99	98	93	89	96	95	81	89	96
29	91	92	89	99	95	96	96	100	87	96	95
31	81	96	82	96	91	95	90	93	100	100	97

[a]RELATIVE PURITY is defined in the discussion of Table 3 in the text. Each paint is designated in this table by the library entry number which was assigned to the composite spectrum used initially to build the library.
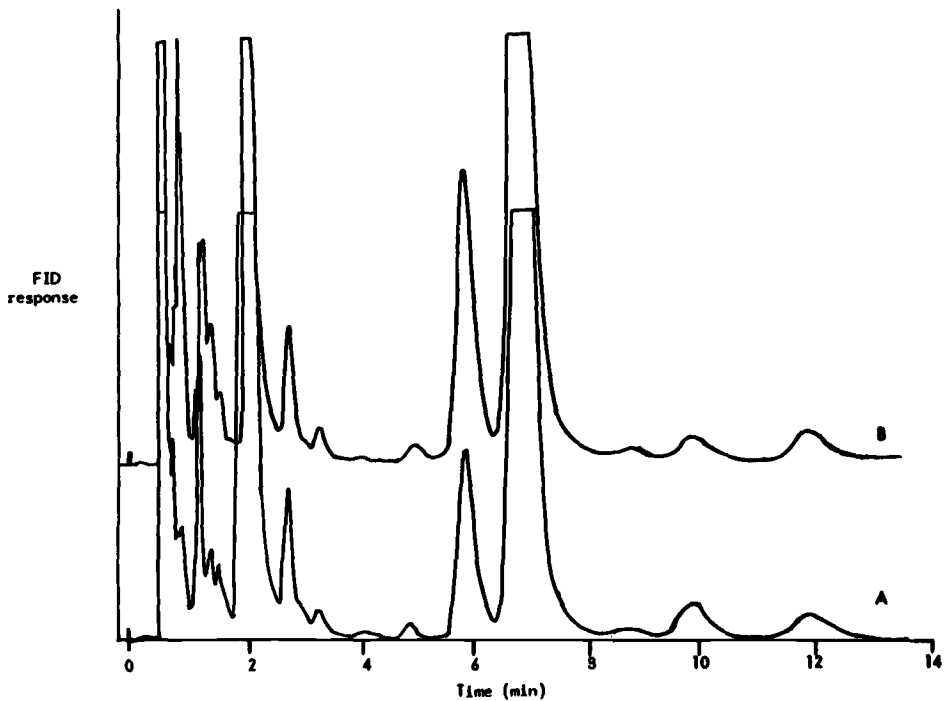

FIG. 3—*Packed column pyrograms of black paints:* (a) *library Entry 34;* (b) *library Entry 35.*

100% obtained when the composite spectra were compared to library Entry 4. The other values (92, 76, and 86%) are the RELATIVE PURITY values for paint Entry 4 compared to library Entry 1, again illustrating that the computer search discriminates the two paints adequately. An examination of the data for white paints (Table 5b) and brown paints (Table 5c) made to the same specifications but by different manufacturers shows that, in most cases, the correct choice has the highest RELATIVE PURITY within the group, but the discriminations are not as distinct. Also, in those cases where the highest RELATIVE PURITY shown is less than 100%, a library entry other than a paint from the particular color group being compared gave the best match. Although the discrimination was not as good, the results from the computer library searching would still be useful to guide the analyst to the best choices for further examination. In all of the nine groups of paints differing only in manufacturer, a study of the capillary pyrograms enabled the paints to be differentiated.

In the current study, no attempt was made to optimize the capillary GC conditions. The potential for using fused silica capillary columns can be demonstrated, however, by looking at pyrograms from the black paints (Entries 34 and 35). Figure 3 shows pyrograms from a typical packed column run, while those from a capillary system are shown in Fig. 4. Differentiation of the two paints based on the capillary traces is much easier than from the packed column work.

Conclusion

Although only a small fraction of the total FBI National Automotive Paint File was used in this preliminary study, the results are encouraging enough to suggest that a searchable data
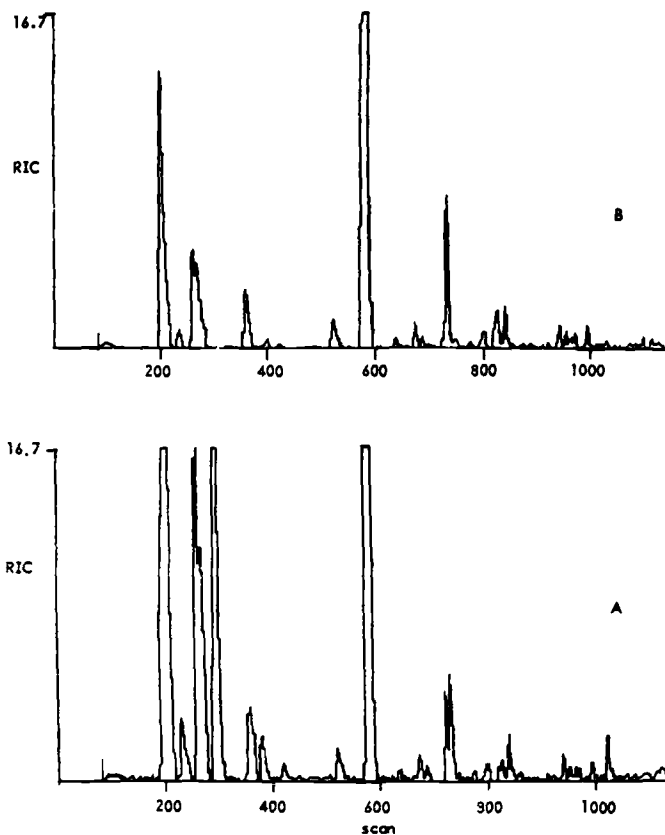

FIG. 4—*Capillary column pyrograms of black paints using conditions in Table 2b, fast run:* (a) *library Entry 34;* (b) *library Entry 35.*

base might be established by utilizing the composite mass spectra as proposed here. Other information available about the sample will allow the search to be narrowed sufficiently so that only a workable number of choices will be included. The problems associated with standardization of GC conditions are minimized, although capillary gas chromatography may be necessary to differentiate the more closely related paints. Since many forensic science laboratories now use pyrolysis-GC and since many also have GC/MS available, the potential for widespread use is apparent.

Even when the comparison which needs to be made is between questioned and known samples, the investigator may well compare the questioned material to the library entries to see if there are other possible matches which should be considered before a conclusion is reached. Wheals [2] has pointed out the difficulty in deciding when enough possibilities have been included in the matching process, and commented on the limited significance of analytical "identity" in the absence of a significant data collection.

The comparison of suspect paint samples with reference paint samples by PGC suffers because the suspect paint will have been exposed to many conditions (such as weathering, environmental contamination, waxing) which might cause the profile not to match the reference paint. While performing the comparison by pyrolysis-capillary gas chromatography-mass spectrometry does not offer a ready solution to this problem, the tremendous separating power of the capillary column coupled with the ability, using the mass spectrometer, to identify the individual components separated should prove useful. In addition, it seems plausible that the library building and search sequence suggested here has application in other forensic areas where an objective means of sample comparison is desired.

References

[1] Thornton, J. I., "Forensic Paint Examination," in *Forensic Science Handbook*, R. Saferstein, Ed., Prentice-Hall, Englewood Cliffs, NJ, 1982, pp. 529–571.

[2] Wheals, B. B., "Analytical Pyrolysis Techniques in Forensic Science," *Journal of Analytical and Applied Pyrolysis*, Vol. 2, No. 4, April 1981, pp. 277–292.

[3] Wheals, B. B. and Noble, W., "The Pyrolysis-Gas Chromatographic Examination of Car Paint Flakes as an Aid to Vehicle Characterization," *Journal of the Forensic Science Society*, Vol. 14, No. 1, Jan. 1974, pp. 23–32.

[4] Cartwright, N. S. and Rodgers, D. G., "A Proposed Data Base for the Identification of Automotive Paint," *Canadian Society of Forensic Science Journal*, Vol. 9, No. 9, Sept. 1976, pp. 145–154.

[5] Martz, R. M., Munson, T. O., and Lasswell, L. D., III, "Identification of Smokeless Powders and Their Residues by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," *Proceedings of the International Symposium on the Analysis and Detection of Explosives, March 29–31, 1983, FBI Academy, Quantico, Virginia,* U.S. Government Printing Office, 1984-426-295, pp. 245–254.

[6] Saferstein, R. and Manura, J. J., "Pyrolysis Mass Spectrometry—A New Forensic Science Technique," *Journal of Forensic Sciences*, Vol. 22, No. 4, April 1977, pp. 748–756.

[7] Hughes, J. C., Wheals, B. B., and Whitehouse, M. J., "Pyrolysis Mass Spectrometry. A Technique of Forensic Potential?" *Forensic Science*, Vol. 10, No. 10, Oct. 1977, pp. 217–228.

[8] Hughes, J. C., Wheals, B. B., and Whitehouse, M. J., "Simple Technique for the Pyrolysis-Mass Spectrometry of Polymeric Materials," *Analyst*, Vol. 102, No. 2, Feb. 1977, pp. 143–144.

[9] Hickman, D. A. and Jane, I., "Reproducibility of Pyrolysis-Mass Spectrometry Using Three Different Pyrolysis Systems," *Analyst*, Vol. 104, No. 4, April 1979, pp. 334–347.

[10] Eichelberger, J. W., Harris, L. E., and Budde, W. L., "Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography/Mass Spectrometry Systems," *Analytical Chemistry*, Vol. 47, June 1975, pp. 995–1000.

[11] *Finnigan MAT 100 Series Operators Manual*, Finnigan MAT Corporation, San Jose, CA, 1981.

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