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Pyrolysis Mass Spectrometry—A New Forensic Science Technique

Pyrolysis gas chromatography (PGC) has found wide acceptance in forensic science laboratories as a technique for identifying and comparing many types of synthetic polymeric materials, particulary paints, adhesives, and fibers [*1–5*]. As a tool for identification, this technique is restricted to assorting polymeric materials into broad classes. Wheals and Noble [*4*] have demonstrated the ease of identifying thermosetting alkyd finishes, acrylic lacquers, and acrylic enamels by PGC. Stewart [*2*] has used PGC to distinguish the three types of nonaqueous dispersion acrylic enamels commonly used by American automobile manufacturers, thereby facilitating the identification of a car's make and model from the pyrogram of its paint binder.

Probably of greater significance to the forensic analyst is the fact that PGC can detect slight differences in the chemical composition of paint binder formulations. The ability to discriminate paints derived from different sources is greatly enhanced by supplementing microscopic and solvent tests with PGC [*6*]. Hence, a careful comparison of the pyrograms of questioned and control paints may reveal slight differences in the chemical composition of their binders even though they may have the same color and belong to the same family of paints. This, of course, would immediately eliminate the possibility that the paints had a common origin. On the other hand, if two paints can be shown to have comparable pyrograms, this would enhance the probability that they originated from the same source.

At present, comparative PGC determinations are confined to intralaboratory analyses where the pyrogram patterns of known and questioned specimens can be compared directly. Owing to the large number of variables associated with the PGC technique (column composition, column length, column temperature, flow rates, and the pyrolyzer system), there seems to be little hope at this time that a standardized system can be implemented to permit the interlaboratory exchange of pyrolysis data and the maintenance of standard pyrogram collections for automobile paints in the United States.

One feasible alternative may be to combine the pyrolysis technique with mass spectrometry, thereby eliminating the gas chromatograph. This alternative has been suggested by DeForest [*7*] while studying the feasibility of individualizing hair through PGC. He later reported [*8*] that a preliminary investigation of high-resolution electron-impact pyrolysis mass spectrometry (PMS) showed some promise for the forensic individualization of hair and paint; however, the resultant fragmentation patterns were apparently too complex, limiting the applicability of the technique. Work has been in progress on "fingerprinting" biological material by PMS for a number of years. Zemany

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[*9*] first published mass pyrographs of albumin and pepsin in 1952. Other workers have since identified bacteria and other microorganisms by PMS [*10–13*].

This paper reports the results of our initial efforts at characterizing paint and synthetic fibers by PMS. In contrast to the studies cited above, we chose to simplify the resultant mass pyrograph (*pyro*lysis-spectro*graph*) by incorporating a chemical ionization (CI) source into our mass spectrometer. The CI process basically involves the reaction of an ionized reagent gas with the sample molecules in the mass spectrometer's source. By selecting the proper reagent gas, a proton transfer will ensue between the reagent gas and the sample causing the formation of a protonated molecular ion, $(MH)^+$. The major advantage of this approach is the ability to control the complexity of the fragmentation patterns. For example, by selecting isobutane as a reagent gas, the predominant mass spectral ions are expected to be $(MH)^+$ arising from a proton transfer between the *tert*-butyl ions and the sample molecules [*14*]. Few other fragmentation ions are normally present in an isobutane CI spectrum.

The simplicity of the resultant isobutane CI mass spectrum makes it amenable to the analysis of multicomponent mixtures. By inserting the mixture directly into the CI source one can correlate the resultant ions with the molecular weight plus one for many organic compounds. Forensic scientists have already used this approach for analyzing drugs [*15–18*] and explosive residues [*19–22*]. All of this work has been accomplished without resorting to a prior chromatographic separation technique.

With this approach various paints and fibers were pyrolyzed and their degradation products transferred directly to the CI source. Fragmentation patterns were generated and the resultant mass pyrographs were recorded on an oscillographic recorder.

Experimental Procedure

All CI spectra were taken on a Du Pont 21-490 single focusing magnetic sector mass spectrometer. The instrument was fitted with a dual EI/CI source and differential pumping. The unit has resolution of 600 with a 10% valley. The reagent gas selected was isobutane (99.9% pure) at a source pressure of 0.5 to 1.0 torr. The source temperature was 200°C, and the ionizing voltage was set at 420 eV in the CI mode.

The pyrolysis mass spectrometry system is shown in Fig. 1. Briefly, the system consists of a pyrolyzer (Chemical Data System Model 100) connected to the batch inlet of the mass spectrometer with 1/8-in. (3.2-mm) outside diameter stainless steel tubing. The batch inlet was maintained at 150°C. Pyrolysis was accomplished by inserting 0.5 mg

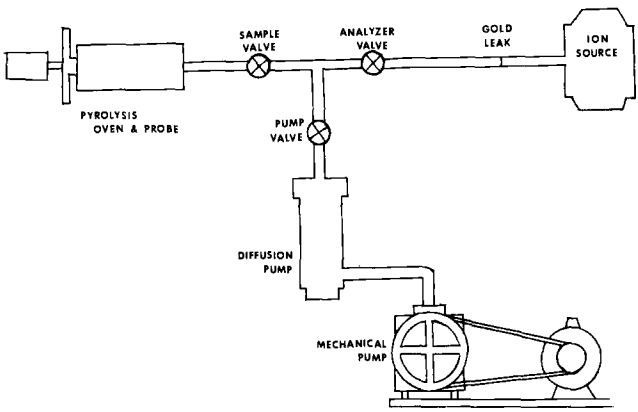

FIG. 1—*Schematic of pyrolysis mass spectrometry system.*

of material into a quartz tube. Each end of the tube was plugged with quartz wool. The tube was positioned into the platinum coiled probe of the pyrolyzer. The pyrolyzer chamber was heated to 150°C. A probe temperature of 800°C was maintained for 20 s to effect the thermal degradation of paint and fiber specimens. The pyrolyzates were passed directly into the evacuated batch inlet. Here the mixture was held for 60 s before the analyzer valve was opened leading to the source of the mass spectrometer. Scans were taken at set time intervals of 30, 60, and 90 s. All data presented in this paper represent spectra recorded at 60 s. All monomeric acrylates were purchased from Theta Corp., Media, Pa.

Results and Discussion

Degradation products frequently arising from the pyrolysis of acrylic polymers were analyzed by isobutane mass spectrometry. These materials were introduced into the CI source through the heated batch inlet. The resultant isobutane CI spectra are listed in Table 1.

TABLE 1—*Isobutane chemical ionization spectra of common thermal degradation products of acrylic polymers.*

Compound	Molecular Weight	MH^+	$MH^+ - H_2O$	Other Ions
Acrylic acid	72	73 (100%)	...	...
Methacrylic acid	86	87 (100%)	...	69 (20%)
Methyl acrylic acid	86	87 (100%)	...	...
Methyl methacrylate	100	101 (100%)	...	...
Ethyl acrylate	100	101 (100%)	...	...
Styrene	104	105 (100%)	...	91 (44%)
Allyl acrylate	112	113 (100%)	...	...
Ethyl methacrylate	114	115 (100%)	...	...
iso-propyl acrylate	114	115 (100%)	...	73 (60%)
2-hydroxyethyl acrylate	116	117 (100%)	99 (39%)	...
Allyl methacrylate	126	127 (100%)	...	...
n-butyl acrylate	128	129 (100%)	...	73 (20%)
sec-butyl acrylate	128	129 (100%)	...	73 (80%)
iso-butyl acrylate	128	129 (100%)	...	73 (20%)
n-propyl methacrylate	128	129 (100%)	...	87 (22%)
iso-propyl methacrylate	128	129 (100%)	...	87 (80%)
2-hydroxypropyl acrylate	130	131 (100%)	113 (46%)	73 (24%)
2-hydroxyethyl methacrylate	130	131 (100%)	113 (23%)	...
n-butyl methacrylate	142	143 (100%)	...	87 (20%)
iso-butyl methacrylate	142	143 (100%)	...	87 (25%)
sec-butyl methacrylate	142	143 (87%)	...	87 (100%)
tert-butyl methacrylate	142	143 (50%)	...	87 (100%)
n-amyl acrylate	142	143 (100%)	...	73 (50%); 71 (11%)
iso-amyl acrylate	142	143 (100%)	...	73 (13%); 71 (56%)
2-hydroxypropyl methacrylate	144	145 (100%)	127 (30%)	87 (30%)
Phenyl acrylate	148	149 (100%)	...	...
n-amyl methacrylate	156	157 (100%)	...	87 (40%)
iso-amyl methacrylate	156	157 (100%)	...	87 (20%); 71 (45%)
Phenyl methacrylate	162	163 (100%)	...	...
2-ethylhexyl acrylate	184	185 (60%)	...	113 (93%); 73 (100%)
2-ethylhexyl methacrylate	198	199 (100%)	...	87 (50%)

The majority of the compounds studied yielded one or two ion isobutane CI spectra. All showed intense protonated molecular ions. The loss of water occurred in those compounds containing an aliphatic hydroxyl group, a situation attributable to the loss of a protonated hydroxyl group from $(MH)^+$. Not surprisingly, de-esterification was the primary mode of fragmentation for many of the acrylic and methacrylic esters studied. Protonation of the carbonyl oxygen and a subsequent rearrangement analogous to the McLafferty rearrangement [*23*] (see Fig. 2) can explain the phenomenon.

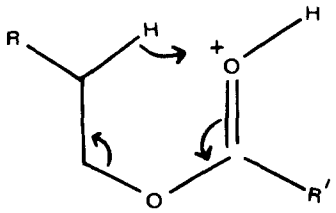

FIG. 2—*Mechanism for fragmentation of acrylic esters.*

One major disadvantage in selecting isobutane as the reagent gas was its inability to distinguish compounds having the same molecular weight. Often, for this reason, the absence of detailed fragmentation patterns limits the amount of structural information that can be derived from the isobutane CI spectrum. However, with isobutane as a reagent gas the components of a complex mixture of acrylic and methacrylic esters could be tentatively identified by correlating the spectra's major ions with $(MH)^+$ for specific acrylic and methacrylic esters (see Table 1).

Paint panels received from the Law Enforcement Standard Laboratory of the National Bureau of Standards were used for testing automotive paints by PMS. These finishes are actual production coatings obtained from automobile paint suppliers. Samples of various sizes were pyrolyzed into the mass spectrometer's source in an effort to obtain mass pyrographs repeatable to within 10% at each mass unit detected. A sample size of 0.5 mg was chosen to meet this criterion. Unfortunately, at this time, it is possible to retain this repeatability for only 6 h, a situation that limits the PMS technique to the direct comparison of known and questioned specimens within a given day.

Mass pyrographs produced by the PMS technique for different classes of automotive paints are listed in Table 2. As shown, a nonaqueous dispersion acrylic enamel, a water-based acrylic enamel, and an acrylic lacquer are readily differentiated from each other by PMS. The mass pyrographs of four paints of indistinguishable color are listed in Table 3. Again, no difficulty is encountered in differentiating these specimens by their mass pyrographs.

Finally, the mass pyrographs of eight paints, supplied to us by an outside source as part of a collaborative study [*24*], are shown in Table 4. Seven of the paints were white automobile finishes representative of the types of finishes common to American automobiles. The eighth was an unknown selected from one of the seven paints. The finishes were identified as follows:

(1) Du Pont, WA-2661, 1968 GM (acrylic lacquer);
(2) Du Pont, WA-2661, 1965 GM (acrylic Lacquer);
(3) PPG Industries, Ayl-EWI, 1972 Chrysler (acrylic enamel);
(4) Cook, M-1525A-NAD, 1973 Ford (acrylic enamel);
(5) Mt. Clemens, JWFAXXA (M-1619), 1973 Ford (acrylic enamel);
(6) Inmont, M-1619A, 1973 Ford (acrylic enamel);
(7) Mt. Clemens, M-1619 NAD, 1973 Ford (acrylic enamel); and
(8) unknown (one of the above).

TABLE 2—*Mass pyrographs of automobile paint, NBS standards.*

m/e	Nonaqueous Dispersion Enamel	Water-Based Enamel	Acrylic Solution Lacquer
201	...	2	3
161	9	6	...
160	4	...	...
156	...	1	...
149	...	...	1
145	7	2	...
144	11	6	2
143	100	64	15
133	5	...	...
131	11	7	1
129	6	21	...
127	4	...	...
119	20	3	...
117	9	...	...
113	10	3	...
110	7	...	...
106	4	2	...
105	27	21	...
104	5	5	...
103	...	...	1
102	...	6	6
101	5	100	100
100	4	...	...
99	4	...	...
91	...	6	...
87	8	6	1
86	6	...	...
85	6	1	...
73	19	4	1
71	8	2	2

Eight forensic science laboratories participated in the study. All differentiated the seven finishes from each other by PGC and identified the unknown as Sample 3. Our laboratory subjected these specimens to PMS. Our conclusion was similar to the other participants: the unknown compared with Sample 3. Furthermore, the mass pyrographs of each of the seven paints were distinguishable from each other.

The mass pyrographs of the acrylic lacquers are easily recognizable by their relative simplicity. Gas chromatographic pyrograms of this type binder are characterized by a predominant methyl methacrylate peak [*4*], a situation that is repeated in their mass pyrographs. The acrylic enamels present a far more complex spectra. In the paints examined butyl methacrylate and styrene contributed strong ions to the acrylic enamel mass pyrographs. Many of these paints also contained ions that could tentatively be correlated with many of the compounds listed in Table 1. Undoubtedly, the significant degree of variation existing between the mass pyrographs of acrylic enamel paints lends greater weight to their individualization by this technique and hence to their probative value as physical evidence.

The application of PMS is not restricted to paints. Table 5 shows the mass pyrographs obtained for three different types of acrylic fibers. Each fiber is readily differentiated by its fragmentation pattern.

Although this work is preliminary and more research remains to be done to establish the value of the technique for forensic science applications, it is interesting to speculate as to the potential of PMS as well as to its advantages over PGC. Determinations by

TABLE 3—*Mass pyrographs of automobile paint, metallic green.*

m/e	PPG Industries Acrylic Solution Lacquer	Inmont Acrylic Solution Lacquer	PPG Industries Water-Based Enamel	Inmont Water-Based Enamel
201	4	3	...	2
161	...	...	9	6
156	...	...	...	1
149	4	1	5	...
145	...	...	...	2
144	...	2	9	6
143	...	15	100	64
131	1	1	...	7
129	7	...	10	21
119	...	...	...	3
113	...	...	...	3
111	...	...	36	...
106	...	...	...	2
105	...	...	...	21
104	...	...	...	5
103	1	1	3	...
102	...	6	6	6
101	100	100	94	100
99	...	...	4	...
97	...	...	6	...
91	...	...	...	6
89	1	2	...	...
87	...	1	9	6
85	...	...	7	1
73	1	1	24	4
71	1	2	12	2

TABLE 4—*Proficiency test on white automobile paints.*

m/e	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Unknown
185	...	...	3	...	4	...	...	8
149	20	1	...	...	...	...	...	...
143	...	...	45	75	100	98	100	45
131	...	...	...	...	...	10	...	...
129	10	...	...	25	5	3	8	...
127	2	...	...	20	15	8	10	...
113	...	...	45	20	30	10	17	45
105	...	...	73	69	42	45	80	70
104	...	...	73	64	45	45	82	71
102	12	5	...	...	...	...	...	...
101	100	100	100	...	40	...	92	100
100	10	5	...	...	...	...	...	...
91	...	2	60	85	45	35	75	60
89	8	1	...	...	...	...	...	...
87	...	...	40	...	95	100	98	40
85	7	3	15	65	...	...	10	10
81	9	3	10	50	...	...	10	10
73	8	2	35	100	20	5	25	35
71	6	4	37	75	22	2	27	39

PMS are rapid; they can be performed in less than 5 min, a significant reduction in analysis time when compared with PGC. Furthermore, all pyrolysis products volatile enough to pass into and through the vapor chamber (batch inlet) will contribute to the

TABLE 5—*Mass pyrographs of acrylic fibers.*

m/e	Orlon® Type 42	Acrilan® 16	Teklan
177	15	16	...
165	22	15	...
163	20	28	...
151	18	13	...
149	...	...	37
147	...	...	10
143	...	...	11
129	...	...	18
126	10	...	...
124	25	13	...
123	...	...	22
117	...	...	70
115	...	...	21
113	14	13	23
107	10	12	...
103	...	...	10
101	...	...	11
99	6	10	18
97	8	9	16
95	9	10	10
91	...	...	53
88	...	100	...
87	...	...	12
85	9	8	18
77	...	...	11
75	7	...	10
74	100	12	11
73	38	44	100
71	16	18	33
70	10	9	15
69	12	9	16
68	13	10	...

final mass spectrum. With PGC this situation is different as some degradation products such as free acids may not be able to be chromatographed and hence will not reach the detector of the gas chromatograph. Even more important is the ability of PMS to record and store voluminous numbers of pyrographs in a computer that has been interfaced to the mass spectrometer. The ability to store and retrieve this type of information would give forensic scientists a feasible means for creating and searching extensive pyrograph libraries composed of different automotive paints. This situation would enhance the crime laboratories' ability to identify the minute quantities of paint that are found at many crime scenes. Of course, the feasibility of this approach would also depend on the creation of a comprehensive program aimed at collecting paint standards from the various automotive manufacturers and suppliers, a considerable undertaking in itself. Pyrolysis mass spectrometry does, however, offer a reasonable solution for the storage, retrieval, and dissemination of the large numbers of spectra that would be generated from such a program.

Another point is that the PMS technique may be amenable to generating standardized and reproducible pyrolytic data because it does not have to contend with the many variables associated with gas chromatography, a situation that at present makes PGC unsuitable for creating standard pyrogram libraries. The potential for developing reproducible mass pyrographs may make feasible the interlaboratory exchange of data and the development of reproducible "fingerprint" libraries for the identification of paints. In this

context, the present utility and availability of mass spectral libraries for the identification of drugs should be remembered when one ponders the potential for creating mass pyrograph libraries.

A number of alternatives exist for improving the sensitivity and day-to-day reproducibility of the PMS technique. First, it is essential that additional work with PMS be computer-assisted. Our present capabilities allow us to record only a single mass spectrum at arbitrarily chosen time intervals. Poor reproducibility and low sensitivity can be expected with this approach. Having the ability to continuously scan the relevant mass range of the spectrum and being able to sum the entire series of scans with the aid of a computer should dramatically enhance the sensitivity and reproducibility of the resultant mass pyrographs. Second, the pyrolysis procedure described was performed in a static mode, that is, in the absence of a gas flow. The primary disadvantage of this approach is that it enhances the occurrence of recombination reactions in the pyrolysis chamber, resulting in a reduction in sensitivity and repeatability. A planned modification of our pyrolyzer system will allow the reagent gas (isobutane) to flow through the pyrolyzer chamber while the sample is being heated. The flowing gas will quickly move the pyrolytic products out of the heated zone and into the batch inlet, thus minimizing residence time in the pyrolyzer chamber. It is expected that this modification should reduce secondary recombination reactions and result in enhanced sensitivity and repeatability.

The initial data from this study are encouraging. The immediate advantage of PMS is that it expands the utility of the mass spectrometer in the crime laboratory. In past years, many forensic science facilities purchased mass spectrometers solely for drug identification. Now there is the potential for applying the mass spectrometer to the comparison and identification of other types of physical evidence. At this time, PMS has been found suitable for the direct comparison of paints and fibers.

Summary

A CI mass spectrometer has been modified to monitor the pyrolysis products of paints and fibers. Materials were pyrolyzed by a heated platinum coil directly into the batch inlet of a CI mass spectrometer. The simple fragmentation patterns produced by isobutane CI permits the operator to correlate a large number of the resultant ions with the thermal degradation products of acrylic polymers. The mass pyrographs generated are sufficiently detailed to allow the operator to distinguish various types of automotive finishes and acrylic fibers. The technique has been successfully used for the direct comparison of a variety of automotive paint specimens.

Potentially, PMS may provide forensic scientists with a technique for collecting and disseminating mass pyrograph libraries for the identification and comparison of various types of synthetic polymeric physical evidence.

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