TECHNICAL NOTE

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Applications of Pyrolysis Gas Chromatography/Mass Spectrometry to Toner Materials from Photocopiers

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ABSTRACT: Analytical pyrolysis, pyrolysis gas chromatography (GC), and pyrolysis gas chromatography/mass spectrometry (GC/MS) have been used extensively in forensic science laboratories for the identification of difficult samples. Much of the original work concerned samples of paint—generally from cases involving automobiles. Since then many other materials have been examined, including fibers from clothing, hair, and a variety of polymeric substances. Other investigators have used pyrolysis GC to examine cellulose products such as wood, bark, paper, and so forth, and yet others have used the technique to look at pigments, coatings, and inks. This paper presents the analysis of a variety of photocopies produced by different manufacturers of copying instruments. Sections of the printed paper were pyrolyzed, and the pyrolysates were analyzed by GC/MS. Specific differences were noted to be dependent on the type of toner material used in the photocopying process of each make of copier. Significant peaks were selected and identified by their mass spectra to indicate the chemical differences in toner material. Pyrograms and mass spectral data are presented for the toner material, toner on paper, and blank paper for subtraction from the pyrograms of toner material on paper.

KEYWORDS: forensic science, photocopiers, chromatographic analysis

Forensic chemists are frequently responsible for the analysis of evidence which consists of a nonsoluble, nonvolatile solid material. As in other analytical fields, pyrolysis permits the investigation of these substances via gas chromatography (GC) by fragmenting the materials and producing volatile compounds.

Automobile paint flakes from accident scenes provide the most readily recognized examples of forensic pyrolysis, as it is a sample type analyzed by many laboratories using a variety of procedures. A number of papers have been published on this topic (Refs *1* to *3*, for example), and over the last decade, the technique has become routine. Other samples pyrolyzed in forensic science laboratories include house paint, adhesives, and fibers, as reviewed by Wheals [*4*]. Similar samples are discussed by Saferstein and Manura [*5*] using pyrolysis mass spectrometric (MS) techniques. Cellulose, paper, and wood products have also been extensively studied by pyrolysis [*6*], using a variety of analytical schemes, including pyrolysis MS [*7*].

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The problem addressed here was whether or not pyrolysis and pyrolysis GC/MS could be used to distinguish among various brands of photocopiers, based on the pyrolysis of the black toner material while it was still attached to the paper onto which it was printed. Nine samples of photocopies were obtained representing four manufacturers, and labeled K-1, K-2, M-1, S-1, S-2, X-1, X-2, X-3, and X-4.

Experimental Procedure

Samples of the photocopier papers with and without toner material were pyrolyzed at 650°C for 10 s using a Chemical Data Systems Pyroprobe 120 Pyrolyzer. The pyrolysis runs were performed on paper samples measuring 1 by 10 mm and 1 by 1 mm, which were inserted into a quartz tube. The tube was placed into the platinum coil of the Pyroprobe for pyrolysis. The pyrolysates were analyzed originally using split capillary GC. A 50-m by 0.25-mm SE54 fused silica capillary column was programmed from 25 to 290°C at 6°/min with a 60:1 split of the helium carrier and a flame-ionization detector (FID). Differentiating peaks were identified and repeat runs were performed using pyrolysis GC/MS to identify the significant peaks.

Results and Discussion

Initial pyrolyses were performed on sections of the copier paper only (without toner) followed by pyrolyses of the paper with toner to look for the addition of significant peaks. It was assumed that many of the peaks in the chromatogram would result from the pyrolysis of the paper itself, and in fact, there were some differences in the relative peak intesities seen from brand to brand in the paper alone.

Original runs were performed on slices of paper 1 by 10 mm at 650°C. Examples of each brand of photocopier toner on paper are shown in Figs. 1 to 5. These initial runs showed that many of the peaks differentiating the photocopier brands were significant contributors to the chromatograms. A second series of pyrolyses was carried out using paper slices 1 by 1 mm, again at 650°C for 10 s. From these chromatograms, 15 peaks were identified which indicate differences between brands (and sometimes between model numbers within a brand). Chromatograms of the smaller samples are shown as Figs. 7 to 11, while Fig. 6 shows the pyrolysis of a piece of white paper only, without toner. In each figure, the numbers indicate a significant peak (or show where it would appear in chromatogram if it were present). The 15 peaks were chosen as indicators of differences among the various brands of photocopiers, and a summary of their presence or absence in each make and model of photocopier is compiled as Table 1.

It can be seen from the chromatograms (and the table) that there are several major peaks that are present in each separate brand of photocopier. Brand S for example is the only one that shows strong peaks at Numbers 14 and 15. Brand K has no 14 or 15, but has a major Peak 13, and it is the only one that does. Brand K also has a large Peak 8, which Brand S does not, but Peak 8 is also present in Brand X. X, however, also contains a major Peak 10 shared by neither Brand S nor Brand K.

Within a manufacturer, there was little difference seen in the toner formulations used for different models, with the exception of Brand X. Here, Models 1, 2, and 3 all used similar (or the same) toner formulations, and the chromatograms greatly resemble each other. Brand X-4, however, differs significantly from the others, most noticeably in the absence of Peaks 8 and 10.

The most similar of the brands were seen to be M and X. Here only minor peaks and peak intensities differentiate the brands, and it is possible that the toner formulation used for both of the photocopiers is essentially the same.

In an effort to identify some of the materials used in the photocopying process, specific peaks were analyzed by GC/MS. The results of these analyses indicate that Peak 1 is methyl methacrylate, Peak 2 is toluene, Peak 4 is glycidol, and Peak 7 is furfural. Peaks 8 and 10,

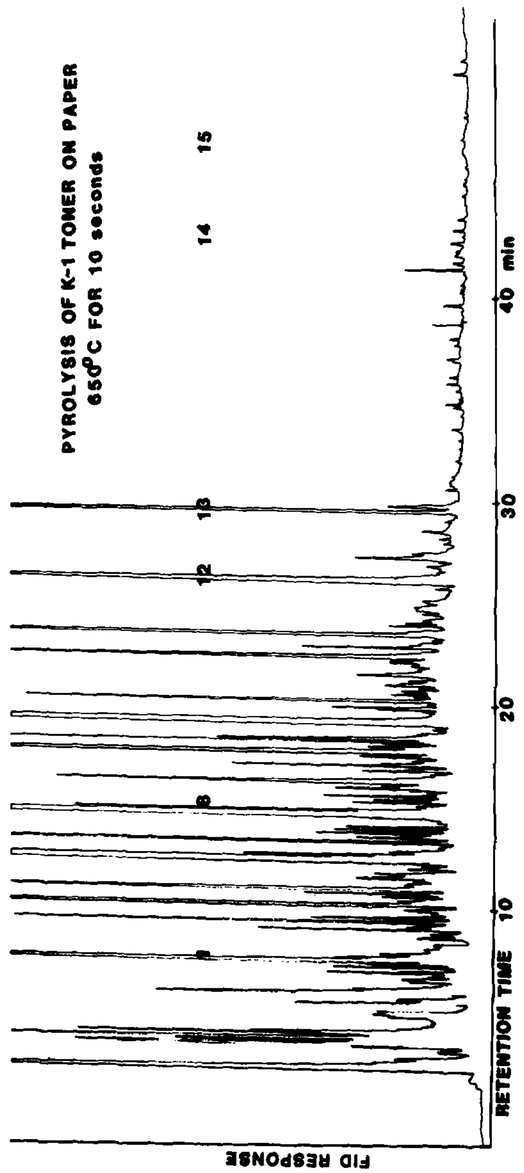

FIG. 1—Pyrolysis of K-1 toner on paper at 650°C for 10 s.

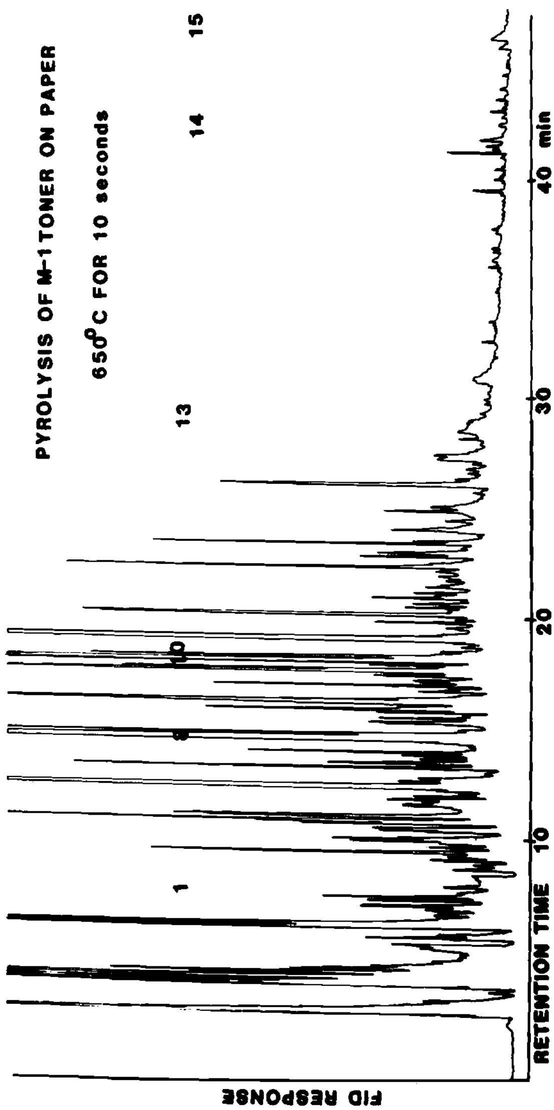

FIG. 2—*Pyrolysis of M-1 toner on paper at 650°C for 10 s.*

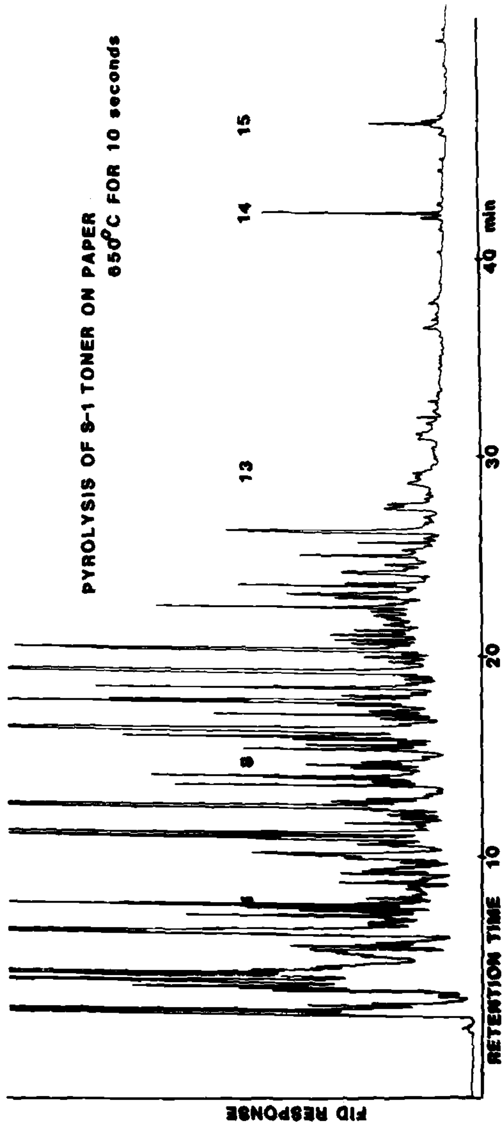

FIG. 3—*Pyrolysis of S-1 toner on paper at 650°C for 10 s.*

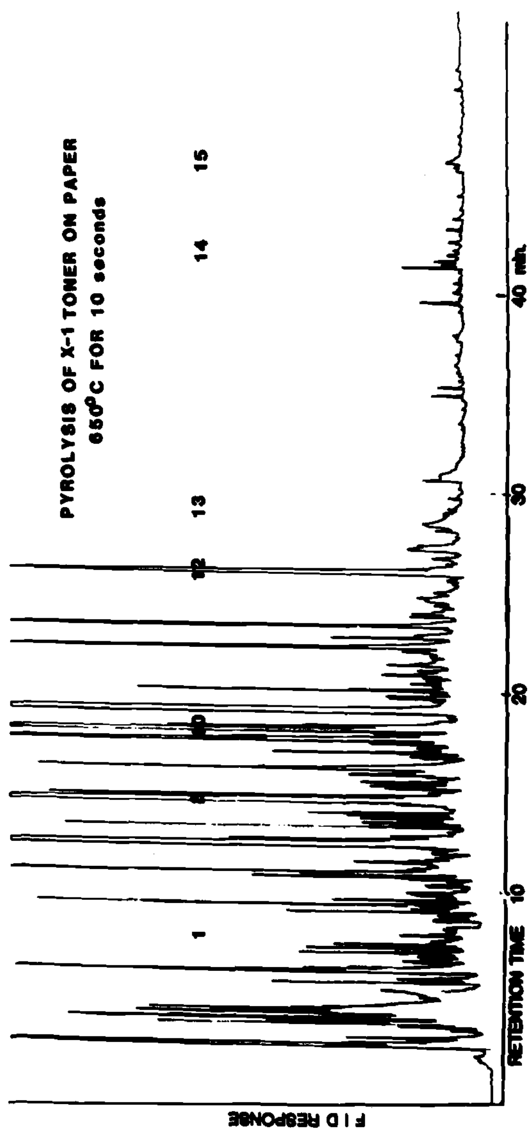

FIG. 4—*Pyrolysis of X-1 toner on paper at 650°C for 10 s.*

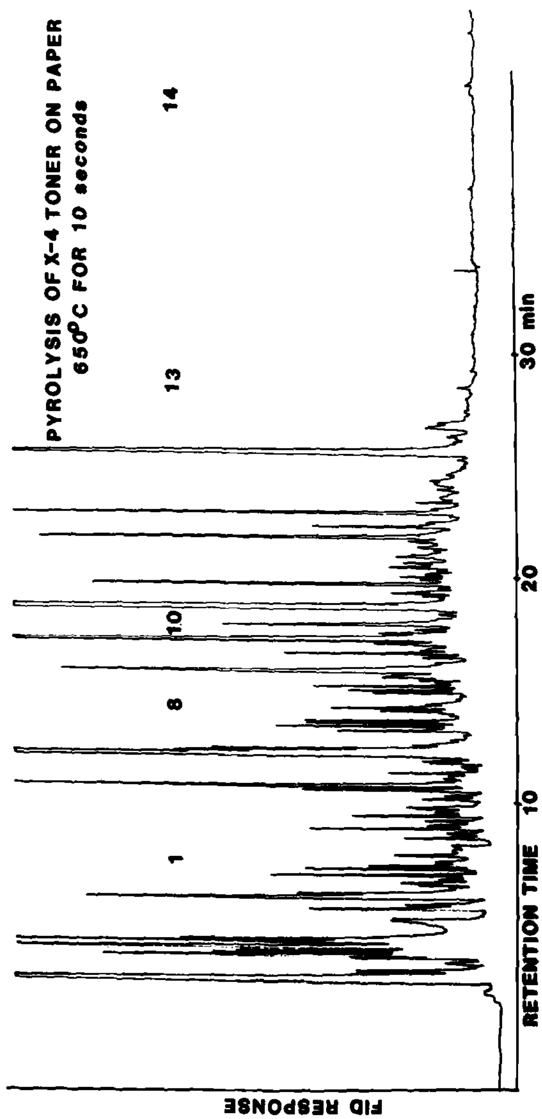

FIG. 5—*Pyrolysis of X-4 toner on paper at 650°C for 10 s.*

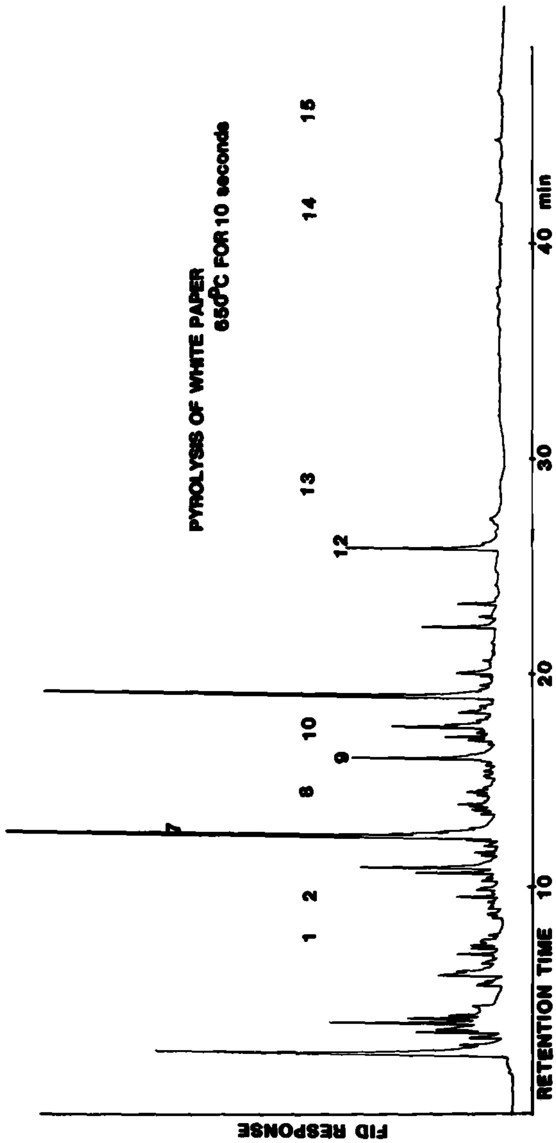

FIG. 6—*Pyrolysis of white paper at 650°C for 10 s.*

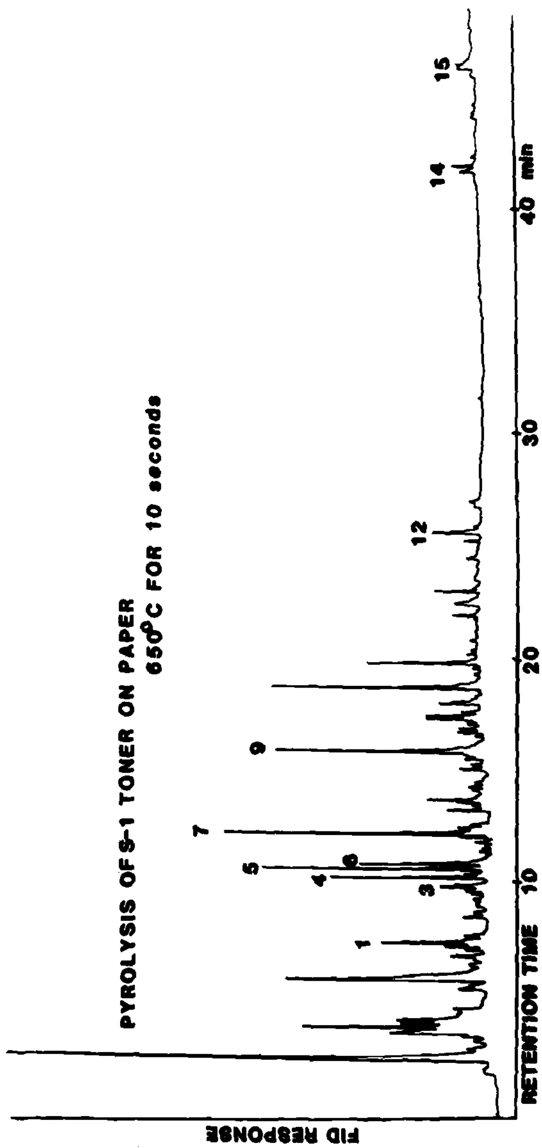

FIG. 7—*Pyrolysis of S-1 toner on paper at 650°C for 10 s.*

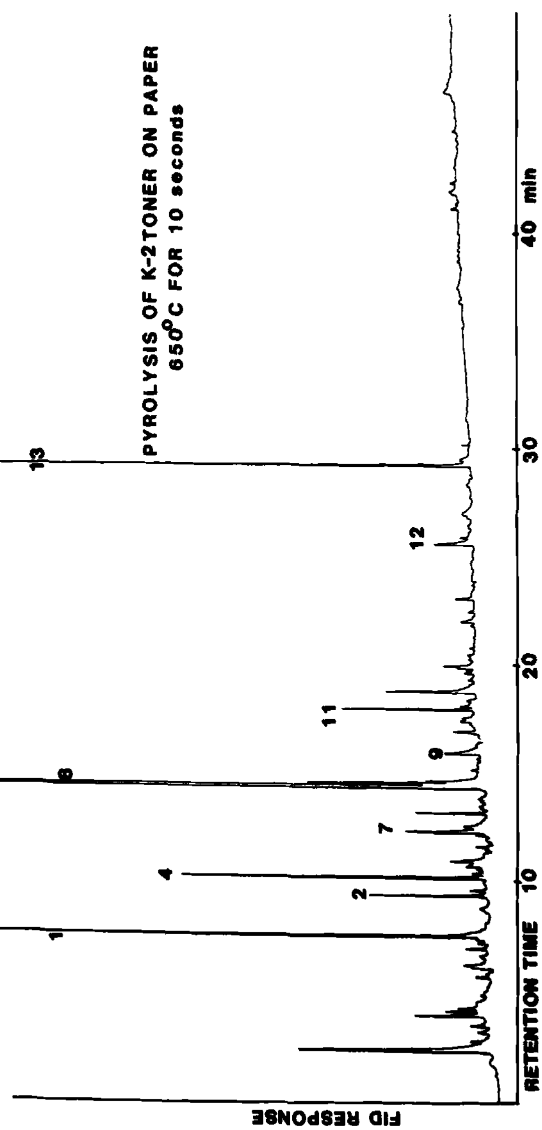

FIG. 8—*Pyrolysis of K-2 toner on paper at 650°C for 10 s.*

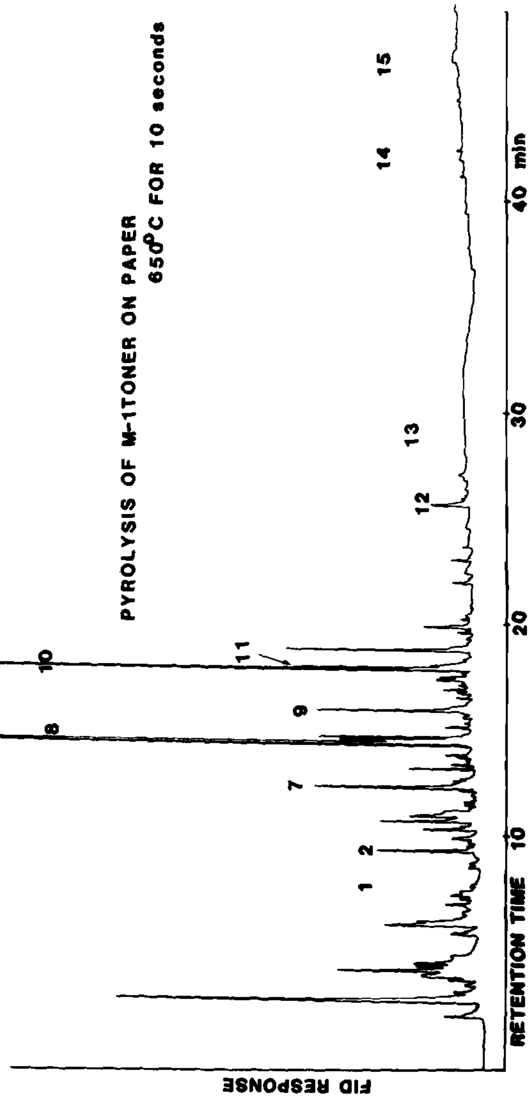

FIG. 9—*Pyrolysis of M-1 toner on paper at 650°C for 10 s.*

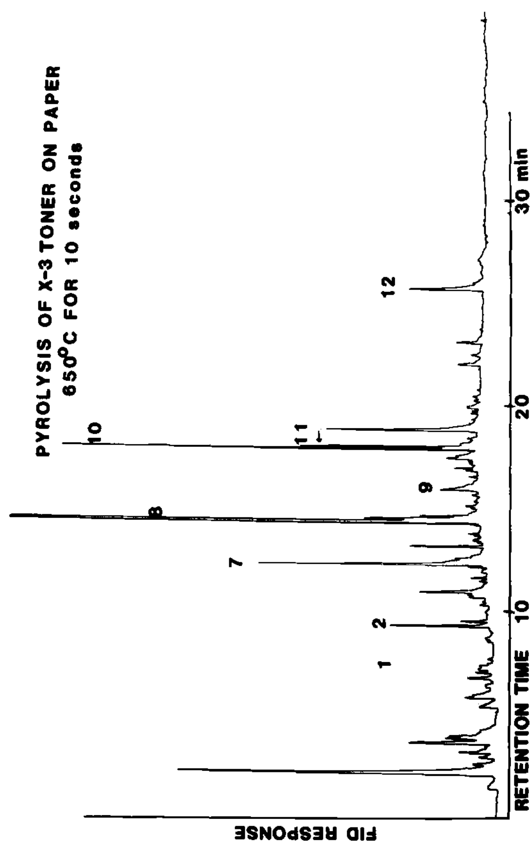

FIG. 10—*Pyrolysis of X-3 toner on paper at 650°C for 10 s.*

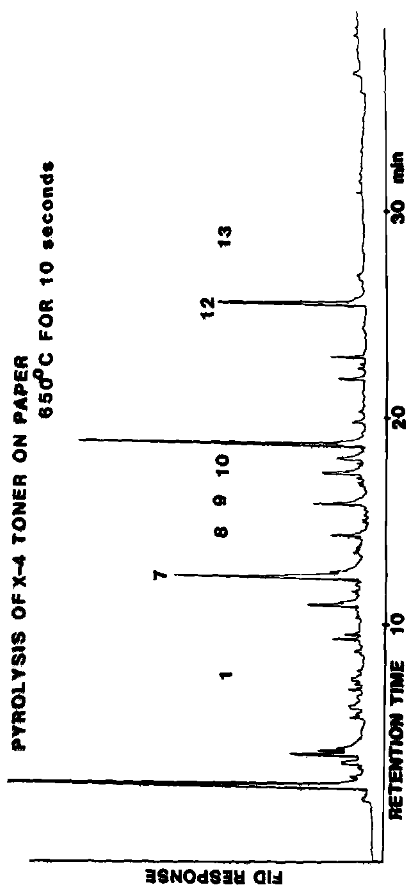

FIG. 11—*Pyrolysis of X-4 toner on paper at 650°C for 10 s.*

TABLE 1—*Peaks associated with various toner systems.*

	Peaks														
Toner System	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
K-1	X	X		X			X	X	X		X	X	X		
K-2	X	X		X			X	X	X		X	X	X		
M-1		X					X	X	X	X	X	X			
S-1	X		X	X	X	X	X		X			X		X	X
S-2	X		X	X	X	X	X		X			X		X	X
X-1		X					X	X	X	X	X	X			
X-2		X					X	X	X	X	X	X			
X-3		X					X	X	X	X	X	X			
X-4							X		X			X			

which are important in the distinction of Brand X-4 from the other X models (and Brands K and S from X-1, X-2, X-3, and M-1), are styrene and butyl methacrylate, respectively. In addition, dodecyl methacrylate and tetradecyl methacrylate have been identified, as well as 1-dodecene and 1-tetradecene.

Conclusions

Photocopying processes generally involve the application of a polymer-based toner to white paper. Several different polymer systems are in general use and may easily be differentiated using pyrolysis GC and pyrolysis GC/MS. This not only provides a tool for the analysis of document photocopies by forensic science laboratories, but suggests the applicability of pyrolysis GC/MS to the analysis of other ink and paper systems involved in the evaluation of documents as evidence.

References

[1] May, R., Pearson, E., Porter, J., and Scothern, M., "A Reproducible Pyrolysis Gas Chromatographic Systems for the Analysis of Paints and Plastics," *The Analyst*, Vol. 98, 1973, p. 364.

[2] Stewart, W. D., Jr., "Pyrolysis-Gas Chromatographic Analysis of Automobile Paints," *Journal of Forensic Sciences*, Vol. 19, No. 1, Jan. 1974, pp. 121-129.

[3] Wheals, 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, 1974, p. 23.

[4] Wheals, B., "Analytical Pyrolysis Techniques in Forensic Science," *Journal of Analytical and Applied Pyrolysis*, Vol. 2, 1980/1981, p. 277.

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

[6] Schfizadeh, F., Furneaux, R., Cochran, T., Scholl, J., and Sakai, Y., "Production of Levoglucosan and Glucose from Cellulose Material," *Journal of Applied Polymer Science*, Vol. 23, 1979, p. 3525.

[7] Franklin, W., "Direct Pyrolysis of Cellulose and Cellulose Deriv. in an M.S. with Data Systems," *Analytical Chemistry*, Vol. 50, 1978, p. 992.

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