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The Classification of Photocopies by Pyrolysis Gas Chromatography-Mass Spectrometry

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ABSTRACT: Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) was used to compare photocopy toner material from photocopies from 62 different (brand name or model number or both) photocopy machines. A simple sample lifter was developed for obtaining a specimen of toner from the copy free of paper fibers. Toner obtained from a single, standard typewriter-sized character usually provided enough organic material to give a satisfactory pyrogram. Based upon the presence or absence of peaks in the pyrograms, the toners were separated into 18 classes. Most of the toner classes fell into 2 general groups: those containing a large amount of styrene, usually with smaller amounts of butyl methacrylate or other methacrylates or acrylates, or some combination of these chemicals; and those toners consisting mainly of some type of epoxy resin.

KEYWORDS: questioned documents, photocopiers, chemical analysis, pyrolysis gas chromatography, mass spectrometry

In an investigation to determine the source of a photocopied document, the identification of photocopy machines which would produce copies most closely resembling the questioned copy is a considerable help to the investigator. The Federal Bureau of Investigation (FBI) Laboratory maintains two files of information which are used for the classification of photocopies—the Office Copier Standards File and the Similar Models File. The methods used for classification of photocopies at the FBI Laboratory have recently been reviewed [*1*]. Document examiners in the FBI Laboratory use ten class characteristics to classify photocopy machines: paper type, toner type, toner application, reduction, enlargement, magnetic properties, paper supply, marks, fusion method, and color. While some of these characteristics are fairly obvious, discerning several of these class characteristics requires considerable skill and discretion on the part of the document examiner. Unfortunately, the most discriminating class characteristic, the fusion method (the means by which the toner is permanently affixed to the sheet of paper), is the most subtle and the most difficult to determine.

Any additional method for classifying photocopies would be useful, because when a photocopy has been classified using the above ten class characteristics, the number of possible source machines for the questioned photocopy can still be quite large.

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Several studies have been reported in which instrumental methods have been used to compare photocopies. Kemp and Totty scraped toner from photocopies and used infrared spectroscopy (IR) for the comparison [*2*]. Wampler and Levy compared toners still attached to paper by pyrolysis-gas chromatography (Py-GC) [*3*] and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) [*4*]. Zimmerman et al. [*5*] examined raw photocopy toners and toners dissolved from photocopies by both IR and Py-GC. All of these studies indicated that classification of photocopies by chemical analysis of the toners might be a useful addition to the classification by physical characteristics. Each of the instrumental techniques cited above, however, presents the examiner with considerable difficulties in sample handling and data interpretation. This report summarizes the results of the comparison of photocopies from 62 different (brand name or model number or both) photocopy machines by Py-GC-MS using a simple technique for obtaining a specimen of the toner from the copy free of paper fibers.

Materials and Methods

Of the 62 different photocopy samples used for this study, 57 were from exemplars contained in the Office Copier Standards File. The additional 5 specimens were from machines in use at FBI Headquarters or the FBI Academy. All of the copies were made on machines which were operated using the "name brand" toner specified by the manufacturer. The toner specimens to be analyzed were removed from the photocopies using a technique developed as part of this project and described in detail elsewhere [*6*]. Briefly, a sample lifter (a glass microslide approximately 1.5 by 4.0 mm) placed over the character on the document to be sampled is touched for several seconds with a hot soldering iron to melt the toner. After being allowed to cool for about 5 min, the sample lifter is pried loose from the document with the tip of a scalpel. A substantial portion of the toner releases from the paper and adheres to the sample lifter. Figure 1 shows a typical example of toner lifted from a photocopy using this technique. The toner specimen adhering to the sample lifter is then analyzed as described below.

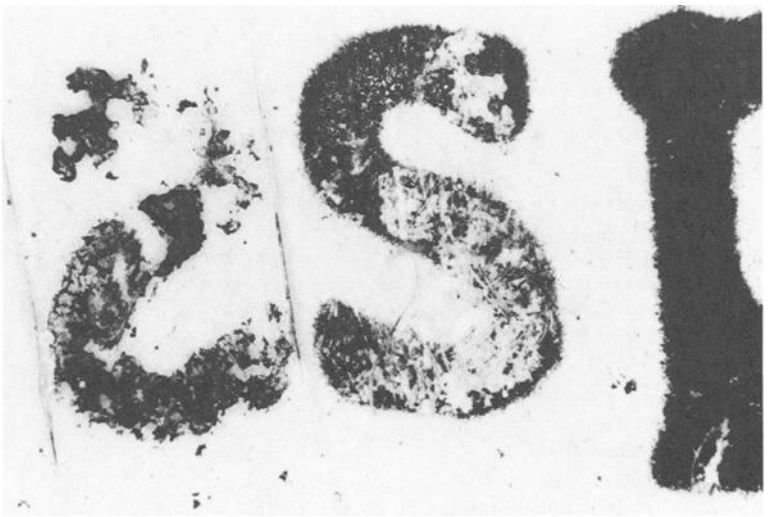


FIG. 1—*A sample lifter (the glass rectangle with the backwards letter "s") has been used to remove a portion of the toner from the letter "s" displayed. A fiber is visible which has been ripped up from the page in the process (shown at about ×40 magnification).*

All of the data presented in this report were generated using a Hewlett-Packard (HP) 5890 gas chromatograph connected to an HP 5970B Mass Selective Detector controlled by an HP 236 computer (HP 59970 MS Chemstation using the 3.1 revision software, Hewlett-Packard Company, Avondale, PA). This instrument performs 70 electron volt electron impact ionization MS. The figures were drawn by the computer software using an HP 7475A plotter.

A DB-5 bonded-phase fused silica GC column, 22-m by 0.25-mm internal diameter with a 0.25-μm film thickness (J & W Scientific, obtained from Alltech Associates, Deerfield, IL) was used. The pyrolysis was performed with a CDS Model 122 Pyroprobe system using a coil filament with a quartz sample tube (Chemical Data Systems, Oxford, PA). The sample lifter described above was designed so that the lifter with the attached specimen could be inserted into the quartz sample tube for the analysis. The Py-GC-MS system was set up and tested as described elsewhere [*7*]. Presumptive identification of some of the compounds encountered was performed by searching the spectra of the unknowns against the database resident on the instrument (PBM Search and Parametric Retrieval Software using a NBS/NIH/EPA/MSDC database, copyright 1984, 1986). The matching spectra were compared to the complete spectra published in the EPA/NIH Mass Spectral Data Base [*8*]. The experimental conditions used are presented in Table 1.

Results and Discussion

The letters of a photocopy formed by the dry toner process consist of the coloring material (for instance, iron oxide or carbon black) imbedded in a matrix of organic material bonded on top of the paper. A single, standard typewriter-sized character usually transfers enough organic material to the sample lifter to give a usable pyrogram (for example, the amount of material adhering to the sample lifter shown in Fig. 1).

Two dry toners were encountered in this study, however, which transferred very little organic material to the sample lifter, presumably because the toner on the finished copy contained very little organic material. A copy from a Clark CMC 2000 photocopy machine

TABLE 1—*Experimental conditions.*

Pyrolysis	
ramp	off
temperature setting	850°C
time	20 s
interface temperature	200°C
carrier gas flow rate	35 mL/min
Gas chromatography	
injector temperature	250°C
linear velocity at 50°C	50 cm/s
carrier gas	helium
oven temperature program	50°C for 0 min 25°C/min to 200°C 10°C/min to 300°C hold 300°C for 5 min
split ratio	20 to 1
septum purge	0.5 mL/min
Mass spectrometry	
transfer line temperature	250°C
electron multiplier voltage	−1800 to −1900 V
scan range	35 to 350 amu[a]
scan rate	1.5 scans/s

[a]amu = atomic mass unit.

yielded a pyrogram with no peaks other than a small carbon dioxide peak; and a copy from a 3M 379 copier, upon repeated attempts, yielded only a weak pyrogram (Class 13 in Fig. 2). In their study of toners by IR, Kemp and Totty [*2*] also observed that some toners appear to consist mainly of carbon black with very little organic material. This method for the examination of photocopies fails completely with those copies which are formed by the liquid toner process, in which the liquid toner (ink) flows into the paper fibers without leaving a substantial layer of polymeric material on the surface of the paper to stick to the sample lifter. Figure 2 shows typical toner pyrograms. The similarities and differences are readily apparent because these pyrograms do not contain a forest of peaks originating from the pyrolysis of paper [*3,4*].

Toner Classification

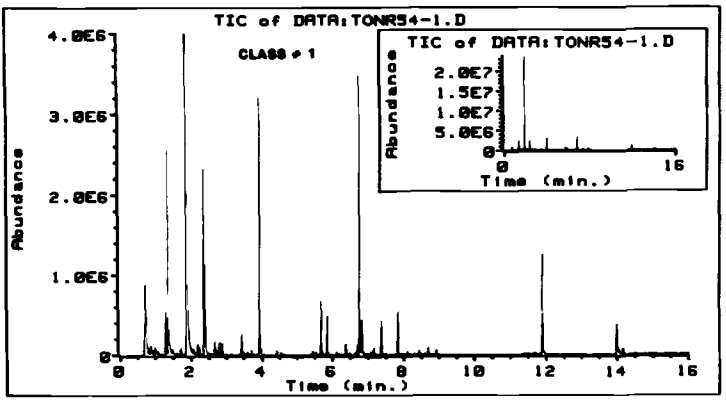
After most of the photocopies used in this study had been run once, it became apparent that more than a dozen different patterns were present in the pyrograms, but not a different one for each different photocopier. This result was not unexpected.

Although there are hundreds of different photocopy machines, there are fewer (several dozen) different photocopy "engines" (the mechanism inside the machine which actually produces the copy on the paper). It seemed reasonable at the outset to expect that the number of different toner formulations would be equal to or less than the number of different photocopy engines (ignoring "off-brand" toners). Upon examination of the pyrograms, it became apparent that the toner pyrograms could be sorted into classes based solely upon a few of the GC peaks. Table 2 displays a key for the classification of the photocopies examined in this study and shows the members of each class.

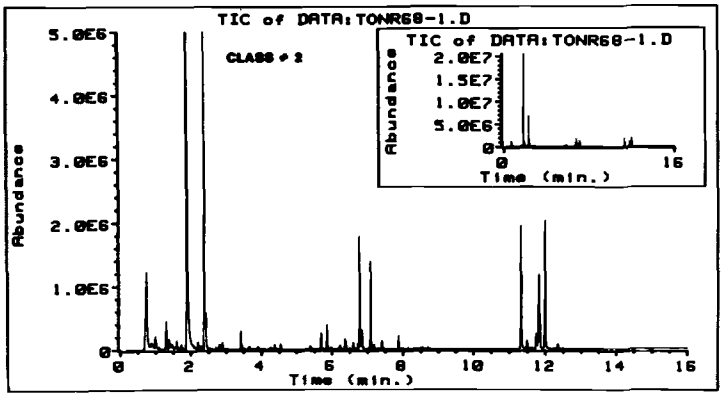
Included in the table are the presumptive identities of some of the peaks used for the classification. These identifications should be considered as tentative because, although the unknown spectra were matched against those in the EPA/NIH Mass Spectral Data Base, standards were not run to confirm the spectra and the GC retention times. No corresponding spectra were found for the peaks at 11.8 min (designated unknown A) and 12.0 min (assumed to be styrene trimer). A peak frequently seen at 6.8 min (but not included in the classification key) and the peak at 12.0 min gave related spectra which are consistent with the assumption that these compounds are styrene dimer and trimer (based solely upon the mass fragments in the spectra, since reference spectra for these compounds were not available).

Most of the toner pyrograms fell into two general types: those which were dominated by a large styrene peak, usually with additional peaks of butyl methacrylate or other methacrylates or acrylates or some combination of these chemicals; or those which exhibited no styrene or acrylates but instead a series of later eluting peaks appearing to be a homologous series of compounds. The first series is made up of those toners which have the coloring material embedded in a styrene-acrylic copolymer. Figure 2, Class 1 shows a typical example of the pyrogram of such a toner. The mass spectral data suggest the presence of styrene (the peak at 1.9 min), butyl methacrylate (2.4 min), methylheptyl acrylate (3.9 min), styrene dimer (6.8 min), and styrene trimer (12.0 min) in this pyrolyzate. A number of variations on this general pattern were observed as are shown in Fig. 2, Classes 1 through 13. In addition to the presence or absence of the compounds shown in the Class 1 pyrogram, methyl methacrylate (1.1 min), decyl methacrylate (11.3 min), and unknown A (11.8 min) were present in some of the pyrograms. Classes 14 through 16 in Fig. 2 show typical examples of the second type of toner pyrogram. Few of the components of these pyrograms gave mass spectra which were contained in the EPA/NIH Mass Spectral Data Base. In addition to phenol and phthalic anhydride, the spectrum of one of the earlier peaks was tentatively identified as bisphenol A [4,4′-(1-methylethylidene)bisphenol].

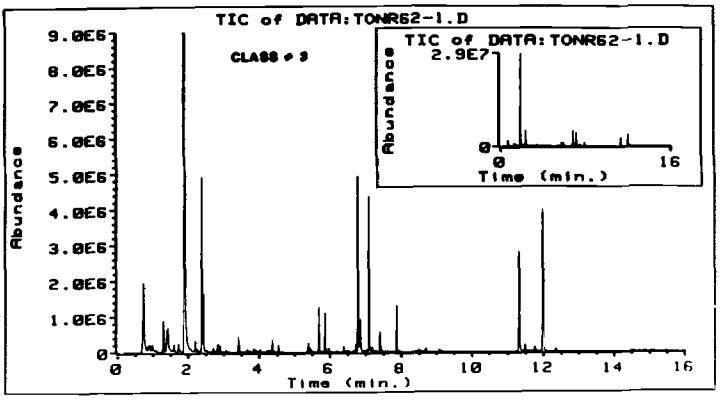
The most commonly used epoxy resins are diglycidyl ethers of bisphenol A cured with various polyamines, polyaminoamides, polyphenols, polymeric thiols, polycarboxcylic acids,



Class 1: Pitney Bowes PB2000

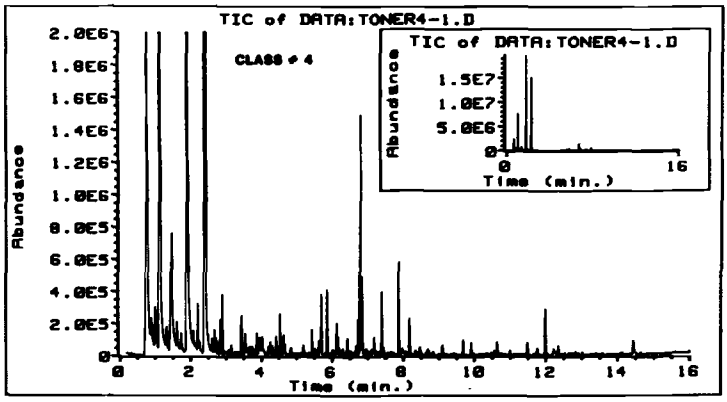


Class 2: Develop 100

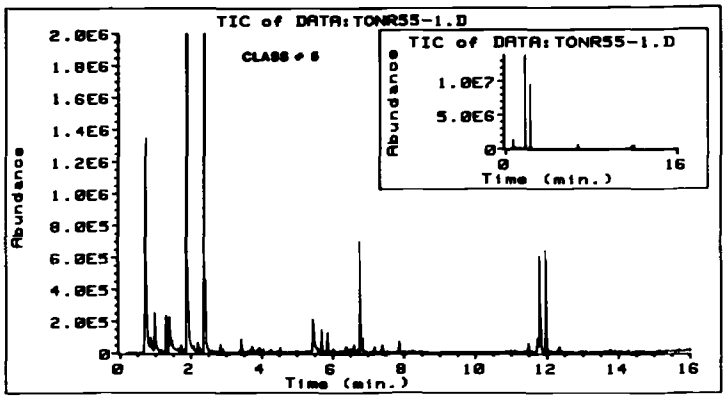


Class 3: Adler/Royal TA 230Z

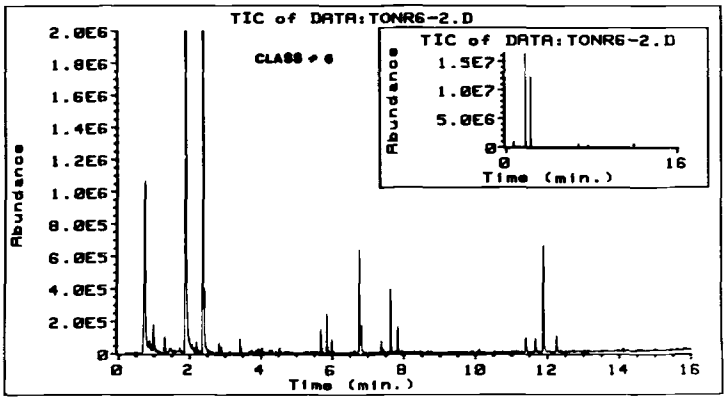
FIG. 2—*Representative pyrograms from each class of toner. The total ion current profile from the analysis by Py-GC-MS is shown with the abundance scale magnified to show the smaller peaks, and with all of the peaks on scale (inset).*



Class 4: Royal Copier 122

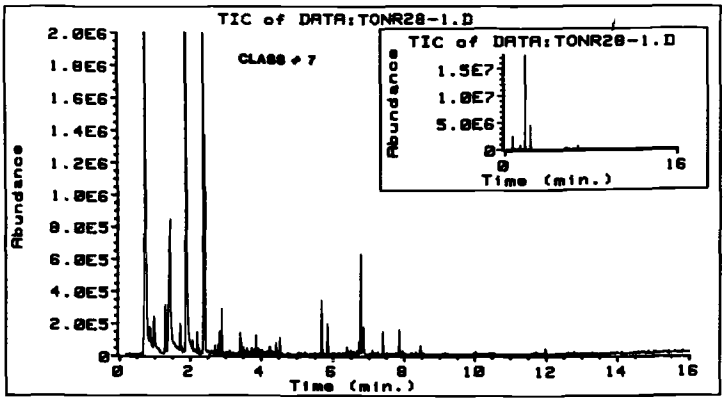


Class 5: Minolta EP 310

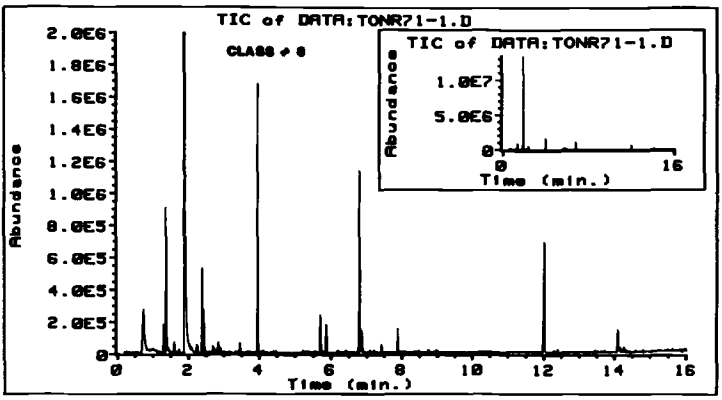


Class 6: Xerox 1075

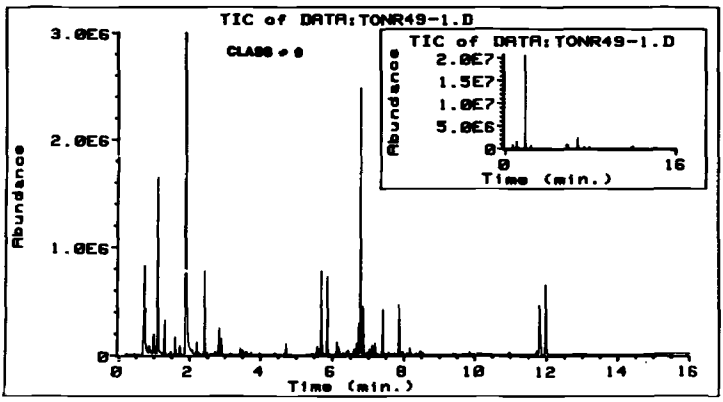
FIG. 2—*Continued.*



Class 7: Xerox 1050

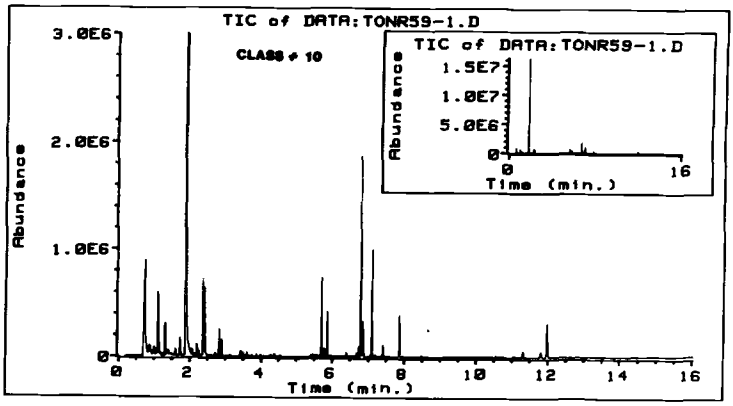


Class 8: Ricoh FT-2010

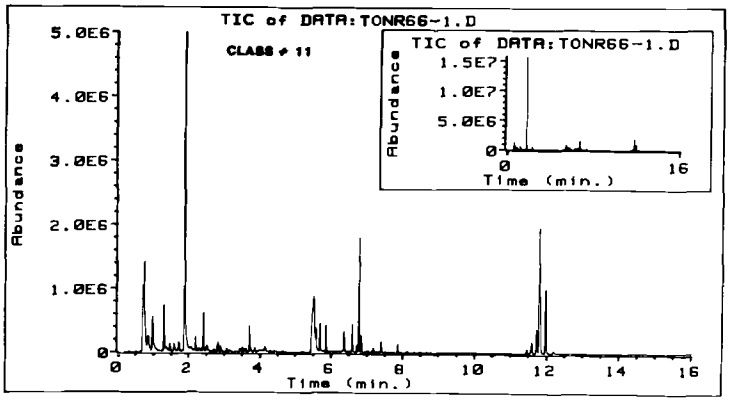


Class 9: 3M 516

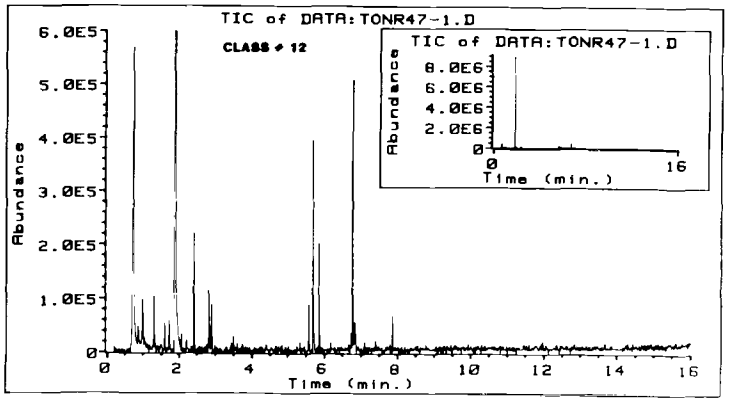
FIG. 2—*Continued.*



Class 10: Gestetner 2110C

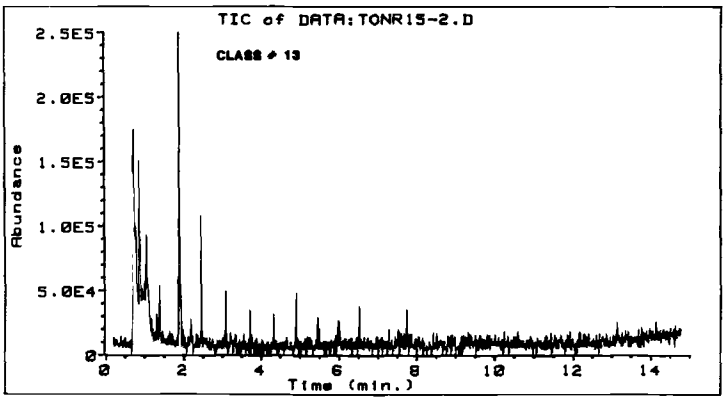


Class 11: Canon NP-400

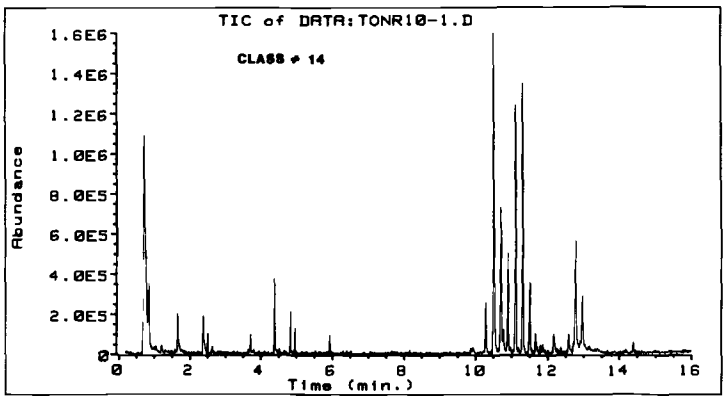


Class 12: A. B. Dick 988RE

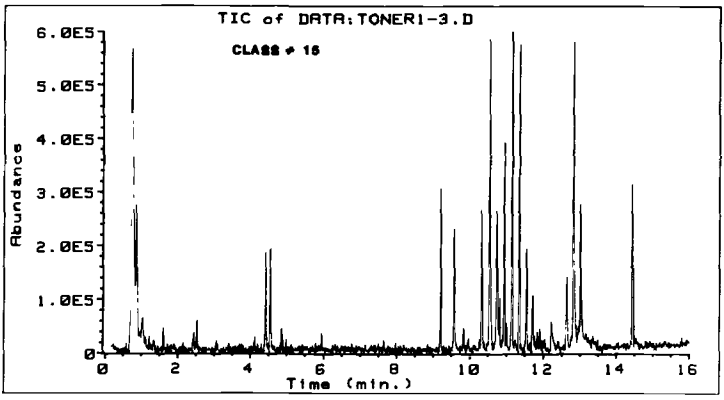
FIG. 2—*Continued.*



Class 13: 3M 379

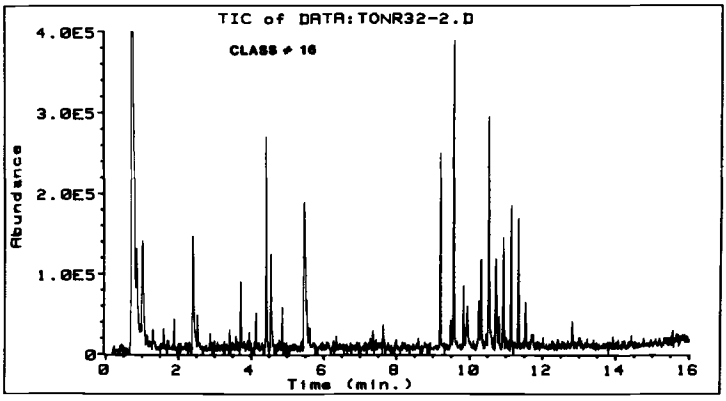


Class 14: Oce 1825

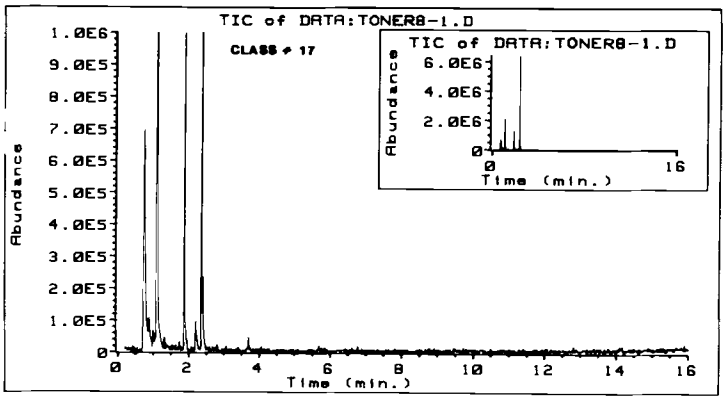


Class 15: Royal 1803ZMR

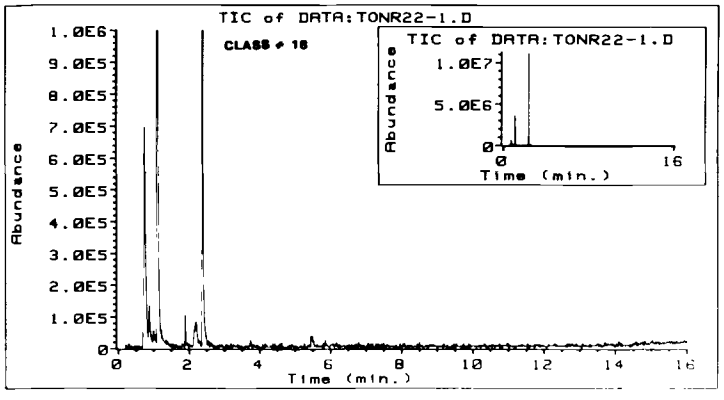
FIG. 2—*Continued.*



Class 16: Minolta EP 870



Class 17: IBM 85



Class 18: IBM Copier II

FIG. 2—*Continued.*

TABLE 2—*Photocopy classification key.*

1. Is the peak at 1.9 min (styrene) the largest in the pyrogram?
   yes = go to 2.
   no = go to 12.
2. Is the peak at 2.4 min (butyl methacrylate) greater than or equal to 10% of the peak at 1.9 min (styrene)?
   yes = go to 3.
   no = go to 10.
3. Is there a peak at 3.9 min (methylheptyl acrylate) equal to or greater than the peak at 12.0 min (styrene trimer)?
   yes = Class 1: Savin 5015RE; Savin 5020; Ricoh FT 4480; Ricoh FT 3050; Pitney Bowes PB2000.
   no = go to 4.
4. Is there a peak at 11.3 min (decyl methacrylate) which is equal to or greater than 50% of the peak at 12.0 min (styrene trimer)?
   yes = go to 5.
   no = go to 6.
5. Are there peaks at 11.8 (unknown A) and 12.0 min (styrene trimer) which have height ratios between 1:2 and 2:1?
   yes = Class 2: Develop 100.
   no = Class 3: Monroe RL-710; Monroe RL-735Z; Mita DC-313Z; Mita DC-111; Gestetner 2130Z; Adler/Royal TA 210C; Adler/Royal TA 230Z.
6. Is there a peak at 1.1 min (methyl methacrylate) which is greater than the first peak?
   yes = Class 4: Royal Copier 122; Royal 115.
   no = go to 7.
7. Are there peaks at 11.8 (unknown A) and 12.0 min (styrene trimer) which have height ratios between 1:2 and 2:1?
   yes = Class 5: Standard 225; IBM 102; Minolta EP 310.
   no = go to 8.
8. Is there a peak at 12.0 min (styrene trimer) which is at least 50% of the peak at 7.8 min?
   yes = Class 6: Toshiba BD-4810; Xerox 1075; Ricoh FT-6200; A. B. Dick K555; Pitney Bowes 9600.
   no = Class 7: Xerox 1050.
9. Is there a peak at 3.9 min (methylheptyl acrylate) equal to or greater than the peak at 12.0 min (styrene trimer)?
   yes = Class 8: Ricoh FT-2010; Sharp SF-811.
   no = go to 10.
10. Is there a peak at 1.1 min (methyl methacrylate)?
    yes = go to 11.
    no = go to 12.
11. Are there peaks at 11.8 (unknown A) and 12.0 min (styrene trimer) which have height ratios between 1:2 and 2:1?
    yes = Class 9: Sanyo SFT 600; Sanyo SFT Z116; RC Allen RC2001; Royal 1200mc; Towa T-1000 (red); 3M 516; 3M 586; Toshiba BD-8812; Toshiba BD-3301; Panasonic FP4520.
    no = Class 10: Gestetner 2110C.
12. Is there a peak at 12.0 min (styrene trimer) which is at least 50% of the peak at 7.8 min?
    yes = Class 11: Xerox 1012; Canon NP-400; Canon NP-270; Panasonic FP-2520; A. B. Dick 998RE; A. B. Dick K122; Sharp Z50; Sharp SF-7200; Sharp SF-8200VMR; Minolta EP 870.
    no = go to 13.
13. Is the peak at 1.9 min (styrene) two times larger than the next largest peak?
    yes = Class 12: A. B. Dick 988RE.
    no = Class 13: 3M 379.
14. Are there two or more peaks between 10 and 12 min?
    yes = go to 15.
    no = go to 17.
15. Are there two or more peaks between 8 and 10 min?
    yes = go to 16.
    no = Class 14: Oce 1725; Oce 1825; Towa T-1000 (black).
16. Are there two or more peaks between 12 and 14 min which are equal to or greater than the peaks between 8 and 10 min?
    yes = Class 15: Kodak 85; Royal 250ZMR; Royal 1803ZMR; Royal 4003ZMR.
    no = Class 16: Canon NP-7050; Minolta EP 870.
17. Is a peak present at 1.9 min (styrene)?
    yes = Class 17: IBM 85; IBM 40; IBM 70; Konica/Royal 700 mm.
    no = Class 18: IBM Copier II.

and anhydrides depending upon what final properties are desired [*9*]. The mass spectrum of the diglycidyl ether of bisphenol A is present in the Data Base and is very similar to the mass spectrum for bisphenol A—very little fragmentation, with the base peak (the most abundant ion) being 15 mass units less than a strong molecular ion. Many of the chromatographic peaks which eluted after the bisphenol A peak in this type of toner pyrogram gave similar spectra, with the ions shifted to higher masses. It seems most likely that these types of toners have epoxy resins as the bonding material. While interpreting the data of Kemp and Totty [*2*] using infrared group frequency analysis, Williams concluded that one of their toner classes was made up of epoxy resin-based toners [*10*]. The pyrograms of the epoxy containing toners all showed a cluster of peaks between 10 to 12 min and sorted into three groups depending upon the presence or absence of two other groups of peaks occurring between 8 to 10 min and 12 to 14 min. As shown in Fig. 2, Class 14 contained peaks at 12 to 14 min but not 8 to 10 min, Class 15 contained peaks at both 8 to 10 min and 12 to 14 min, and Class 16 contained peaks only at 8 to 10 min.

The toners in the remaining two classes consist mainly of the methacrylate esters, butyl methacrylate, and methyl methacrylate. The toners in Class 17 also contain styrene, while the toner in Class 18 does not.

Reproducibility

Reproducibility is a critical consideration when one attempts to interpret the results of the comparison of materials by Py-GC. The reproducibility of the Py-GC technique, that is, the production of identical pyrograms from repeated analyses of identical specimens, is well established. Judging from the published reports, toner specimens taken from different places on a photocopy page are nearly identical. Wampler and Levy [*3*] calculated peak height ratios for the major components in pyrolyzates of toner specimens taken from a photocopy and reported percent relative standard deviations for the averages of five runs to be less than 5%. Kemp and Totty also examined reproducibility [*2*] and reported that if "sufficient paper free toner was used, sampling from different parts of the same document, sampling from different documents from the same machine and sampling from different documents from different machines of the same type had little effect on the spectra, apart from slight variation in relative absorptions." Similar observations about reproducibility can be made based upon the results of this study. In addition to the examples cited by Kemp and Totty, in this study, specimens from different machines of the same type but separated in time by several years were found to be very similar (that is, showing only minor variations which would not cause them to be classified as different).

Also, it was noticed that a new shipment of toner being used in a Xerox 1075 machine, while being the same stock number, was designated as being made in the Netherlands rather than in the United States, as was the previous shipment. The photocopies from the two toners were very similar (a Xerox representative verified that these two toners were, in fact, produced, rather than just packaged, at the different locations).

Future Work

In retrospect, the instrumental conditions used for this study may not be ideal for detailed comparisons of toners by Py-GC. The pyrolysis temperature used may seem excessively high (even considering that the specimen inside the quartz tube experiences 100 to 125°C less than the set temperature in the CDS Pyroprobe instrument used). However, with samples such as these, which might be somewhat heterogeneous, it is very important to pyrolyze the specimen to completion to achieve reproducibility [*7*]. If a specimen is pyrolyzed at a particular set temperature with the GC column held at an elevated temperature (such as 300°C), the pyrolyzate will elute from the column as a single peak with the retention time of an unretained solute (1 to 2 min). If the specimen were completely consumed during the pyroly-

sis time, a second firing of the pyrolysis probe at 1000°C would not give a second peak. Such a test with the styrene-acrylic toners indicated that a set temperature of 650°C pyrolyzed the specimen to completion in 20 s, but 625°C did not.

For the epoxy resin toners, however, pyrolysis at a set temperature of 700°C left a second peak of about 20% by this test. A set temperature of less than 850°C might give pyrograms with a higher percentage of late eluting peaks and possibly better discrimination, but this possibility has not been adequately tested yet.

The GC conditions were chosen to rapidly screen the toners and provide adequate separation of the peaks, but at the same time not to miss any late eluting components. Better conditions could be chosen for photocopy toner comparisons in light of the data presented in this report. Even though the GC runs proceeded for 22 min, no peaks eluted after 15 min in any of the toner analyses. Conditions should be adjusted to give better separation of the early eluting components, some of which are important to the classification of the toners. The extra time consumed with the early peaks could be regained by shortening the time the GC column is at an elevated temperature. Using a shorter capillary GC column with a thicker stationary phase (1 to 5 μm) would provide better separation of the more volatile (early eluting) components and shorten the overall analysis time. The data presented in this report would still be useful for comparison to samples run under different GC conditions if the retention times of the key components were established using the new conditions.

This report has not addressed "off-brand" toner use at all. For a file of pyrograms to be useful, some attention needs to be given to this area. Unless an off-brand toner were the name-brand toner being marketed under a different label, one would expect the formulation to be at least slightly different to avoid patent infringement problems. Such differences may or may not cause the toner to fall into a different class.

Summary and Conclusions

The results presented here clearly support the earlier claims that Py-GC is a useful technique for the examination of photocopied documents. While many unanswered questions remain, enough information has been generated about the examination of photocopies by Py-GC (and Py-GC-MS) to allow useful comparisons using this technique. For instance, if two photocopies were produced on the same machine at the same time (or very close in time), they would almost certainly give very similar toner pyrograms. Or if a photocopy showed marks characteristic of several photocopy machines (by being a photocopy of a photocopy), a comparison of the toner pyrograms could likely determine which machine made the last copy. Also, sequential pages in a photocopied document should most likely have matching toner pyrograms.

For the examination of photocopies by Py-GC-MS to be a useful method for searching for possible sources of a particular photocopy, many more photocopies of known origin would need to be analyzed.

Because one might expect the number of different classes of toners to be only a few dozen, a manual method for handling the pyrograms, such as presented in this report, would probably still be sufficient. Even without this additional work, Py-GC could be useful for selecting the most likely source machine from amongst a group of suspected sources.

References

[1] James, E. L., "Classification of Photocopy Machines by Physical Characteristics," *Crime Laboratory Digest*, Vol. 14, No. 2, April 1987, pp. 54-73.

[2] Kemp, G. S. and Totty, R. N., "The Differentiation of Toners Used in Photocopy Processes by Infrared Spectroscopy," *Forensic Science International*, Vol. 22, No. 1, July 1983, pp. 75-83.

[3] Wampler, T. P. and Levy, E. J., "Pyrolysis GC in the Analysis of Inks and Papers," *Liquid Chromatography-Gas Chromatography*, Vol. 4, No. 11, Nov. 1986, pp. 1112-1116.

[4] Levy, E. J. and Wampler, T. P., "Applications of Pyrolysis Gas Chromatography/Mass Spectrometry to Toner Materials from Photocopiers," *Journal of Forensic Sciences*, Vol. 31, No. 1, Jan. 1986, pp. 258-271.

[5] Zimmerman, J., Mooney, D., and Kimmett, M. J., "Preliminary Examination of Machine Copier Toners by Infrared Spectrophotometry and Pyrolysis Gas Chromatography," *Journal of Forensic Sciences*, Vol. 31, No. 2, April 1986, pp. 489-493.

[6] Munson, T. O., "A Simple Method for Sampling Photocopy Toners for Examination by Pyrolysis Gas Chromatography," *Crime Laboratory Digest*, in press 1989.

[7] Munson, T. O., "Getting Started with Pyrolysis Capillary Gas Chromatography," *Crime Laboratory Digest*, Vol. 13, No. 3, July 1987, pp. 82-91.

[8] Heller, S. R., Milne, G. W. A., and Gevantman, L. H., *EPA/NIH Mass Spectral Data Base*. U.S. Government Printing Office, Washington, DC, 1983.

[9] Elam, E. U., "Epoxy Resins," in *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, R. E. Kirk, D. F. Othmer, M. Grayson, and D. Eckroth, Eds., John Wiley & Sons, Inc., New York, 1985, pp. 432-433.

[10] Williams, R. L., "Analysis of Photocopying Toners by Infrared Spectroscopy," *Forensic Science International*, Vol. 22, No. 1, July 1983, pp. 85-95.

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