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Forensic discrimination of photocopy and printer toners. III. Multivariate statistics applied to scanning electron microscopy and pyrolysis gas chromatography/mass spectrometry

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Abstract Copy toner samples were analyzed using scanning electron microscopy with X-ray dispersive analysis (SEM–EDX) and pyrolysis gas chromatography/mass spectrometry (Py–GC/MS). Principal component and cluster analysis of SEM data for 166 copy toner samples established 13 statistically different subgroups, with the presence or absence of a ferrite base being a major division. When toners were compared for which both SEM and reflection–absorption infrared spectral data were available, 41% of the samples could be assigned to specific manufacturers. Py–GC/MS on poly(styrene:acrylate)-based toners produced eight peaks relevant to toner differentiation. One third of the toners clustered in a small group that contained five statistically different subgroups. Of the 57 ton-

ers for which both Py–GC/MS and SEM data were available, 31 could be differentiated using the combined analytical results. The synergy of the complementary information provided by Py–GC/MS and SEM narrows matching possibilities for forensic investigations involving copied or laser printed documents.

Keywords Principal component analysis · Cluster analysis · Questioned documents · Copy toner · Scanning electron microscopy · Pyrolysis gas chromatography/mass spectrometry · Infrared microspectroscopy.

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Introduction

Use of photocopying machines and laser printers has increased dramatically over the last 20 years [1, 2, 3]. Because of the speed, simplicity, and accessibility of photocopying, forensic examiners are now encountering photocopies as questioned documents with increasing frequency. Among other criminal activities, photocopied documents are involved in counterfeiting, false documents, fraud, threatening letters, confidential materials, and acts of terrorism. Because of the large number of manufacturers producing photocopy machines and toners, identifying the possible source of photocopied documents is not an easy task for the forensic scientist. Our two previous papers on the forensic analysis of photocopy and printer toners dealt with discrimination achievable by reflection–absorption (R–A) IR spectroscopy [4, 5].

Analysis of photocopies often starts with determination of class characteristics such as paper type, supply marks, toner type, toner application, fusion method, and magnetic properties [6, 7, 8, 9]. The composition of toners can be particularly discriminating among toner classes [6, 7]. For example, common black dry toner has opaque solid material imbedded in a matrix of organic binder which bonds to the surface of the paper. Typical binders include variations of styrene, methacrylate polymers, and epoxy resins, sometimes cured with other organic components [10]. The toner itself is usually iron oxide or carbon black

with additional elements that may vary systematically with manufacturing origin. Liquid toners generally do not contain significant inorganic elemental traces, while dry powdered toners do. Single component ferrite based toners have higher levels of iron, often combined with traces of manganese and chromium. Elemental combinations observed in these single component toners include: iron and silicon (high levels), iron and calcium, barium and sulfur, and sulfur (high levels) and chlorine [11]. Dual-component toners have low silicon content and high levels of organic components. Toner may also be grouped by the fusion method used to affix toner to paper. For cold-press fusion, used by older photocopiers, four of ten toners could be differentiated on the basis of low iron or high iron and silicon content [12]. Photocopy samples processed by heat fusion could be differentiated into three groups: dual-component toners, dual-component toners containing copper but not silicon, and high organic backgrounds with medium iron and sulfur content [12]. Paper samples have been differentiated by multivariate statistical analysis of their elemental compositions [13, 14]. SEM-EDX has been previously employed used to characterize photocopy toners and the results have been compared to that produced by FTIR [15, 16, 17].

Organic toner components may also be characterized by analytical pyrolysis [18, 19], a technique which has proven useful in forensic investigations [6, 20, 21, 22, 23, 24, 25, 26]. Pyrolysis-based methods extend gas chromatography (GC) to enable the analysis of organic materials that are not volatile due to their high molecular weight, such as the polymeric matrix found in copy toners. Following a fast temperature jump in the absence of oxygen, thermal fragments are separated by GC and detected by mass spectrometry (MS) or flame ionization detection. The resulting chromatogram (or pyrogram) is a fingerprint with contributions from the structural components of the original sample. By avoiding derivatization or other sample pretreatment, speed of analysis is increased; however, relating the complex mixture of pyrolysis products to the composition of the sample can be difficult without knowledge of the chemical markers that might be generated from characteristic structures. Levy and Wampler [27] used pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) to distinguish toners from four different manufacturers using 15 peaks including methyl methacrylate, toluene, glycidol, furfural, styrene, butyl methacrylate, dodecyl methacrylate, tetradecyl methacrylate, 1-dodecene, and 1-tetradecene. Zimmerman et al. [28] reported the Py-GC differentiation of eight toners that could not be distinguished by IR spectroscopy. Munson [29] compared Py-GC/MS data from 62 photocopy machines differing by brand name and/or model number and developed a classification scheme based on 17 decision branches. The majority of the toners fell into two groups: the first group had a large styrene peak accompanied by varied acrylates; the second group lacked those compounds, but included a later eluting series of homologous compounds indicative of an epoxy resin base. Compounds used to classify toners in the first group included styrene,

butyl methacrylate, methylheptyl acrylate, decyl methacrylate, styrene trimer, methyl methacrylate, and a peak of unknown composition. Chang et al. [30] used a library search of Py-GC retention indices to differentiate 14 toner samples by their pyrolysis products. Brandi et al. [10] found Py-GC to not provide any greater discriminating power than IR for copy toners. More recently, Armitage et al. [31] employed filament and laser Py-GC/MS for analysis of 11 different photocopy toner, detecting over 100 pyrolysis products including styrene, various alkylbenzenes, furans, unsaturated cyclic hydrocarbons, phenols, and polycyclic aromatics.

A driving force behind current research has been development of simple and rapid analytical methods that can be applied directly to toners with little or no sample destruction. The ease of sample preparation and the discriminating information on polymer and organic components produced by IR spectroscopy of toners has been demonstrated. Merrill et al. [4] have developed a library of reflection-absorption (R-A) IR spectra from dry toners and have separated the spectra into distinguishable groups. Egan et al. [5] have verified the grouping of copy toners in this library by achieving 96% correct classification into the previously defined groups using multivariate discriminant analysis on 430 selected toner spectra. Linear discriminant analysis applied to R-A IR spectra of poly(styrene:acrylate) based toners was able to discriminate several individual toners (AB Dick, Brother, Copystar, Okidata, Newgen, and Texas Instruments), while C. Itoh, Hewlett-Packard, Mannesman, and Qume toners could not be distinguished [32]. The present paper reports the application of multivariate statistics to explore the clustering and the discrimination of photocopy and printer toners by SEM and Py-GC/MS. A fundamental question is whether SEM and Py-GC/MS add sufficient additional discrimination beyond that achievable by R-A IR to be routinely employed for the forensic analysis of copy toners.

Experimental

Scanning electron microscopy

A total of 166 samples of photocopier and printer toners were analyzed. Small squares of print, 2 mm×2 mm, were cut from one letter with a "thick" application of toner. The toner sample was removed from the paper by making vertical cuts on each side of the sample, then inserting the blade under the toner in a plane parallel to the paper, removing a minimum of paper fibers. The toner sample was attached to double-sided tape applied to a carbon planchet and made conductive by coating with carbon by vacuum evaporation. Carbon coating was mandated by the sample characteristics (conductivity and size), operating environment (pressure), and analytical requirements (beam voltage and current).

Elemental analysis of toner samples was performed using a Jeol JSM-35CF SEM (Peabody, MA, USA), with a Noran TN-5500 EDXA attachment (formerly Tracor Northern, Middleton, WI, USA). For X-ray analysis, spectra were obtained using 25 KeV beam voltage, ca. 1.3 nA beam current (adjusted to yield a dead time of 30%), and 100 s live time. The instrument design employed a 39 mm working distance to provide optimal sample/detector geometry. The scan was rastered over the surface of an area of intact toner. For each sample, relative abundances for ten elements

(Al, Si, S, Cl, Ca, Ti, Cr, Mn, Fe, and Zn) were calculated by dividing the net peak counts (above background) of the principal (strongest) peak for each element by the sum of counts from all elements present.

Pyrolysis gas chromatography/mass spectrometry

A total of 93 toner samples, representing 38 different brands of poly(styrene:acrylate) based toners, were analyzed. Clean aluminum foil (solvent washed with methanol followed by acetone and then hexane) was placed over a glass microslide and the photocopy was placed toner side down on top of the foil. A soldering iron (288 °C tip temperature) was used to melt the toner by heating the back of the photocopy for 10–20 s. A portion of the toner adhered to the aluminum foil, which was cut into a small square, slightly curled, and then inserted into a quartz sample tube.

Pyrolysis was performed using a CDS Model 2000 Pyroprobe system with a platinum coil probe (Chemical Data Systems, Oxford, PA, USA). A CDS Valved Interface was coupled to a Hewlett-Packard (HP, Palo Alto, CA, USA) G1800A GCD system. Quartz tubes containing toner samples were held in the platinum coil probe, which was then inserted into the interface. Samples were pyrolyzed at a setting of 850 °C for 20 s at the fastest ramp rate (off mode). An HP-5 fused silica capillary column (30 m×0.25 mm×0.25 µm film thickness) was used for separation of pyrolysis products. The split ratio was 50:1. The GC oven temperature was programmed over 50–300 °C at 10 °C min⁻¹ and was then held at 300 °C for 1 min (26 min total run time). The valved interface, injection port, and transfer line temperatures were set at 250, 250, and 280 °C, respectively. The mass spectrometer (EI ionization) was tuned daily with PFTBA at 70 eV. A mass range of *m/z* 35 to 350 was used for data acquisition. Samples of toner from an Advanced Matrix Tracet were pyrolyzed each day as a control to check day-to-day reproducibility.

Data analysis

Due to their wide intensity ranges, all elemental abundances determined by SEM were median autoscaled as previously described [5]. The median autoscaled data set was analyzed by PCA to reduce the data dimensionality to a manageable level and to see if any major trends or clusters were evident in plots of the first few principal components [33, 34]. In projections of the data into the space of the first few PCs, toner samples were labeled according to the reflection-absorption infrared (R-A IR) spectra grouping scheme previously established [4]. Agglomerative hierarchical cluster analysis [35, 36] was used in an exploratory fashion to group the samples analyzed by SEM without regard to their R-A IR classification. Ward's measure of information loss was used because single linkage clustering appeared to chain nearest data points into clusters regardless of the global cluster structure [37]. Ward's algorithm clusters samples one by one, forming groups which minimize the sum of squares adjusted for the mean within each growing cluster. Identification of groups by cluster analysis does not necessarily imply that those groups are truly different. Hotelling's T^2 test was applied to pair-wise comparison of groups to assess their separation [38, 39, 40]. Despite the assumption of equality of covariance matrices for groups being compared and the loss of control of the type I error rate [41], such multiple pair-wise tests are useful as relative indicators of group separability.

The analysis of Py-GC/MS data by pattern recognition techniques requires some method for taking the mass spectral information unique to each peak into consideration when determining the identity of a peak in multiple chromatograms. A previously developed algorithm was used to create a consistent data matrix containing peak areas for 42 peaks whose retention times and mass spectra matched across all samples [42]. Mass spectra were used to validate peak identities in these comparisons. All peak areas were preprocessed by scaling relative to the large styrene peak present in all the samples at 3.86 min to correct for possible variations in sample size. Styrene itself was not included in the data matrix. After this preprocessing, pattern recognition was applied to the relative peak areas and mass spectral data were not used further. PCA was applied to the pre-processed Py-GC/MS data in an exploratory data analysis mode to create a reduced dimensionality view of the data by finding those directions in multivariate space which best describe the overall variation in the data. Peaks contained within the feature array were examined by R-mode PCA and cluster analysis [43, 44] to determine if any peaks were redundant or lacked information relevant to classification. R-mode PCA weights each variable (peaks in the present case) equally by performing PCA on the correlation matrix of the data. Then, instead of examining the normalized principal component (PC) scores (the projections of the pyrograms into the space of the first few PCs), the loadings (weights of the original variables) were examined to evaluate the relatedness of the original peak variables. The PCA results and a priori knowledge of printer and copier manufacturers and engines were combined to establish subgroups of the toners. Linear discriminant analysis (LDA) was used to construct linear combinations of the original variables (canonical variates) which best separate the predefined groups by maximizing the ratio of their between- to within-group variances [45, 46, 47]. Group definitions followed the R-A IR classification scheme [4]. Leave-one-out cross validation was used to estimate the predictive ability of classification models and Hotelling's T^2 test was applied to pair-wise comparison of groups to assess their separation. Univariate Fisher ratios [5, 48], which represent the ability of each peak variable to separate groups based on the ratio of between- to within-group variability, were calculated to see which pyrolysis peaks best separated groups of toner samples.

Data was preprocessed and analyzed using Microsoft Excel (Microsoft Corporation, Redmond, WA, USA), Omnic 3.0 (Nicolet Analytical Instruments, Madison, WI, USA), custom programs written in MatLab for Windows (The MathWorks, Inc., Natick, MA, USA), and Systat v. 8.0 (SPSS, Chicago, IL, USA).

Results and discussion

Scanning electron microscopy

The data set of abundances for 10 elements for each toner sample can be conceptualized as a set of 166 points in a

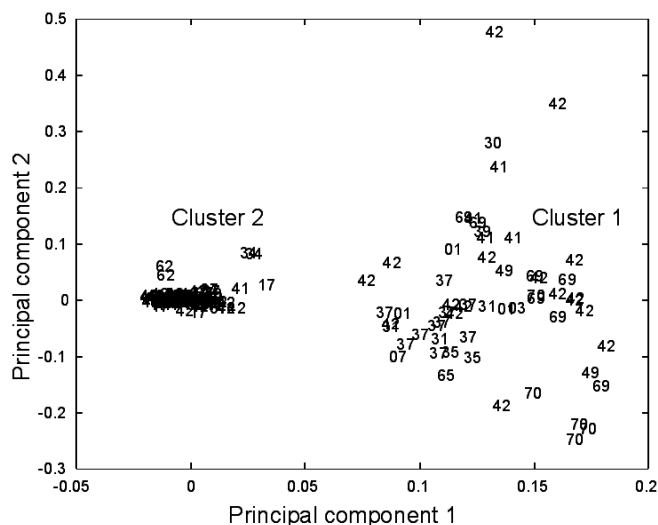


Fig. 1 Bi-plot showing projections of all SEM data into the space of the first two principal components. Cluster 1 has low Fe concentrations and no Mn. Cluster 2 contains much higher Fe and Mn abundances. The first two PCs account for 56.02% of the variation in the data. Samples are labeled with their group numbers previously determined by R-A IR [16, 17]

10-dimensional space. While this 10-dimensional space cannot be easily visualized, the projection of the SEM elemental data into the space of the first two principal components revealed two extremely different groups (Fig. 1). Cluster 1 contains 58 samples in a group spread over the positive region of the first PC. Cluster 2 contains the remaining 108 toner samples, tightly grouped in the left center of the bi-plot. The first two PCs account for 44.27% and 11.75%, respectively, of the variation in the autoscaled data. Examination of the loadings (the vectors defining the principal components) for the first two PCs shows that the elements manganese and iron have the only negative weights for the first loading vector and very small weights on the second loading vector. The mean abundances of manganese and iron for cluster 1 were 0.00 and 13.25, while the mean abundances of manganese and iron for cluster 2 were 1.07 and 92.39, respectively. Since the PCA results provided such a major division between toners incorporating iron and manganese and those lacking iron and manganese (thus correlating well with magnetic properties), these two groups were analyzed separately by cluster analysis and PCA to provide insight into how the toner samples naturally grouped together within each cluster. Figures 2 and 3 show the resulting dendrograms and include group assignments (designated by alphabetic letters) based on their interpretation. A total of 13 groups (A–M) were assigned for the SEM samples. Finally, Fig. 4 shows the projection of the groups A–F and G–M plotted in their respective PC-spaces. Excellent clustering is now visually present, even though the projections into the space of the first three PCs each explain less than 60% of the total variance.

Visual examination of PCA plots, unfortunately, cannot be relied on to determine if the groups really exist, es-

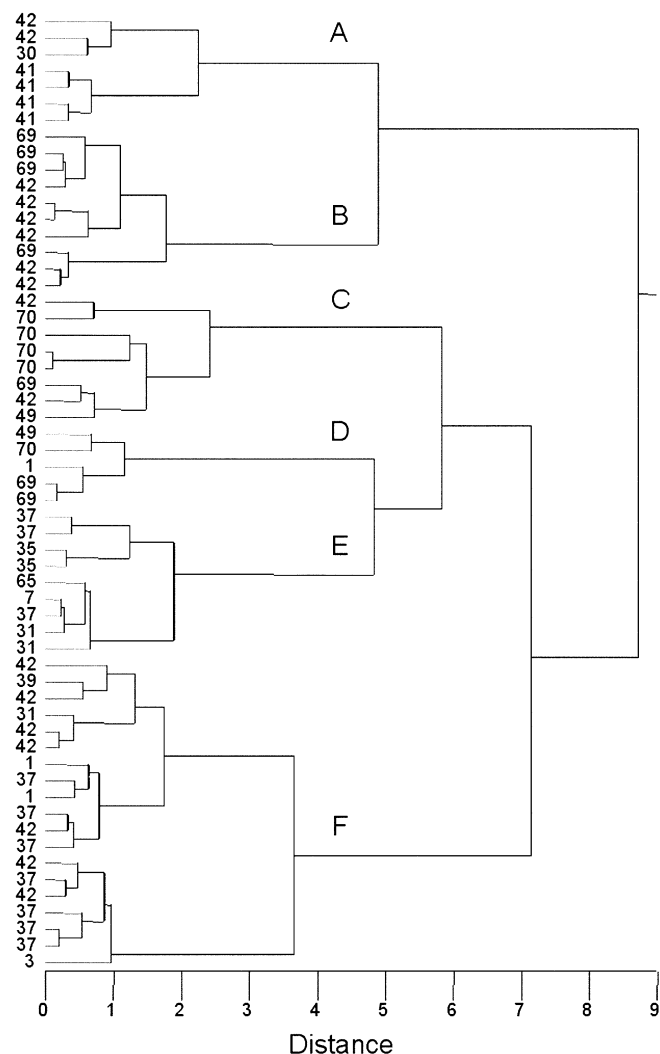
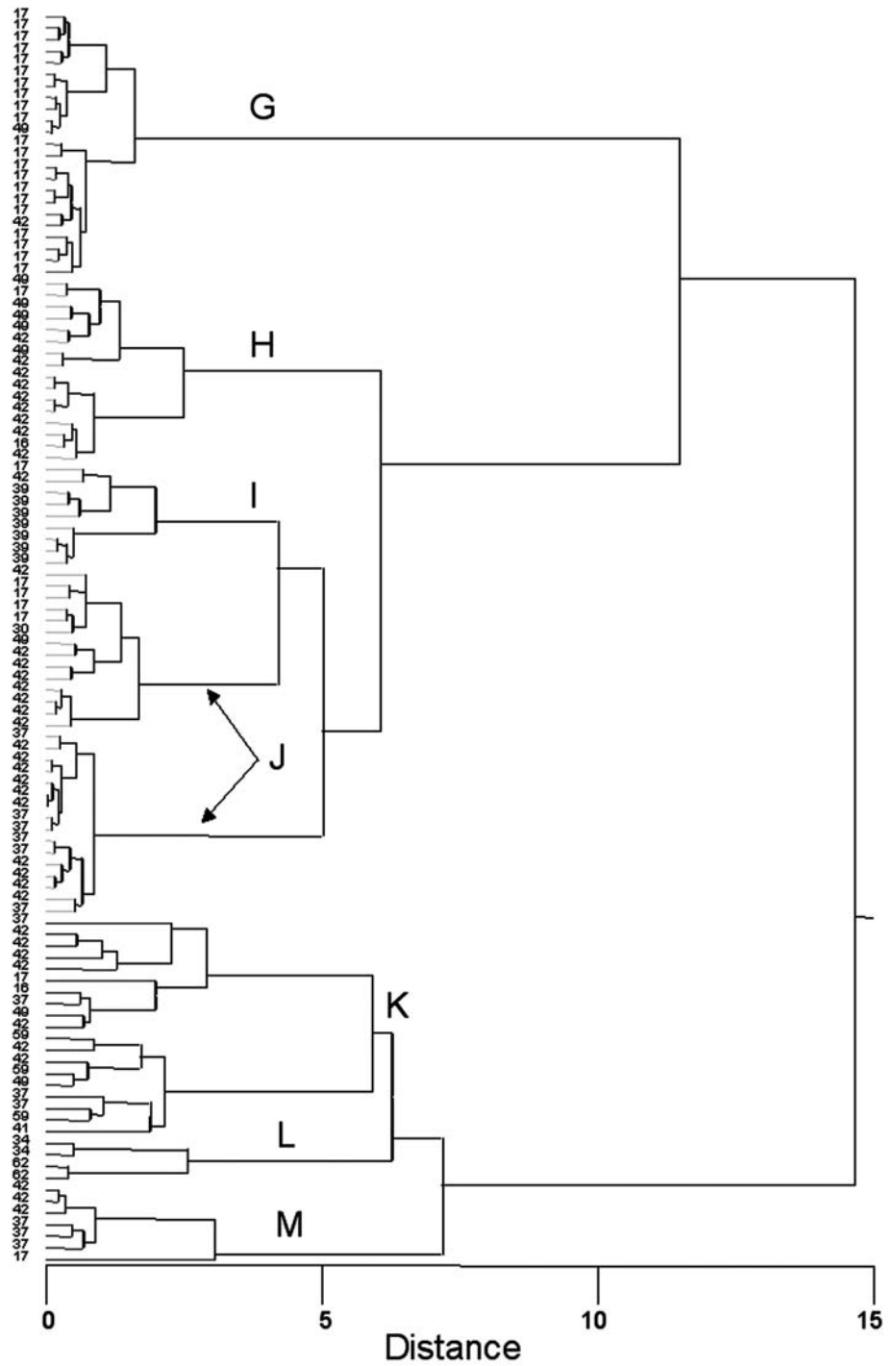


Fig. 2 Hierarchical clustering dendrogram for SEM data from cluster 1. The 58 samples were divided into six groups (A–F)

pecially with less than 60% of the variance available for inspection in a tri-plot. Hotelling's T^2 test was used to compare the multivariate means of the groups within their respective clusters. A 95% confidence level ($p=0.05$) was felt to be appropriate for determining the statistical significance of differences in group means. For cluster 1, all p -values were <0.01 , except for two comparisons: A and D ($p=0.0412$) and D and E ($p=0.0260$). For cluster 2, all p -values were <0.01 , except for two comparisons: I and L ($p=0.0111$) and L and M ($p=0.0561$). Group J was initially considered to be two different groups (see Fig. 3), but Hotelling's T^2 test found the difference between the two groups was not significant ($p=0.2655$). The two clusters on the dendrogram were combined to form group J. Since no p -value exceeded 0.0561 after the group J fusion, the null hypothesis that the group means are equal can be rejected with confidence.

Once the validity of the SEM groupings was established, the next question was: how well would these groupings perform when used in a classification system? As shown

Fig. 3 Hierarchical clustering dendrogram for SEM data from cluster 2. The 108 samples were divided into seven groups (G–M)



in Table 1, 149 of 166 samples (89.8%) were correctly classified into the groups defined above. The chemical interpretation of the SEM analysis is relatively straightforward. The two clusters separate the samples between the dual-component (Si present, but little to no Fe) and the single-component (high in Fe, low in Mn) toners.

Pyrolysis–gas chromatography/mass spectrometry

The similarity (or dissimilarity) of replicate measurements establishes the standard for judging the significance of observed differences between two or more sample patterns. Although replicate pyrograms of the control toner samples exhibited variations in absolute peak intensity, excellent reproducibility of relative peak heights was observed. When PCA was performed on the Py–GC/MS data (Fig. 5), two tight clusters separated by the second PC and a number of

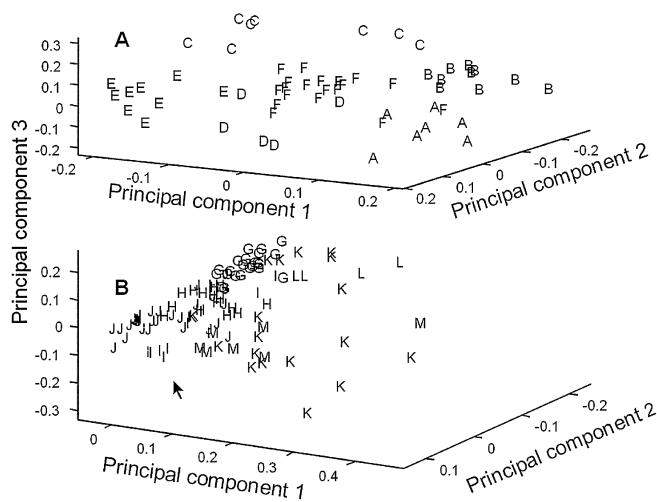


Fig. 4 Tri-plots showing projections of the SEM data into the space of the first three principal components. (A) The first three PCs explain 58.13% of total variation in the data for cluster 1. Note that groups A and D extend out of the page, towards the reader. (B) The first three PCs explain 57.79% of total variation in the data for cluster 2. Samples are labeled according to their SEM group assignments from Figs. 2 and 3

outlying points were clearly evident. The two clusters in Fig. 5 do not represent groupings similar to that seen previously in Fig. 1 for the SEM data; the SEM and Py-GC/MS data sets are based on different toner samples.

The PC loadings defining the composition of the second PC for the Py-GC/MS data are shown in Fig. 6A. The loadings for PC 2 highlight the importance of peaks at 2.73, 3.25, 8.58, and 21.37 min in discriminating the two

clusters shown in Fig. 5. As shown in Figs 6B and 6C, the average pyrograms (normalized to styrene) for the two clusters clearly reveal differences. Toners in cluster 1 have peaks at 2.73, 3.25, and 8.58 min, while cluster 2 toners lack these peaks. With three exceptions, cluster 1 toners lack the peak at 21.37 min, while toners in group 2 have this peak. Table 2 lists the peaks in the pyrograms which best differentiate and serve as chemical markers for these groups. Because of the proprietary nature of toner formulations and because adequate fits to mass spectral libraries were not possible, the exact chemical identity of these peaks are unknown. The peaks selected as important features were examined to determine their interrelationships using R-mode PCA, cluster analysis, and visual inspection. Peaks were deleted from the data set that were either: (1) present in all samples, or (2) all but one of any group of peaks that were identical in their presence or absence without considering abundance, i.e., containing the same information. The number of peaks used for further data analysis was thus reduced from 42 to 21, decreasing data set complexity while still retaining information of discriminatory value.

The 33 toner samples in cluster 1 were analyzed separately by PCA using the 21 features selected above. A plot of the first three PCs (Fig. 7) separates two groups of toners from the rest: AB Dick (labeled 4–6) and Fujitsu (labeled 46 and 47). Close examination of various bi-plots of the PCs, coupled with the knowledge that many of the toners in this group were produced by machines with Ricoh or Pentax engines, led to the hypothesis that there were five subgroups within cluster 1 (AB Dick (1-1), Pentax (1-2), Ricoh (1-3), a mixed group (1-4), and Fujitsu (1-5)). Univariate Fisher ratios [5, 25, 36] measuring the

Table 1 Cross-validated classification results for SEM data from cluster 1 (A–F) and cluster 2 (G–M)

SEM group	Correctly classified	Fraction correct	Incorrect (group×count)	Copier (R-A IR group)×count
A	100%	7/7	–	IBM(41)×2, Lexmark(41)×2, Ricoh(42,42,30)×3
B	100%	10/10	–	Canon(42), Fujitsu(69)×4, Hitachi(42), OKI Electric(42)×2, Ricoh(42)×2
C	87.5%	7/8	B×1	Fujitsu(69), Minolta(70)×4, OKI Electric(42), Ricoh(42), Toshiba(49)
D	100%	5/5	–	Canon(49), Kyocera(69)×2, Minolta(1), Minolta(70)
E	88.9%	8/9	D×1	Copal(35)×2, Kentex(31)×2, Kyocera(65), MITA(37)×2, Panasonic(7)×2
F	84.2%	16/19	B×2, D×1	Hitachi(42), Kentex(31), Minolta(1), OKI Electric(42), Printware(37), Sanyo(37), Sharp(1), Sharp(42)×5, Toshiba(3), Toshiba(37)×5, Xerox(39)
G	100%	23/23	–	Brother(17), Canon(17)×20, Casio(42), Sharp(49)
H	87.5%	14/16	G×1, J×1	Canon(16), Canon(17), Canon(42)×8, Sharp(49)×4, Tokyo Electric(42), Xerox(49)
I	88.9%	8/9	H×1	Canon(17), Casio(42), Ricoh(39)×7
J	86.7%	26/30	G×3, I×1	Canon(17)×4, Canon(42)×2, Casio(42), Fujitsu(42)×2, Konica(37)×6, Matsushita(42)×2, Pentax(42)×3, Ricoh(30), Sharp(49), Tokyo Electric(42)×8
K	73.7%	14/19	H×2, I×2, J×1	Canon(16), Canon(17), Canon(42)×3, Casio(42), Konica(59)×2, Kyocera(37)×4, Matsushita(49), Sharp(49), Tokyo Electric(42)×2, Troy(41), Varityper(42), Xerox(59)
L	100%	4/4	–	Matsushita(62), NEC(34)×2, Panasonic(62)
M	100%	7/7	–	Canon(17), Kyocera(37)×2, MITA(37), Tokyo Electric(42)×3
Total	89.8%	149/166		

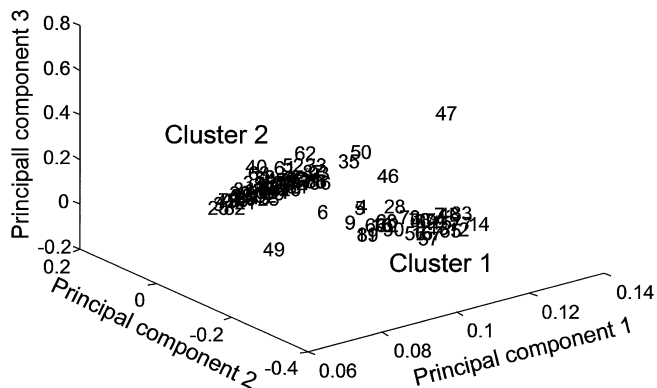


Fig. 5 Projections of Py-GC/MS data into the space of the first three principal components showing the normalized scores of all 93 toner samples based on the original 42 peaks. The first three PCs explain 94.13% of the variation in the data

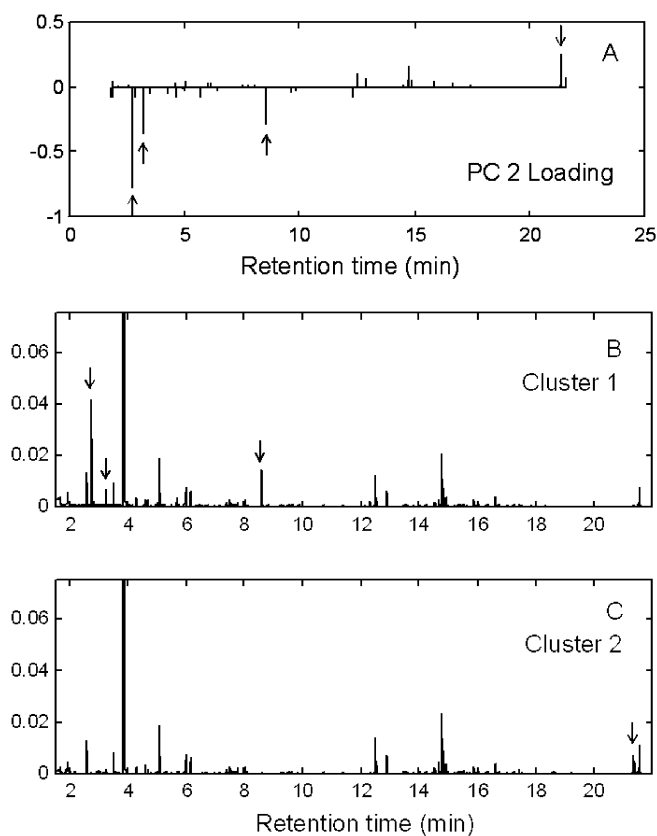


Fig. 6 (A) PCA loadings for principal component 2 for Py-GC/MS data. The four peaks (marked with arrows) with large loadings differentiate the two clusters. (B, C) Plots of the average pyrograms for clusters 1 and 2. Peaks are scaled relative to styrene (3.86 min), which is shown off-scale. Peaks important for discrimination are marked with arrows

individual ability of each feature to separate groups based on the ratio of between- to within-group variability were calculated to see which pyrolysis peaks best separated the five groups. A feature with no discriminatory power has a Fisher ratio of zero; there is no upper limit on the ratio.

Table 2 List of the Py-GC/MS peaks important for classification and the groups/subgroups to which they apply

Retention times (min)	Presence/absence (+/-)	Classification
2.73, 3.25, 8.58	+	Cluster #1
21.37	-	Cluster #1 (except AB Dick toners)
21.37	+	AB Dick (1-1)
6.42, 9.87	+	Pentax Engines (1-2)
4.99	+(higher)	Ricoh LP 1060 Engines (1-3)
4.99, 6.42, 9.87, 12.3, 21.37	-	Mix of Okidata, HP, Newgen, C. Itoh, Gestetner (1-4)
3.25	+	Fujitsu (1-5)
21.37	+	Cluster #2

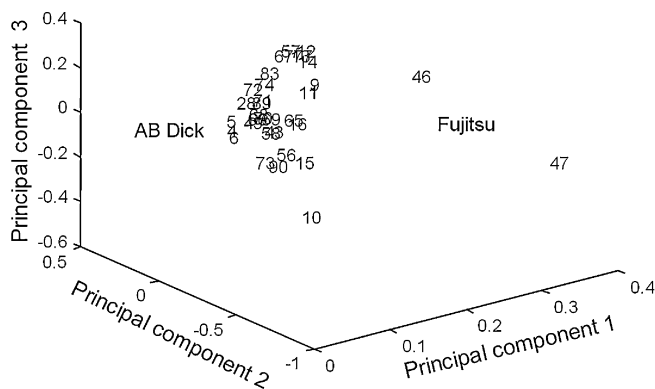


Fig. 7 Projections into the space of the first three principal components for Py-GC/MS data from samples in cluster 1. The first three PCs explain 98.32% of the total variation. Three AB Dick (4-6) and two Fujitsu (46 and 47) toners are well separated

Two peaks at retention times 2.15 and 21.3 min were not present in any cluster 1 samples. Nine peaks whose univariate Fisher ratios exceeded 2.5 were chosen for linear discriminant analysis. Figure 8 shows the projection into the space of two pairs of canonical variates (CVs) from LDA on this reduced feature data set. The extreme differences between the AB Dick and Fujitsu subgroups and the other three subgroups are clearly shown by CVs 1 and 2, which account for 83.85% of the total dispersion. However, only the fourth CV separates the toners from Pentax engines from the subgroup of mixed composition. That subgroup contains toners produced by machines with Okidata, Newgen, HP, Gestetner, and C. Itoh engines. The cross validation classification results correctly assigned 93.9% of the toners to the subgroups. Subgroups 1-2 and 1-3 each had one toner incorrectly classified, both as subgroup 1-4, and had correct classification rates of 88.9% and 83.3%, respectively. The Fujitsu engine subgroup, which contained only 2 samples, was excluded from significance testing for differences in group means. Using projections into the space of the first three PCs (93.83% of total variation), the largest p -value for Hotelling's T^2

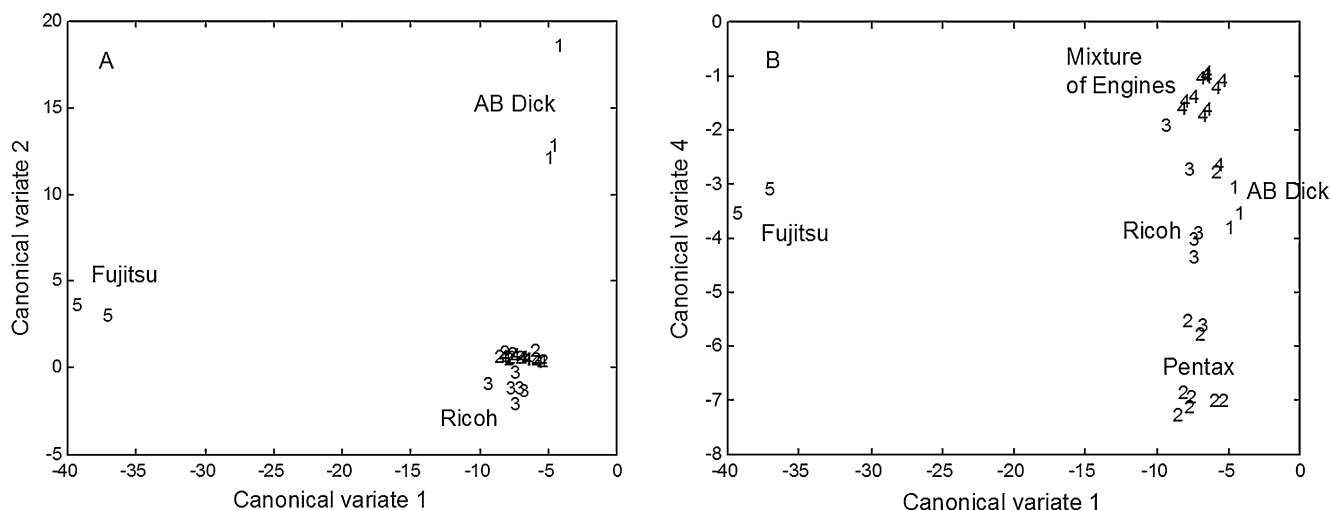


Fig. 8 (A) Projections into the space of canonical variates 1 and 2 for cluster 1; toners from AB Dick, Ricoh, and Fujitsu engines are well separated. (B) Projections into the space of canonical variates 1 and 4 for cluster 1; toners from Pentax engines are separated from the group of mixed composition

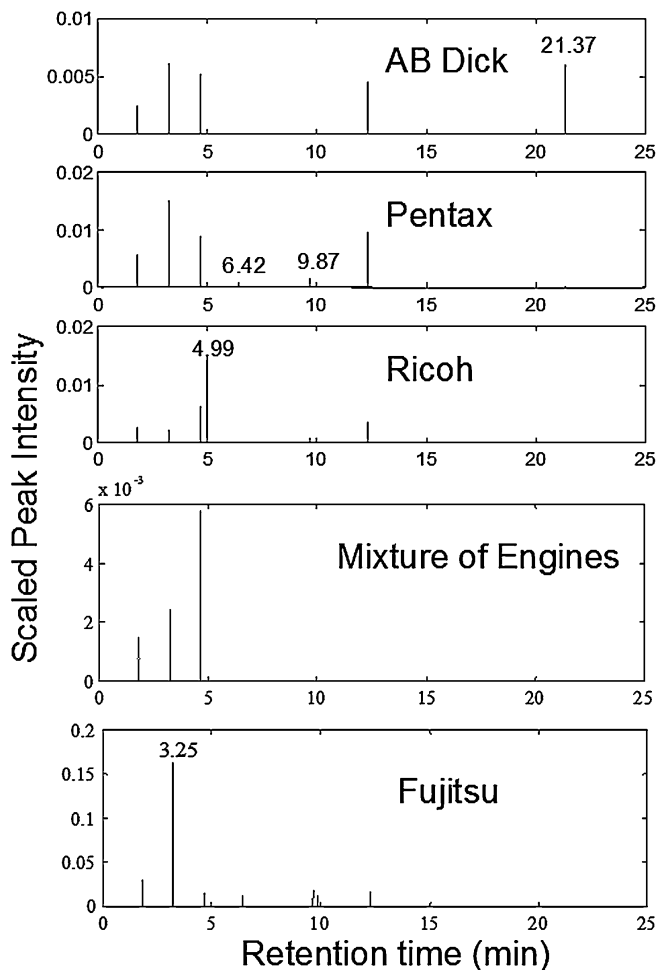


Fig. 9 Average scaled peak intensities (relative to styrene) for toners in five subgroups of cluster 1. Labeled peaks are markers for the individual subgroups. The Fujitsu subgroup is marked by the presence of the peak at 3.25 min

was 0.0028 (for subgroup 1-1 compared with 1-3). The means of the four subgroups tested were thus all statistically different at high levels of confidence.

Figure 9 shows average scaled values for the pyrograms of each subgroup in cluster 1. Peaks important for subgroup separation are labeled where they occur. The mixed subgroup that cannot be further subdivided lacks peaks at 4.99, 6.42, 9.87, 12.3, and 21.37 min. Most of the toner samples in subgroup 1-2 were the replicates of the Advanced Matrix Tracjet used to determine day-to-day reproducibility. Cluster analysis grouped the replicates together. In Fig. 7, the Advanced Matrix Tracjet samples are labeled 9–15, and the other toner sample produced by a Pentax engine is labeled 77 (in the center of the cluster to the right). These samples form a vertical line in the center of the three-dimensional plot.

This group of toners found in cluster 2 of the Py-GC/MS data was composed of 60 samples acquired from machines with AB Dick, Canon, Casio, Copystar, Eastman Kodak, Harris/3 M, Hitachi, Matsushita, Sharp, Tokyo Electric, and Varityper engines. PCA and knowledge of the printers and photocopiers suggested several groupings, e.g., engines manufactured by Canon or Sharp. However, no statistically significant groupings were found and the results from LDA were extremely poor. The 42 peak feature array was used to test if peaks which were deleted in the initial analysis would improve the results. Unfortunately, no improvement was seen, suggesting that Py-GC/MS cannot differentiate between these samples, presumably because they are all based on the same polymer mixture.

Comparisons of SEM and Py-GC/MS results with RA-IR classification

A particular interest of this study was to learn if R-A IR and SEM could be employed together in a synergistic fashion to identify a toner sample's origin. Table 1 shows the relationship between R-A IR and SEM group assignments for the toners. Each listing follows the format given at the top center of the table. For example, SEM Group A con-

Table 3 Listing of toner samples found in Py-GC/MS cluster 1, with their SEM group assignments

Py-GC/MS Subgroup	SEM Group	Brand name	Model	Engine
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Advanced Matrix	Tracjet	Pentax Tech PLF 0301
1-2	J	Atari	SLM 804	Tokyo Electric LB1301
1-2	J	Pentax	PL-F 0242 Laser	Pentax
1-3	A	Ricoh	PC Laser 6000	Ricoh LP 1060
1-3	A	Texas Instruments	Omnilaser 2106	Ricoh LP 1060
1-3	A	Texas Instruments	Omnilaser 2106	Ricoh LP 1060
1-3	B	IBM	4216	Ricoh LP 1060
1-3	C	Epson	GQ 3500	Ricoh LP 1060
1-4	B	Okidata	Laserline 6	Ricoh LP 1060
1-4	C	Okidata	Okilaser 800	OKI Electric 800
1-4	F	Okidata	Okilaser 830	OKI Electric OL 8
1-4	J	C. Itoh	8	TEC
1-4	K	Newgen	Turbo PS 480	Canon
1-4	K	Newgen	Turbos PS 630	Canon LPX SX
1-4	K	Newgen	Turbo PS 880	Canon LPX SX
1-5	J	Fujitsu	RX 7100 PS	Fujitsu M 3701 M
1-5	J	Fujitsu	RX 7100 S2	Fujitsu RX 7100

tains two samples of toner from machines with IBM engines belonging to R-A IR group 41.

Toners in R-A IR group 42, composed of a poly(styrene:acrylate) base, comprise a significant number of the commercial toners used in modern photocopiers and printers. Visual discrimination of R-A IR spectra for these toners has been unsuccessful, although discriminant analysis has been useful [32]. SEM analysis, however, is somewhat more successful for discrimination of toners in R-A IR group 42. SEM groups D, E, and L do not contain any group 42 samples. Group 42 engines manufactured by Ricoh are found in SEM groups A–C. Sharp engines in group 42 are found only in SEM group F. OKI Electric group 42 engines are found in SEM groups B, C, and F. Tokyo Electric engines in group 42 are found in SEM groups H, J, K, and M. Canon engines in group 42 fall into SEM groups B, H, J, and K, which include both the ferrite and nonferrite based toners. This particular manufacturer exemplifies one of the main problems in the classification of toners. Chemically different toners may be used by the same engine manufacturer. The SEM results for R-A IR group 42 toners thus suggest that SEM may provide limited discrimination among this large group of toners.

Toners not classified as R-A IR group 42 were found to separate well when their SEM results were analyzed. Fujitsu engines in R-A IR group 69 are found in SEM groups B and C, while Kyocera engines in the same R-A IR group are in SEM group D. For R-A IR group 37, Toshiba engines are classified as SEM group F, while Konica engines are SEM group J. MITA engines are found in both SEM groups E and M, and Kyocera engines in R-A IR group 37 are also classified in SEM group M.

To estimate the effect of combining results from the SEM and R-A IR analyses on toners, the 166 samples were sorted by SEM group and then by R-A IR group. Once sorted, groups of differing combinations of SEM and R-A IR groups were identified. To determine the number of toners defined by a particular combination, the brand name and engine manufacturer were checked. For SEM cluster 1, there were 58 samples which could be split into 23 separate combinations of SEM and R-A IR groups. When the brand names and engine manufacturers were checked, 31 of the 58 toners (53.45%) could be assigned to either a brand name or engine manufacturer. For SEM cluster 2, there were 108 samples which could be split into 27 separate combinations of SEM and R-A IR groups. When the brand names and engine manufacturers were checked, 37 of the 108 toners (34.26%) could be assigned to either a brand name or engine manufacturer. Overall, 40.96% of the samples were specified by brand name or engine manufacturer. For the remaining samples, the number of possible brand names or manufacturers ranged from two to six.

A total of 57 poly(styrene:acrylate) based toner samples had both SEM and Py-GC/MS results available for comparison. Table 3 lists 24 toners classified in the Py-GC/MS cluster 1 and their SEM groups. Interestingly, cluster 1 toners contain both ferrite and nonferrite based toners. Pentax and Fujitsu engines, differentiable by Py-GC/MS, are both SEM group J. Newgen engines, part of the subgroup 1-4, which had a mix of manufacturers, are all SEM group K and thus may be separated from the other toners in 1-4. Also in subgroup 1-4 were three toners from Okidata brand machines, all in nonferrite based SEM

Table 4 Listing of toner samples found in Py-GC/MS cluster 2, with their SEM group assignments

Py-GC/MS subgroup	SEM group	Brand name	Model	Engine
2	F	Alps	LPX 600	Sharp JX 9300
2	F	Qume	Scripten	Hitachi SL 100
2	F	Sharp	JX 9700	Sharp JX 9700
2	F	Sharp	JX 9300	Sharp
2	F	Texas Instruments	Microlaser Turbo	Sharp JX 9500
2	F	Texas Instruments	Microlaser XL	Sharp JX 9701
2	G	Fortis	DP 600 W	Casio LCS 130
2	H	Brother	HL 4 PS	Canon LBP 4
2	H	Brother	HL 4 V	Canon LBP SX
2	H	Canon	LBP 4 Plus	Canon P 110
2	H	Canon	LBP 4 Plus	Canon P 110
2	H	Canon	LBP 4	Canon P 110 LBP4
2	H	Epson	EPL 6000	Tokyo Electric
2	H	Hewlett-Packard	Laserjet II P Plus	Canon
2	H	Hewlett-Packard	Laserjet III P	Canon LBP LX
2	H	Newgen	Turbo PS 400 P	Canon LX
2	H	QMS	PS 410	Canon LBP LX
2	I	Qume	Crystalprint Publisher	
2	J	C. Itoh	4	Tokyo Electric
2	J	C. Itoh	8 E	TEC
2	J	Eastman Kodak	Ektaplus 7008	
2	J	Facit	P 6060	Tokyo Electric
2	J	Hewlett-Packard	Laserjet	Canon CX
2	J	Hyundai	HLP 8000	Tokyo Electric
2	J	Qume	Crystalprint Series II	Casio
2	J	Seikosha	OP 115	Matsushita
2	J	Toshiba	Pagelaser GX 200	Tokyo Electric LB
2	J	Vistron	V 5000	Matsushita
2	K	Mannesmann	MT 908	Tokyo Electric
2	K	Varietyper	VT 600	Proprietary
2	M	Mannesmann	MT 905	TEC
2	M	Mannesmann	MT 906	TEC
2	M	Microtek	Truelaser	Tokyo Electric

groups (B, C, and F). The last toner in subgroup 1-4 was a C. Itoh brand classified in SEM group J. Thus, subgroup 1-4, the “mixed group”, may be separated on the basis of SEM results for those toners. Subgroup 1-3 contains all Ricoh engines with toners classified in SEM groups A, B, C. As stated above, 33 toner samples that were classified in Py-GC/MS cluster 2 (Fig. 5 and 4) did not exhibit statistically significant clustering behavior. Aside from 6 toners classified in SEM group F all but one with Sharp engines, the remaining toner samples in this cluster were all from SEM groups G–M, the ferrite based, single component toners. Toners from machines with Canon engines are, with one exception, all in SEM group H. Toners from machines bearing Mannesmann, Microtek, and Varietyper brand names, with four out of five engines being made by Tokyo Electric, are classified in SEM groups K and M. Qume and Fortis machines were each unique, being the only toner samples with SEM groups G and I, respectively. Five out of ten toners in SEM group J had Tokyo Electric engines.

Conclusions

Several differences between this investigation and our previous work involving RA-IR [4, 5] should be noted. The RA-IR study involved analysis of a total of 430 photocopy and toner samples. The SEM study was conducted on a more limited set of 166 toner samples, and Py-GC/MS study involved only 93 poly(styrene:acrylate) based samples. The SEM and Py-GC/MS data sets were not only smaller in number than that analyzed by RA-IR, but also did not include all the same samples. Another important difference is that the RA-IR study applied multivariate classification to group copy toners into RA-IR classes established previously by visual comparison and computer-assisted spectral matching [4]. These RA-IR groups did not represent toners from single manufacturers or from single toner engines. The more limited SEM and Py-GC/MS data in the present study provide some discrimination relevant to the more challenging goal of classifying samples into individual manufacturer or toner engine groups.

While individual elements may be recognized to discriminate various toner groups, discriminating among dif-

ferent types and manufacturer's brands of toner by visual examination of SEM data for multiple elements is time-consuming and subjective. The multivariate pattern recognition methods used here took into account the entire chemical characterization of the toners based on all 10 elements simultaneously. Multivariate techniques also provide a greater ability to discriminate between groups in large sample sets than is achievable by visual analysis. Interpretation time can be reduced because the approach also has the potential to be automated. Principal component analysis and cluster analysis of the SEM results for 166 toner samples established 13 statistically different subgroups. A major division among these toner subgroups was the presence or absence of a ferrite base, matching reports in the literature. The detection of further subgroups within these toners may enable greater accuracy in the determination of a toner's origin, especially for those cases where SEM provides information unavailable from R-A IR. When toners for which there were both SEM and R-A IR data available were compared, 40.96% of the samples could be assigned to specific brand names or manufacturers. The number of potential brand names and/or engine manufacturers was reduced for the remaining toner samples. SEM analysis is a complementary technique to R-A IR, further enhancing the ability to classify toner samples.

The statistical validity of observed differences in Py-GC/MS patterns was assessed and the combination of PCA and CVA identified eight peaks relevant to differentiation between groups. Two main clusters were found. The smaller cluster, roughly one-third of the toners, contained 5 statistically different subgroups. While it is not the objective of this work to identify the chemical nature of discriminating features, pyrolysis products that differentiate certain toner types were identified and characterized by their mass spectra. Considering the 57 toners for which there were both SEM and Py-GC/MS data, 31 could be well differentiated from the information provided by both analyses. SEM data allowed almost unambiguous determination of Fortis, Fujitsu, Newgen, Pentax, Qume, Ricoh, and Sharp engines (two toners did not come from engines with those manufacturers, but those engines could have been marketed "private label"). The remaining 26 samples fell into somewhat broad groupings, but the list of possible manufacturers was still narrowed. The improvement in classification of this common type of toner based on the combined SEM and Py-GC/MS data over that offered by R-A IR may be worth the additional effort involved in the application of these analytical methods.

These results have direct applicability to the forensic investigation of criminal acts involving the duplication or production of documents, e.g., fraud, counterfeiting, the transmission of sensitive or confidential materials, anonymous letters. By subjecting copied or laser printed documents of unknown origin to R-A IR, SEM, and Py-GC/MS analyses, forensic scientists may obtain a substantial amount of information regarding the probable origin of the document. The synergy between the complementary information provided by these different analytical approaches has the potential to narrow the number of possi-

ble machines which could have produced the document and thus speeding up investigations. For a significant number of the toners, unambiguous determination is possible. The application of multivariate statistics to data from these different analytical methods allows comparisons of the discriminating ability of each method and evaluation of the variability of analytical results within groups of toners. It is important to remember, however, this work is only preliminary and that the results demonstrate the potential of using multivariate statistics to discriminate copy toners. Further work is required to realize the full potential and to validate the methods for forensic applications. It will be necessary to build toner libraries with information of toner product numbers, the machine engines, and machine models that the toners are used with. To be most effective in forensic casework, extensive collections that contain results from all three analytical techniques are needed and it is necessary to expand the number of samples to remain current with changing technologies.

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