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Forensic Characterization of Papers. II: Determination of Batch Differences by Scanning Electron Microscopic Elemental Analysis of the Inorganic Components

Paper is often used in the course of criminal activities, including kidnapping, bombings, forgery, conspiracy, threatening letters, and gambling. Thus the examination of paper is a common task for the document examiner [1].

The characterization methods commonly used in forensic laboratories [2,3] are generally based on those developed by ASTM and the paper manufacturing industry [4-6]. They focus on the measurement of gross physical properties such as thickness, weight per unit area before and after ashing, and strength as well as the qualitative characterization of color, fluorescence ("brightness"), and fiber content. It has been noted [7] that the scanning electron microscope (SEM) may be very useful for the study of the surface morphology and fiber content of paper. Further, wire and water marks provide very useful information when present.

However, the individualization of paper, whether as to manufacturer or identity of source with another sample, is made difficult by the very large number of manufacturers producing similar papers and by the variability in samples of a given brand of paper as a result of the use of different naturally occurring and recycled materials. Additionally, many of the characterization techniques listed above have a low ability to discriminate between similar papers.

Quantitative elemental analysis of the inorganic components of paper can provide additional points of comparison. In addition to the fibrous material generally constituting the bulk of a paper, paper usually contains inorganic additives which serve as fillers, coatings, and whiteners or pigments. Such substances include clays, talc, silica, calcium carbonate, titanium dioxide, zinc oxide, barium sulfate, and calcium sulfate. These materials generally have particle sizes of less than 0.1 to 5 μm [7] and are finely dispersed throughout the paper. These additives provide the bulk of the metallic elements present in modern papers.

In two studies [8,9] the forensic usefulness of quantitative elemental analysis of paper by neutron activation analysis (NAA), with emphasis on trace elements, was investigated; the results indicated that such analyses can indeed provide a useful further characterization of paper. In a recent study [10], pattern recognition methods were applied to the data obtained in the earlier studies [8,9]. Since NAA is not readily available to most labora-

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tories, alternative analytical techniques would be desirable; potential methods include X-ray fluorescence, atomic absorption, and emission spectroscopy.

A previous paper of this series [11] reported the initial results of a study designed to investigate the application of SEM microanalysis to paper. Fifty-four different papers, primarily writing papers, were analyzed; the wide variation of elemental content confirmed the forensic usefulness of such an analysis. In addition, the compositional uniformity of two common writing papers was examined more closely; even for very small test areas ($\sim 0.06 \text{ mm}^2$), the apparent compositional variations across the sheet were much less than those between different papers.

Further, for several different sheets from one specific box of paper the differences in the spectra were found to be small and similar to those found within one sheet. However, it is known [1] that different sheets within one box of writing paper can have markedly different properties since sheets from different rolls of paper are generally interleaved during the slitting, cutting, and boxing process. The compositions of individual rolls may vary since they may have been made from different batches of ingredients; such variations are expected to be especially large when some recycled paper is incorporated into the final product.

This paper reports the results of a continuation of the previous study [11] in which attention is now focused on the compositional variations among identically labeled sheets of paper.

Experimental Procedure

As in the previous study [11], samples for SEM X-ray microanalysis were taken in the form of $\frac{1}{4}$ -in. (6.35-mm) disks which were ashed under controlled conditions. The ashing procedure eliminated the Bremsstrahlung radiation originating from the organic fibers and thus improved the sensitivity of the analysis of the metallic components, giving a better statistical determination of the relative peak heights of different elements. The ashed samples were mounted on carbon disks using Duco cement diluted with acetone.

Samples were irradiated with 30 keV electrons in an AMR 1000 SEM. Generally the spectra were obtained by electron beam scanning a sample area of approximately 6 mm^2 , corresponding to the full SEM screen at a magnification of $\times 50$. Since the paper shrinks upon ashing, this area represents a somewhat larger section of the original paper. The fluorescent X-radiation was acquired with an Ortec Si(Li) detector of 170 eV resolution; the energy spectra were analyzed by a Nuclear Data PHA. The spectra were then plotted by an x - y point plotter and printed in tabular form. With the exception treated below, peak heights were used to determine intensities; in this case, data were digitized by recording the peak heights above background and then scaling them such that the height of the major peak was set as 100. Samples were counted until the count in the channel corresponding to the maximum of the highest peak reached about 125 000; typically, this took about 20 min. The following series of typewriter paper samples were examined:

- (1) samples from a single sheet of paper;
- (2) different sheets of paper from the same box;
- (3) sheets from identically labeled boxes purchased from different stores;
- (4) manufacturer-supplied samples originating from different rolls of paper which were to be identically labeled for sale and had been produced during a period of two days; and
- (5) samples as in No. 4, but produced during a period of several months.

The variability within a single sheet (No. 1) was determined using peak area rather than peak height as in the earlier study [11] and the other data reported here; this reexamination served as a check on the adequacy of the simpler peak height method.

Results

As an example, Fig. 1 shows the spectrum obtained from an ashed sample of Eaton's Corrasable typewriter paper (Sample 19B). The peaks superimposed on the background

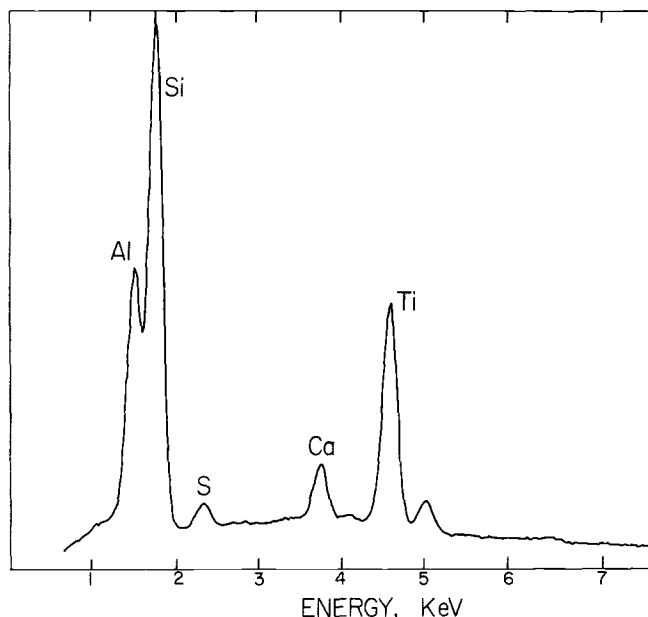


FIG. 1—Energy spectrum of the fluorescent X-rays obtained from an ashed sample of Eaton Corrasable typewriter paper, characteristic of the spectra used to obtain the data in Tables 1 through 9.

originate from the metallic elements which are present at major concentration levels; in order of increasing energy, they are aluminum- K_{α} , silicon- K_{α} , sulfur- K_{α} , calcium- K_{α} , and the titanium- $K_{\alpha\beta}$ doublet. Because different elements have different excitation efficiencies and there may be preferential absorption of the X-rays emitted from different elements, the relative peak heights are not directly proportional to the relative concentrations of the elements; however, although the peak heights only approximate the relative concentrations, they do provide a useful reproducible "fingerprint" of the paper. (The titanium- K_{β} peak is proportional to the titanium- K_{α} peak and hence is not listed in the tables.) Results for the five categories of samples listed above are presented in the following.

Samples from a Single Sheet of Paper

The compositional variations within a sheet had been examined in the previous study [11]. The first four lines of Table 1 present a reexamination of the reproducibility within one sheet of Eaton's Corrasable paper. In this case the area under each peak was measured and each peak area is given as a percentage of the total of the areas of the individual peaks. As expected, the variation is less than that found [11] with only peak height measurement. The average values and associated standard deviations (given in parentheses both as absolute numbers and as percentages of the average) are aluminum-24.56 (0.32, 1.3%); silicon-48.44 (0.64, 1.3%); sulfur-2.17 (0.038, 1.7%); calcium-4.65 (0.020, 4.3%); and titanium-20.17 (0.69, 3.4%).

TABLE 1—Spectra from Eaton Corrasable paper, based on peak area, of four samples (FA, FD, FE, FF) from one sheet and two samples (FG, FH) from different, randomly selected sheets from the same box.

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium
FA	25.57	48.57	2.19	4.37	19.29
FD	24.02	49.32	2.17	4.55	19.93
FE	24.38	48.31	2.24	4.81	20.25
FF	24.27	47.54	2.09	4.87	21.22
FG	23.73	46.92	2.14	5.02	22.21
FH	20.62	43.23	2.11	5.97	28.07

Sheets from the Same Box of Paper

In the previous study [11], six randomly selected sheets from one box of Eaton's Corrasable were found to have compositional variations similar in magnitude to those found in one sheet by using peak-height measurements with the associated standard deviations ranging up to 10% for the smallest peaks. To increase the information available on intra-box variations, the present study was made on three different types of paper.

The first example of intra-box analysis is given for Eaton's Corrasable Typewriter paper in Table 1. Three different, randomly selected sheets were examined: the reference sheet for which four samples were analyzed (FA, FD, FE, FF) as discussed above and two other sheets (FG, FH). Using the criterion that sheets are distinguishable when at least one elemental concentration of the questioned sheet differs from the average derived from the reference sample by $\pm 3\sigma$ (corresponding to a 99.7% confidence level that they are different), FG cannot be distinguished from the sheet analyzed for lines FA, FD, FE, and FF. However, FH is distinguishable since the aluminum, silicon, calcium, and titanium levels are outside of the $\pm 3\sigma$ interval. This ability to distinguish sheets within the box of Eaton's Corrasable, in contrast to the earlier study [11] where sheets were indistinguishable, is due to the significantly smaller standard deviations found in the present study using peak area; Sample FH would be indistinguishable from the other two sheets if the standard deviations observed [11] for peak height characterization were used.

Table 2 displays the spectra from eight consecutive sheets from a box of Coupon Bond produced by the Eagle A/Linweave Division of Brown Co. In this case, the sheet-to-sheet variations are much greater than the standard deviations for peak height characterization found in Ref 11 within one sheet. It appears that the sheets have a compositional periodicity of four, though the second and fourth sheets within one period are not distinguishable, suggesting that four rolls of paper were cut and interleaved in the packaging of this box.

TABLE 2—Spectra from eight consecutive sheets from a box of Eagle A Coupon Bond.

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium
90A	36.8	31.9	4.1	4.2	100.0
90B	18.2	12.0	4.6	4.6	100.0
90C	28.8	22.3	5.6	6.3	100.0
90D	20.3	13.5	4.2	3.8	100.0
90E	37.1	31.7	4.3	3.9	100.0
90F	17.9	12.2	4.9	5.2	100.0
90G	27.6	21.5	5.5	5.8	100.0
90H	19.3	12.0	4.2	3.7	100.0

Table 3 contains the spectra from eight consecutive sheets from a box of Trojan Bond, also produced by Eagle A, with each sheet analyzed twice. Again, the sheets within the box differ but a periodicity of three can be seen. It is also noted that these two boxes of different papers produced by the same company are, on the basis of their aluminum, silicon, and titanium contents, compositionally distinct and do not overlap.

TABLE 3—*Spectra from eight consecutive sheets from a box of Eagle A Trojan Bond (each sheet was analyzed twice).*

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium
91A	100	40.7	10.5	16.3	56.8
91A	100	39.5	9.4	14.7	47.5
91B	100	76.8	3.0	6.6	33.8
91B	100	72.2	3.1	6.7	33.9
91C	100	44.2	11.9	19.5	35.4
91C	100	42.2	9.5	18.0	37.3
91D	100	43.7	11.5	18.8	47.8
91D	100	39.4	9.0	15.6	56.6
91E	100	77.0	2.9	6.0	31.1
91E	100	73.6	2.7	5.8	35.5
91F	100	44.3	10.7	18.6	36.0
91F	100	45.9	9.7	17.8	38.0
91G	100	39.6	10.7	16.3	51.9
91G	100	40.5	8.7	15.8	58.8
91H	100	79.1	3.2	5.6	27.2
91H	100	76.7	2.6	6.2	33.4

Sheets from Different, Identically Labeled Boxes of Paper

Table 4 contains the spectra from single sheets selected from seven different boxes of Eaton's Corrasable purchased from different stores. On the basis of the previously observed standard deviations [11], these sheets are generally distinguishable from each other by this analysis. The variations are, in this case, seen to be much greater between boxes than those observed within one box, as reported for Eaton's Corrasable in Ref 11 and above.

Sheets from Different Rolls Produced During a Short Time

Two examples for this case are presented. Table 5 contains spectra from samples of Coupon Bond taken from individual rolls produced during two days in August, 1975, arranged in the order of production. Again, significant compositional variations are seen, with the samples appearing to fall into groups, namely, A to C, D, E to G, H-I, and J-K. The compositional variation of titanium is especially large, ranging from being the major element to being essentially absent.

Table 6 lists the spectra obtained from samples of Trojan Bond taken from separate rolls which had been manufactured during two days in July, 1975, also arranged in the order of production. Once again, groupings do exist (for example, Samples H to L), though the variations are significantly greater than those found for the box of Trojan Bond, reported in Table 3, which appeared to represent only three rolls.

Sheets from Rolls Produced During a Long Period

Three types of paper, each produced during a three to nine-month interval, were

TABLE 4—Spectra from seven sheets of Eaton Corrasable paper, each having been selected at random from boxes purchased at different stores.

Sample	Sodium	Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Potassium	Calcium	Titanium	Iron
19B	...	52.5	100	...	5.2	10.1	38.7	0.5
19C	6.2	73.1	100	8.5	2.8	8.7	2.1	10.7	2.0	3.1
19D	...	50.2	100	...	8.3	18.9	18.9	0.4
19E	...	22.3	100	...	0.8	7.8	22.3	0.3
19F	5.2	87.8	100	7.5	5.5	14.6	11.0	3.1
19G	2.0	64.0	100	...	10.2	16.1	33.3	0.4
19H	1.5	49.7	100	...	5.3	8.8	...	9.4	2.4	1.2

TABLE 5—*Spectra from samples from individual rolls of Eagle A Coupon Bond produced during a period of two days.*

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium	Iron
83A	45.3	5.3	13.2	3.3	100	3.1
83B	38.3	4.1	10.4	2.8	100	2.5
83C	48.7	5.6	12.0	1.9	100	2.6
83D	100	10.1	28.9	6.8	17.3	5.6
83E	100	7.0	22.7	6.5	7.6	5.5
83F	100	7.3	24.7	6.5	4.2	6.0
83G	100	6.8	26.8	6.8	6.5	6.0
83H	100	6.6	22.4	6.9	2.4	4.7
83I	100	7.6	21.4	7.6	2.6	4.9
83J	100	7.8	20.6	8.4	51.6	8.6
83K	100	6.6	21.2	7.1	64.8	6.1

TABLE 6—*Spectra from samples from individual rolls of Eagle A Trojan Bond produced during a period of two days.*

Sample	Aluminum	Silicon	Phosphorus	Sulfur	Calcium	Titanium
84A	100	59.7	...	11.1	26.6	36.3
84B	100	33.7	...	21.8	39.6	38.6
84C	100	26.2	...	33.2	52.3	27.6
84D	100	24.1	...	43.1	63.8	13.1
84E	100	39.3	...	28.0	47.7	38.3
84F	100	28.7	...	24.2	42.6	32.1
84G	100	29.1	...	31.8	54.7	36.7
84H	81.6	21.8	...	22.4	28.9	100
84I	94.1	18.8	...	18.6	28.8	100
84J	67.3	23.0	...	14.3	26.3	100
84K	76.6	26.2	...	14.4	26.0	100
84L	77.8	22.7	...	17.3	28.5	100
84M	100	27.4	...	26.7	44.7	22.6
84N	100	24.7	...	27.6	45.8	61.3
84O	83.8	26.3	...	21.4	33.2	100
84P	93.6	29.0	9.5	12.0	17.5	100
84Q	69.5	26.4	14.1	12.7	18.7	100
84R	100	43.5	...	19.3	36.5	36.7

examined. Table 7 displays spectra from samples of Coupon Bond produced during a six-month period and Table 8 similarly gives spectra of Trojan Bond produced during a nine-month period, each being listed in order of production. Interestingly, the variation over the six-month period for the Coupon Bond (Table 7) is significantly less than that over the short period of two days at a later time when the paper detailed in Table 5 was produced; the titanium content as reported in Table 5 no longer dominated the metal content to such a degree as in the earlier production characterized in Table 7. This change may reflect, for example, a decision to incorporate less titanium dioxide into the paper or the incorporation of different amounts or types of recycled paper into the final product. By contrast, for the Trojan Bond the variability of the analysis was of the same order at different times, as seen by a comparison of Tables 6 and 8; however, the relative calcium, sulfur, and silicon content of the later production (Table 6) is higher on average.

Table 9 contains the spectra from six sheets of Green Label Xerographic Copy paper of Groveton Papers Co. which were produced during a three-month interval and are

TABLE 7—Spectra from samples of Eagle A Coupon Bond produced during a six-month period.

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium
81A	9.3	0.8	6.2	6.0	100
81B	11.3	1.1	5.0	4.2	100
81C	6.2	3.1	2.5	2.5	100
81D	3.3	...	2.9	3.3	100
81E	5.0	0.8	4.6	6.3	100
81F	24.7	3.2	8.6	13.1	100

TABLE 8—Spectra from samples of Eagle A Trojan Bond produced during a nine-month period.

Sample	Aluminum	Silicon	Sulfur	Calcium	Titanium
80A	63.2	6.4	5.8	16.7	100
80B	39.1	8.8	9.8	17.5	100
80C	39.1	21.7	14.4	26.5	100
80D	18.1	1.2	5.8	11.7	100
80E	52.6	8.1	7.5	16.4	100
80F	99.3	14.8	15.1	31.9	100
80G	100	19.1	8.0	12.7	28.4
80H	100	18.3	13.5	29.8	55.0
80I	30.8	8.4	4.3	11.1	100
80J	47.2	13.6	6.4	10.2	100

TABLE 9—Spectra from samples of Groveton Paper Green Label Xerographic Copy paper produced during a three-month period.

Sample	Magnesium	Aluminum	Silicon	Titanium	Iron
82A	0	99.2	100	12.1	3.2
82B	0	100	99.9	9.6	3.5
82C	18.4	56.6	100	4.7	6.9
82D	15.7	67.4	100	8.1	6.2
82E	17.1	62.9	100	6.1	6.4
82F	16.6	60.6	100	21.0	6.6

listed in order. Two distinct groups are apparent, those with and those without significant amounts of magnesium.

Discussion

The data reported above indicate that chemical analysis of the inorganic components of paper can provide forensically useful information. Such an analysis is of special value when two sheets of paper are indistinguishable on the basis of their commonly examined physical characteristics; elemental analysis may then be capable of distinguishing them (an important capability for the detection of forgery) or may provide strong, additional support for the likelihood of common origin.

Each group of papers analyzed for this report appears similar on cursory visual examination and possesses identical watermarks; thus the analysis presented here has detected individualizing batch differences. These batch differences obviously depend on the manufacturing procedure followed by each company. While it would be necessary to determine an approximate range of batch differences to be found for each type of paper,

the analyses of the four types of typing paper from three manufacturers examined here demonstrate that significant batch differences are common, occurring during both long and short time periods.

Such batch differences are a mixed blessing. Clearly, they are useful since the ability to discriminate between identically labeled papers is based on such differences. However, the practice of interleaving sheets cut from different rolls of paper makes matching of a sheet to a suspect box more difficult since many sheets in it have to be analyzed and the chance of an accidental match is greater.

The batch differences demonstrated in Tables 2 to 9, when combined with the observed standard deviations for samples from within one sheet, also provide the basis for estimating the probability for an accidental match. While the limited data accumulated here are not sufficient to provide the basis for conclusive, quantitative statements as to the general probability of an accidental match, it can be said that the observed intra-batch standard deviation is very much less than the inter-batch variations; thus, a usefully low chance of accidental matches can be achieved. However, it should be emphasized that, as with all other characterizations based on a limited number of points of comparison, chemical analyses which are identical (within statistical fluctuation) cannot provide absolute identification of paper.

The large range of values found and their variability with time suggests that the analysis may also be of assistance in providing limits on the date of manufacture of paper. This would be possible when the content of at least one of the major inorganic components is changed radically, for example, by no longer adding a component or by adding a new one. This might be the case for the papers listed in Table 9, where there appears to be a change in the "recipe" between the period when A and B were made and the following period: magnesium appears and the relative aluminum content decreases. The same effect may account for the fact that titanium is very dominant in the older Coupon Bond (Table 7) while being less dominant or even a minor element in more recent production (Table 5). In fact, the use of titanium dioxide as a whitener is being reduced by some paper manufacturers in favor of the inclusion of an organic whitener.

The present study suggests the direction for future work: an important goal would be to provide a statistical base for the technique used here.

Because paper is produced from a large vat of slurry that is mechanically stirred and the inorganic ingredients are of a small size, one would expect the paper to be relatively homogeneous; however, as reported above, careful SEM microanalysis gave standard deviations of under 2% for the aluminum, silicon, and sulfur and about 4% for the calcium and titanium. Because the ability to discriminate effectively between different papers of nominally similar compositions depends on the knowledge of these standard deviations, a study to determine if the standard deviations are due primarily to inherent compositional variability, the sample size, or analytical limitations would be desirable. In particular, it would be desirable to determine the intra-sheet standard deviations for many different manufacturers and types of paper; if they were similar, fewer samples would need to be analyzed for each comparison.

It is also noted that additional information as to the inorganic content can be obtained by analyzing for the trace metal content; inclusion of this information would provide still greater discriminating power and reduce the chance of an accidental compositional match. Atomic absorption spectrometry is suitable for such an examination; a study by this technique has been completed² and will be published; a study combining both data bases and applying pattern recognition methods to them is in progress.

²P. Simon, T. Copeland, and B. C. Giessen, unpublished data.

Summary

Previous work has demonstrated the potential usefulness of elemental analysis in the forensic examination of paper. The examination with SEM microanalysis of compositional variations found within individual boxes of paper, between identically labeled boxes purchased from different stores, and between manufacturer-supplied samples of identically labeled papers produced during short and long time periods has been reported. For each paper, significant batch differences have been observed; thus, papers with identical watermarks and very similar physical properties can generally be further individualized. This can be useful, for example, in determining the likelihood that a given sheet of typewriter paper came from a given box of that type of paper or in providing limits on the date of manufacture of a paper.

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