

CASE REPORT

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Comparison of the Elemental Composition of Office Document Paper: Evidence in a Homicide Case

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ABSTRACT: Fraudulent substitution of a page within a multiple page document such as a will or business contract, the counterfeit manufacture of paper banknotes, and linking ransom or extortion notes have all been the focus of criminal investigations at one time or another. In a recent homicide investigation, document examiners were requested to compare a threatening letter received by a business partner of the deceased with paper samples seized under warrant from a suspect's house. Through a quantitative elemental analysis of the concentrations of nine elements (Na, Mg, Al, Mn, Sr, Y, Ba, La, and Ce) within the questioned and specimen documents, determined by inductively coupled plasma-mass spectrometry (ICP-MS), it was concluded that (i) the paper of the threatening letter originated from a different source to that of the paper seized from the suspect's house and (ii) all six pages of paper seized from the suspect's house originated from the same source. This discrimination of paper is presented as both a statistical *t*-test analysis (99.9% confidence limit) as well as construction of an elemental fingerprint for individual replicates within the questioned and specimen sample populations. This is the first reported use of the comparison of the elemental composition of document paper, determined by ICP-MS, to assist in a criminal investigation.

KEYWORDS: forensic science, document examination, document paper, elemental composition, inductively coupled plasma-mass spectrometry, elemental profile, elemental fingerprinting

Pertinent to a recent homicide investigation was the question of authorship of a threatening letter received by a business partner of the deceased. While initially the document examination focused on the nature of the typewritten entries, the submission for analysis of six blank pages of paper seized under warrant from a suspect's house opened a further avenue of analysis. Both the paper of the questioned document (threatening letter), and the paper of the specimen document (seized from the suspect's house) were white, A4,

80 gsm, i.e., paper readily accessible from many sources and retailers. Historically, characterizing paper through the measurement of gross physical properties (strength, thickness, mass per unit area) or variables such as fluorescence, color, and fiber content (1) has not proven to match paper with a high degree of certainty (2). Recent forensic studies by Fourier Transform Raman spectrometry (3) and Fourier Transform Infrared spectrometry (4) are of limited value, for either the finished paper product was not analyzed or the samples could be visually discriminated. However, very recently Byrne et al. (5) successfully discriminated seventeen different samples of commonly used office document paper (white, A4, 80 gsm) through the use of elemental compositions determined by inductively coupled plasma-mass spectrometry. Not only was the discrimination of different papers reported, but separate batches of a single product line from the same mill, manufactured at monthly intervals, were also discriminated. It is the purpose of this article to report the first application of the research by Byrne et al. (5) to a criminal investigation to determine whether the paper of specimen and questioned documents could be concluded as originating from a common source.

Method

The documents submitted for analysis were the one page threatening letter (questioned document denoted Q_1) and six pages of paper seized from the suspect's house (specimen documents denoted S_1 through S_6 , respectively). As per the method in Byrne et al. (5) samples in the mass range of 100 to 110 mg (approximate area 30×40 mm) were removed from the margin area of each document so as to maintain the integrity of its contents. Five samples were removed from documents Q_1 and S_1 , and one sample was removed from documents S_2 through S_6 . Samples were digested with 3.0 mL of HNO_3 (69% AR, BDH, Victoria, Australia), 1.5 mL of H_2O_2 (30% AR, BDH, Victoria, Australia) and 2.0 mL of deionized H_2O using a CEM MDS2100 microwave digestion unit (Matthews, North Carolina). The program used for the microwave digestion is given in Table 1. Upon completion, the sample digests were diluted to 40.0 mL with deionized water.

The elemental composition analyses were performed using an Agilent 7500a ICP-MS (Yokogawa, Japan) with a Babington nebulizer, quartz spray chamber, and CETAC 500 autosampler. According to Byrne et al. (5), following detailed validation work, nine elements were suitable as discriminators of document paper:

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Na, Mg, Al, Mn, Sr, Y, Ba, La, and Ce. Therefore, the instrument was operated in quantitative mode measuring for those nine elements. The instrumental and data acquisition parameters are given in Table 2. For Na, Mg, Al, Mn, Sr, and Ba the calibration response curve for each element was generated through measurement of a zero reagent blank, 100 μgL^{-1} and 1000 μgL^{-1} standards. Linear calibration responses ($r > 0.999$) were generated for all six elements. For Y, La, and Ce the linear calibration curve for each element was generated through measurement of a zero reagent blank and 100 μgL^{-1} standard. The standards were prepared by serial dilution in 2% v/v HNO_3 of a mixture of two multielement standards (Hewlett-Packard, Palo Alto, California). Calibration was repeated after each set of five samples and a procedural blank had been analyzed.

TABLE 1—Microwave digestion program.

Step	Power (W)	Time (min.)
1	190	5
2	475	5
3	800	5
4	950	2
5	950	3

TABLE 2—ICP-MS operating and data acquisition parameters.

R _f Power (W)	1300
Carrier Gas Flow Rate (l/min)	1.03
Makeup Gas Flow Rate (l/min)	0.34
Sampler and Skimmer Cone Composition	Ni
MS Resolution	0.75 μ at 10% peak height
Oxide Ratio $^{156}\text{CeO} : ^{140}\text{Ce}$	<0.5%
Doubly Charged Ratio $^{70}\text{Ce}^{2+} : ^{140}\text{Ce}^+$	<2.0%
Mode of Data Acquisition	Quantitative
Dwell time/point (ms)	
^{23}Na , ^{24}Mg , ^{27}Al	30
^{55}Mn , ^{88}Sr	300
^{89}Y , ^{137}Ba , ^{139}La , ^{140}Ce	500
Points/spectral peak	3
Sweeps/reading	7

TABLE 3—Elemental concentrations (μgg^{-1}) of questioned and specimen documents.

Element	LOD (n = 9)	Q ₁ (n = 5)	%RSD	S ₁ (n = 5)	%RSD	S ₂ -S ₆ (n = 5)	%RSD	Instrumental Precision (%RSD) (n = 7)
Na	84	2300 ± 100	4.3	580 ± 30	5.2	560 ± 30	5.4	1.4
Mg	78	420 ± 30	7.1	400 ± 80	20	420 ± 60	14	1.5
Al	26	178 ± 7	3.9	140 ± 40	29	150 ± 30	20	1.7
Mn	0.7	4.55 ± 0.16	3.5	5.37 ± 0.06	1.1	5.4 ± 0.2	3.7	2.2
Sr	1.4	13.4 ± 0.7	5.2	12.8 ± 1.2	9.4	12.9 ± 0.9	7.0	1.6
Y	0.007	0.102 ± 0.004	3.9	0.199 ± 0.004	2.0	0.203 ± 0.008	3.9	2.4
Ba	0.5	0.86 ± 0.07	8.1	1.1 ± 0.3	27	1.08 ± 0.14	13	1.8
La	0.015	0.049 ± 0.003	6.1	0.233 ± 0.006	2.6	0.238 ± 0.011	4.6	2.7
Ce	0.03	0.047 ± 0.004	8.5	0.429 ± 0.009	2.1	0.441 ± 0.019	4.3	2.7

Results

Using the analytical method described, five samples were analyzed from documents Q₁ and S₁, while one sample was analyzed from documents S₂ through S₆. For comparison purposes, three sample populations were constructed: Q₁, S₁, and S₂-S₆, each consisting of five samples. The elemental concentrations as determined by the mean and standard deviation of the five samples within each population is shown in Table 3. Also presented for each element are the limits of detection ($3\sigma_{\text{blank}}$), relative standard deviations, and instrumental precision.

Cursory examination of the data in Table 3 would suggest that on the basis of the Na, Y, La, and Ce concentrations, the paper of the questioned document originates from a different source to that of the paper of the specimen documents. Legally, however, such preliminary scrutiny of the results is insufficient if required as evidence. Therefore, a variety of techniques were employed to determine if the paper of the questioned and specimen documents had been discriminated. The null hypothesis theorem, Student's *t*-test, was used to decide if the papers could be discriminated on the basis of their elemental concentrations. The results of this statistical analysis are shown in Table 4. With the null hypothesis, papers are discriminated if the calculated *t*-statistic is greater than the *t*-critical of 5.04 at a 99.9% confidence level. Table 4 shows that on the basis of Na, Mn, Y, La, and Ce the questioned document can be discriminated from both specimen paper S₁ and the specimen population S₂ through S₆ at a 99.9% confidence level.

In addition to the comparison between the questioned and specimen populations, a further analysis can be conducted between the

TABLE 4—*t*-test analyses of questioned and specimen documents ($t_{\text{critical}} 99.9\% = 5.04, n_1 = n_2 = 5$)

Element	Q ₁ vs. S ₁	Q ₁ vs. S ₂ -S ₆	S ₁ vs. S ₂ -S ₆
Na	36.8	37.3	1.1
Mg	0.5	0.0	0.4
Al	2.1	2.0	0.4
Mn	10.7	7.4	0.3
Sr	1.0	1.0	0.1
Y	37.9	25.5	1.0
Ba	1.7	3.1	0.1
La	66.3	37.4	0.9
Ce	88.4	45.5	0.3

six pages of the specimen document S_1 through S_6 seized from the suspect's house. While the assumption may exist that all six pages were derived from the same ream of paper, persons responsible for the seizure were unable to provide confirmation. From the method, it was seen that five samples were removed from specimen S_1 while one sample was removed from each of specimens S_2 through S_6 . Therefore, two sample populations for comparison purposes can be constructed, containing all five S_1 samples to be compared against the five samples from S_2 through S_6 . While it may be argued that such an analysis assumes common origin of specimen pages S_2 through S_6 , a cost effective and timely analysis precludes analyzing five samples from each individual sheet. More importantly, however, were one of the specimen pages S_2 through S_6 to have originated from a different source (i.e., containing significantly different elemental concentrations), then the magnitude of the relative standard deviations within the sample population would indicate this. It can clearly be seen in Table 3 that across the nine elements there is no significant difference between the relative standard deviation of the five samples removed from S_1 compared to that of the one sample removed from each of S_2 through S_6 . Combined with the results of the t -test analysis in Table 4 it must be concluded, therefore, that all six pages of the specimen document S_1 through S_6 originate from the same source.

While there is no doubt regarding the conclusion of differing origins for the specimen and questioned documents, a table full of statistical values may not be the most effective method of presenting that evidence in court. Rather, an elemental fingerprint can be constructed for the specimen and questioned documents as illustrated in Fig. 1. Appropriate scaling factors were used for some elemental concentrations; these are shown in the legend of Fig. 1. To reinforce the strength of the conclusions reached, instead of simply graphing the mean and standard deviation of each sample population, individual replicates of each of the questioned Q_1 and speci-

men S_1 documents were graphed. As statistical analysis has already shown that S_1 and S_2 through S_6 were of common origin, results for S_2 through S_6 were not plotted. The elemental fingerprints clearly illustrate not only the differences between the questioned and specimen documents but also the uniform distribution of elements within each sample population.

In referencing both the limits of detection in Table 3 and those reported in Byrne et. al. (5), it is apparent that in this case report, the measured limits of detection are approximately an order of magnitude higher than those measured by Byrne et. al (5). They are, however, still approximately an order of magnitude lower than the concentrations of the discriminating elements measured in paper. The validity of our conclusions are therefore unaffected. In the previously reported work of Byrne et. al (5), samples were digested in Spectrosol grade H_2O_2 and Analytical Reagent grade HNO_3 purified by sub-boiling distillation in a quartz still. Due to the unavailability of certain laboratory chemicals and techniques in the current case, samples were only digested in Analytical Reagent grade H_2O_2 and Analytical Reagent grade HNO_3 , resulting in obviously higher limits of detection. While lower limits of detection are preferable, those measured in this case are still sufficiently below the discriminating element concentrations so as not to affect the validity of the conclusions.

One final note is the high magnitude of the aluminum and magnesium relative standard deviations, especially from the specimen document. Upon digestion of the paper samples, a substantial quantity of undigested particulate matter was observed that had not been oxidized in the nitric acid-hydrogen peroxide. In the paper manufacturing process, fillers are frequently added to the paper to fill in the spaces and crevices between the fibers, producing a denser, brighter, and more opaque sheet. Common fillers include kaolin clay (hydrated aluminosilicate), calcium carbonate, and titanium dioxide and normally constitute 5 to 15% of the sheet weight (6).

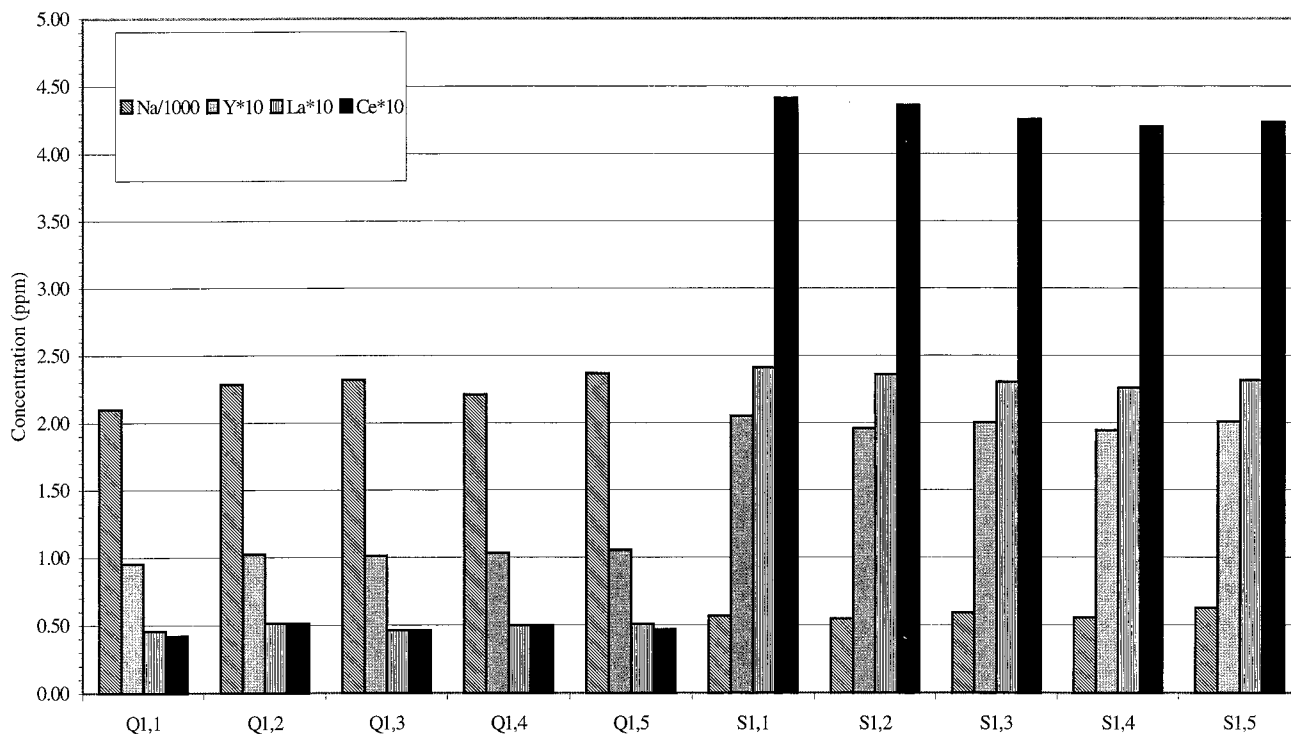


FIG. 1—Elemental fingerprint for five individual replicates of each of the questioned (Q_1) and specimen (S_1) documents.

Other fillers include talc (hydrated magnesium silicate), zinc oxide, and calcium sulfate. The undigested particulate in the above digests combined with the high relative standard deviations of the aluminum and magnesium concentrations would suggest the existence of kaolin clay and/or talc fillers in the questioned and specimen documents. While hydrofluoric acid could be substituted for the nitric acid to ensure complete digestion of the silicates, the nature of HF does not lend itself to routine analyses. Moreover, there are a sufficient number of discriminating elements with low relative standard deviations (suggesting complete dissolution) enabling conclusions to be drawn without a reliance upon hydrofluoric acid.

Discussion

The results of this case report show that trace element concentrations, measured using inductively coupled plasma-mass spectrometry, can effectively be used to compare office document paper of questioned and specimen documents. While the technique is relatively new, with this being the first reported application to a criminal investigation, there is no doubting its capacity for rapid, precise multielement results in sheet to sheet comparisons.

In this case, the alternate hypothesis of a real difference existing between the questioned and specimen documents was accepted. Now it may be argued that a negative result contributes little value to the homicide investigation. However, objectivity and impartiality are fundamental to any forensic analysis and an exclusionary result such as that obtained can direct an investigation in just the same way as an inclusionary result. There exists a wide variety of situations apart from the above case in which the technique may be employed. Fraudulent substitution of a page within a multiple page document such as a will or business contract; the counterfeit manufacture of paper banknotes; or linking ransom, extortion, or threatening notes are all scenarios that may in the future employ this technique to assist the criminal investigation.

The forensic examination of evidence concentrates on maintaining the integrity of the sample as well as preserving it in such a way that further tests may be conducted at a later date. The obvious disadvantage of the ICP-MS analysis is the destructive nature of the technique with the sample being taken into solution through a nitric acid/hydrogen peroxide digest. However, the analysis only requires a 100 mg paper sample of an approximate 30 × 40 mm area. Consider a piece of A4, 80 gsm paper with default margins (2.54 cm on all sides). If sampling is done strictly from the margin to maintain the integrity of the document content, a substantial eighteen (18) samples can be removed per sheet. Therefore, while it is destructive in nature, the impact on the document is minimized by a small sample size and through sampling strictly from the margins. Moreover, the amount of sample required for analysis could be reduced by a factor of two or three (i.e., less than 50 mg) without compromising the analysis method.

Offsetting this disadvantage is the fact that ICP-MS is a rapid, extremely sensitive, precise, multielement technique. In less than 90 s

(post digestion) an analysis is able to provide the concentration of 74 elements within the sample at an instrumental precision of under 2%. There has yet to be an alternate technique published, applying to the characterization of paper, that has the sensitivity, precision, speed of analysis, and discriminating power that ICP-MS offers.

Routine document examination involves the application of fingerprint reagents (e.g., Diazafluorenone (DFO), ninhydrin, and metal salt treatment) to ascertain the evidential value of any latent prints realized. Due to the nondestructive nature of these reagents they would be applied prior to a trace element analysis by ICP-MS. While in this case the exhibits were not to be submitted for fingerprint analysis, there exists concern regarding the potential contamination, which may result from the addition of these reagents. Future work must be undertaken to ascertain the potential for such contamination. One must consider the value that fingerprint evidence produces compared to the evidential value of a trace elemental profile. Perhaps the probative value of a trace element profile outweighs the likelihood that a comparable print may exist on the analyzed portion of the margin. These are valid issues that need to be addressed in the future.

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