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ORIGINAL ARTICLE

Trace Elements Analysis in Paper Using Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)

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ABSTRACT

The forensic examination and dating of documents is important in our society, because documents are used throughout our lives to record everything we do. The analysis of questioned documents therefore involves different types of analysis including comparison of the handwriting, ink, typescript or print, as well as physical and chemical characterization of the paper itself. Inductively coupled plasma mass spectrometry (ICP-MS) has already successfully been applied to applications in geology, forensics, ceramics, metals, glasses and a wide variety of environmental and industrial materials. In this study the use of elemental compositions, determined by ICP – MS to differentiate paper samples was investigated. Paper samples of commonly used office document paper from different sources were first microwave – digested in nitric acid – hydrogen peroxide solution and then trace elements concentrations were determined using ICP – MS.

Key Words: *Forensic analysis, questioned documents, inductively coupled mass spectrometry (ICP-MS.)*

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1.INTRODUCTION

Questioned documents like checks, business contracts, passports are submitted to the forensic laboratory for many reasons: authenticity and the printer/typewriter determination, writing author identification and the most important source of paper determination. Also source identification of successive pages can provide important forensic evidence in cases of forgery, counterfeiting and the felonious use of certificates, securities, or wills. It is important to be able to determine whether all pages come from the same source or if one or more pages of the document have been fraudulently interleaved with different paper [1].

From the literature review, some of the following elements were identified as potentially useful for discrimination: Li, Na, Mg, Al, Sc, Mn, Cr, Rb, Fe, Co, Cu, Zn, Sr, Y, Zr, Ag, Cd, Sb, Ba, La, Ce, Nd, Pb and Th. However based on the full mass scan Li, Na, Cr, Rb, Co, Cu, Cd, Sb and La were removed from the list as the concentrations of these elements were below background levels. So the list of elements to be considered in further analysis consisted of the following elements: Mg, Al, Sc, Mn, Fe, Zn, Sr, Y, Zr, Ag, Sn, Ba, Ce, Pb and Th. If papers are to be discriminated effectively, using their trace element concentrations, then the elements chosen as discriminators must satisfy certain criteria. A suiTable discriminating element must be present at a concentration significantly above its limit of detection (LOD), be uniformly distributed throughout the sheets of paper, be unaffected by any spectral interference, and show a statistically significant variation in concentration from one paper source to another.

Traditional analysis of paper involves comparison of the physical properties (dimensions, color and weight) and the fluorescent ones which are used to determine the presence of optical brighteners in the paper. The fiber content in the paper can be determinate microscopically and an experienced examiner can even identify the pulping process used during manufacture. The problem with characterizing papers by these methods has been the inability to match two sheets of paper with a high degree of certainty [2-4].

The first attempts to distinguish papers using their elemental composition were made in the 1970s. Schlesinger and Settle [5] used thermal neutron activation analysis (NAA) to determine the elemental composition of 120 paper samples from nine manufacturers. Blanchard and Harrison [6] determinate an elemental fingerprint based on the clay content of specific paper using NAA. Five paper samples were prepared from pulp with 15% of different clay added to each, then analyzed by NAA. The five paper samples were correctly associated with the clays that were added as fillers. Although successful for this application, NAA is limited by the lack of availability in forensic labs and the need for a nuclear reactor.

Copeland [7] attempted to classify papers from their trace element concentrations, determined using electro thermal atomic absorption spectrometry (ETAAS). Nineteen paper types from seven manufacturers were analyzed for Cd, Cu, Cr, Mn, Sb, Co, Ag, Pb, Mg and Fe content. Moreover, this solid sampling technique can be prone to significant and irreproducible loss of volatile elements, such as Ag, Cd and Pb, during the ashing stage.

Polk et al. [8] used scanning electron dispersive X-ray spectroscopy (SEM - EDS) to determine elemental composition of several writing papers. The most abundant elements detected in the paper samples were Al, Si, S, Ca and Ti. Relative standard deviation (RSD) values for a single sheet and within a box of paper for all these elements, was low (<5% for sheet and <10% for box), which enabled discrimination of sheets from different but identically labeled boxes. However, SEM – EDS has limited sensitivity for elements with atomic numbers larger than Na and relative, rather than absolute, concentrations are used for discrimination.

Inductively coupled plasma mass spectrometry (ICP-MS) provides an alternative technique for the determination of trace element profiles of papers. This technique allows for rapid, quantitative multi-element determination of trace elements, with good sensitivity and precision; it has the potential for a range of sample introduction techniques, suited to both solution and solid sampling (solution nebulization, laser ablation and electro thermal vaporization) [9-10].

Spence et al. [11] considered 17 different paper manufacturers: one ream was selected from each of 16 manufacturers and six reams were obtained from a single manufacturer. Five sheets were selected at random from each ream and a sample was cut from each sheet. Nine elements (Na, Mg, Al, Mn, Sr, Y, Ba, La and Ce) were selected as potential discriminating elements; concentrations of these elements did not vary significantly in sheets from the same ream.

Elizabeth A. McGaw et al. [12] differentiated paper based on significant differences in Ba, Sr, Ce and Nd concentrations. Differences in concentration were assessed statistically using two-way ANOVA and Tukey’s honestly significant differences test.

The objective of this article is to report the results for the ICP-MS analysis of the trace element content of five differently labeled brands of white A4 photocopy paper, with a view to discriminating papers produced by different manufacturers.

2. EXPERIMENTAL

Reagents and materials:

All reagents and solvents were of analytical grade: nitric acid (Merck, suprapur), hydrogen peroxide (30 % AnalR). The paper chosen for analysis was the most commonly used office document paper, i.e., white, A4 (210/ 297 mm), 80 grams per square meter printer/copy paper labeled acid- and chlorine- free. We used five different brands of paper:

Paper 1 – STORAENSO, multilaser;

Paper 2 – XEROX, business;

Paper 3 – UNI COPY, laser copier;

- Paper 4 – NAVIGATOR, universal;
- Paper 5 – SKY COPY, paper.

Apparatus:

Micro-analysis was performed using NexION 300 ICP-MS (Perkin Elmer Co., Beaconsfield, Bucks, UK) with S10 auto sampler. A Meinhard concentric nebulizer attached to a glass cyclonic spray chamber was used for sample introduction.

The spectral data were processed with the Chromera® (Perkin Elmer Co., Beaconsfield, Bucks, UK). A microwave digestion unit (Ethos 1, Milestone, Inc.) was used for the digestion of the samples.

The instrumentation and data acquisition parameters are given in Table 1.

Table 1. ICP - MS operating and data acquisition parameters.

ICP - MS mass spectrometer	
Rf power (W)	1300
Argon flow rates (L/min) Outer Auxiliary Nebulizer	 12,5 0.8 0.81-0.85
Sampler and skimmer cone	Ni
MS resolution	Unit mass
Data acquisition	
Mode	Selected ion recording – peak jumping
Dwell time (ms)	30
Point / spectral peak	1
Sweeps / reading	10 survey 40 main
Number of replicates	5
Autosampler	
Sample read delay (s)	60
Wash time (s)	60

Procedures

Samples in the mass range 140 to 150 mg (approximate area 25 mm x 70 mm) were cut from the four corners and centre of each sheet of paper with plastic scissors. All samples were subsequently handled using plastic tweezers and gloves to prevent any elemental composition using acid washed plastic scissors and handled with acid washed plastic tweezers. Paper samples were digested with 7 mL of HNO_3 and 1 mL of H_2O_2 in a microwave digestion unit, fitted with PTFE vessels and equipped with an internal temperature probe. Four samples and one procedural blank (prepared in the same way but without paper present) were prepared at once using the program for the microwave digestion given in the Table 2.

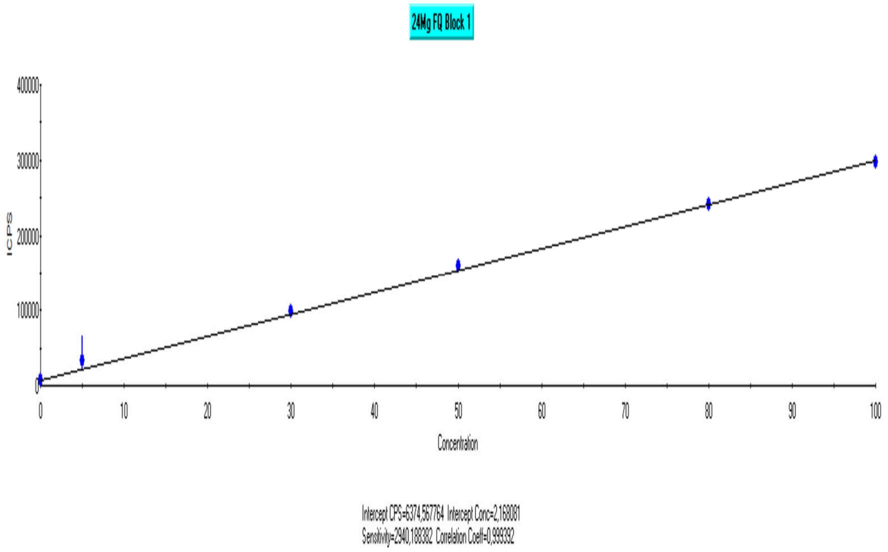
Table 2. Microwave digestion program.

Step	**Power (W)**	**Time (min.)**	**Temp. ^{0}C**
1	1200	15	Room temp - 200
2	1200	15	200

Following digestion, the Teflon vessels were allowed to cool to below 60^{0}C. The sample digest were transferred to 100 mL polyethylene calibrated flask and diluted to 100 mL with ultrapure water. In order to reduce the possibility of carryover between digestions, the vessels were soaked in 4M HNO_3 and then cleaned by reheating in the microwave unit with 4 mL HNO_3 and 4 mL H_2O_2 using the same program. Upon completion of this procedure, the vessels were repeatedly washed with ultra-pure water.

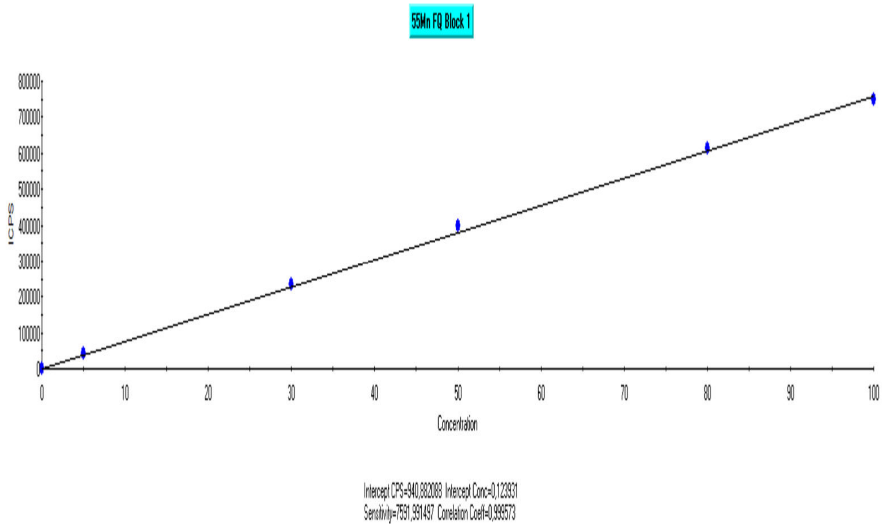
3. RESULTS AND DISCUSSION

Tune conditions were optimized daily using a 10 ppb solution of Li, Be, Co, In, Ba, Ce, Pb, Ti, Tl and U prepared in a 2 % HNO_3 solution. The instrument was calibrated using multi – element external calibration standards prepared in 2 % HNO_3 solution (concentrations range 5 – 100 ppb in each element). Calibration curves for a few elements are shown in Figures 1-4.



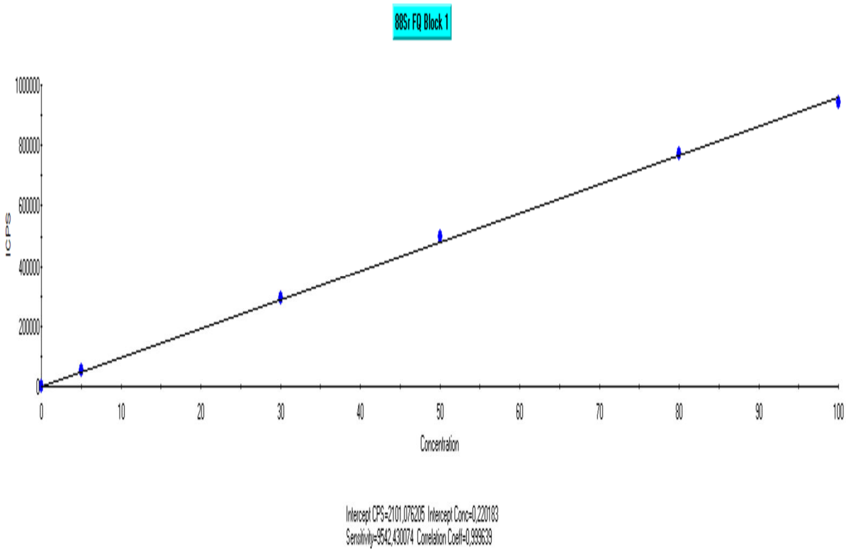
Intercept CPS=6374,567764 Intercept Conc=2,168081
Sensitivity=2940,188382 Correlation Coeff=0,999392

Figure 1. Calibration curve for Mg



Intercept CPS=940,882088 Intercept Conc=0,123931
Sensitivity=7591,991497 Correlation Coeff=0,999573

Figure 2. Calibration curve for Mn.



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Intercept CPS=2101,076205  Intercept Conc=0,220183
Sensitivity=9542,430074  Correlation Coeff=0,999639
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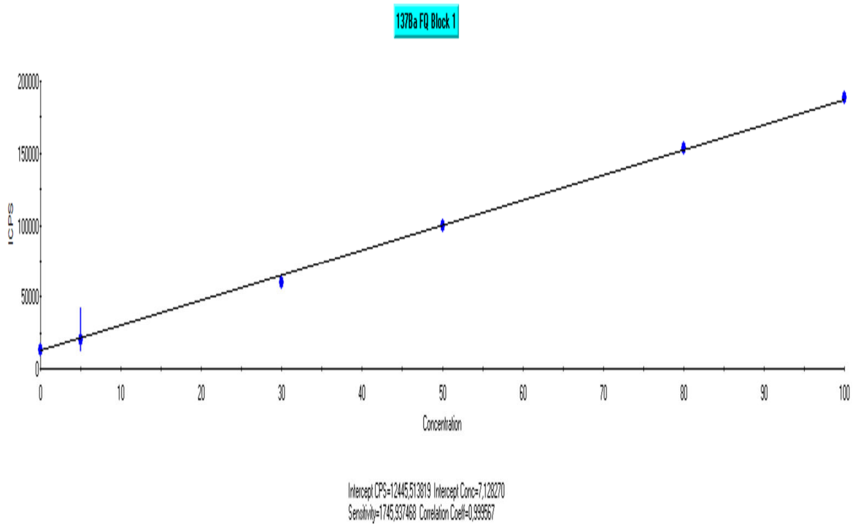
Figure 3. Calibration curve for Sr



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Intercept CPS=12445,513819  Intercept Conc=7,128270
Sensitivity=1745,937468  Correlation Coeff=0,999567
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Figure 4. Calibration curve for Ba

For each of the different brands of paper, five sheets were chosen at random from the ream. The samples were digested and analyzed using the methods described in the previous section. A typical set of results, for one of the manufactured papers are presented in Table 3, while Figure 5 presents a standard spectrum.

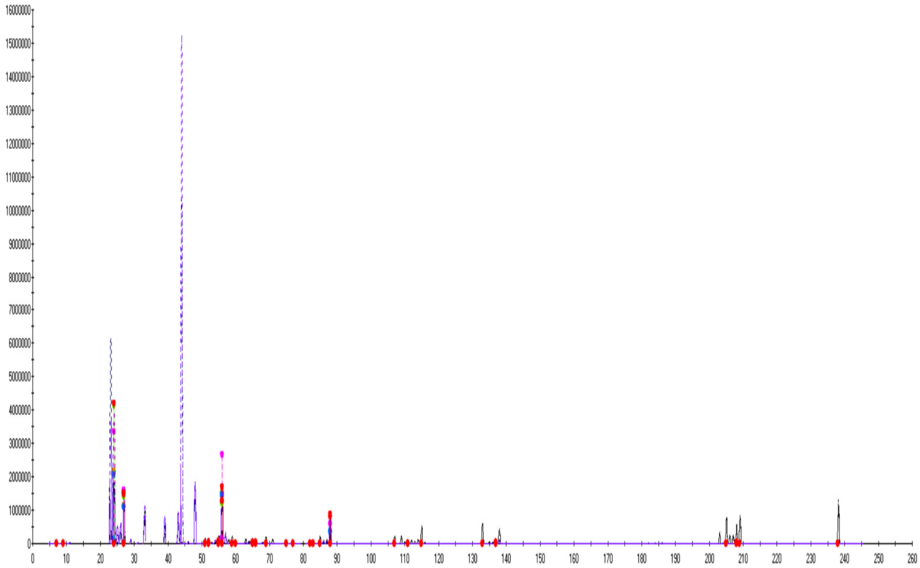

Figure 5. Spectra for paper

Table 3. Limits of detection, typical concentrations and instrumental precision for 8 elements measured in paper.

Element	**LOD (µg/g) (n=10)**	**LOQ (µg/g) (n=10)**	**Concentration in paper (µg/g) (n=5)**	**%RSD**	**Instrumental precision (%RSD) (n=5)**
Mg	1	3	525	1.6	0.6
Al	1	3	183	1.4	1.2
Mn	0.1	0.3	4.3	1.9	1.2
Fe	1	3	135	2.3	1.6
Zn	0.1	0.3	0.93	4.9	2.1
Sr	0.1	0.3	27	1.7	0.6
Ba	0.1	0.3	10	1.1	0.6
Pb	0.01	0.03	0.23	1.5	0.7

The concentrations (µg/g) of the discriminating elements for this paper are shown. The RSD for each elemental concentration (based on five measurements) is shown in the adjacent column. These RSD can be compared with the instrumental precision measured for each element. This precision was determined from five repeat measurements of the one digest solution. These results show that these 8 elements have a reasonably uniform distribution throughout the sampled sheets, with a mean RSD <5%. The limits of detection and quantification are also shown in Table 3. These were determined from the measurement of ten reagent blanks, prepared using the same digestion and dilution procedure as used for the samples. The values shown are paper LODs, which take into account the dilution factor (140 - 150 mg paper to 100 mL of solution).

Although the composition of the digest matrix is not known, for most papers very high count rates were observed for C and Ca. This is not surprising, since the two major components of most modern papers are cellulose (>80%) and $CaCO_3$ filler (5-15%). The presence of these matrix components, at relatively high concentrations could cause spectral interferences from polyatomic ions formed from oxides, carbides and argides of C and Ca. The polyatomic ions listed include oxides and argides of the five most abundant elements found in paper samples i.e., C, Ca, Na, Mg and Al.

The variability in elemental concentration across a single sheet of paper was then assessed. Because only a portion of the sheet would be sampled in a forensic analysis scheme, it is important that a sample is representative of the whole sheet.

RSD values were calculated for each sheet of paper based on the five samples analyzed per sheet (one from each corner and one from center).

If the RSD was greater than 15% the element was eliminate from suite of discriminatory elements. In general the RSD for an elemental concentration within a sheet was 5-10% (Table 4).

Table 4. The results obtained for papers analysis*.

Element	**Concentration in paper (μg / g) (n=5)**	**Average**	**%RSD**
Mg	525 540 570 530 500	533	5.87
Al	183 171 199 205 167	185	9.04
Mn	4.3 4.1 4.6 3.9 4.4	4.26	6.34
Fe	135 145 120 124 104	125.6	10.37
Zn	0.93 0.85 0.95 0.99 0.87	0.92	6.27
Sr	27 23 28 25 24	25.4	8.16
Ba	10 9.2 11 10.8 9	10	9.05
Pb	0.23 0.20 0.26 0.24 0.25	0.24	9.75

*Four corner and center of sheet

Also, in forensic cases where only a small sample is available, it is important the sample analyzed is representative of the whole sheet. Further – more, a single sheet that has been removed from the ream will have the statistically indistinguishable elemental concentrations compared to other sheets in that ream. Also, there did not appear to be any contamination from contact with the paper wrappers on the reams as the top and bottom sheets were sampled and did not show significant elemental differences from a sheet sampled in the middle.

The five different manufactured papers were sampled, digested and analyzed using the analytical protocols previously described.

The large amount of data produced (5 papers, 5 replicates per paper, 8 elements per samples) presents some problems in terms of its visual representation and analysis, if the similarities and differences between papers are to be demonstrated effectively. The process adopted was to first compare the papers, based on a single elemental concentration (Mn), and determine which could be discriminated. For those papers that could not be distinguished using this one element, a second element (Sr) was then used to test the remaining papers. This process can be continued, using all eight elemental concentrations, until all papers are successfully discriminated or the papers are considered indistinguishable (an example of discriminating papers is shown in Table 5).

Table 5. Comparison of elements concentration measured in the analyzed papers.

Element	**Paper 1** (µg / g)	**Paper 2** (µg / g)	**Paper 3** (µg / g)	**Paper 4** (µg / g)	**Paper 5** (µg / g)
Mn	4.3	5.7	6.7	6.63	4.1
Sr	27	38	61	58	29
Al	183	210	226	230	440
Mg	525	721	1019	961	1001
Ba	10	6.5	1.8	2.3	7.2
Fe	135	226	113	101	154
Zn	0.93	5.9	7.38	11.55	2.4
Pb	0.23	0.97	0.70	0.87	0.1

CONCLUSIONS

The results of this study show that trace element concentrations measured using ICP – MS, can be used for discrimination of white photocopy papers. Five different brands of paper could be distinguished using few elemental concentrations. ICP – MS offers an excellent method for sheet to sheet comparison, given its capacity for rapid, precise, multielement analysis at low concentration levels. The method is particularly apt for paper whose major component is wood pulp. Elemental concentrations in wood are higher than in ground water, and derive from root uptake from the soil as well as absorption from resuspended dust and aerosols. The results show that elemental analysis, using ICP-MS, provides an effective and robust technique for the discrimination of document paper.

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