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Trace Element Profiles and Ratios Determined by Instrumental Neutron Activation Analysis for Fine Paper Identification

Instrumental neutron activation analysis (INAA) has been applied to virtually every type of evidentiary material for forensic purposes, including glass, rubber, narcotics, soil, and paper [1-5]. Literature to date on sample identification of fine paper (book or bond-type writing papers) by INAA has not emphasized the value of trace element concentration profiles or elemental ratios. It is to this area of sample identification that this investigation was directed. Some assets of INAA that make it suitable for forensic analysis are (1) the often nondestructive nature of the technique, which is valuable in many legal situations; (2) extremely high sensitivity, allowing small samples of evidentiary material to be used when mutilation is permitted; and (3) the ability to analyze for many elements in a single sample.

The forensic significance of determining if separate pieces of fine papers have the same elemental profiles is often of interest in judicial proceedings as supportive evidence. For example, if all the sheets of paper, except one, that compose a will or contract have the same trace element profiles, such data may be important supportive evidence. Because trace element data obtained by INAA would be useful in such areas of supportive evidence, a two-part study was undertaken.

The first part was directed toward determining if clays, internationally used as the primary pigment filler in paper, varied substantially in their trace element profiles. Such an elemental profile data base must be provided from the filler within the paper since unfilled paper provides a very weak data base because of the low level and small number of trace elements present. For this study twelve different clays used in the paper industry were analyzed for their trace element content.

The main objective of the second part of this study was to ascertain if the resultant trace element profiles and respective elemental ratios of clay-filled papers could serve as a "fingerprint" of that specific piece of paper. If such a fingerprint exists, it could be determined by INAA profiles that one sheet of paper was different from another sheet or from a group of similar sheets. The study involved preparing pieces of paper, each of which was filled with one of the clays analyzed in the first part of the study. These papers were then subjected to INAA to obtain trace element profiles, ratios, and relative distinctiveness of the data.

Analytical Procedure

Two types of samples had to be prepared for analysis: clay and paper. Because the experimental purpose was forensic, it was important that a small sample size be used so as not to sacrifice a significant portion of a limited amount of evidence. In a piece of filled paper, most of the trace elements are due to the small amount of clay filler rather than the bulk, which is fiber. Therefore, a preliminary experiment was undertaken to determine the smallest sample of clay that could be reliably analyzed for its trace element profile.

Five samples of a blended kaolin clay were prepared for analysis, the weights being approximately 10, 25, 50, 100, and 200 mg each. The samples were sealed in precleaned polyethylene bags and encapsulated in polyethylene pneumatic transfer containers ("rabbits") for irradiation. Two irradiations of each sample were made: first, a short one for 10 min in a thermal neutron flux of 1.6×10^{11} n/cm$^2 \cdot$ s, and then a long one of 1 h in a neutron flux of 5×10^{13} n/cm$^2 \cdot$ s. The samples were counted a single time for 15 min following the short irradiation. The samples were allowed to decay radioactively for at least a week before being repackaged for the long irradiation. Three gamma-ray spectra were taken after the long irradiation at decay times of 24 h, 5 days, and 3 weeks.

From the results of this preliminary experiment, it was decided that 25 mg would be a suitable sample size of clay. Twelve different clays (eight kaolin types and four nonkaolin types) were packaged for irradiation as described above. In addition to the clays, unfilled paper samples had to be analyzed to determine background contributions for subsequent filled paper analyses. The unfilled paper samples analyzed were (1) pulp, (2) pulp plus alum, and (3) pulp plus alum plus rosin size. (Alum and rosin size are typical components of fine paper.) A 25- to 35-mm square sample ($\sim$150 mg) of each unfilled paper was cut from handsheets 89 by 178 mm with clean stainless steel scalpel blades. These square pieces of paper were folded into quarters, then sealed in polyethylene bags and encapsulated in "rabbits."

For cataloging the trace element profiles of clay and for analyzing unfilled papers, the two irradiations used were 1 min at a flux of 1×10^{13} n/cm$^2 \cdot$ s, to determine elements producing short-lived isotopes, and 2 h at a flux of 5×10^{13} n/cm$^2 \cdot$ s, to determine elements producing medium- to long-lived isotopes. The same counting scheme as described above was used.

For the final part of the study, analysis of unknown clay-filled papers, the same packaging and analysis procedure was used as for the unfilled papers. In both cases, the paper samples were handsheets prepared basically by Technical Association of the Pulp and Paper Industry (TAPPI) Standard T218 OS-75. Pulp composition was 70% softwood bleached sulfite/30% hardwood bleached sulfite. All the clay-filled sheets included (on bone-dry fiber) 3.0% iron-free alum, 2.5% rosin size, and 15% pigment filler added. Therefore, a 150-mg sample of a filled paper theoretically would contain about 23 mg of pigment. This weight is approximately equal to the 25-mg clay sample size determined to be suitable for analysis in the first experiment. Therefore, with the same irradiation and counting procedure, the pigment analysis and the unknown filled paper analysis should produce statistically comparable results, as they are both based on approximately 25 mg of clay.

For the quantification of trace element concentrations, primary standards made from solutions of reagent-grade chemicals and a National Bureau of Standards (NBS) Standard Reference Material, 1633—Coal Fly Ash, were prepared and irradiated under the same conditions as the samples.

The counting equipment and data reduction procedures used were the same for all sample sets. Two Ge(Li) semiconductor detectors, with 2.1-keV peak resolution for the ^{60}Co 1332-keV gamma-ray peak, each coupled with a 2048-channel analyzer, were used

to acquire the gamma spectra. All data were stored on magnetic tape. Peak integration was completed by using the ALSPIC program with the assistance of the NBS Univac 1108 computer [6].

Results and Discussions

Thermal neutron irradiation of a sample causes nuclear reactions, primarily of the (n,γ) type, on stable isotopes. The radioactive species produced by neutron irradiation observed in this study after the short and long irradiations are listed in Tables 1 and 2. Not all listed radioactive products were observed in all samples.

After it was determined that 25 mg would be a suitable sample size for clay analysis, the twelve clays were analyzed for all trace elements that could be determined instrumentally with the irradiation and counting conditions outlined above. The results of this part of the study amounted to a cataloging of the trace element profiles of the clays for later unknown filled paper analyses.

The following elements were quantitatively determined in some or all of the samples: aluminum, vanadium, manganese, sodium, chlorine, titanium, calcium, magnesium, arsenic, samarium, gallium, lanthanum, tungsten, antimony, ytterbium, lutetium, scandium, thorium, cobalt, chromium, cerium, tantalum, europium, cesium, barium, and iron. Quantification was carried out by using the sample/standard comparator technique. It was felt that presentation of all of the data accumulated would be cumbersome; therefore, in Table 3, data are given for only those elements later found to be useful in the identification of unknowns. Results for elements listed above but not in Table 3 are available.

The maximum expected analytical error per determination was $\pm 20\%$. Some of the lowest concentrations determined for a given element have errors greater than this, but these values were not used in the sample identification process. Occasionally, electronics difficulties caused degradation of the counting system resolution, resulting in an overlap of peaks and possible suspect values. A good example of this is thorium and chromium determinations in the duplicate analyses of Clay 4.

In addition to clays, samples of unfilled papers were analyzed to determine their contributions to background. All the filled papers contained both alum and rosin size. Therefore, in Table 3 duplicate Samples 1 to 3B are the background controls for the unknown filled clay sheets.

It can be seen from the data in Table 3 that there is considerable sample-to-sample

TABLE 1—*Nuclear data for isotopes observed after short irradiation* [7].

Target Nuclide	Natural Abundance, %	Thermal Neutron Cross Section, barns[a]	Product Nuclide	Half-Life	Gamma-Ray Energy Used for Analysis in This Work, keV
^{27}Al	100	0.235	^{28}Al	2.3 min	1779
^{51}V	99.25	4.9	^{52}V	3.8 min	1434
^{50}Ti	5.25	0.14	^{51}Ti	5.8 min	320
^{48}Ca	0.18	1.1	^{49}Ca	8.8 min	3084
^{26}Mg	11.3	0.027	^{27}Mg	9.5 min	1014
^{37}Cl	24.47	0.43	^{38}Cl	37 min	2168
^{55}Mn	100	13.3	^{56}Mn	155 min	1811
^{23}Na	100	0.53	^{24}Na	15 h	1368/2754

[a]1 barn = 1.00×10^{-28} m^2.

TABLE 2—*Nuclear data for isotopes observed after long irradiation* [7].

Target Nuclide	Natural Abundance, %	Thermal Neutron Cross Section, barns[a]	Product Nuclide	Half-Life	Gamma-Ray Energy Used for Analysis in This Work, keV
^{151}Eu	47.8	2 800	^{152m}Eu	9.3 h	963/344
^{41}K	6.8	1.20	^{42}K	12.4 h	1525
^{71}Ga	39.8	5.0	^{72}Ga	14.1 h	834
^{68}Zn	18.6	0.10	^{69}Zn	14.1 h	439
^{23}Na	100	0.53	^{24}Na	15.0 h	1368/2754
^{186}W	28.4	40	^{187}W	23.9 h	686
^{75}As	100	4.5	^{76}As	26.4 h	559
^{81}Br	49.5	0.20	^{82}Br	35 h	776
^{139}La	99.9	8.9	^{140}La	40.2 h	1596
^{152}Sm	26.6	210	^{153}Sm	47 h	103
^{121}Sb	57.3	6.0	^{122}Sb	64 h	564
^{174}Yb	31.8	55.0	^{175}Yb	4.2 days	396
^{176}Lu	2.6	2 000	^{177}Lu	6.7 days	208
^{130}Ba	0.10	8.8	^{131}Ba	12 days	216
^{232}Th	100	7.4	^{233}Th → ^{233}Pa	27 days (^{233}Pa)	312
^{50}Cr	4.3	17	^{51}Cr	28 days	320
^{168}Yb	0.14	11 000	^{169}Yb	32 days	198
^{140}Ce	88.5	0.60	^{141}Ce	32.5 days	146
^{58}Fe	0.31	1.1	^{59}Fe	46 days	1292
^{123}Sb	42.7	3.3	^{124}Sb	60 days	1691
^{84}Sr	0.56	0.80	^{85}Sr	64 days	514
^{159}Tb	100	46.0	^{160}Tb	72 days	qualitative only
^{45}Sc	100	13.0	^{46}Sc	84 days	889
^{181}Ta	100	21.0	^{182}Ta	115 days	1221
^{74}Se	0.87	30.0	^{75}Se	120 days	265
^{64}Zn	48.9	0.46	^{65}Zn	243 days	1115
^{133}Cs	100	28.0	^{134}Cs	2.05 years	797
^{59}Co	100	19.0	^{60}Co	5.26 years	1332
^{151}Eu	47.8	5 900	^{152}Eu	12.7 years	1408

[a] 1 barn = 1.00×10^{-28} m^2.

TABLE 3—*Trace element concentrations,*

| | | Pulp + Alum | Pulp + Alum + Rosin | | | | Sample | Clays |
	Pulp 1	2	3A	3B	4A	4B	5	6
Element								
Al	21	2600	3400	ND	2.2×10^5	1.6×10^5	1.6×10^5	1.6×10^5
Sc	ND	0.0096	0.0087	0.011	*18*	*17*	*3.8*	*5.0*
Th	ND	ND	ND	0.0085	*35*	*15*	*15*	*10*
Co	ND	0.037	0.052	0.038	*5.3*	*5.1*	*1.2*	*0.48*
Cr	ND	ND	ND	0.25	*10*	*109*	*9.2*	*32*
Ce	0.47	0.52	0.17	0.052	*108*	*116*	*52*	*52*
Sm	0.0064	0.014	0.011	ND	*13*	*12*	*8.7*	*4.5*
Eu	ND	ND	0.0026	0.0071	*1.9*	*1.9*	*1.1*	*1.3*
La	0.15	0.19	0.096	0.076	*66*	*59*	*20*	*28*

[a] ND = not determined.
[b] *Italicized* values are greater than the minimum concentration in clay, which is detectable in filled papers.
[c] $C_{z,min}$ = the minimum concentration in clay which would be detectable in a filled paper.

variation in the concentrations of most trace elements. To determine which of these concentration values are sufficiently above the background from the unfilled paper, calculations were carried out.

The following assumptions were made to answer the question, "What is the minimum concentration of an element in a clay ($C_{z,min}$) which would be detectable in a filled paper as a substantial increase over the background concentration of that element, in other words, the concentration in the unfilled paper?"

1. Assume an 8% loading of clay on a filled paper. (Although 15% by weight is added, substantially less than this adheres.)

2. Assume 2.5 is a minimum factor detectable as an increase above background (unfilled paper). (This factor is high to account for large concentration variations observed in the unfilled paper.)

3. Assume the highest elemental concentration detected in any of the unfilled papers (Samples 1 through 3B, Table 3) is the background value and is given as $C_{b,z,max}$.

By using these assumptions, a relationship for computing $C_{z,min}$, where z is the element of interest, was derived. If an 8% clay loading is assumed, then 92% of the total filled paper is background, as defined.

$$0.92C_{b,z,max} + 0.08C_{z,min} = 2.5C_{b,z,max}$$

$$C_{z,min} = (2.5C_{b,z,max} - 0.92C_{b,z,max})/0.08$$

$$C_{z,min} \simeq 20C_{b,z,max}$$

Example: The highest concentration for scandium detected in the unfilled papers is 0.011 μg/g. Therefore, the minimum concentration of scandium in clay that would be detectable above background in the filled papers is 20 × 0.011 μg/g, or 0.22 μg/g.

The last column in Table 3 lists this "minimum detectable limit" for all elements. All concentrations for an element which exceed the minimum are indicated by italics.

The final portion of the study was the analysis of unknown clay-filled papers. Five sheets were prepared by using one of the previously analyzed clays as a filler in each. They were submitted as unknowns for INAA and the results appear in Table 4. As in Table 3, only a partial listing of the elements determined appears.

in μg/g, of unfilled papers and clays.[a,b]

					Numbers				

7	8	9	10	11	12	13	14	15	$C_{z,min}$[c]
1.6×10^5	1.5×10^5	1.9×10^5	1.7×10^5	1.6×10^5	1.3×10^5	0.90×10^5	1.3×10^5	0.10×10^5	0.07×10^5
11	5.3	7.8	2.8	2.1	6.5	8.9	5.8	0.049	0.2
15	1.4	1.9	3.4	17	14	17	10	4.4	0.2
<0.16	4.4	12	4.1	1.3	<0.3	<0.08	<0.3	0.086	1.0
5.3	4.7	8.1	4.6	4.0	6.5	6.3	16	7.6	5
27	71	75	130	60	36	94	72	30	10
2.2	7.6	7.2	14	4.1	2.1	4.0	12	4.6	0.28
0.37	1.7	1.7	3.2	0.73	0.25	0.67	0.39	0.089	0.14
20	24	25	152	47	26	55	37	17	3.8

TABLE 4—*Trace element profiles of unknown filled papers (concentration in μg/g).*

Sample	A	B	C	D	E
Identification by analysis[a]	6	4	10	7	ND[b]
Known identification[a]	6	4	10	7	unfilled paper
Element					
Al	1.2×10^4	1.2×10^4	1.2×10^4	0.71×10^4	0.33×10^4
Sc	0.382	1.30	0.180	0.660	0.0069
Th	0.64	2.2	0.16	0.85	0.01
Co	0.075	0.39	0.17	0.044	0.027
Cr	2.6	0.74	0.61	0.92	0.18
Ce	3.6	8.9	6.4	1.9	<0.07
Sm	0.24	0.64	0.85	0.10	0.0076
Eu	0.062	0.14	0.21	0.018	<0.002
La	1.6	2.5	9.2	0.10	0.083
Qualitative	. . .	. . .	Tb	. . .	. . .

[a] Identification refers to sample numbers in Table 3.
[b] ND = not determinable because the percentage of clay in paper is too low.

Since it could not be assumed in a real situation that the amounts of pigment retained in various sheets were the same, the identification of unknown papers (Table 4) filled with clays (Table 3) were evaluated by three criteria independent of load level. First, those trace elements with relatively high concentrations in a given unknown were marked as key identifying elements for that unknown. Second, the ratios of the concentrations of these key elements and other well-determined elements were computed for the unknowns and possible clay knowns. Third, any qualitative data such as unique elements were noted. The following discussion will show how these three factors were used in concluding unknown identification.

Unknown Sample C was the easiest to identify because of the qualitative information that terbium was observed in the sample. Terbium had been observed in only one clay sample (Sample 10). Since supporting data were available, they were used to confirm the identification. Unknown C has the highest concentrations of samarium and europium of any of the unknown papers. One would expect that the clay used as a filler in Unknown C would also have relatively high samarium and europium concentrations. Clays 10 and 4 are the two samples from Table 3 that best fit this criterion. By using the technique of elemental ratios, Unknown C is compared to Clays 10 and 4 in Table 5. The elemental ratios for Unknown C compare better with those for Clay 10 than those for Clay 4. The correct identification of Unknown C having Clay 10 as a filler was made.

Unknown Sample B contained many elements with high concentrations relative to the other unknown filled papers. Scandium, thorium, cobalt, and cerium all appeared in higher concentrations in Unknown B than any other unknown. Clay 4 is the only clay with high values for all four elements. Other clays with high values for three of the four elements would be Clays 9 and 13. Some elemental ratios are compared for the four samples in Table 6. Of the three clays, Samples 4, 9, and 13, the elemental ratios for Clay 4

TABLE 5—*Comparison of Unknown C with Clays 10 and 4.*

Ratio	Paper Unknown C	Clay 10	Clay 4
Ce/Sm	7.5	9.3	9.0
Eu/Sm	0.25	0.23	0.15
La/Sm	11	11	5.0

TABLE 6—*Comparison of elemental ratios for four samples.*

Ratio	Paper Unknown B	Clay 4	Clay 9	Clay 13
Th/Sc	1.7	(0.9–1.9)[a]	0.24	1.9
Co/Sc	0.30	0.30	1.5	<0.009
Ce/Sc	6.8	6.4	9.6	11
Sm/Sc	0.49	0.71	0.92	0.45
Eu/Sc	0.11	0.11	0.22	0.075
La/Sc	1.9	3.6	3.2	6.2

[a]The duplicate analyses of clay (4A-4B) show very different values for thorium and chromium because of the poor resolution of the adjacent peaks, 312-keV ^{233}Pa (used to determine ^{233}Th) and 320-keV ^{51}Cr. In one series of counts, the detector-analyzer system was not operating at optimum resolution, degraded to greater than 3 keV, resulting in overlapping of the 312-keV and 320-keV peaks. The program used was unable to resolve overlapping peaks properly. The true values for thorium and chromium probably lie somewhere between the two values given for each in Table 3. This problem would not arise when equipment operating at optimum resolution is used.

compare best with Unknown B. None of the three clays compared well with the unknown for the lanthanum/scandium ratio. Clay 13 has a closer samarium/scandium ratio to Unknown B than Clay 4. However, the analytical error for each value is about 20%, making the error on the ratio of the two numbers 28%. Therefore, the confidence intervals for the samarium/scandium ratios for Unknown B and Clay 4 do overlap.

Since Clay 4 is the only clay with high values for scandium, thorium, cobalt, and cerium, and it has a better elemental ratio comparison to Unknown B than the two next best choices, it was correctly concluded that Unknown B contained Clay 4 as a filler.

Similar data interpretations were successfully made for Unknowns C and D with data from Tables 3 and 4.

The final unknown, E, had extremely low concentrations for all elements. The first step was to determine if any of the elements in Unknown E had concentrations above the background of the unfilled paper, $C_{b,z,\max}$. This comparison is given in Table 7. For all cases, the concentration in Unknown E is less than $C_{b,z,\max}$ except for thorium, in which case they are approximately equal. The conclusion was that either Unknown E is an unfilled paper or the percentage of loading of clay on paper was much less in Unknown E than in the other unknowns. The true identification was that Unknown E is an unfilled paper.

In the relationship for determining minimum detectable limits, an 8% loading of clay on paper was assumed. From the identified unknowns, this assumption can be verified. In each filled paper, an element was chosen whose concentration was sufficiently high

TABLE 7—*Comparison of Unknown E to highest determined value in background samples,* $C_{b,z,max}$ *(concentration in $\mu g/g$).*

Element	Unknown E	$C_{b,z,\max}$
Al	3.3×10^3	3.4×10^3
Sc	0.0069	0.011
Th	0.010	0.0085
Co	0.027	0.052
Cr	0.18	0.25
Ce	0.070	0.52
Sm	0.0076	0.014
Eu	0.002	0.0071
La	0.083	0.19

to make the contribution from the unfilled paper negligible. Then the following equation was used to determine the percentage of clay in paper:

$$\frac{(\text{grams element } x)/(\text{grams paper})}{(\text{grams element } X)/(\text{grams clay})} \times 100\% = (\text{grams clay})/(\text{grams paper}), \%$$

$$= \% \text{ clay in paper}$$

Table 8 lists the elements used to determine the approximate concentrations of clay in each of the filled papers. These results validate the assumption made earlier.

TABLE 8—*Experimentally determined clay loading of unknown papers.*

Unknown	Element Used	Clay in Paper, %
A	Cr	8
B	Sc	7
C	Eu	7
D	Sc	6

Conclusions

It was determined that clays vary substantially in their trace element profiles and provide a data base for the identification of unknown filled papers.

Successful identification of unknown clay-filled sheets indicates that analysis of fine papers by INAA, utilizing trace element profiles and concentration ratios, is a viable instrumental technique in determining "fingerprint" profiles of such sheets. Therefore, such an INAA technique should be useful for acquiring supportive evidence for forensic purposes in determining similarities or differences in fine papers.

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