

TECHNICAL NOTE

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Characterization of Undigested Particulate Material Following Microwave Digestion of Recycled Document Papers

ABSTRACT: Recycled document paper was microwave digested in a solution of HNO₃ and H₂O₂ prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS) to determine the trace elemental concentrations within the paper. Undigested particulate material was observed and subsequently characterized as a mixture of kaolin (clay) and TiO₂ by Fourier transform infrared spectroscopy and X-ray diffraction spectroscopy. The effect of the particulate material on the elemental concentrations was then investigated. Paper samples were completely digested in hydrofluoric acid (HF) and element concentrations determined in the HF and HNO₃/H₂O digests were statistically compared using Student's *t*-test (95% confidence limit). Statistical differences in element concentrations between the two digests were observed for only four elements and there was no evidence of element adsorption by the particulate material. Hence, the HNO₃/H₂O₂ digestion proved sufficient to digest paper for ICP-MS analysis, eliminating the need to use the hazardous and corrosive HF matrix.

KEYWORDS: forensic science, inductively coupled plasma mass spectrometry, microwave digestion, trace elements, document paper, undigested particulate material

During an investigation into the potential for associating and discriminating 100% recycled document (multipurpose copy) paper based on trace element concentrations, white document papers from two different vendors were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (1). Prior to analysis, paper samples were microwave digested in a HNO₃/H₂O₂ matrix. However, following the digestion procedure, white particulate material remained, settling to the bottom of the digestion vessels. During paper manufacture, several inorganic additives (e.g., clay, titanium dioxide, mica, and talc) are added to change the physical properties such as the brightness or texture of the paper. These inorganic additives are likely the portion of the paper sample that did not break down during the standard digestion procedure. Hence, a chemical characterization was undertaken to determine the identity of the white particulate material.

Based on known additives in paper, it was suspected that the particulate matter may include kaolin, titanium dioxide (TiO₂), and silicon dioxide (SiO₂). About one-half of the kaolin mined today is used in paper-making processes (2). Kaolin is an aluminosilicate clay material (Al₂Si₂O₅(OH)₄) that is commonly used as a filler material for paper to give it color, opacity, and good printing quality (3). TiO₂ is an inorganic material that is commonly used as a white pigment in a wide variety of materials such as paint, cosmetics, and toothpaste. This pigment is also commonly added to paper to enhance the whiteness (3). SiO₂ is a filler material used in papers. Hence, kaolin, TiO₂, and SiO₂ are likely to be found in

paper samples but are not expected to be fully digested in a matrix of HNO₃ and H₂O₂.

The undigested particulate matter was chemically characterized using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) spectroscopy. The effect of the white particulate on the element concentrations determined in the paper samples was then assessed by comparing the elemental concentrations in the partial digest obtained using a HNO₃/H₂O₂ matrix with concentrations in a complete digest obtained by adding hydrofluoric acid (HF) to the matrix. Finally, the potential for the particulate to adsorb elements from the HNO₃/H₂O₂ matrix digest was investigated to assess the effect of the particulate presence on the element concentrations determined in the paper samples.

Materials and Methods

Five reams of white document paper made from 100% post-consumer waste were obtained from two different vendors (Vendors A and B), that were chosen due to their ready availability in the Lansing, MI area. All reams were 20 lb in weight and were labeled as acid-free and chlorine-free.

The undigested particulate matter was observed in digestions of paper samples obtained from both Vendors A and B. The particulates analyzed for this work are all from paper samples from Vendor A, as it was assumed that the nature of this particulate matter was similar in both. Because the amount of particulate remaining in each digestion was very small, samples from several sheets of paper from two reams were combined to obtain a sufficiently large sample of material for characterization.

Microwave Digestion of Paper Samples

Paper samples were digested in a microwave digestion unit (Ethos EX; Milestone, Inc., Shelton, CT) equipped with an internal

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temperature probe. The paper samples, *c.* 23 mm × 18 mm, corresponding to a mass of 0.029 g ± 0.001 g, were placed individually into quartz vessels (Milestone, Inc.) that had previously been acid-washed. To the quartz vessel, 1.5 mL of Optima grade nitric acid (69%; Fisher Chemicals, Pittsburg, PA) and 0.75 mL of hydrogen peroxide (30%; J.T. Baker, Phillipsburg, NJ) were added. The quartz vessel was then capped and placed into an outer Teflon® vessel (Milestone, Inc.) to which 11 mL of ultra-high purity water (Barnstead, Dubuque, IA or Millipore, Jaffrey, NH) and 1 mL of hydrogen peroxide (J.T. Baker) were added. The Teflon® vessel was then sealed with a Teflon® cap. Five samples plus one procedural blank (prepared in the same way but without paper present) were digested at once using the following digestion program: heat from room temperature to 210°C over a 15 min period, and then hold at 210°C for 10 min. The system automatically adjusted applied microwave power (wattage) to obtain and maintain the desired temperature.

Following digestion, the Teflon® vessels were allowed to cool to below 100°C. The quartz vessels were removed from the Teflon® vessels and allowed to cool to room temperature with the quartz tops in place to prevent evaporative changes in volume. The paper in the quartz vessel was partially digested; the resulting solution was clear with a small amount of white particulate matter. The particulate matter was collected from the bottom of 20 vessels from the standard HNO₃/H₂O₂ digestion, washed with ultra-pure water, and allowed to air dry on filter paper overnight. The collected particulates were used for spectroscopic analysis, aiming to characterize the particulates.

FTIR Spectroscopy of Undigested Particulate Material

A potassium bromide (KBr, IR Spectral Grade; Spectrum Chemical, Gardena, CA) pellet was made of the dried particulates using approximately a 1:100 dilution of the sample particles with KBr. The mixture was pressed (Carver Laboratory Press, Fisher Scientific, Pittsburg, PA) and the resulting pellet analyzed by FTIR, using a Mattson Galaxy Series 3000 FTIR spectrometer (Mattson Instruments, Madison, WI) in the transmittance mode. The sample was scanned from 350 to 4000 cm⁻¹ with the instrument resolution set at 4 cm⁻¹. The spectrum was recorded using WinFirst software (Mattson Instruments) and compared with spectra for kaolin (clay), TiO₂, and SiO₂ obtained from the literature (4–6).

XRD Spectroscopy of Undigested Particulate Material

A sufficient volume of particles to cover approximately 1 cm² was mounted onto a glass slide using double sided tape. The XRD spectrum was collected using a Rigaku Rotaflex RU 200B XRD instrument (Rigaku Corporation, Tokyo, Japan). The X-ray beam was generated by accelerating electrons (45 kV, 100 mA) at a rotating Cu-anode. The Cu K1- α line was used and the instrument was run in the 2 θ / θ mode. Scans were performed at a speed of 1°/min.

HF Digestion of Paper Samples

HF was added to the digestion matrix to obtain a complete dissolution of the paper components. Because HF can dissolve glass and quartz vessels, only the Teflon® vessel was used without the quartz insert. The Teflon® vessel is much larger than the quartz and requires a minimum solution volume of 10 mL. To make sure that approximately the same elemental concentration was obtained

using this procedure, compared with that described in the accompanying manuscript (1), a paper sample, about four times larger (approximately 0.12 g) was necessary.

A paper sample was added to each Teflon® vessel followed by 6 mL of Optima grade HNO₃ (69%; Fisher Chemicals), 3 mL of H₂O₂ (30%; J.T. Baker), and 1 mL of HF (48%; Columbus Chemical Industries, Columbus, WI). The vessels were then sealed with the Teflon® tops and digested using the same digestion program as described previously. Following digestion, a clear solution with no particulate matter remained in the Teflon® vessels.

The HF was removed from the sample solutions before ICP-MS analysis by evaporating to dryness. Following evaporation, 10 mL of 2% nitric acid (Optima grade; Fisher Chemicals) was added to reconstitute the sample, which was subsequently analyzed by ICP-MS.

Results

FTIR Spectroscopy of Undigested Particulate Material

A KBr pellet was prepared from the particulate material and an IR spectrum was collected as shown in Fig. 1. The spectrum was compared with reference IR spectra of kaolin (clay), TiO₂, and silicon dioxide (SiO₂) obtained from the literature (4–6). These components are expected to be present in paper but are not expected to be digested in the HNO₃/H₂O₂ matrix.

The absorption frequencies from the particulate sample and the reference materials are listed in Table 1. From the table, it is clear that the particulate sample is a combination of both kaolin and TiO₂. There is no clear evidence for the presence of SiO₂, although there is one peak present that cannot be attributed to kaolin or TiO₂ at 1636 cm⁻¹. However, this is not close to the 1620 cm⁻¹ peak expected from SiO₂. Three other peaks would be expected if SiO₂ was present: 3425, 1100, and 475 cm⁻¹. While there are peaks in the spectrum that are close to these values it is more likely that these peaks are due to either kaolin or TiO₂ because there are additional peaks that support the presence of these two components. On assessing the spectrum of the particulate sample, the strongest peaks are from the kaolin while the TiO₂ peaks are not as strong, suggesting that the particulate sample contains a larger proportion of kaolin.

There is a strong peak in the sample IR spectrum at 1384 cm⁻¹ that could possibly be from the TiO₂ (expected at 1375 cm⁻¹) but the intensity of this peak is much larger than the other peaks

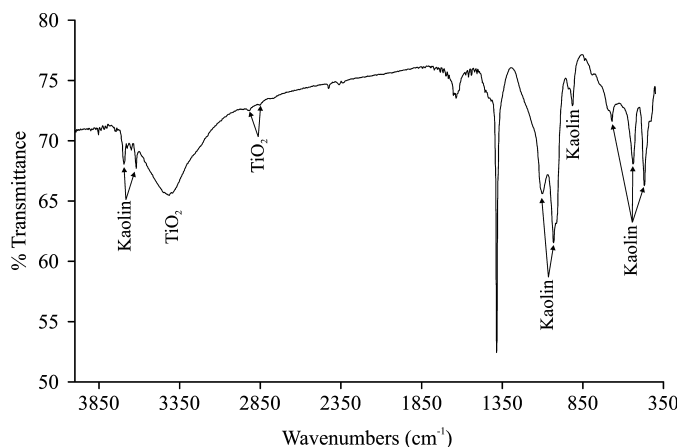


FIG. 1—FTIR spectrum of undigested particulate material from paper digestion in HNO₃/H₂O₂ matrix.

TABLE 1—Comparison of absorption frequencies in IR spectra of particulates and reference materials.

IR Absorption Frequencies (cm ⁻¹)			
Undigested Particulate	Kaolin (clay)	Titanium Dioxide	Silicon Dioxide
3695	3690	—	—
3619	3620	—	—
3414	—	3400	3425
2919	—	2915	—
2850	—	2840	—
1636	—	—	1620
—	—	1455	—
1384	—	1375	—
1101	1100	—	1100
1031	1030	—	—
—	1005	—	—
913	910	800–400 (broad peak)	—
669	695	—	—
538	535	—	—
468	460	—	475

— Indicates not present.

Absorption frequency of kaolin, titanium dioxide, and silicon dioxide is from references (4–6), respectively.

attributed to TiO₂ (5). However, this peak is in the range of a normal vibration of an inorganic nitrite (7). As the paper samples were digested in HNO₃ it is possible that an insoluble inorganic nitrite species was formed that absorbs at 1384 cm⁻¹.

XRD Spectroscopy of Undigested Particulate Material

An XRD spectrum was collected for residual particulates from the HNO₃/H₂O₂ digestions (Fig. 2). All of the peaks visible in Fig. 2 are consistent with TiO₂ (8).

There is one small peak correlating to a lattice spacing of 7.187 Å that can be seen in the expanded spectrum (Fig. 3). From the IR spectrum, it was apparent that some component of the undigested particulate material is kaolin. The kaolinite group of clays has a lattice spacing of 7.15–7.20 Å (9). The peak in the sample spectrum lies within this range at 7.187 Å and therefore it was determined the kaolin was the likely source of this peak. Because clay materials are not perfectly crystalline, relatively weak signals are observed in XRD (9). This is apparent in this case based on the

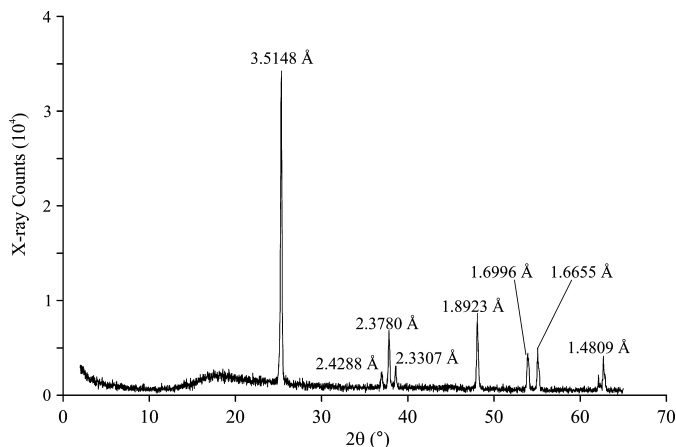


FIG. 2—XRD spectrum of undigested particulate material from paper digestion in HNO₃/H₂O₂ matrix.

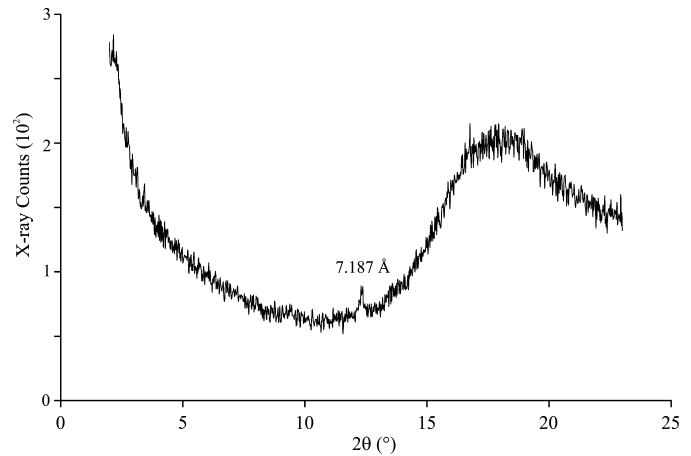


FIG. 3—Kaolin peak in the XRD spectrum of undigested particulate material from paper digestion in HNO₃/H₂O₂ matrix.

relative intensity of the kaolin peak to the TiO₂ peaks, which is in contrast to the stronger kaolin signals observed in the FTIR spectrum. No evidence of SiO₂ was found in the XRD spectrum.

Approximate Concentration of Al and Ti in Particulate Material

To determine the element concentrations attributable to TiO₂ and kaolin in the particulate material, paper samples were completely digested with the addition of HF to the digestion matrix. Digests were then analyzed by ICP-MS, following the same procedure as described in the accompanying manuscript (1). Digests were analyzed in the selected ion recording mode, specifically for ²⁷Al, ²⁸Si, and ⁴⁸Ti. Concentrations of these three elements in the HF digest (no particulates present) were compared with the corresponding concentrations in the HNO₃/H₂O₂ digest (particulate material present), as shown in Table 2. As the same sheet of paper was used for both digestions, it was assumed that any differences in the concentrations of these elements were due to the material in the particulate matter.

The standard deviation in the Ti concentration in the HNO₃/H₂O₂ digestion mixture was very high because two of the samples had low Ti concentrations (7 and 9 µg/g) and two had high Ti concentrations (21 and 69 µg/g). As only these four HNO₃/H₂O₂ digestions were analyzed for Ti it is unclear if the Ti concentration is so variable through all the samples. However, Ti was not an element that was chosen for statistical comparison between vendors (1). Even though the standard deviation is high, the concentration in the complete digest is clearly higher than in the HNO₃/H₂O₂ digest and, for the purpose of this investigation, can still give an approximate estimation of the Ti contribution in the particulates.

TABLE 2—Average concentrations of ²⁷Al, ²⁸Si, and ⁴⁸Ti in paper digested in HNO₃/H₂O₂ matrix compared with HF matrix.

Digestion Matrix	Average Concentration (µg/g paper)		
	Al	Si	Ti
HNO ₃ /H ₂ O ₂ (n = 4)	380 ± 40	800 ± 100	50 ± 50
HF (n = 3)	1020 ± 40	ND	179 ± 3

ND, not detected; HF, hydrofluoric acid.

Differences in element concentrations by each digestion procedure were observed. The concentrations of Al and Ti were approximately three times higher in the HF digest, as expected, however the Si was no longer detectable in the HF digest solution. An HF digest cannot be used to quantify Si because during the digestion, the Si and F will form a volatile complex SiF_4 (10–12). The boiling point of this compound is -86°C , hence the Si is lost from the digestion solution prior to quantification (13).

Assuming the additional Al present in the HF digest is from kaolin the approximate concentration is $3100 \mu\text{g}$ kaolin/g paper. A similar calculation for TiO_2 yields a concentration of *c.* $220 \mu\text{g}$ TiO_2 /g paper. Based on these approximate calculations, kaolin is the major component of the particulate material, confirming results obtained based on the FTIR spectrum.

Comparison of Element Concentration in Paper Digests Using $\text{HNO}_3/\text{H}_2\text{O}_2$ and HF as Digestion Matrices

To determine if complete dissolution of the particulate matter had any significant effects on the element concentrations being determined in the paper samples, a comparison was made between the two digestion methods. Four paper samples were digested using $\text{HNO}_3/\text{H}_2\text{O}_2$ and three were digested using HF; all samples were again from the same sheet of paper. Digests were then analyzed by ICP-MS and elemental concentrations were determined for ^{23}Mg , ^{27}Al , ^{55}Mn , ^{56}Fe , ^{64}Zn , ^{88}Sr , ^{89}Y , ^{138}Ba , ^{140}Ce , ^{146}Nd , and ^{208}Pb , following procedures described in reference (1). Concentrations of corresponding elements using each digestion procedure were statistically compared using Student's *t*-test with a 95% confidence limit, as shown in Table 3.

The concentrations of Mg, Al, Fe, and Pb varied significantly between the two digestion procedures. The increase in concentration of Al was expected, as it was determined that the major proportion of the particulate sample consisted of an aluminosilicate clay. Other sheet silicate minerals are known to contain Mg (e.g., serpentine [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$]) and Fe (e.g., mica [$\text{K}(\text{Mg},\text{Fe})_3(\text{Al}-\text{Si}_3\text{O}_{10})(\text{OH})_2$]) and could be minor components of the clay as well (9). The increase in Pb concentration in the HF digest is significant but Pb is not a major component in any of the expected filler materials. There is heterogeneity of Pb across a single sheet of paper which is why it was eliminated for statistical comparisons between the two vendors as described in reference (1). It is possible that the increased Pb concentration is simply a manifestation of the

heterogeneity and a small sample set or that it was a contaminant present in the HF used.

Elemental Adsorption by Undigested Particulates

Another concern of the incomplete digestion was that the undigested particulates in the paper digest could potentially adsorb elements from the liquid portion of the digest. The particulate matter was determined to contain clay materials that adsorb cations. If this occurs the adsorption of elements by particulates will cause variation in the elemental concentrations determined in the digests and affect statistical comparisons of these concentrations.

To determine if the elemental concentrations in the paper digests varied with time (decrease due to adsorption by the particulates), a single sheet of paper was digested in $\text{HNO}_3/\text{H}_2\text{O}_2$ using the previously described digestion procedure (1). The digest was allowed to remain in contact with the particulates for up to 180 min before decanting the solution for ICP-MS analysis. Because the digestions occur at an elevated temperature in a sealed vessel, the minimum contact time was 20 min to allow the solution to cool below the boiling point before opening the vessel. The subsequent elemental concentrations determined by ICP-MS are shown in Table 4 throughout the 180 min interval.

Element concentrations do not significantly change over the time period investigated: there is no pattern of decreasing or increasing concentration with time. It seems that by the first time point (20 min) the particulate matter has reached equilibrium with the elements in the solution and no further changes are observed. Hence, over the time period under investigation, the presence of undigested particulate matter does not change elemental concentration in the digest solution. There is a difference in elemental concentrations between the $\text{HNO}_3/\text{H}_2\text{O}_2$ digest and the complete (HF) digest; even though some of these changes were expected based on the nature of the particulate, it cannot be said that the particulates do not adsorb material from the digest solution. It is possible that if the amount of kaolin present were changed it could adsorb more of the elements present in the digest solution. However, this technique is being used as a comparison between the samples; a difference in the amount of kaolin present that may affect the elemental concentrations would also constitute a difference between the paper samples. Therefore, although the $\text{HNO}_3/\text{H}_2\text{O}_2$ matrix does not fully digest the paper sample, subsequent element concentrations are appropriate for comparisons, allowing the use of this matrix rather than the more corrosive HF matrix.

TABLE 3—Average element concentrations in paper digested in $\text{HNO}_3/\text{H}_2\text{O}_2$ matrix compared with HF matrix.

Element	Average Concentration ($\mu\text{g}/\text{g}$ paper)		Significant Difference at 95% Confidence Interval?
	$\text{HNO}_3/\text{H}_2\text{O}_2$ Digestion	HF Digestion	
Mg	1200 ± 100	1460 ± 60	Yes
Al	390 ± 40	1200 ± 300	Yes
Mn	4.7 ± 0.4	6.0 ± 0.1	No
Fe	100 ± 10	129 ± 3	Yes
Zn	12 ± 2	15 ± 5	No
Sr	38 ± 3	43 ± 1	No
Y	0.14 ± 0.02	0.16 ± 0.02	No
Ba	12 ± 1	13.9 ± 0.6	No
Ce	0.34 ± 0.01	0.7 ± 0.2	No
Nd	0.19 ± 0.01	0.22 ± 0.03	No
Pb	0.11 ± 0.01	1.21 ± 0.03	Yes

HF, hydrofluoric acid.

TABLE 4—Elemental concentration of paper samples digested in $\text{HNO}_3/\text{H}_2\text{O}_2$ and allowed to equilibrate in the presence of the particulates for various time intervals.

Element Concentration ($\mu\text{g}/\text{g}$ paper)	Equilibration Time (min)			
	20	60	120	180
^{23}Mg	791	961	800	848
^{27}Al	431	328	370	373
^{55}Mn	3.84	4.12	3.94	4.18
^{56}Fe	70.1	74.3	75.2	77.9
^{63}Zn	8.00	4.12	9.31	5.07
^{88}Sr	63.0	69.6	63.6	67.2
^{89}Y	0.094	0.094	0.148	0.099
^{138}Ba	1.99	2.18	2.20	2.12
^{140}Ce	0.244	0.263	0.259	0.258
^{146}Nd	0.131	0.132	0.129	0.139
^{208}Pb	0.656	0.752	0.721	0.674

Discussion

With a matrix of only HNO_3 and H_2O_2 , complete digestion of document paper samples was not possible. The undigested particulate material was characterized as a mixture of kaolin (clay) and TiO_2 by FTIR and XRD. The presence of this particulate matter does not appear to have a significant effect on several element concentrations (Mn, Zn, Sr, Y, Ba, Ce, and Nd) determined in the paper digest, as determined by comparing the $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion (particulates present) with an HF digestion (no particulates present). The clear digest solution reaches equilibrium elemental concentrations of Al, Mg, and Pb within the time of the normal procedure, making these concentrations suitable for comparisons as well. HF is a very corrosive acid; it is hazardous to work with, requires a larger paper sample, and an additional evaporation step prior to ICP-MS analysis. As the elemental concentrations determined using the $\text{HNO}_3/\text{H}_2\text{O}_2$ digest are suitable for comparison, this matrix was deemed sufficient for microwave digestion of paper samples.

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