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DETERMINATION OF TRACE ELEMENTAL CONCENTRATIONS IN DOCUMENT PAPERS FOR FORENSIC COMPARISON USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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DETERMINATION OF TRACE ELEMENTAL CONCENTRATIONS IN DOCUMENT PAPERS FOR FORENSIC COMPARISON USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

By

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ABSTRACT

DETERMINATION OF TRACE ELEMENTAL CONCENTRATIONS IN DOCUMENT PAPERS FOR FORENSIC COMPARISON USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

By

Elizabeth Ann McGaw

Traditional document paper analysis involves examining mostly physical characteristics of the paper: weight, size, color, opacity, brightness, and watermarks. While these are useful characteristics they are usually uniform for a specific brand and type of paper because these are carefully controlled by the manufacturer. Trace elemental concentrations are not specifically controlled and can vary between batches of the same brand and type of paper making this type of analysis more selective.

In this work microwave digestion was used to dissolve the paper samples prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS) This technique was successfully applied to paper samples from two vendors (New Leaf Paper® and Staples®). Five reams from each vendor were sampled and it was determined that the elemental concentration (Mg, Al, Mn, Fe, Sr, Y, Ba, Ce and Nd) was consistent across single sheets as well as throughout a single ream of paper. Statistically significant differences were observed between reams and between vendors. The most useful elements for discrimination were Al and Ba for reams of New Leaf Paper® and Mg, Mn, and Sr for reams of Staples® paper. The best element to discriminate between the vendors was Ba.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1. Background

Documents have become an important part of our society. Nearly every major life event involves a document: birth certificate, death certificate, property deed, marriage certificate. Documents are used in all sorts of transactions daily for example, checks, passports, wills, contracts and loans. While documents may not be common evidence in violent crimes, crimes committed with false documents (e.g., forged checks, embezzlement, tax fraud, altered wills) cost our country billions of dollars each year.[1]

Questioned document analysis involves a wide variety of analyses including handwriting, ink, typescript, printed and copied materials and the paper itself. Document examiners are also trained to visualize entries that have been erased or obliterated and even to visualize indented writing. Recently there has been considerable emphasis in research on comparing the ink[2-9] and toner[10-14] used in a document and even studies to determine age of the ink.[15-21] While identifying the ink is certainly important there are other aspects of document analysis that can be equally valuable.

The research presented herein will focus on the chemical composition of the document paper itself, specifically the trace elemental components. Since paper is created from natural materials (e.g., wood pulp, clays) and recycled consumer waste, it is highly unlikely that different paper manufacturers will produce a product with identical chemical composition.[1] While only chemical

analysis of the paper will be discussed in this work this is just one portion of a comprehensive document analysis. There are many different types of papers available commercially and the samples chosen for this work were document papers (multipurpose copy paper) made from 100% recycled materials, since such paper is commonly used in everyday activities.

1.2. Document Paper Production

Paper is composed of natural fibers, usually cellulose fibers (e.g., wood pulp, hemp, cotton), that are combined and flattened by heat or pressure. Although other fibers such as asbestos, silk, wool, glass, and plastic can be used, cellulose is the least expensive and therefore the most commonly used in paper manufacture.[22] The samples used in this research were made of cellulose fibers so only this production method will be discussed.

Pulp is the raw material that makes up the paper. This pulp can come from a number of sources however in the United States wood is typically the source of virgin raw fiber.[23] Most paper mills now use a mixture of virgin and secondary (recycled wastepaper) pulps.[23] The wood for pulp is usually material left over from creation of higher value lumbers and the residual wood from these processes is then chipped into small pieces (approximately 20 mm x 5 mm), which are turned to pulp by either mechanical or chemical methods. Mechanical methods grind the wood and typically create much shorter fibers that make a much weaker paper but 90-95% of the input material is retained in the final pulp.[23] The most common chemical pulping method, called the Kraft process, is accomplished by cooking the wood chips in a solution of sodium hydroxide

(NaOH) and sodium sulfide (Na_2S). The solution is very basic (pH >13) and will attack lignin, the highly polymerized substance found in the intercellular spaces of the wood. Since lignin is undesirable in high quality papers, the Kraft process is used to solublize the lignin and free up the cellulose fibers. Chemical pulping creates longer fibers but has lower yields (45-50%) so usually some combination of mechanical and chemical pulping is used to obtain the highest yield of pulp while maintaining longer fibers for good paper strength.

Once the pulp is created it is refined and must go through a series of processing steps. The pulp is washed to remove residual chemicals (e.g., NaOH, Na_2S) from the chemical pulping process. It is then screened to remove any large (> 3/8 inch) or unwanted particles from the "good" fibers. The pulp is then bleached to obtain the desired brightness. Chlorine was commonly used as a bleaching agent until the 1990s. However, since it is known to be a major producer of toxic chlorinated organic compounds, chlorine has been phased out.[23] Now the most common bleaching sequence includes oxygen extraction, alkaline extraction, and peroxide steps. After completion of these steps the pulp can then be shipped to paper manufacturers.

Wastepaper can be repulped for use and goes through many of the same steps described above. The wastepaper is first dispersed and broken up into a water solution. It is then cleaned and chemically deinked followed by a very similar screening and bleaching processes as the virgin fibers. The difference is that the recycled pulp samples will always contain some amount of contaminants;

waxes, glues, inks, and various other dissolved solids that may affect the end paper product.

The paper manufacturer will generate a wet stock by dispersing the pulp fibers into a water slurry. At this point the manufacturer mixes the desired amount of virgin and secondary (recycled) paper pulp. To this wet stock a variety of paper chemicals are added to give the end product certain qualities.[23] Acids or bases are added to control the pH of the paper to prevent yellowing. Starches are added to improve the tensile strength of the paper. Fillers such as clay, talc, and titanium dioxide are added to improve the opacity. Chemical dyes are also added at this point for whitening or color.

The pulp is then placed on large screens and the water is allowed to drain off. Physical watermarks may be introduced onto the paper by adding a pattern to the screen on which the paper is formed. The resulting paper sheet is then squeezed between rollers to remove remaining water and ensure smoothness and uniform thickness. The paper will also pass through large heated rollers to remove any remaining water before being cut to the appropriate dimensions.

There are many points during this process in which different chemicals and trace components can be introduced into the paper. An overview of this process is shown in Figure 1.1, the steps where chemicals may be added to the process are displayed in italics and possible chemicals that made be added are noted in the boxes.

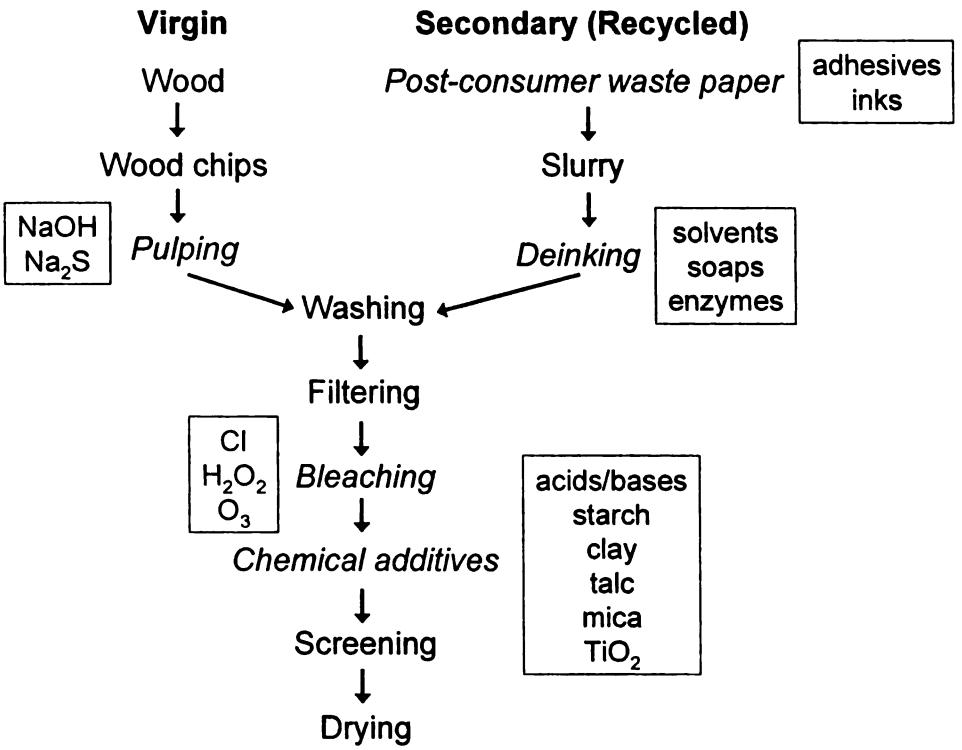

Figure 1.1. Overview of the papermaking process for both virgin and secondary fibers. The steps where chemicals are added are shown in italics and the additives are shown in the boxes.

1.3. Document Analysis

1.3.1. Traditional Analysis

The physical properties of the paper are typically examined first.[1] These include the size, weight, opacity, color, brightness and fluorescent properties of the paper. Opacity is a measure of the amount of light that passes through the paper. The color of many papers is slightly yellow so some manufacturers may add blue dyes to make the paper appear whiter, fluorescent dyes are also used for this purpose. The color, and presences of visible dyes, can be measured using UV/visible spectroscopy. The presence of fluorescent dyes and the intensity of the fluorescence can also be measured by spectroscopy. Most of these physical characteristics are carefully controlled by the manufacturers during

their quality control procedures and will not be very discriminating for paper produced by the same manufacturer.

Watermarks, imparted during paper manufacture, also serve as an important characteristic of the paper. These watermarks are usually trademarked property of a manufacturer and many manufacturers will use different watermarks for different grades of paper.[22] Watermarks are generated in several different ways: imprinted into the wet sheet (conventional method), mechanically embossed after drying, or chemically added. The watermarks that are mechanically embossed cause a compression of the fibers and will have a raised appearance and feel, different from the conventional or chemical methods. A conventional and chemical watermark can be differentiated under ultraviolet light where the conventional one will appear lighter and the chemical one darker than the paper. The watermarks are not only helpful in identifying the source of the paper but may also narrow dates of production based on manufacturer's codes or design changes.

The next step in the analysis would be to examine the fiber content. Different papers have different fiber types (e.g., wood, cotton) and an examiner can even determine if different pulping processes (e.g., mechanical, chemical) were used. This is typically done using microscopic analysis and observing the morphology of the fibers present. The paper sample must be defibered, which involves tearing it into small pieces, boiling in water and shaking vigorously to produce a suspension. This suspension is then placed on a carefully cleaned microscope slide. Once the sample is mounted different stains can be used to

differentiate different wood types, for example a Stellger stain (calcium nitrate and potassium iodide) can differentiate coniferous and hardwood pulps.[22] Other stains can be used to determine the content of bleached pulp by determining the amount of lignin still present. While staining can identify the types of fibers present this is still a class characteristic and many papers of the same type may also contain the same mixture of fibers. The technique is tedious, requires an experienced scientist, and is destructive.

The last part of the document analysis is the analysis of the chemical composition of the paper. Many chemical additives are used during the production of the paper to improve its color, strength, opacity, adjust pH, and even to prevent growth of microorganisms (e.g., fungi).[23] Infrared reflectance spectroscopy can be used to determine the coating contents based on characteristic adsorption bands for the different coating materials (e.g., starch, calcium carbonate, casein). The fillers and pigments in papers (e.g., titanium dioxide) are typically crystalline in nature and therefore can be determined by x-ray diffraction analysis. Typical fillers such as kaolin clay, calcium carbonate, talc, mica, and titanium dioxide can be identified at concentrations of less than 2% by weight.[22] X-ray diffraction is also a non-destructive method. There are many other methods that can be used to determine specific chemical components through extraction methods and additional information about these tests can be obtained from Browning's work.[22]

While all of the tests described above are useful for the paper analysis there may be many papers that have all the same characteristics, for example,

two paper samples of the same type from the same manufacturer. Manufacturers strive to produce a product that is very uniform and have greatly improved the quality control of the manufacturing processes. Therefore there are fewer differences among paper samples of the same type. However, even if the main components are the same there can still be variation at the trace level especially in the case of recycled materials.

1.3.2. Elemental Analysis

Elemental analysis of paper samples can increase the significance of an association and can also be helpful in determining approximate production times if suitable references are available. Elemental analysis has been performed on paper samples using a variety of techniques including neutron activation analysis (NAA),[24-26] scanning electron microscopy coupled with electron dispersive x-ray spectroscopy (SEM-EDS),[27] atomic absorption spectroscopy (AA),[28] and inductively coupled plasma mass spectrometry (ICP-MS).[29, 30]

Schlesinger and Settle did some of the initial elemental characterization of paper samples using NAA in the early 1970s.[24] A total of 102 pairs of paper samples were obtained from nine manufacturers, each pair containing a sample from the beginning and end of a production run. Relative standard deviations for elements in these pairs were relatively high, ranging from 12-20%. However, when only sample pairs containing high Al and Ti concentrations (filler components added deliberately by the manufacturers) were considered, relative standard deviations of <10% were obtained. No specific elemental markers were identified for any of the manufacturers.

Blanchard and Harrison developed a method to determine a "fingerprint" based on the clay content of the specific papers using NAA.[25] Initially 12 clay samples (8 kaolin and 4 non-kaolin) were analyzed and it was determined that the trace elemental profile of these clays was different. Five paper samples were then prepared from pulp with 15% of a different clay filler added to each, then analyzed by NAA. Elements with relatively high concentrations were marked as key identifying elements, the ratio of the key elements to other key elements was calculated, and the presence of unique elements was noted. These features were used to compare the results in the paper samples to the results from the clay samples. The five paper samples were correctly associated with the clays used to produce them. While this is a useful analysis for papers with a high clay content more modern copy papers have replaced much of the clay with calcium carbonate.[29]

Brunelle and coworkers also used NAA and found that some elements were more likely to be present (Na, Mn, Ag, and Cu) but elements that were less common (Ta, As, and Sn) were more valuable for distinguishing samples.[26] Brunelle was able to distinguish papers from different manufacturers, 600 samples from 10 manufacturers. The papers were distinguished based on which elements were present as well as the concentration of the elements. The disadvantage to NAA analysis is the need for special irradiation facilities that makes this a less universal method and not commonly available in forensic crime labs.

Polk and coworkers used scanning electron microscopy with electron dispersive x-ray spectroscopy (SEM-EDS) to determine elemental composition of several writing papers.[27] SEM is typically used for high power magnification and can be used as an imaging technique for fiber morphology. However, in conjunction with EDS this technique is also able to give elemental analysis. The most abundant elements detected in the paper samples were Al, Si, S, Ca, and Ti. The relative standard deviation on a single sheet and within a box of paper for all these elements was low (<5% for sheet, <10% for box). They were able to distinguish sheets from different but identically labeled boxes. The disadvantage of SEM-EDS is that it has limited sensitivity for elements with atomic numbers larger than Na and relative, rather than absolute, concentrations are used for discrimination.

Copeland and coworkers ashed and directly analyzed paper samples using atomic absorption spectroscopy (AA).[28] They determined ten elemental concentrations (Cu, Pb, Mn, Sb, Cr, Co, Cd, Fe, Mg, and Ag) present in the mid ppb to ppt range. They then used clustering algorithms (Q mode and Zahn minimal spanning tree) to group the samples. Using Co, Cr, Cu, Mn and Sb concentrations 12 of the 19 papers were differentiated using the Zahn minimal spanning tree algorithm and 16 of the 19 were differentiated using the Q-mode algorithm. The 3 samples that could not be differentiated, using Q-mode, had high relative standard deviations (>10%) for all of the elements used, which likely affected the differentiation capability. The limitations of this method seem to be due to variation in the measurements which may be limited by the reproducibility

of the dry ashing technique. AA is also typically a single elemental analysis and can be time consuming to perform multi-element analysis.

1.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS has been used as a method for trace elemental analysis since the 1980s.[31-33] ICP is an efficient ion source used to generate ions to be separated and detected by MS. This technique has several advantages, rapid multielement analysis, low detection limits (ppt), wide linear dynamic range (5-6 orders of magnitude), and high precision (0.5 – 5%).[33]

A plasma is a gas cloud of particles including radicals, free electrons, ions and neutral species. The plasma is formed in a torch that consists of 3 concentric quartz tubes, see Figure 1.2, and the end of these tubes are placed in a copper induction coil. Argon gas flows between the two outermost tubes and an electric spark is used to introduce free electrons. The induction coil has an oscillating (RF) frequency that will accelerate the electrons in alternating directions. These accelerated electrons will collide with Ar atoms and can cause them to lose an electron. This will continue until the rate of Ar ions forming is equal to the rate of electrons recombining with Ar ions and the plasma reaches a steady state. The plasma consists mostly of Ar atoms with a small fraction of free electrons and Ar ions.

The plasma is very efficient at generating ions which results in low detection limits for most elements. Solution samples can be directly analyzed using ICP as an atomization and ionizationmethod. An aerosol is generated from the solution using a nebulizer. This aerosol is introduced into the plasma where

the temperature ranges from 6000 – 10,000 K and is typically 6000 – 6500 K in the analytical zone where ions are sampled.[34] The particles will spend milliseconds in the plasma which is sufficient time to desolvate, atomize, excite, and ionize the atoms, forming a high density of positive sample ions.[31] The ionization efficiency is described by the Saha equation.[35] Thompson and Houk[36] calculated the degree of ionization (M^+/M) for many of the elements using this equation and these calculations are shown as percentages in Figure 1.3.

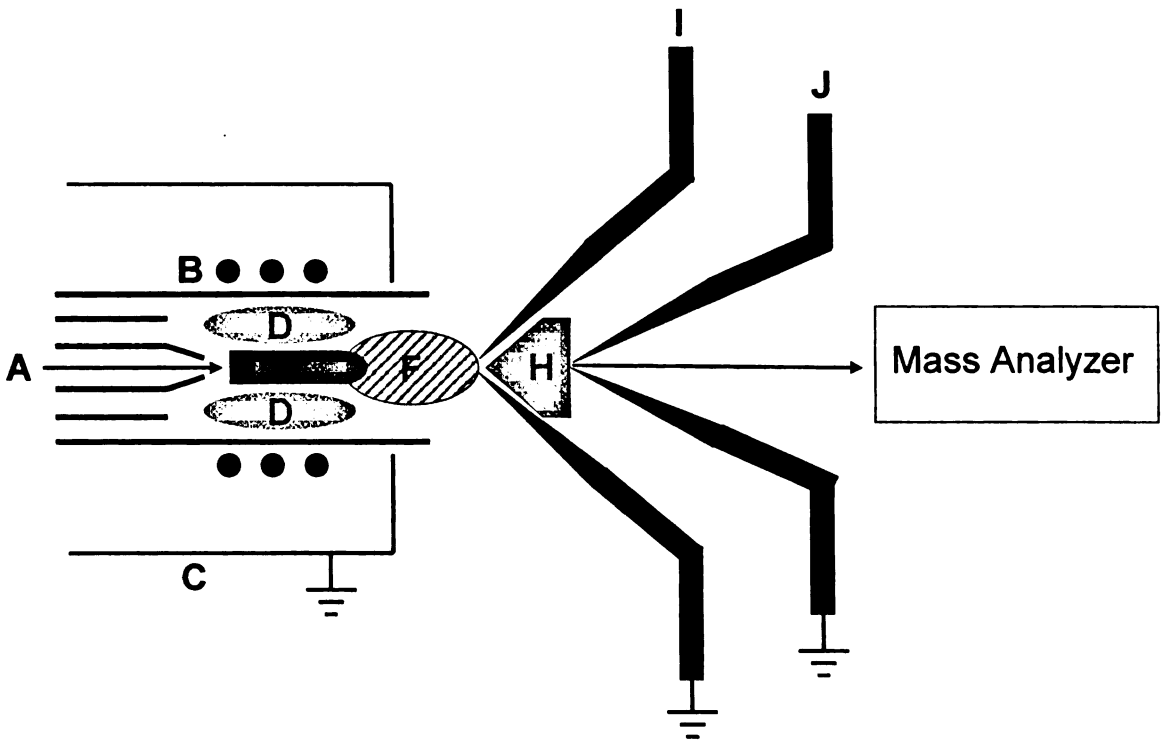

Figure 1.2. ICP torch and sampling interface. (A) solution aerosol injection, (B) RF induction coils to sustain plasma, (C) shielding box, (D) induction region, (E) initial reaction zone of the plasma, (F) analytical zone, (H) expanding gases sampled from plasma, (I) sampling cone and (J) skimmer cone.

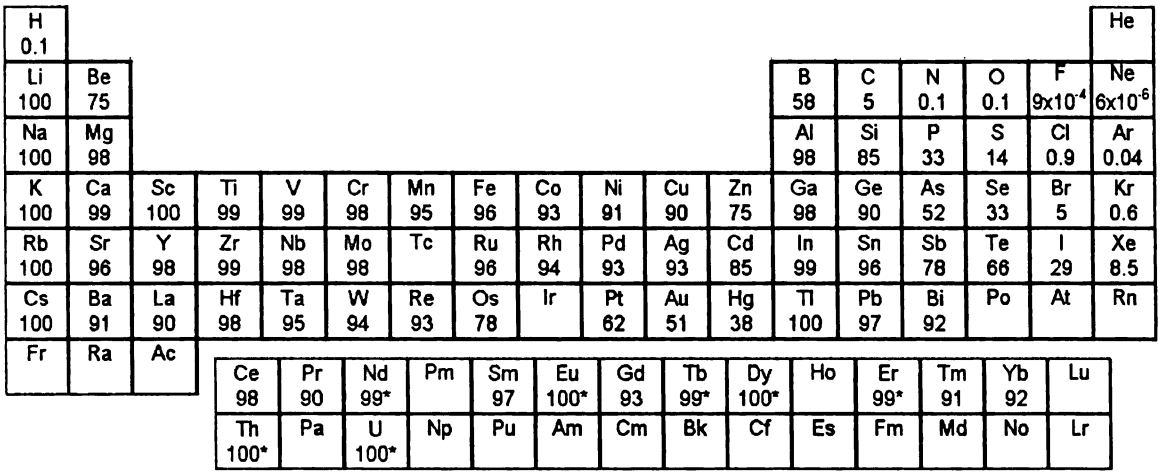

Figure 1.3. Calculated values for degree of ionization (M^+/M) reported as a percentage.[36] Elements with * also form a significant portion of M^{2+}.

The calculations from this equation indicate that the efficiency of forming singly charged ions is very high and these are the most abundant ionic species generated. This is important because it greatly simplifies the mass spectra that are obtained.

The ICP generates ions at atmospheric pressure however mass spectrometers require low operating pressures ($<10^{-5}$ torr) therefore these ions must be introduced to the MS through a differentially pumped vacuum system. The interface (Figure 1.2) is designed to extract a small amount of the plasma gas along with the ions into the vacuum system. A sampling cone is positioned to extract just above the hottest part of the plasma where the highest density of ions exist. The sample gas is directed through the sampling cone to a region where the pressure is approximately 1 torr. The gas expands in the vacuum region forming a plume. The skimmer cone is positioned just behind the sampler

cone and is designed to transmit as much of the sample as possible into a second vacuum chamber.

After the ions have entered the second vacuum chamber they are focused with ion lenses and accelerated toward the mass analyzer. In some cases a collision cell is used to remove some of the interfering species. Interfering species (Ar_2^+, ArN^+, ArO^+ etc.) are likely to be formed in clustering reactions that occur in the ion sampling interface.[32] The collision cell is a multipole (4, 6, or 8) chamber with only AC voltage at RF frequency applied to the poles to act as a high-pass mass filter allowing all ions over a predetermined mass pass through. The chamber is filled with a reaction gas, typically hydrogen or helium. The hydrogen and helium promote collision induced dissociation (CID) of the clustered ions and therefore reduce the interference of these molecules in the final mass spectrum.[37]

The typical mass analyzer used in commercial ICP-MS instruments is a quadrupole (Figure 1.4). The quadrupole consists of 4 parallel metal rods with opposite pairs electrically linked together. On each of these pairs a DC and AC voltage (with RF frequency) are applied. For one pair the DC voltage is positive and for the other it is negative and the AC voltages have the same amplitude but are 180° out of phase with one another. The ions enter the quadrupole region and the oscillating electric fields cause the ions to travel in oscillatory paths along the z-axis. At particular settings for the DC and AC voltages only ions with a particular mass to charge (m/z) ratio will have a stable path and will travel through the field and reach the detector. All other ions with different m/z values

than the selected value will impact the rods and become neutralized and will not be detected. By scanning the voltage (DC and AC) settings, ions of different m/z values will be selected for detection, allowing full mass scan of ions.

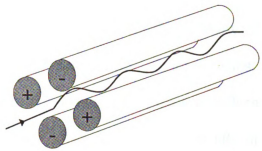

Figure 1.4. Diagram of a quadrupole. An example of a stable ion's oscillatory path is drawn down the center of the four parallel rods.

ICP-MS has been used by Spence and co-workers to differentiate document paper from 17 manufacturers around the world based on trace elemental concentrations.[29, 30] A single sample (30 mm x 40 mm) was taken from 5 random sheets in each ream, only 1 ream was selected from each manufacturer, except the Australian manufacturer where 6 reams were obtained. These samples were microwave digested and analyzed using ICP-MS. Nine elements (Na, Mg, Al, Mn, Sr, Y, Ba, La and Ce) were selected as potential discriminating elements because they showed low relative standard deviations over the sheets from one ream and had minimal interferences from polyatomic ions. All 17 paper manufacturers could be distinguished based only on elemental concentrations of Mn and Sr. Papers from the same Australian manufacturer but four different batches (sampled monthly) were able to be statistically

distinguished using Al, Zr, and Mn; however, differences in consecutively manufactured rolls could not be determined.

1.5. Thesis Overview

Forensically it would be useful if paper of the same type from the same manufacturer or vendor could be differentiated. Many of the current document analysis techniques are based on characteristics that vary between manufacturers and paper types but do not explore differences between batches or reams of the same paper. Being able to detect differences between reams of the same paper would add another level of specificity to the document analysis and serve to narrow the number of potential sources.

This thesis describes studies of the trace elemental composition of 100% recycled document (multipurpose copy) paper as determined by ICP-MS. These studies were intended to build on previous work and expand the study of differentiation of papers from the same vendor, specifically looking at differentiation of papers from separate reams.

Samples were studied from two U.S. vendors, five reams from each. Several levels of comparisons were made to assess the potential of differentiating paper samples based on elemental composition. First the homogeneity of the element composition across a single sheet and within a ream of paper was determined to choose elements suitable for comparison between reams. Next a statistical comparison was made between reams from the same vendor to differentiate the reams. Finally a comparison among papers from the

two vendors was made, aiming to distinguish different vendors based on elemental content of the papers.

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CHAPTER 2

EXPERIMENTAL MATERIALS AND METHODS

2.1. Paper Samples

Paper samples consisted of two brands of 20 lb. weight white document paper (8½ x 11 inches) made from 100% post-consumer waste which were acid-free and chlorine-free processed. The brands chosen were New Leaf Paper® - Encore 100 (San Francisco, CA) and Staples® 100% Recycled Copy Paper (Item #620016) (Framingham, MA). These brands were chosen because they were readily available in the East Lansing, MI area.

Five reams (500 sheet units) were selected from each brand. The New Leaf Paper® had the following markings on the ream wrappers for reams one through five respectively: JD6041015, JC6041115, JD6041015, JD6041115 and JD6041015. It is suspected that these codes relate to batches or production time frames. The company was contacted but the meaning of these codes was not positively determined. New Leaf Paper® reams one through four were obtained from different offices in the Chemistry building at Michigan State University and ream five was obtained from Kinko's Copy Center, East Lansing, MI. The Staples® brand papers had no individual markings on ream wrappers and all of these reams were obtained from Staples®, Lansing, MI. From each of the reams, for both vendors, 3 sheets were selected, the top sheet, a sheet in the middle and the bottom sheet of each ream. These 30 sheets of paper (3 sheets from 5 reams from each of 2 vendors) were used in this study.

From each sheet of paper, 5 samples were obtained, one from each corner and one from the center of the page. Samples (approximately 23 mm x 18 mm) were cut from the paper using plastic scissors and handled using plastic tweezers and gloves to prevent any elemental contamination. Each sample was weighed on a Mettler H80 balance by first weighing a quartz vessel, then the paper sample was added and the total mass recorded. The sample mass was determined as the difference between these masses and each sample weighed approximately 0.03 g (0.029 ± 0.001).

A numbering system was used to easily identify the origin of each individual sample. The first letter(s) in the numbering system referred to the vendor, NL for New Leaf Paper® and S for Staples®. The first number referred to the ream (1-5) and the second number referred to the location of the sheet in the ream with 1 indicating the top, 2 the middle, and 3 the bottom sheet in the ream. The last number in the numbering system referred to the sampling position on the sheet, 1 was the top left corner, 2 was the top right corner, 3 was the bottom left corner, 4 was the bottom right corner, and 5 was the center of the page. For example, the sample NL335 referred to a sample from New Leaf Paper®, ream 3, bottom sheet cut from the center of the page. On some occasions replicates were sampled from a single digest of one paper sample and lower case letters were used after the numbers to indicate these replicates.

2.2. Microwave Digestion

Microwave digestion is a sample preparation technique used for trace metal analysis. This technique involves a high temperature, closed vessel acid

digestion that is able to shorten digestion times and use less acid than conventional hot plate digestions. Because the digestion is done in a sealed vessel, elevated pressures can be used with the elevated temperature to help digest difficult matrices.

Paper samples were digested using a microwave digestion unit (Ethos EX, Milestone, Inc., Shelton, CT) equipped with an internal temperature probe. Quartz liner vessels (Milestone, Inc.) were used to minimize contamination and allow for smaller volumes of acids to be used. The procedure used for microwave digestion was suggested by the manufacturer for the type of samples used in this work. First the clean quartz vessels were weighed then a paper sample added and re-weighed to obtain an accurate sample mass. To the quartz vessel, 1.5 mL of Optima grade nitric acid (69%) and 0.75 mL of hydrogen peroxide was added. In the outer Teflon® vessel 11 mL of DI water and 1 mL of hydrogen peroxide were added. The quartz vessel was placed inside the Teflon® vessel (Milestone, Inc.) and capped with a quartz top. The Teflon® vessel was then sealed with a Teflon® cap. This assembly was placed in a segmented rotor and held in place with a screw tightened to the manufactures specifications using a torque wrench. The sealed assembly can hold up to 100 bar of pressure and retains volatile components produced during digestion.

Five vessels were loaded onto the rotor that rotates during digestion to evenly heat all vessels. The temperature probe was placed in a reference vessel to monitor temperature. The system automatically adjusted applied microwave power (wattage) to obtain and maintain the desired temperature. The

temperature program used to digest the paper samples is shown in Table 2.1. A maximum wattage is set as a safety precaution in case the temperature probe is not working. The wattage set is based on the number of vessels loaded and the desired maximum temperature.

Table 2.1. Microwave digestion temperature program

Step	Time (min)	Temperature	Maximum Wattage
1	15	Ramp to 210 °C	300
2	10	Hold at 210 °C	300

Following digestion, the Teflon® vessels were allowed to cool to below 100 °C before being opened in order to prevent loss of solvent. The quartz vessels were then 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 liquid in the Teflon® vessels was discarded.

The paper contained in the quartz vessel was partially digested; the resulting solution was clear with a small amount of white particulate matter. The particulate matter was chemically characterized and is discussed in more detail in Chapter 3. The solution initially consisted of 1.5 mL nitric acid (69%) and 0.75 mL hydrogen peroxide, during the digestion the hydrogen peroxide was broken down to water and the resulting solution was 47% nitric acid.

The digested sample was further diluted to a nitric acid concentration of 2% for ICP-MS analysis by adding 429 µL of the decanted digestion solution to 10 mL of ultra pure water. The diluted digest was stored in 15 mL polystyrene conical vials (BD Falcon™, BD Biosciences, Franklin Lakes, NJ) that were

previously acid washed. The digests were stored in the vials for up to 4 weeks prior to analysis.

The acid washing procedure for the conical vials was a 3 step process: 1) vials were filled with 15% hydrochloric acid, soaked in a water bath at 45 °C for 24 hours, 2) acid was removed, vials were triple-rinsed and soaked in ultra pure water for 24 hours 3) vials were triple-rinsed in ultrapure water and allowed to dry.

Procedural blank samples were run daily along with the paper digest samples. The same procedure described above was used to prepare these samples, except no paper was added to the quartz vessel. Over the course of the digestions 11 procedural blank samples were created.

2.3. Particulate Characterization

The particulate matter was collected from the bottom of twenty vessels from the standard nitric acid/hydrogen peroxide digestion. The collected particulate matter was washed with ultrapure water and allowed to dry. The collected particulates were used for spectroscopic analysis, aiming to characterize the particulates.

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

A potassium bromide (KBr) 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.

An IR spectrum was collected on a Mattson Galaxy Series 3000 FTIR (Madison, WI) in the transmittance mode. The sample was scanned from 350 cm^{-1} to 4000 cm^{-1} with the instrument resolution set at 4 cm^{-1}. WinFirst software (Mattson Instruments, Madison, WI) was used to record the spectrum.

2.3.2. X-ray Diffraction Spectroscopy (XRD)

The particles were mounted onto a glass slide using double sided tape. A spectrum was taken on a Rigaku Rotaflex RU 200B XRD instrument (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 2θ/θ mode. Scans were performed at a speed of 1 degree per minute.

2.3.3. Dissolution/Hydrofluoric Acid Digestion

In order to characterize the elemental make up of the particles, a complete digestion was performed to be analyzed by ICP-MS. Microwave digestion was again used to obtain a complete dissolution of the paper components but hydrofluoric acid (HF) was added to the digestion matrix. 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. In order to make sure approximately the same elemental concentration was obtained using this procedure, compared to that described in section 2.2, a paper sample, approximately four times larger, was necessary.

The Teflon® vessels were initially weighed then a paper sample was added and the vessel was reweighed. The sample mass was calculated from the

differences in weights and was approximately 0.12 g. To these vessels, 6 mL of Optima grade nitric acid, 3 mL of hydrogen peroxide, and 1 mL of hydrofluoric acid were added. The vessels were then sealed with the Teflon® tops, placed in the segmented rotor, and tightened to the manufacturer's specifications using a torque wrench. The same temperature program described in Table 2.1 was used for these samples. Following digestion a clear solution with no particulate matter remained in the Teflon® vessels.

The hydrofluoric acid was removed from the sample solutions before ICP-MS analysis since HF is a highly corrosive acid that will shorten the lifetime of the instrument. To remove HF, the samples were evaporated to dryness and reconstituted to the proper dilution with nitric acid. From the digestion solution 427 µL was removed and placed in a small Teflon® container. These were placed on a hot plate in a hood and allowed to evaporate over approximately one hour. Following evaporation of all the solution, 10 mL of 2% nitric acid (Optima grade) was added to reconstitute the sample. This reconstituted sample was used for the ICP-MS analysis.

2.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Samples were analyzed on a Micromass Platform quadrupole ICP-MS (Thermo Electron Corp, Waltham, MA) with hexapole collision cell using a CECTAC ASX-500 autosampler (Omaha, NE). Tune conditions were optimized using a 10 ppb solution of Be, Co, In, Ce, Bi, and U prepared in a 2% nitric acid solution. Nebulizer (Ar gas) flow rate, was 0.71 - 0.73 L/min and hexapole

helium and hydrogen gas flow rates ranged from 1.8 - 4.0 mL/min. Samples were scanned for 2.75 min using a dwell time of 0.1 s for each element.

Paper digests were prepared in a 2% nitric acid solution as described above. Each sample was mixed 2:1 with an internal standard solution containing 20 ppb of Bi and In. The instrument response was corrected using ^{115}In as an internal standard for ^{24}Mg, ^{27}Al, ^{45}Sc, ^{55}Mn, ^{56}Fe, ^{66}Zn, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{120}Sn, ^{138}Ba, ^{140}Ce and ^{146}Nd while ^{209}Bi was used for ^{208}Pb, ^{232}Th and ^{238}U. Final sample concentrations were quantified using a set of multi-element external calibration standards prepared in 2% nitric acid solution. Three ranges of calibration standards were used because the elements had a wide range of concentrations. The ranges were 5 to 1000 ppb for Mg, Al and Fe, 0.1 to 100 ppb for Sc, Mn, Zn, Sr, Zr, Sn, Ba, Pb and U, and 0.05 to 10 ppb for Y and Nd.

The autosampler probe was flushed with 2% nitric acid, for 90 seconds, between every sample, "blank" samples (pure 2% nitric acid) were run between every 10 samples, and the calibration standards were run approximately every 20 samples. To correct for any instrument drift, new calibration curves were generated after each calibration standard run. Each calibration curve was generated using two sets of standards, the standards run just before and just after the set of samples. Both sets of data were plotted on the same curve and the line generated was representative of both sets of standards. The concentrations for the paper digest samples were calculated using the calibration curve generated using calibration standards run immediately before and after the sample. A single digest sample was run in triplicate and yielded concentrations

that had less than 3% relative standard deviation, indicating that the concentrations determined by ICP-MS were consistent run-to-run.

2.5. Chemicals

All solutions were prepared using ultra high purity water (> 17 MΩ–cm) from a Barnstead E-pure or Millipore Milli-Q system. Nitric acid (69%) was obtained from Fischer Chemical (Pittsburg, PA) and was Optima grade (low ppt levels of metal contaminants) to reduce trace element contamination of the sample. Hydrogen peroxide (30%) was obtained from J.T. Baker (Phillipsburg, NJ) and was ACS reagent grade and used without additional purification. Hydrofluoric acid (48%) was obtained from CCI (Columbus Chemical Industries, Columbus, WI) and used without additional purification. Potassium bromide was IR spectral grade, stored dry, was obtained from Spectrum Chemical (Gardena, CA).

Elemental standards were ICP standard grade (Spex Certiprep, Metuchen, NJ) and were premixed in 1000 µg/L concentration in a 2% Optima nitric acid solution. One multielement standard was used for Ce, Nd, and Y but all other standards were single element solutions. These standards were used without any additional purification.

Ar used for ICP-MS was reagent grade and obtained from Linde Gas (Independence, OH).

2.6. Statistical Analysis

Prior to any statistical analysis, the elemental concentrations obtained from the ICP-MS were corrected for dilution factors and normalized to the paper

weight measured prior to digestion giving the concentration in μg element/g paper.

The average elemental concentration was calculated for each sheet (n=5) along with relative standard deviation (RSD). Q-tests were performed on all data sets that had RSDs higher than 15%, removing the data points that were determined statistically to be outliers (confidence limit of 95%). After the q-test the relative RSDs of elemental concentrations for each sheet was re-calculated. Any elements with an RSD greater than 15%, for any of the sheets tested were not used in any further analysis.

At this point, the samples are grouped by vendor and are treated as two separate groups. Two-way analysis of variance (ANOVA) was applied to the average elemental concentration for each sheet tested. The two variables in ANOVA were sheets within a ream (n=3) and the reams (n=5). ANOVA was used to determine which elements showed significant differences within a ream and between reams. To investigate these differences further, Tukey's HSD (honestly significant difference) test was performed to determine which reams differed from each other. This test has also been used by Almirall and co-workers for his work on forensic glass samples also analyzed by ICP-MS.[1, 2]

Tukey's HSD completes pairwise comparisons of all the data sets. The equation (2.1) is shown below.

$$t_s = \frac{M_i - M_j}{\sqrt{\frac{MSE}{n_h}}} \qquad (2.1)$$

where M_i - M_j is the difference between the i^{th} and j^{th} means, MSE is the mean square error and n_h is harmonic mean (equation 2.2) of sample sizes of groups i and j. If the sample sizes are even as they are in this case n_h is equal to the number of items per group.

$$n_h = \frac{2n_i n_j}{n_i + n_j} \tag{2.2}$$

where n_i is the number of samples in group i and n_j is the number of samples in group j. The Tukey statistic (t_s) is compared to a table of values based on the number of samples and degrees of freedom to determine the level of statistical significance of the difference between the two values.

To determine significant differences between the elemental concentrations between the two vendors, a t-test analysis was performed. The average concentration of each element was calculated for all of the paper samples from the vendor (n=75). This was then compared to the average for the other vendor. An F-test was performed for each element to compare the variance of the elemental concentrations for each vendor (confidence limit 95%). If the variances were statistically different the degrees of freedom (df) for the t-test comparison were calculated with equation 2.3.[3]

$$df = \frac{\left(\frac{s_i^2}{n_i} + \frac{s_j^2}{n_j}\right)^2}{\frac{\left(\frac{s_i^2}{n_i}\right)^2}{n_i + 1} + \frac{\left(\frac{s_j^2}{n_j}\right)^2}{n_j + 1}} - 2 \tag{2.3}$$

Where s_i^2 is the variance of group i, n_i is the number of data points in group i and similar for group j.

The t-statistic was calculated with equation 2.4.

$$t = \frac{\left|\bar{x}_i - \bar{x}_j\right|}{\sqrt{\frac{s_i^2}{n_i} + \frac{s_j^2}{n_j}}} \qquad (2.4)$$

Where $\bar{x}_i$ is the mean of group i and similar for group j. The t-statistic was compared to tables of values at the 95% and 99% confidence limits (two-tail) using 8 (n-2, n=10) or the value calculated from equation 2.3 for the degrees of freedom.

All statistical analyses were performed with either OriginPro for windows 7.5 SR 4 (v7.5853, OriginLab Corp., Northampton, MA) or Excel 2000 (Microsoft® Corp.)

2.7. References

(1) Trejos, T.; Montero, S.; Almirall, J. R. *Analytical and Bioanalytical Chemistry* **2003**, *376*, 1255-1264.

(2) Montero, S.; Hobbs, A. L.; French, T. A.; Almirall, J. R. *Journal of Forensic Sciences* **2003**, *48*, 1-7.

(3) Harris, D. C. *Quantitative Chemical Analysis*, 6th ed.; W. H. Freeman and Company: New York, 2003.

CHAPTER 3

PARTICULATE CHARACTERIZATION

3.1. Introduction

With a standard microwave digestion matrix of HNO_3 and H_2O_2, the paper samples were not completely digested. There was a white particulate matter remaining that settled to the bottom of the quartz vessels. During manufacture several inorganic additives (e.g., clay, titanium dioxide, mica, talc) are added to paper 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. Based on what is known about the additives in paper, it was suspected that the particulate matter include kaolin and TiO_2.

Kaolin is an aluminosilicate clay material ($Al_2Si_2O_5(OH)_4$) that is commonly used as a filler material for paper to give it color, opacity and good printing quality. About one half of the kaolin mined today is used in paper making processes.[1] TiO_2 is an inorganic material that is commonly used as a white pigment in a wide variety of materials such as paint, cosmetics, and toothpaste, which is also added to papers to enhance their whiteness.[2]

Kaolin and TiO_2 are likely to be found in paper samples but are not expected to be digested just with HNO_3 and H_2O_2. Two types of spectroscopy, infrared and x-ray diffraction were used to determine the composition of the undigested particulate matter. These two types of spectroscopy were chosen because they can give information about the structure of the material and identify

the materials present. Additional digestions and analysis with ICP-MS were conducted to determine the effect of the particulate matter on the composition and reproducibility of the digestion solution.

3.2. Particulate Identification

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

A KBr pellet was prepared from the particulate material and an IR spectrum was collected (Figure 3.1).

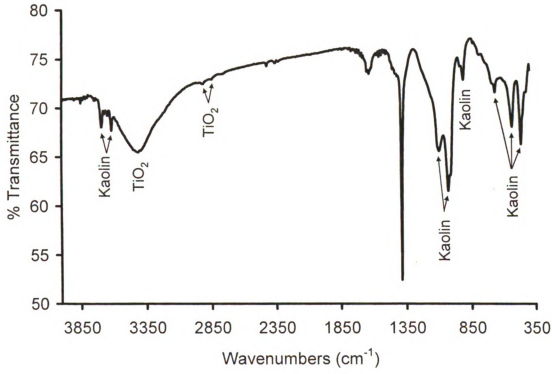

Figure 3.1. FTIR spectrum of particulates from paper digestion

The spectrum was compared to reference IR spectra of kaolin (clay), TiO_2, and silicon dioxide (SiO_2); possible materials that would be expected in paper samples. SiO_2 is a filler material used in papers that also will not dissolve in the HNO_3/H_2O_2 digestion. The absorption frequencies from the particulate sample

and the reference materials are listed in Table 3.1. From the table it is clear that the IR spectrum of the particulate sample is a combination of both kaolin and TiO_2. The strongest peaks are from the kaolin and the TiO_2 peaks are not as strong, suggesting the particulate sample contains a larger portion of kaolin.

Table 3.1 Comparison of absorption frequencies in IR spectra of particulates and reference materials

Sample (cm^{-1})	**Kaolin (clay)[3] (cm^{-1})**	**Titanium Dioxide[4] (cm^{-1})**	**Silicon Dioxide[5] (cm^{-1})**
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

There is a strong peak in the sample IR spectrum at 1384 cm^{-1} that could possibly be from the TiO_2 but it is much strong than the other peaks. This peak is in the range of a normal vibration of an inorganic nitrite.[6] Since the paper samples were digested in HNO_3 it is possible that an insoluble inorganic nitrite species was formed, and absorbs at 1384 cm^{-1}.

3.2.2. X-ray Diffraction Spectroscopy

X-ray diffraction spectroscopy is based on the principle of diffraction and is commonly used to identify crystalline materials. In order for diffraction to occur

the spacing of scattering centers must be similar to the wavelength (λ) of the light being scattered. The spacing between atoms in crystal structures is approximately the same as the wavelength of x-rays, in the range of Å.

When an incident beam of x-rays bombard an atom they can be elastically scattered (i.e., maintains same λ as incident beam). When several atoms are close to one another, such as in a crystal lattice, the x-ray waves scattered from the different atoms can interfere either constructively or destructively. Constructive interference occurs when the lattice spacing is an integer multiple of the wavelength of the incident radiation as described by Bragg's law (equation 3.1),

$$n\lambda = 2d \cdot \sin\theta \qquad (3.1)$$

where n is an integer, λ is the wavelength of incident light, d is the distance between scatters (lattice spacing), and θ is the angle of refraction. Based on this equation, if the wavelength and the scattering angle are known then the lattice spacing can be determined.

In an x-ray diffraction experiment a single wavelength is focused onto the sample and the x-ray scattering is measured at a range of angles. The data is plotted as x-ray intensity versus angle. The angles that have x-ray scattering intensity above the background result in a peak. From the angle where a peak occurs the lattice spacing (d-spacing) can be determined using equation 3.1. Every crystalline material has a specific lattice structure in which the atoms are in a certain configuration (e.g., face centered cubic) and there are several distances within a single lattice (e.g., between atoms in the same plane, atoms in different

planes). The pattern of d-spacing and the relative intensity of these peaks are characteristic to the crystal and can be used to identify the material. If the sample is a mixture of multiple materials the intensity of the x-ray scattering is related to both the concentration as well as how strongly the material scatters.

The particulates that were collected from the HNO_3/H_2O_2 digestions were mounted on a glass slide. The sample was scanned between 2 and 65° at a rate of 1°/min and the resulting XRD spectrum is shown in Figure 3.2.

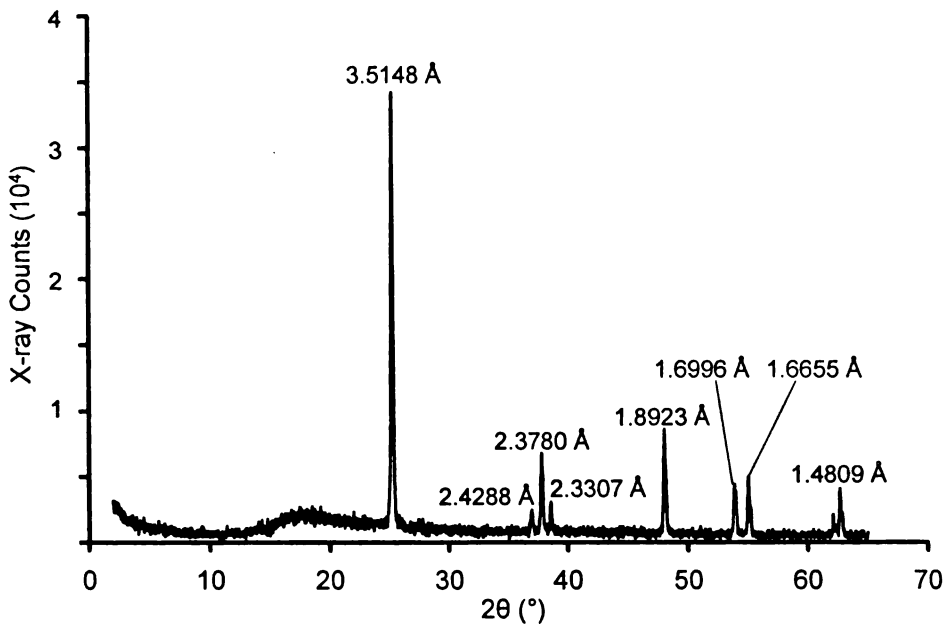

Figure 3.2. X-ray diffraction spectrum of undigested material from the HNO_3/H_2O_2 digestion.

The peaks expected for TiO_2 and their relative intensities are shown in Table 3.2, all of the peaks visible in Figure 3.2 are consistent with TiO_2.[7]

Table 3.2. X-ray diffraction peaks for TiO_2[7]

d (Å)	I/I_1
3.52	100
2.431	10
2.378	20
2.332	10
1.892	35
1.6999	20
1.6665	20
1.4930	4
1.4808	14

There is one small peak correlating to a lattice spacing of 7.187 Å that can be seen in the expanded spectrum (Figure 3.3). From the FTIR spectroscopy it was apparent that some component of this mixture is kaolin. The kaolinite group of clays has a lattice spacing of 7.15 – 7.20 Å.[8] The peak in the sample spectrum is in the middle of 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 x-ray diffraction.[8] This is apparent in this case based on the relative intensity of the kaolin peak to the TiO_2 peaks, which is in contrast to the stronger kaolin signals observed in the FTIR spectrum. Neither XRD nor FTIR was used to quantify the TiO_2 and kaolin concentration in the undigested particulate matter.

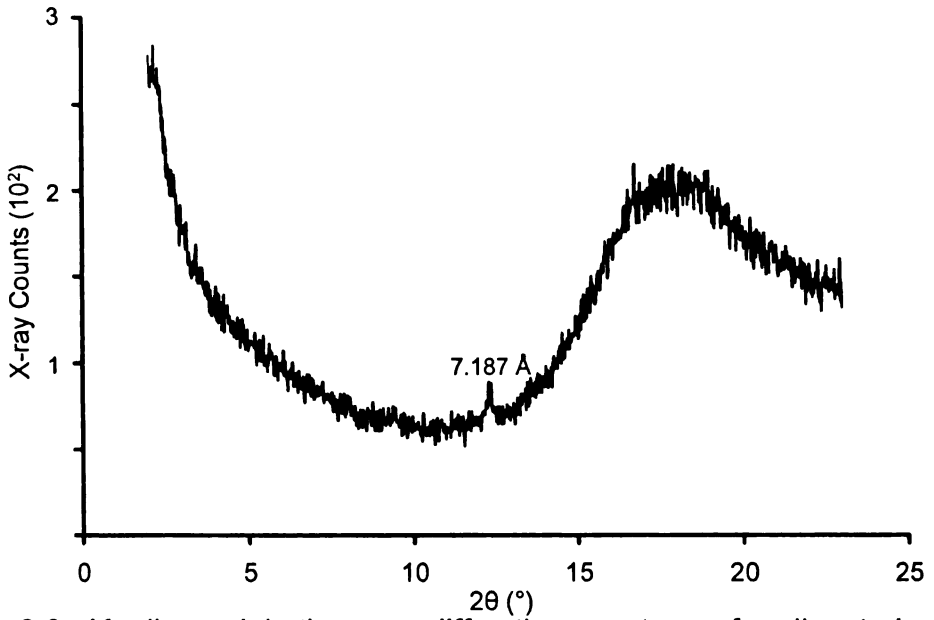

Figure 3.3. Kaolin peak in the x-ray diffraction spectrum of undigested material from the HNO_3/H_2O_2 digestion.

3.2.3. Elemental Analysis of Hydrofluoric Acid (HF) Digest

In order to determine the concentration of TiO_2 and kaolin in the particulate material, paper samples were completely digested with the addition of HF to the digestion matrix, as described in section 2.3.3. Levels of Ti, Al and Si levels were determined by ICP-MS for both digestion procedures: HNO_3/H_2O_2 (particulates present) and HF (no particulates present). The same sheet of paper was used for both digestions therefore it was assumed that any difference in the concentrations of these elements was due to the material in the particulate matter. The concentration of Al, Si and Ti under both digestion conditions are presented in Table 3.3.

Table 3.3. Comparison of Al, Si and Ti concentrations, determined by ICP-MS, in solutions from HNO_3/H_2O_2 and HF digestions.

	Al (µg/g)	Si (µg/g)	Ti (µg/g)
HNO_3/H_2O_2 Digest (n=4)	380 ± 40	800 ± 100	50 ± 50
HF Digest (n=3)	1020 ± 40	0	179 ± 3

There was a difference between the concentrations determined with each of these digestion methods. The Al and Ti were about 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 use to quantify Si because during the digestion the Si and F will form a volatile complex SiF_4.[9-11] The boiling point of this compound is -86 °C hence the Si is lost from the digestion solution prior to quantification.[12]

Assuming the additional Al present in the HF digest is from kaolin the approximate concentration is 3100 µg kaolin per g paper. A similar calculation for TiO_2 yields a concentration of approximately 220 µg TiO_2 per g paper. Based on these rough calculations kaolin is the major component of the particulate matter, confirming results obtained from FTIR.

3.3. Effect of Particulate on Elemental Analysis

3.3.1. Comparison of Nitric Acid/Hydrogen Peroxide and Hydrofluoric Acid Digestion

In order to determine if complete dissolution of the particulate matter had any significant effects on the element concentrations being determined, a

comparison was made between the two digestion methods. Four paper samples were digested using HNO_3/H_2O_2 and three were digested using HF; all samples were from the same sheet. All digests were then analyzed by ICP-MS, using the same calibration curve, to quantify elemental concentrations. The results are shown in Table 3.4. Significant differences between the digests, based on a t-test with a 95% confidence limit, were observed in the concentrations of Mg, Al, Fe and Pb.

Table 3.4 Comparison of elemental concentrations in solutions from HNO_3/H_2O_2 and HF digestions.

	HNO_3/H_2O_2 Digest (n=4) (µg/g)	HF Digest (n=3) (µg/g)	Significant Difference (95% CL)
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
Pb	0.11 ± 0.01	1.21 ± 0.03	yes
Nd	0.19 ± 0.01	0.22 ± 0.03	no

The increase in concentration of Al was expected, as it was determined a large portion of the particulate sample consisted of an aluminosiliate clay. Other sheet silicate minerals are known to contain Mg (e.g., serpentine ($Mg_3Si_2O_5(OH)_4$)) and Fe (e.g., mica ($K(Mg,Fe)_3(AlSi3O_{10})(OH)_2$)) and could be minor components of the clay as well. There was variation in Pb concentration across a single sheet of paper (RSDs 20 – 100%) but the increase in the HF

digest is 1000% so it is more likely that the Pb was a contaminant present in the HF used. No procedural blank was done with the HF solution so this cannot be determined for sure.

3.3.2. Effect of Filtering HNO_3/H_2O_2 Digest

Following digestion in HNO_3/H_2O_2, a small portion of the digestion solution was decanted to be diluted for ICP-MS analysis. It is possible that some small particulates were also sampled and could affect the elemental concentrations and the reproducibility of the analysis. To test this hypothesis, two digested samples from the same sheet of paper were selected. From each of these samples, one aliquot was filtered and a second was not. A new syringe filter (Millex-Ha, 0.45 μm, Millipore) and an acid wash syringe were used to filter each of the samples. Both the filtered and unfiltered solutions were then analyzed by ICP-MS and the elemental concentrations normalized to the mass of the sample. The results are shown in Table 3.5.

Table 3.5. Comparison of elemental concentrations for filtered and unfiltered samples. Errors represent standard deviations.

	Unfiltered (n=2) (μg/g)	Filtered (n=2) (μg/g)	Significant Difference (95% CL)
Mg	1100 ± 70	1130 ± 30	no
Al	670 ± 70	680 ± 60	no
Mn	4.42 ± 0.09	4.5 ± 0.2	no
Fe	90 ± 4	92 ± 6	no
Zn	13 ± 6	1000 ± 1000	yes
Sr	30.5 ± 0.2	31.2 ± 0.5	no
Y	0.13 ± 0.01	0.13 ± 0.01	no
Ba	6.49 ± 0.04	22 ± 10	no
Ce	0.34 ± 0.02	0.34 ± 0.02	no
Pb	0.08 ± 0.01	0.15 ± 0.05	no
Nd	0.18 ± 0.02	0.18 ± 0.01	no

From the results it was clear that filtering the digest did not significantly affect the concentrations of the elements of interest with the exception of Zn, which showed a significant increase. There may be Zn present in the filters or syringes that is washed into the solutions when the 2% HNO_3 matrix passes through the filter causing the increase Zn concentration in the filtered samples. This particular filter material was not rated for trace metal analysis. Because none of the other elemental concentrations were affected by the filtering procedure and to avoid the possibility of sample contamination decanting of the digestion liquid was determined to be sufficient.

3.3.3. Elemental Absorption by Particulates

One other concern of having undigested particulates is that the particulates could have absorbed some of the elements in the digestion solution and subsequently altered the concentrations determined. The particulate matter did contain clay material that could absorb cations. In soil analysis a cation exchange capacity (CEC) is used to gauge how well the soil will hold nutrients (e.g., Ca^{2+}, Mg^{2+}, K^{+}). Since this property is a measure of how well the material will absorb cations in this application CEC was related to how much effect the clay had on the digestion solution.

The previously described studies determined that the type of clay present in the papers is kaolin. Kaolin has a relatively low CEC of 3.0 – 3.7 meq/100 g clay, where meq is mol M^{n+}/n.[13] The average CEC of the Clay Mineral Society source clays is 61 meq/100 g.[13] While kaolin does not have very strong exchange capability for cations it is still possible that it could absorb some of the

elements in the solution. The amount of kaolin that was present is relatively small in regard to the weight of the paper samples; based on estimations of the concentration of kaolin (3100 µg/g paper) it makes up less than 1% of the paper by weight. Even if the kaolin does absorb some of the elements from the digestion solution, if the system has reached equilibrium, the concentration of the elements in the digestion solution will be relatively constant with time.

To determine if there was a time dependent component to the elemental concentrations, a single sheet of paper was sampled and the digestion solution remained in contact with the particulates for various amounts of time before decanting for ICP-MS analysis. Because the digestions are done at an elevated temperature in a sealed vessel the minimum amount of time was 20 minutes to allow the solution to cool below the boiling point before opening the vessel. The results of the time study ICP-MS quantifications are shown in Table 3.6, based on elemental concentrations determined by ICP-MS.

The values for each element do not appear to significantly change with time: 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 changes are seen with time. The particulate matter does not affect the elemental concentration in the digestion solution.

Table 3.6. Elemental concentration paper samples digested with HNO_3/H_2O_2 and allowed to equilibrate in the presence of the particulates for various amounts of time.

	Equilibration Time			
	20 min	60 min	120 min	180 min
Mg (µg/g)	791	861	800	848
Al (µg/g)	431	328	370	373
Mn (µg/g)	3.84	4.12	3.94	4.18
Fe (µg/g)	70.1	74.3	75.2	77.9
Zn (µg/g)	8.00	4.12	9.31	5.07
Sr (µg/g)	63.0	69.6	63.6	67.2
Y (µg/g)	0.094	0.094	0.148	0.099
Ba (µg/g)	1.99	2.18	2.20	2.12
Ce (µg/g)	0.244	0.263	0.259	0.258
Pb (µg/g)	0.656	0.752	0.721	0.674
Sn (µg/g)	8.39	9.25	8.44	9.67
Zr (µg/g)	1.46	1.92	1.55	1.72
Nd (µg/g)	0.131	0.132	0.129	0.139

3.4. Conclusions

With a digestion solution that contained only HNO_3 and H_2O_2, complete digestion of paper samples was not possible. The undigested portion 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 an effect on the reproducibility of the concentrations determined in the digest, as determined by comparing the HNO_3/H_2O_2 digestion (particulates) with an HF digestion (no particulates). 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. Since an HF digest is not necessary the elemental concentrations used for comparisons for the rest of this work were determined using the HNO_3/H_2O_2 digestion.

3.5. References

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CHAPTER 4

RESULTS AND STATISITICAL COMPARISONS

4.1. Introduction

Paper samples from 2 vendors (New Leaf Paper® and Staples®), 5 reams each, were collected to compare the trace elemental content for differences. From each of the reams, 3 sheets were selected from the top, middle, and bottom. On each sheet 5 samples were collected for analysis. The paper samples were digested in a solution of nitric acid and hydrogen peroxide using a microwave system. Following digestion, they were analyzed using inductively coupled plasma mass spectrometry to determine trace elemental concentrations. Several comparisons were made; within sheet, between sheet, between ream and between vendors.

4.2. Method Development

The ultimate goal of the project was to be able to differentiate papers. Therefore it was necessary to determine if significant differences existed in the elemental concentrations of reams of the same type of paper. First a suite of elements to compare had to be determined. This suite of elements was based on the elements that were present above background levels, were not present in the background, and were a consistent concentration throughout the ream. For the comparison to be useful, the elemental concentrations must not be significantly different between sheets from the same ream.

4.2.1. Full Mass Scan

Initially a list of potential elements in the papers was developed from a literature survey.[1-7] This list included: ^{7}Li, ^{23}Na, ^{24}Mg, ^{27}Al, ^{45}Sc, ^{55}Mn, ^{52}Cr, ^{55}Rb, ^{56}Fe, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{107}Ag ^{114}Cd, ^{121}Sb, ^{138}Ba, ^{139}La, ^{140}Ce, ^{146}Nd, ^{208}Pb, ^{232}Th, and ^{238}U. A full mass scan was measured for a digest from a single sheet of paper (New Leaf Paper®), scanning the range of m/z values, between 7 and 240, to determine if all the elements listed above were present and if there were any additional elements to include in the analysis. Figure 4.1 shows the full range of masses, this mass spectrum is dominated at the lower m/z values by smaller atomic weight atoms such as C, Na, Ca and O as well as Ar, H and He from the source and hexapole gases and other interferences. Figures 4.2 through 4.4 show expanded portions of the mass spectrum to identify the other elements present that may be useful for comparisons.

Based on the full mass scan some elements were eliminated from the list (^{52}Cr, ^{55}Rb, ^{59}Co, ^{63}Cu, ^{107}Ag, ^{114}Cd, ^{121}Sb, and ^{139}La) because the concentrations were below the instrument detection limit. ^{7}Li and ^{23}Na were eliminated because the instrument has high levels of contamination at these masses. Additional elements were observed (^{120}Sn and ^{184}W) in the paper digest and were added to the list.

The full mass spectrum as well as previous work on the elemental analysis of document papers was used to develop a list of elements to quantify in the papers. The final list included Mg, Al, Sc, Mn, Fe, Zn, Sr, Y, Zr, Sn, Ba, Ce,

Nd, Pb, and U. One of the elements present in the full mass scan (W) was initially overlooked and was not included in the suite of elements to be tested.

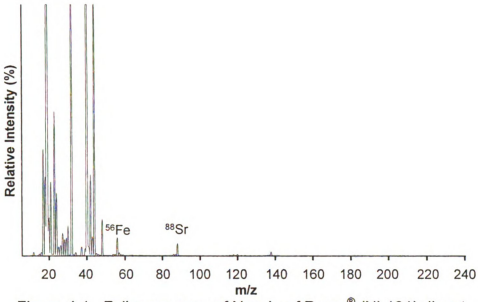

Figure 4.1. Full mass scan of New Leaf Paper® (NL131) digest.

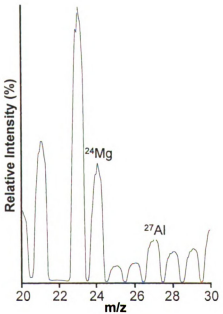

Figure 4.2. Expanded region (m/z 20 – 30) of full mass scan for New Leaf Paper® (NL131) digest.

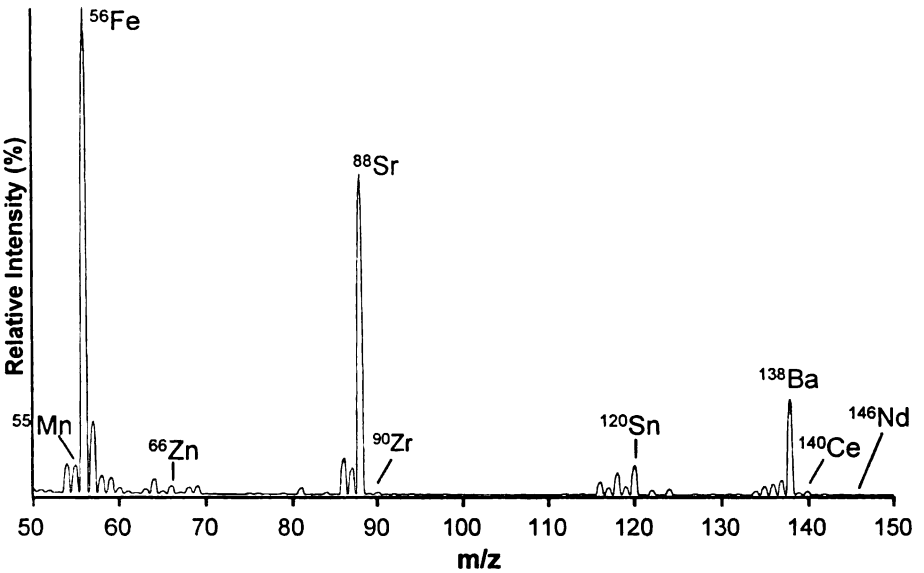

Figure 4.3. Expanded region (m/z 50 – 150) of full mass scan for New Leaf Paper® (NL131) digest.

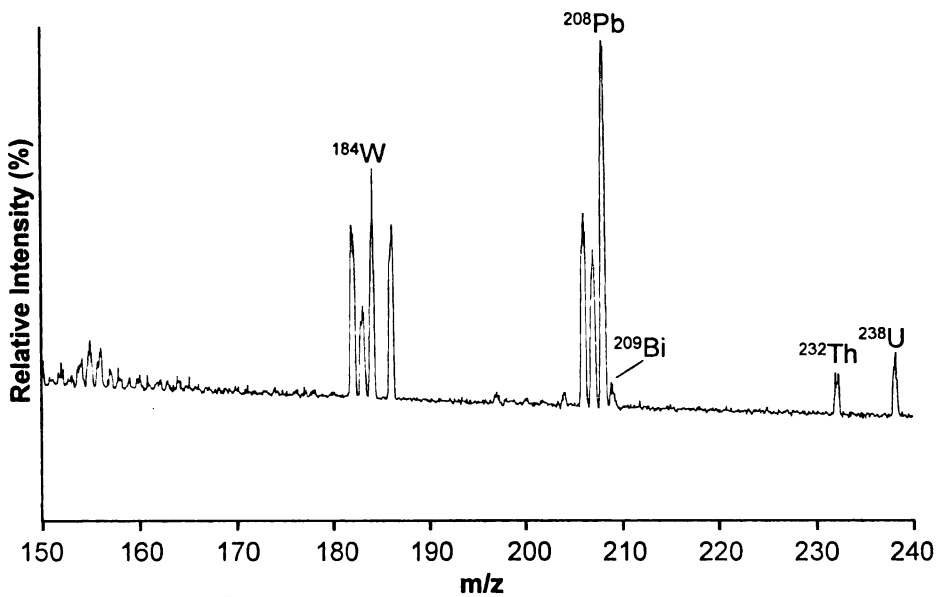

Figure 4.4. Expanded region (m/z 150 – 240) of full mass scan for New Leaf Paper® (NL131) digest.

4.2.2. Calibration

An internal standard (20 ppb Bi and In) solution was added to all samples prior to analysis. All signals were ratioed to either Bi or In signal, depending on mass, to correct for any fluctuation in instrument response. Multi-element calibration standards were prepared containing all of the elements listed above. Because these elements existed in the paper samples over a wide range of concentrations three different ranges were used: 5 – 1000 ppb (Mg, Al, Fe), 0.1 – 100 ppb (Sc, Mn, Zn, Sr, Zr, Sn, Ba, Pb, U) and 0.05 – 10 ppb (Y, Ce, Nd).

Calibration curves were generated for each element based on the signals ratioed to the internal standard. All of the curves were linear and the limits of quantitation for each element are listed in Table 4.1

Table 4.1. Instrument quantitation limits for elements chosen for paper analysis. Sc was not linear so no detection limit is listed

Element	Quantitation Limit (ppb)
^{24}Mg	<5
^{27}Al	10
^{45}Sc	-
^{55}Mn	<0.1
^{56}Fe	<5
^{66}Zn	0.25
^{88}Sr	0.25
^{89}Y	<0.05
^{90}Zr	<0.1
^{120}Sn	<0.01
^{138}Ba	0.25
^{140}Ce	<0.05
^{146}Nd	<0.05
^{208}Pb	<0.1
^{238}U	<0.1

One element, Sc, did not have a linear calibration curve therefore no detection limit is listed. For many of the elements the calibration curve was linear

over the entire range of standards tested so a true quantitation limit could not be calculated and is listed as less than the concentration of the lowest elemental standard analyzed. Because Sc did not have a linear calibration curve it was eliminated from the suite of elements.

4.2.3. Procedural Blanks

Due to the various steps involved in the digestion and analysis procedures as well as the sensitivity of the ICP-MS, some of the elements in the profile could have been environmental contaminants. To determine possible contaminants, procedural blanks were run along with the samples. These samples were handled the same as the paper digests except no paper was added to the quartz vessels prior to the digestion step. A blank sample was generated every day samples were digested giving a total of 11 blank samples.

The procedural blanks were analyzed along with the paper samples and the elements from the suite of elements identified above were quantified with a calibration curve. Shown in Table 4.2 is the average concentration of each element in the 11 blanks along with the lowest concentration of the element found in any of the 150 paper samples analyzed (2 vendors, 5 reams each, 3 sheets per ream, and 5 samples from each sheet). In the last column of Table 4.2 the ratio of the blank to the lowest paper concentration is reported as a percentage. This percentage represents the maximum contribution the background level of an element will have on the concentration determined in a digest sample.

Table 4.2. Elemental concentration of procedural blanks, compared to lowest concentration of the element in any paper digest solutions. ND indicates concentration was below the detection limit

Element	Blank Value (ppb) (n=11)	Lowest Value in Paper (ppb)	Ratio of Blank to Lowest Paper (%)
Mg	1.3 ± 0.7	313	0%
Al	1.0 ± 0.8	131	1%
Mn	0.02 ± 0.01	1.69	1%
Fe	1.0 ± 0.8	30.1	3%
Zn	3 ± 2	1.97	138%
Sr	0.1 ± 0.1	12.6	1%
Y	ND	0.04	-
Ba	0.03 ± 0.02	0.94	3%
Ce	ND	0.11	-
Pb	0.03 ± 0.04	0.05	69%
Sn	5.0 ± 0.2	3.84	129%
Zr	0.09 ± 0.04	0.19	46%
Nd	0.01 ± 0.00	0.05	20%

For some of these elements (i.e., Zn, Pb, Sn, and Zr) a significant portion of the signal is coming from a procedural contamination source, as indicated by the high ratio listed in Table 4.2. Because the background levels could be highly variable and were not representative of the characteristics of the papers, these elements were not used in any future comparisons.

4.2.4. Relative Standard Deviations

The last criterion used to choose elements for statistical comparison among paper samples was the variability in elemental concentration across a single sheet. Because only a portion of the sheet would be sampled in a forensic analysis scheme it is important that no significant differences occur within the single sheet so that the sample analyzed is representative of the whole sheet. For each sheet of paper, five samples were analyzed, one from each corner and

one from the center. These areas were chosen to detect spatial variations in the elements across the page.

Relative standard deviations (RSD) were calculated for each element concentration on a sheet; this was done for all sheets that were sampled. Any element concentration with a RSD larger than 15% was checked for outliers using a q-test. If the RSD was still larger than 15%, after removing any outliers, the element was not considered useful. An RSD of > 15% indicates an elemental concentration that is variable over a single sheet, which is not desirable for forensic analysis.

In general, the RSD for an elemental concentration within a sheet was 5 – 10%, highlighting the acceptable precision in paper, digestion procedure and ICP-MS analysis. Zn had very high variation across the sheets with RSDs of 20 – 50%. Pb and Zr also had high variation within a sheet with RSD values of up to 130% for Pb and around 25% for Zr. The elements with high RSD values (Zn, Pb, and Zr) also had a high contribution from the blank samples. This suggests that the high RSD values are due to varying levels of contamination. Based on the high RSD values as well as the high blank levels, these elements were not used for any statistical comparisons.

The instrumental detection limits, calibration curves, and procedural blank levels were used to narrow the suite of elements for statistical analysis to include: Mg, Al, Mn, Fe, Sr, Y, Ba, Ce and Nd.

It is unclear where these elements come from exactly however Mg and Mn are known micronutrients in plants (i.e., tree cells) and the variation in these

elements could come from variation in the amount present in the trees used for the pulp.[8] Sr is similar to Ca and can be found in cells in place of Ca. Al is a component of some of the filler materials (e.g., clay) however this portion of the paper does not digest in the HNO_3/H_2O_2 digest used for these measurements and so the origin of the Al that was freed during digestion is unknown. Calcium carbonate ($CaCO_3$) is another common filler material for paper[9] and commercial supplies of this chemical can have chemical impurities, Sigma-Aldrich listed potential impurities to include Mg, Fe, and Ba, all are trace elemental components found in the paper digests.[10] Because both the vendors sampled in this work used recycled materials it is impossible to be certain of the source of the trace elements.

4.3. Variation Between Reams

In this section the variation of elemental concentration between the reams of paper is discussed. For simplicity the reams from each vendor, New Leaf Paper® and Staples®, are discussed individually.

4.3.1. New Leaf Paper®

The first analysis performed was a two-way analysis of variance (ANOVA) based on the elemental concentrations of the sheets from five different reams. The two variables tested were the variance among sheets (average of 5 samples from each sheet) and the variance between the reams (average of 15 samples, 3 sheets with 5 samples each). The null hypotheses were that there was no difference in the means of the elemental concentrations of the sheets and that there was no difference in the means of the elemental concentrations of the

reams. The alternate hypotheses were the means of the elemental concentrations of the sheets and reams were not equal. The test generated a p-value, which is a statistical measure of the probability that the null hypotheses were true. A p-value ≤ 0.05 was chosen to define a significant difference between elemental concentrations, at this p-value the probability that the means of the elemental concentrations were the same was 5% or less. Shown in Table 4.3 are the resulting p-values from the two-way ANOVA analysis on the New Leaf Paper®.

Table 4.3. Two-way ANOVA results for New Leaf Paper®. Significant differences defined as p-value ≤ 0.05

Element	sheets (n=3)		reams (n=5)	
	p-value	significant	p-value	significant
Mg	0.491	no	0.007	yes
Al	0.647	no	0.001	yes
Mn	0.676	no	0.064	no
Fe	0.660	no	0.121	no
Sr	0.408	no	0.004	yes
Y	0.495	no	0.258	no
Ba	0.453	no	0.001	yes
Ce	0.453	no	0.405	no
Nd	0.201	no	0.486	no

None of the elements showed significant variation in concentration among all the sheets tested from a single ream; all the p-values were > 0.05. This indicated that the elemental concentrations for all the elements listed were not statistically different for the three sheets in a single ream. If a single sheet of unknown origin were sampled it should have the same elemental concentration as any other sheet in the ream it came from and could be excluded from as originating from a ream that had different elemental concentrations.

The average elemental concentration within an entire ream (15 samples, 3 sheets with 5 samples each) was compared for the 5 reams and the resulting p-values are also displayed in Table 4.3. There are four elements (Mg, Al, Sr, and Ba) that have a significant variation in concentration among the reams. In order to further investigate these differences among the reams (i.e., determine specifically which reams differ from one another), a statistical Tukey test was performed. The Tukey test is a pairwise comparison between each group member, in this case reams, to determine where the statistical differences occur. The null hypothesis was there was no difference between the elemental concentration of the reams and the alternate hypothesis was there is a difference in the mean elemental concentration of the reams. The p-values represent the probability that the null hypothesis is correct. A p-value ≤ 0.05 indicates the mean concentrations are different at a 95% confidence level and similarly for a p-value ≤ 0.01 the confidence level is 99%. The results of the Tukey test are displayed graphically in Figures 4.5 through 4.8.

In Figures 4.5 through 4.8 the bars represent the average element concentration (n=15) for each of the reams. The error bars represent the standard deviation of these measurements. Mean values that are significantly different from one another are connected with a line and the * (p-value ≤ 0.05) and ** (p-value ≤ 0.01) indicate the significance level of the difference. For example in Figure 4.5, the Mg concentration in ream 1 is significantly different than the concentration in ream 2 at a 99% confidence level.

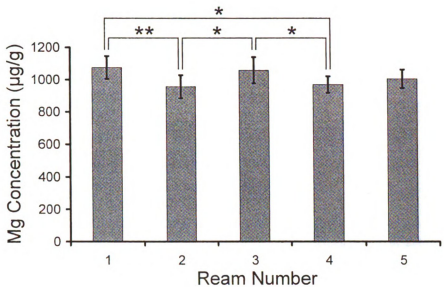

Figure 4.5. Mg concentration in New Leaf Paper®, reported as µg Mg per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

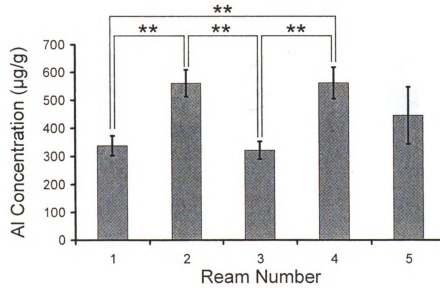

Figure 4.6. Al concentration in New Leaf Paper®, reported as µg Al per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.01$ (**).

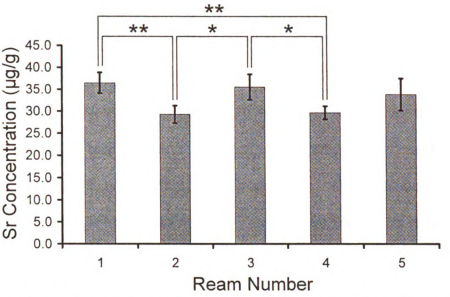

Figure 4.7. Sr concentration in New Leaf Paper®, reported as µg Sr per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

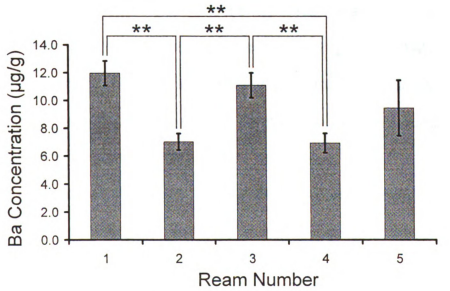

Figure 4.8. Ba concentration in New Leaf Paper®, reported as µg Ba per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.01$ (**).

For the New Leaf Paper®, the same pattern was apparent for all of the elements chosen. The Tukey test was able to group the reams into a few groups. Reams 1 and 3 were distinguished from reams 2 and 4 at the 95% confidence level or higher and vice versa based on all of the elements used for discrimination (Mg, Al, Sr and Ba). Reams 1 and 3 were not distinguished from each other and reams 2 and 4 were not distinguished from each other. Ream 5 was not distinguished from any of the reams. In looking at the elemental concentrations ream 5 has concentrations that were in between the concentrations seen in the group of ream 1 and 3 and the group of ream 2 and 4. This made it statistically indistinguishable from any of the other reams. Interestingly reams 1, 3, and 5 had the same marking on the ream wrapper (JD6041015) and reams 2 and 4 had very similar marking (JC6041115 and JD6041115, respectively). This suggested that these ream markings had some association with a batch or manufacturing time frame because the elemental concentrations were statistically the same for some of the similarly marked reams. It is also interesting to note that ream 5 had the same markings as 1 and 3 and, while it was not a statistically significant difference, the mean concentrations were different than 1 and 3 suggesting that there could be some variation within a single batch.

The other criterion to look at was the level of statistical significance indicated by the * ($p \leq 0.05$) or ** ($p \leq 0.01$) in the figures. Both the Al and the Ba have all of the differences significant at the 99% confidence level. The larger difference in the mean concentration of Al and Ba (Al: 338 ± 35 μg/g for ream 1 and 561 ± 48 μg/g for ream 2, Ba: 12.0 ± 0.9 μg/g for ream 1 and 7.0 ± 0.6 μg/g

for ream 2, vs. Mg: 1070 ± 71 µg/g for ream 1 and 956 ± 72 µg/g for ream 2) led to higher statistical significance of the comparison. Because only a small population of reams was studied it is impossible to make overall conclusions but the preliminary results of this study suggest that Al and Ba would be the best choice for discrimination between reams of New Leaf Paper®.

4.3.2. Staples®

Elemental concentrations in sheets and reams of Staples® paper were statistically compared using the previously described procedures. The two-way ANOVA results are shown in Table 4.4.

Table 4.4. Two-way ANOVA results for Staples® paper. Significant differences defined as p-value ≤ 0.05.

Element	sheets (n=3)		reams (n=5)	
	p-value	significant	p-value	significant
Mg	0.139	no	6.79×10^{-5}	yes
Al	0.512	no	2.07×10^{-4}	yes
Mn	0.539	no	1.95×10^{-4}	yes
Fe	0.193	no	0.0384	yes
Sr	0.384	no	2.08×10^{-6}	yes
Y	0.407	no	1.27×10^{-6}	yes
Ba	0.544	no	0.0258	yes
Ce	0.480	no	0.0302	yes
Nd	0.391	no	0.498	no

Both the New Leaf Paper® and the Staples® showed no statistical difference among concentrations of elements throughout a single ream. There was also no effect of the paper being in contact with the ream wrapper as the very top and bottom sheets were sampled. This is important because in forensic sampling only a small portion of the document will be sampled and it is important that the sampled analyzed is representative of the whole sheet. Also it is important that the ream is consistent so a single sheet that has been removed from the ream

(i.e., questioned document) will have the same elemental concentration of the other sheets in that ream used for comparison.

The variation between the mean elemental concentrations of the reams was calculated (n=15, 3 sheets with 5 samples each) and the resulting p-values are displayed in Table 4.4. Every element, with the exception of Nd, had statistical differences. To investigate further the Tukey test was employed to obtain pairwise comparisons to determine which reams could be distinguished. The results of the Tukey test are displayed graphically in Figures 4.9 through 4.16 for each of the elements that showed a significant difference in concentration among the 5 reams with ANOVA.

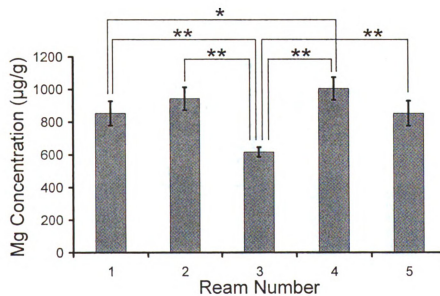

Figure 4.9. Mg concentration in Staples® brand paper, reported as µg Mg per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

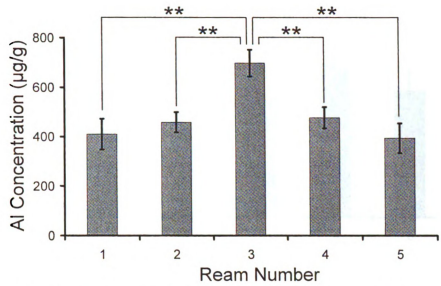

Figure 4.10. Al concentration in Staples® brand paper, reported as µg Al per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.01$ (**).

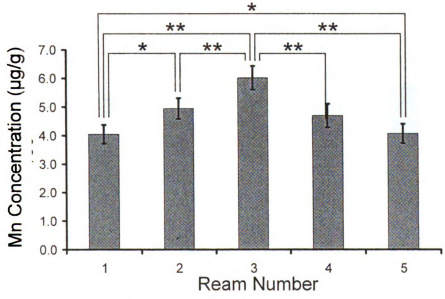

Figure 4.11. Mn concentration in Staples® brand paper, reported as µg Mn per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

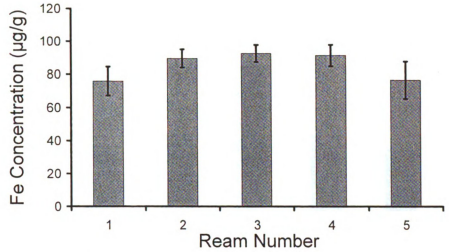

Figure 4.12. Fe concentration in Staples® brand paper, reported as µg Fe per g paper. Error bars represent standard deviation. No significant differences between pairs.

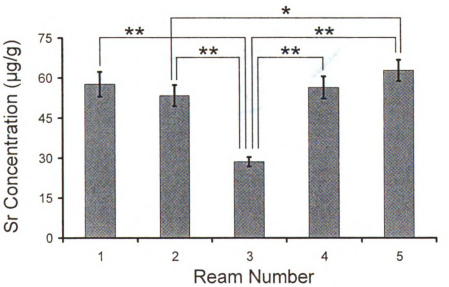

Figure 4.13. Sr concentration in Staples® brand paper, reported as µg Sr per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

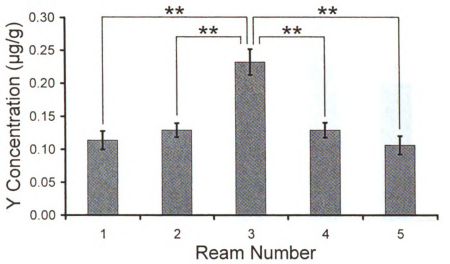

Figure 4.14. Y concentration in Staples® brand paper, reported as µg Y per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.01$ (**).

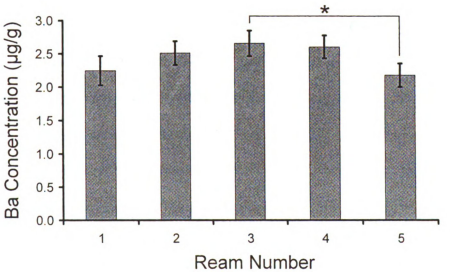

Figure 4.15. Ba concentration in Staples® brand paper, reported as µg Ba per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*).

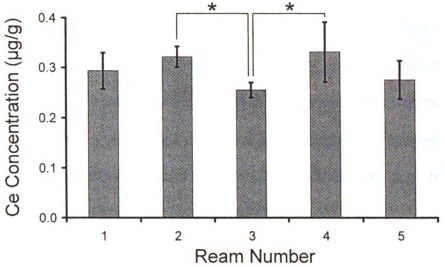

Figure 4.16. Ce concentration in Staples® brand paper, reported as µg Ce per g paper. Error bars represent standard deviation. Significant difference between values with $p \leq 0.05$ (*).

Using the results of the Tukey test, two of the reams of paper (1 and 3) were able to be discriminated from all other reams based on elemental concentration. Ream 3 had different elemental concentrations than all other reams for Mg, Al, Mn, Sr and Y, at a 99% confidence level. Ream 1 was also differentiated from all other reams; the Mn concentration was significantly different from reams 2 and 5 at the 95% confidence level, the Mg concentration was different from ream 4 at the 95% confidence limit and Mg, Al, Mn, Sr and Y concentrations were different from ream 3 at the 99% confidence limit. Ream 2 was found to have a different Sr concentration from ream 5 at a 95% confidence limit. Reams 2 and 4 could not be differentiated from each other nor could reams 4 and 5.

Because nearly all of the elemental concentrations of ream 3 were so different from the other reams, this suggests that ream 3 came from an entirely

different batch. This is not known for sure because there were no markings on the packages. Ream 1 could also be differentiated from all the others but every elemental concentration did not differ from all other reams. This is promising because only a very small population (n=5) of reams was tested, all purchased at the same time, and a significant difference was observed. However, it should also be noted that there were pairs of reams in this sample set (e.g., reams 2 and 4, reams 4 and 5) that could not be differentiated.

Based on these observations it seems that Mg, Mn, and Sr were the most useful elements for comparison of Staples® paper because these elements were able to discriminate the largest number of pairs. No statistically different pairs were observed for Fe, despite a p-value of 0.04 from ANOVA. Even though ANOVA indicated that there was statistically significant variance between the reams the Tukey test did not identify any pairs that were statistically different from one another. The concentration of Ba was relatively constant across all of the reams and the only statistical difference was observed between the highest and lowest values (reams 3 and 5). Ream 3 had very different elemental compositions from all of the other reams. Al and Y were very different in ream 3 as compared to the others but were unable to differentiate any other pairs. While Al and Y were not very useful in this small population (n=5 reams) there was one ream in this population that was different than the other suggesting that if a larger number of reams were tested it is possible that more variations in Al and Y would be observed. Additionally the suite of elements was optimized using New Leaf

Paper® digests so it is possible that elements only present in Staples® were not studied and these elements could offer more discrimination.

4.4. Variation Between Vendors

In these studies, two paper types manufactured in the United States, both of 100% recycled materials, were investigated. Students t-tests were used to determine if there were significant differences in the means of the elemental concentrations between the two sample sets. The average concentrations of each of the samples (n=75, 5 reams, 3 sheets from each and 5 samples per sheet) and the results of the t-test are displayed in Figure 4.17. In this figure, the bars represent the average concentration of the element throughout all the samples taken from the vendor and the error bars represent the standard deviation of these measurements. Similar to the previous figures, pairs of samples with significant differences are connected by a line and the * ($p \leq 0.05$) or ** ($p \leq 0.01$) indicates the significance level. The t-test showed there were differences in the Ba and Nd concentrations at the 99% confidence level and Sr and Ce at the 95% confidence limit.

Ternary plots were used to graphically show the differences in the elemental composition of the papers. These types of plots make it very easy to visually see similarities and differences between the samples and are useful for court presentations to juries.[11] Only three elements can be used for each ternary plot, so two plots were made one with Ba, Nd, and Ce and the second with Ba, Nd, and Sr. The elemental ratios are plotted on three axes as the proportion of each element so the sum was equal to 1.0 (e.g., Ba + Nd + Ce = 1.0).

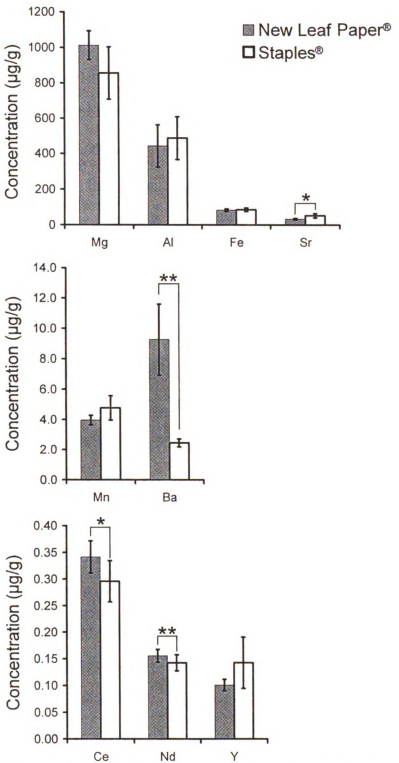

Figure 4.17. Concentration of trace metals found in the paper samples from New Leaf Paper® and Staples® brand. The error bars represent standard deviation of the values n=15. Significant difference between values with $p \leq 0.05$ (*) or $p \leq 0.01$ (**).

Each of the five reams from each vendor is plotted in Figures 4.18 and 4.19. Two groups are clearly formed, each containing the 5 reams from the different vendors, as illustrated in Figures 4.18 and 4.19.

The elements that were most useful for discriminating the reams from the same vendor were Al and Ba for the New Leaf Paper® and Mg, Mn, and Sr for Staples® paper. The Ba (New Leaf Paper®) and Sr (Staples®) were also elements that significantly different concentrations between the vendors. Note in Figure 4.18 the New Leaf Paper® samples are more spread out across the Ba axis than the Staples® because Ba is also a discriminating element for the New Leaf Paper®. Similarly in Figure 4.19 the Staples® samples are more spread across the Sr axis because this is a discriminating element for the Staples® papers. Of the two plots, Figure 4.18 is more useful to display differences between the vendors because the Sr variation in the Staples® makes that grouping much more spread out.

Both the Ba and the Sr have differences between the reams within a vendor and between the vendors. These two elements may originate from trace components of items (e.g., kaolin, TiO_2, pulping chemicals) added during the paper manufacturing process. There is some variation within a vendor of Ba and Sr but there is a larger variation between the vendors suggesting that the concentration of these elements is affected by the manufacturing process used by each vendor. Ba is a trace component in the filler material ($CaCO_3$) which may be added to the paper during the manufacturing. Small variations in Ba concentration among the vendors may occur based on the lot of $CaCO_3$ that is

used. If the different manufacturers who supplied each of the vendors used different amounts of $CaCO_3$ this could cause the large difference in the Ba concentration. If these trace elements were from variation in the wood pulp (i.e., naturally occurring in the tree cells) a difference between the vendors would not be expected.

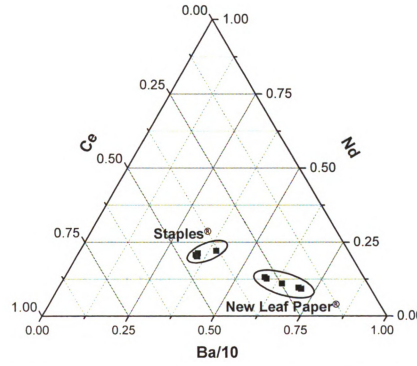

Figure 4.18. Ternary plot of the ratio of Ba, Ce and Nd. The Ba concentration was significantly higher than the Ce or Nd concentrations therefore it was divided by 10 to make the plot easier to read. Each point represents an average ream value, 5 reams from each vendor are plotted.

The Ba concentration of the New Leaf Paper® is approximately 280% greater than the concentration in the Staples® paper (9.3 ± 2.3 µg/g vs. 2.5 ± 0.3 µg/g) but the Nd is only about 10% greater in the New Leaf Paper® (0.16 ± 0.1 µg/g vs. 0.14 ± 0.1 µg/g). Although both of these differences are statistically significant at the 99% confidence limit, Ba would be much easier to use as a

discriminating element for these paper samples because of the larger increase. This is also evident in the ternary plot because the biggest separation in the two groups is along the Ba axis. The other benefit of using the Ba is the concentration is approximately 10 times higher than the Nd, making Ba much higher above the detection limit of the method.

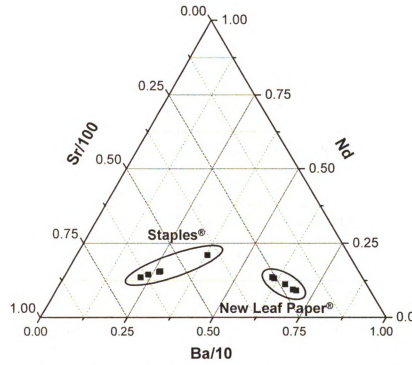

Figure 4.19. Ternary plot of the ratio of Ba, Sr and Nd. The Ba and Sr concentration were significantly higher than the Nd concentration therefore there were divided by 10 and 100, respectively, to make the plot easier to read. Each point represents an average ream value, 5 reams from each vendor are plotted.

4.5. Conclusions

The trace elemental concentrations appeared to be consistent across a single sheet as well as within a single ream. This indicated that each ream can be treated as a single source and it can be assumed that a single sample from

the ream will have the same elemental concentrations as any other sample from the ream.

There were statistically significant differences between the different reams. The different vendors had different discriminating elements. For the New Leaf Paper® the most discriminating elements appeared to be Al and Ba but for the Staples® paper Mg, Mn and Sr were more beneficial.

The papers that came from different vendors were easily discriminated from one another. In the samples that were used here the Ba concentration was the best element to compare, New Leaf Paper® had a concentration that was about 280% higher than the Staples® paper. Other elements (Sr, Ce, and Nd) also had significant differences.

If this technique were to be applied to a case sample the first analysis should be a full mass scan (m/z 7 – 240) for both the questioned document and the exemplar sample. This would determine if the samples had any immediate differences (i.e., presence or absence of element). If there were no immediate differences, based on this study the suggested elements to quantify would be Mg, Al, Mn, Sr, Ba, Ce, and Nd. The digestion and quantification would need to be done on the questioned document as well as exemplar samples from possible reams (sources). The elemental concentrations of the question document would be compared to the exemplar samples using a t-test. If significant differences were found between the questioned document and the exemplar then the paper could be excluded as coming from that source.

This study was only completed on a small number of ream samples collected over a relatively short time frame. A ream is an arbitrary packaging of 500 sheets of paper and it may not be known to a consumer, or forensic scientist, if two reams are from the same batch which may produce thousands of reams of paper. It is possible that the reams from each vendor sampled in this study were from the same batch; however, differences were still observed between the reams. More extensive sampling would be able to determine if the concentrations were consistent for a single batch or if smaller populations existed within a batch. Also additional research of different paper vendors and manufacturers may reveal element concentrations that are characteristic of a particular vendor or manufacturer.

4.6. References

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CHAPTER 5

CONCLUSIONS AND FUTURE WORK

In this work the trace elemental concentrations of document papers were examined to determine the forensic utility of this measurement. The paper that was examined was a common multipurpose copy paper made from 100% post-consumer waste. Two vendors (New Leaf Paper® and Staples®) were selected. From each, 5 reams were sampled and 3 sheets were sampled from each of these reams. A number of comparisons were made to determine the homogeneity of element concentration across a sheet of paper as well as throughout a ream. Statistical comparisons were made of the elemental concentrations of different reams as well as different vendors.

In order to determine the trace elemental concentrations of the paper sample a microwave digestion was performed followed by analysis with inductively couple plasma mass spectrometry (ICP-MS). In a digestion solution that contained only nitric acid (HNO_3) and hydrogen peroxide (H_2O_2), a complete digestion of paper the paper samples was not possible and a small amount of white particulate matter remained in the bottom of the vessel. The undigested portion was characterized by infrared spectroscopy (FTIR) and x-ray diffraction spectroscopy (XRD) and determined to be a mixture of kaolin (clay) and TiO_2, which are common filler materials in papers.

The paper could be fully digested if hydrofluoric acid (HF) was added to the digestion solution. However, this method is not desirable because HF is a very corrosive acid, requires larger paper samples, and additional evaporation

steps prior to ICP-MS analysis. A comparison of the digestion methods (HNO_3/H_2O_2 digestion in which particulates were present and HF digestion in which no particulates were present) showed that the reproducibility of the elemental concentrations was not affected by the presence of this particulate matter. Since an HF digest was not necessary, the elemental concentrations used for comparisons in this work were determined using the HNO_3/H_2O_2 digestion.

Once the digestion procedure was developed a suite of elements to analyze needed to be determined. Based on previous works as well as a full mass scan of one paper sample an initial list of element was generated (^{7}Li, ^{23}Na, ^{24}Mg, ^{27}Al, ^{45}Sc, ^{55}Mn, ^{52}Cr, ^{55}Rb, ^{56}Fe, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{107}Ag ^{114}Cd, ^{121}Sb, ^{138}Ba, ^{139}La, ^{140}Ce, ^{146}Nd, ^{208}Pb, ^{232}Th and ^{238}U). A full mass scan was performed on a single paper sample and some of these elements were eliminated (^{52}Cr, ^{55}Rb, ^{59}Co, ^{63}Cu, ^{107}Ag, ^{114}Cd, ^{121}Sb, and ^{139}La) because they were at concentrations below the instrument detection limit and additional elements were added to the list (^{120}Sn and ^{184}W). The procedural blank samples were analyzed and elements with a significant contribution from the background were eliminated as well as elements that were not homogeneous over a single sheet (relative standard deviation >15%). The final element suite was narrowed to include only ^{24}Mg, ^{27}Al, ^{55}Mn, ^{56}Fe, ^{88}Sr, ^{89}Y, ^{138}Ba, ^{140}Ce, and ^{146}Nd.

Statistical analysis was completed using analysis of variance (ANOVA) and Tukey tests to determine if any statistical differences existed and if so, between which pairs of samples. In all cases the trace elemental concentrations

were consistent across a single sheet as well as throughout a ream. This is important because when sampling only a small portion of a single sheet will need to be analyzed and it will be representative of the entire sheet. Likewise a single sheet that has been removed from a ream (i.e., questioned document) will have the same elemental concentrations of other sheets from the same ream. Therefore it is appropriate to sample a small section of a document for analysis and comparison.

There were statistically significant differences between the reams. For the New Leaf Paper® (NL), reams NL1 and NL3 were distinguished from reams NL2 and NL4 at the 95% confidence level or higher and vice versa based on the elemental concentrations of Mg, Al, Sr and Ba. Reams NL1 and NL3 were not distinguished from each other and reams NL2 and NL4 were not distinguished from each other. Ream NL5 was not distinguished from any of the reams. Interestingly, reams NL1, NL3, and NL5 had the same markings on the ream wrapper and NL2 and NL4 had very similar markings. This suggested that the reams that were grouped with one another were from the same batch and the ream wrapper markings were also correlated to a specific batch.

For the Staples® paper (S), two of the reams (S1 and S3) were able to be discriminated from all other Staples® reams based on elemental concentration. Ream S3 had different elemental concentrations than all other reams for Mg, Al, Mn, Sr and Y, at a 99% confidence level. Ream S1 was also differentiated from all other reams; the Mn concentration was significantly different from reams S2 and S5 at the 95% confidence level, the Mg concentration was different from

ream S4 at the 95% confidence limit and Mg, Al, Mn, Sr and Y concentrations were different from ream S3 at the 99% confidence limit. Ream S2 was found to have a different Sr concentration from ream S5 at a 95% confidence limit. Reams S2 and S4 could not be differentiated from each other nor could reams S4 and S5. The ream S3 was very different from all of the other reams suggesting that it may have come from an entirely different batch.

The different vendors had different elements that offered the best discrimination. For the New Leaf Paper® the best elements were Al and Ba but for the Staples® paper Mg, Mn and Sr were more useful. The Staples® paper had more elements that varied between the reams, but one ream (S3) was different from all others and accounted for a large number of the variations. It is promising to see that a paper of the same brand can vary so much in elemental concentration even when it was purchased from the same store and at the same time as the other reams tested.

A student's t-test was used to compare the elemental concentrations of papers that came from the different vendors. The vendors were easily discriminated from one another. In the samples that were tested in this work, Ba concentration was the best element to compare; New Leaf Paper® had a concentration that was about 280% higher than the Staples® paper. However, Sr, Ce, and Nd also showed significant differences in concentration between the vendors and could also be used for comparison.

Forensically this test is useful because it is known that the elemental concentrations within a ream of paper are consistent but differences exist

between reams therefore two papers can be compared and, if they have different elemental concentrations, they can be excluded from having come from the same source (ream). For example if it was suspected that a page in a will had been added after the original document was created, these two paper samples could be analyzed and compared. If it was found that the two pages had different trace elemental composition they could be excluded from having come from the same source. Based on the small sample used in this study, the recommended elements for comparison would be Mg, Al, Mn, Sr, Ba, Ce, and Nd.

Because this study only use a very small population there are many potential studies that can be done to further assess the utility of this method. First of all it would be difficult to determine how many reams have the same elemental concentrations. Studies need to be completed on papers from the same batch. For this, cooperation of a paper manufacturer would be necessary to obtain several samples from the same batch (i.e., a single pulp mixture) to determine how much, if any, variation is observed. It would also be interesting to investigate the elemental concentrations over time (e.g., months, years) to see how much they varied.

If more samples could be obtained for a larger number of vendors or manufacturers, it would be useful to determine if certain elemental concentrations are characteristic of a particular vendor or manufacturer. For example, all New Leaf Paper® may have a Ba concentration of around 9 μg/g while all other vendors have a much lower Ba concentration. This would be useful to narrow

the source of the paper to a particular vendor or manufacturer. Along the same lines, perhaps a study of different types of paper from the same vendor (e.g., copy paper, laser printer paper, inkjet paper) may point to some characteristic elemental concentrations that are characteristic of the paper type. These variations may be due to different fillers or sizing chemicals used to give the different paper types different characteristics.

In this work only paper used from 100% post consumer use was evaluated. Another study could examine the effect of the percentage of recycled material used in the paper on the variation seen in the elemental concentrations. In preliminary studies done for this work a few sheets of virgin and 30% recycled paper and these samples contained all of the elements that were used for the comparison of the 100% recycled paper, however, no assessment was made as to the discrimination ability of these elements in the other paper types. It is also possible that in paper that is made from recycled material or recycled paper may be easier to distinguish because it has a larger variability in the trace components.

Many of the trace elements in the paper may come from the pulp source (e.g., tree cells). Therefore there could be some variation in the trace element concentration depending on the type of fiber source used (e.g., tree, cotton, hemp). Also the geographical location where the tree or plant was grown may affect the trace elements present based on the composition of the soil.

Overall ICP-MS is promising for forensic analysis of paper. This chemical analysis of the trace elements present would be an addition to the traditional

document analysis. This test appears to be able to distinguish papers of the same type from the same vendor that traditional analysis would not be able to distinguish base only on physical characteristics.