Lynn Brostoff[1] and Sylvia Albro[2]
[1]Research Chemist, Library of Congress
[2] Senior Paper Conservator, Library of Congress

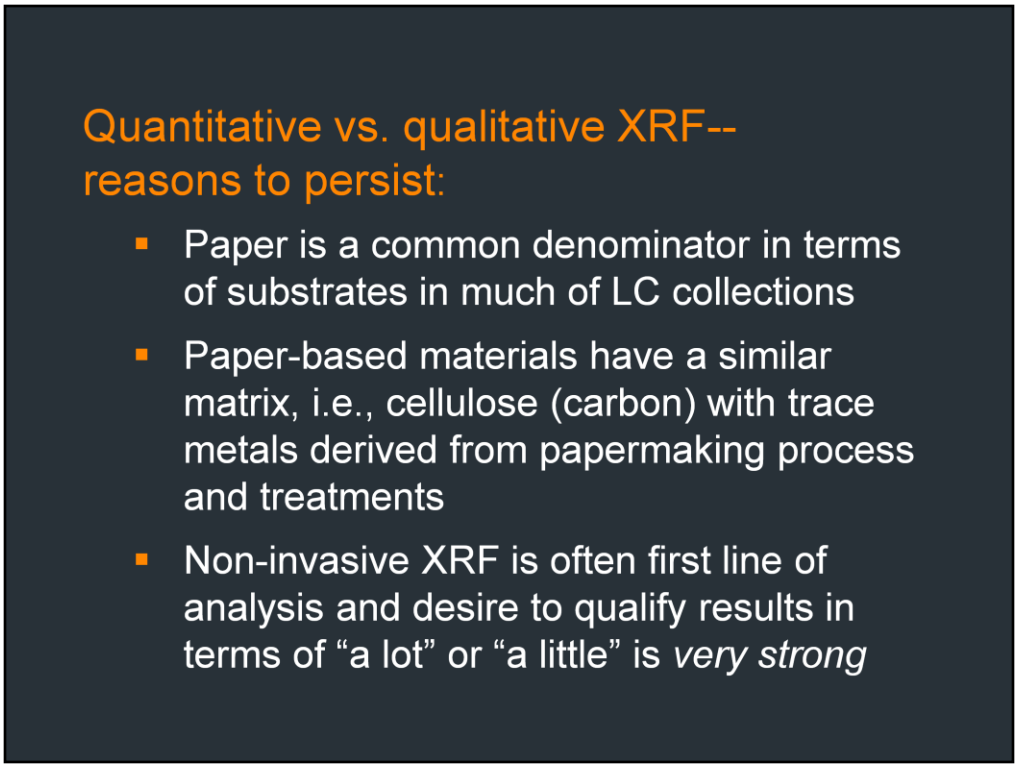
With contributions from:
Alice Han, former Jr. Fellow, Library of Congress; Josefina Maldonado, former HACU Intern, Library of Congress; Jae Anderson, formerly Library of Congress; John W.N. Brown, Student, and Michael Glascock, Director, University of Missouri Research Reactor (MURR) Archaeometry Laboratory.

Presented at the RATS session
40th Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
Albuquerque, NM, May 8-11 2012

Quantitative X-ray Fluorescence Methodology for Examination of Cultural Heritage on Paper

Lynn Brostoff,[1] Sylvia Albro,[1] Alice Han,[2] Josefina Maldonado,[2] Jae Anderson,[2] John W.N. Brown[3] and Michael Glascock[3]

[1]Library of Congress, Washington, DC
[2]former intern, Library of Congress, Washington, DC
[3]University of Missouri Research Reactor (MURR) Archaeometry Laboratory, Columbia, MO



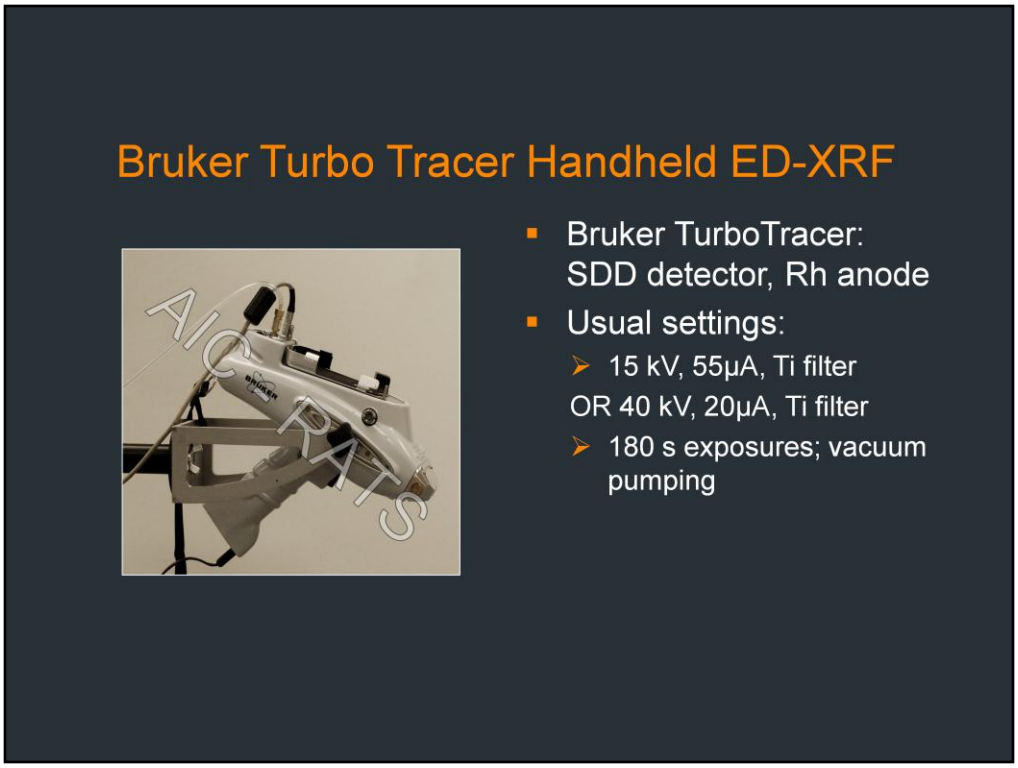
Library of Congress (LC)

Value of quantitative or semi-quantitative XRF results:

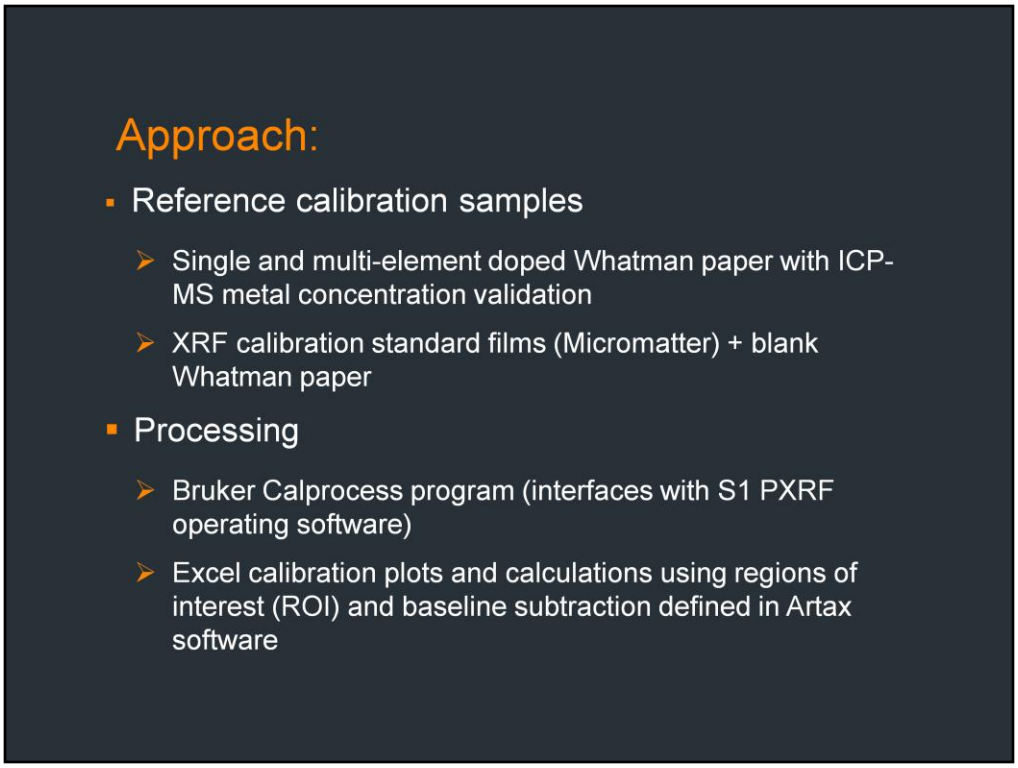
- determination of limit of detection (LOD)
- provenance/method of manufacture information
- treatment history information
- condition information
- treatment monitoring

Problems calibrating XRF spectra:

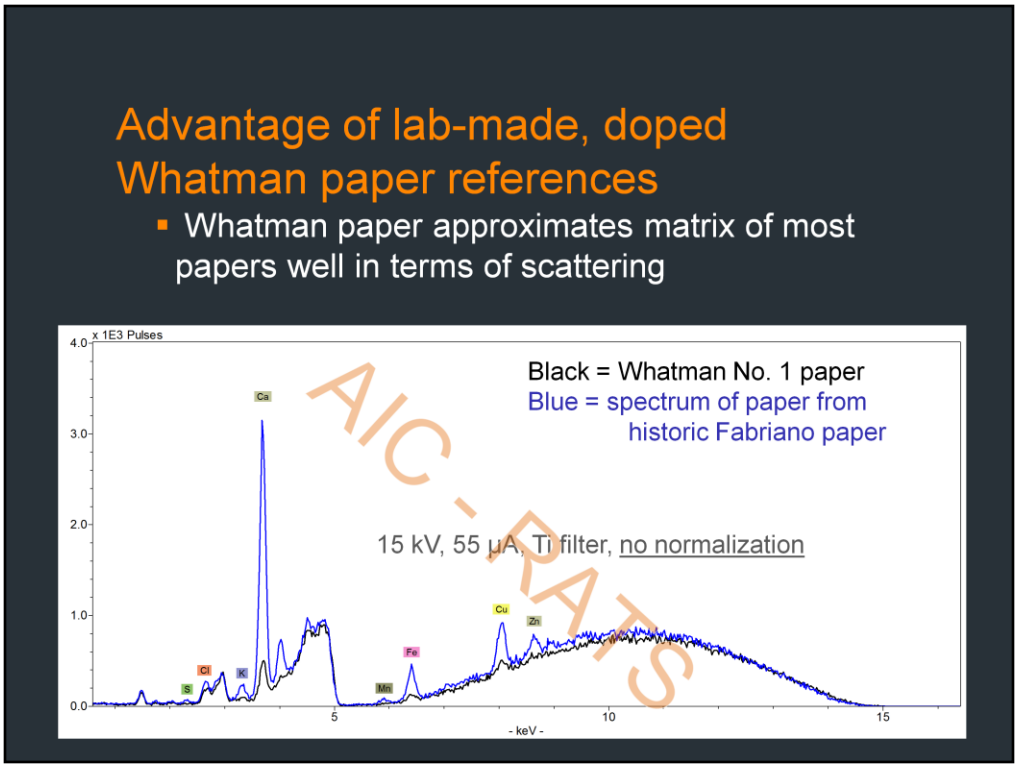
- differences in scattering of X-rays (→ baseline shape) caused by
  - material density
  - material thickness
- other matrix effects
  - inter-element interactions
  - element interferences (overlaps)
- sample non-homogeneity



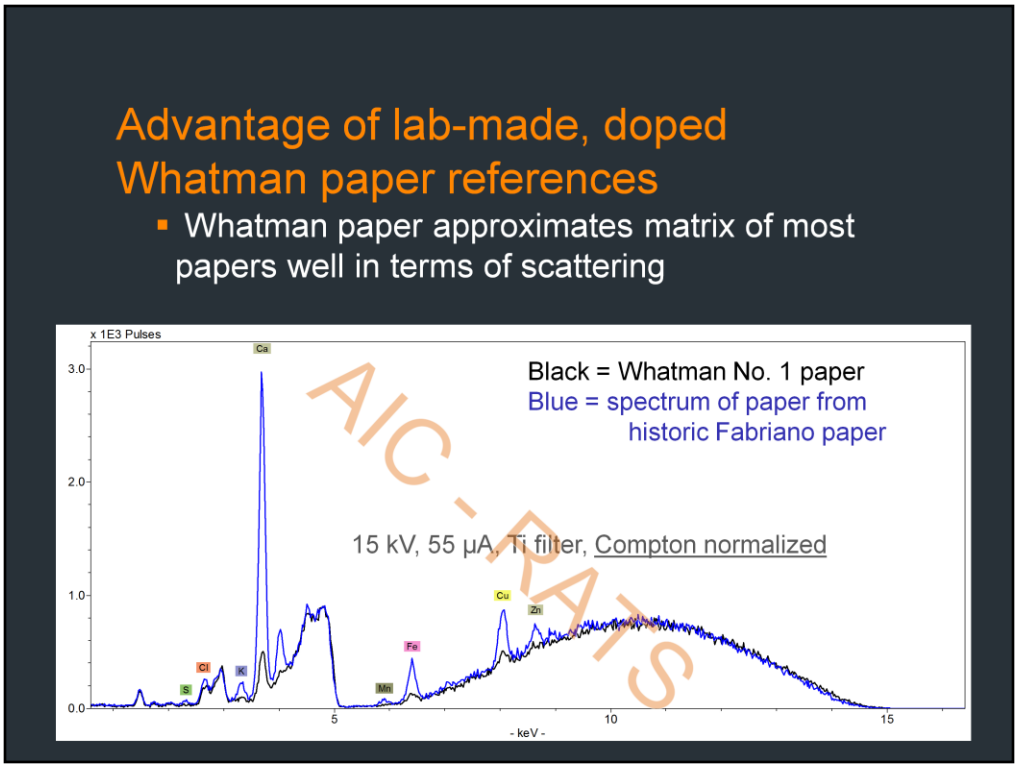
Instrument and common instrumental parameters used in Preservation Research & Testing Laboratory at the Library of Congress.



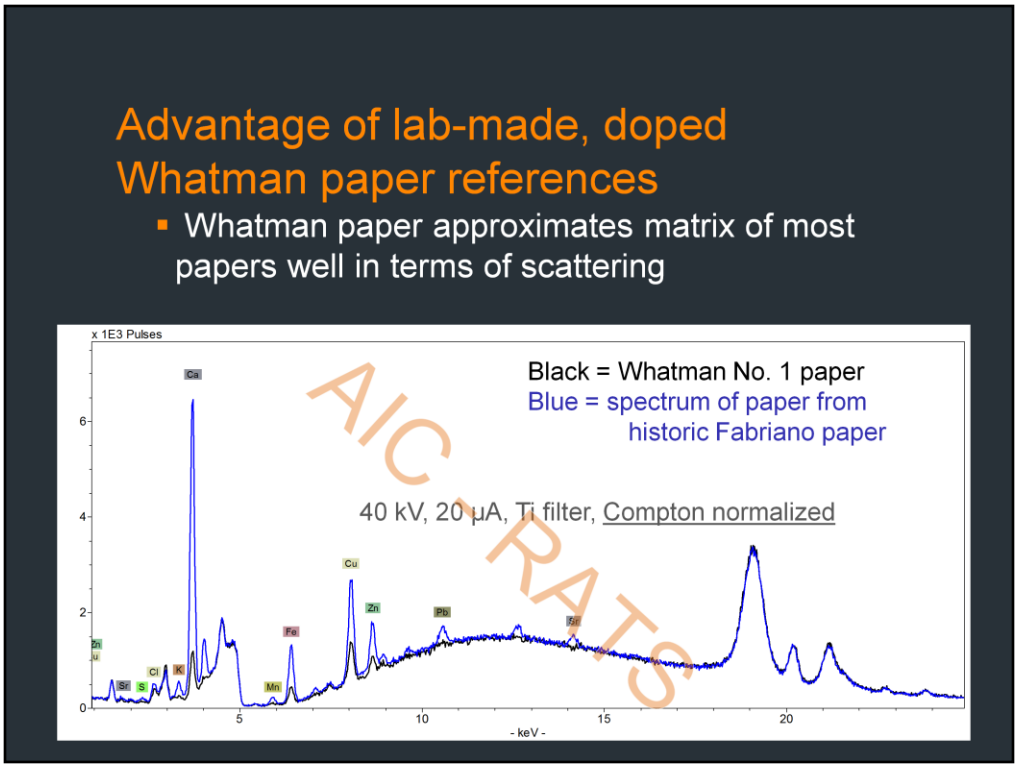
These are the most feasible and practical methods that were found.



The overlaid XRF spectra of a blank piece of Whatman filter paper (black) and an historical 18th century paper from Fabriano, Italy (blue) show that, even without normalization, the scattering characteristics of the two samples are similar at the instrumental settings shown. This indicates that the Whatman filter paper has a suitable matrix for making reference materials.



The same two spectra are normalized to the Compton scattering hump here. This operation allows for minor adjustments in sample thickness before quantification of peak intensities.

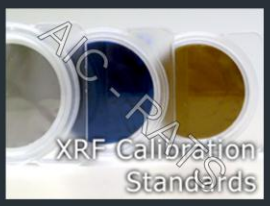


The overlaid XRF spectra of the same blank piece of Whatman filter paper (black) and historic Fabriano paper (blue), show that scattering characteristics of the two samples remain similar at other instrumental settings, as shown. Calibration curves were constructed using Compton normalized spectra of the doped reference papers at both sets of conditions (15 kV/55 µA or 40 kV/20µA with Ti filters).

The set of reference calibration papers used in this study were the first to be manufactured and were not optimal. Despite their flaws, the reference set has proved to be useful for method development and rough quantifications. The reference sample manufacture consisted of immersing the papers into salt solutions and air drying on a sheet of glass in the hood. The drying method was, however, too slow to avoid wicking of metals out to edges, resulting in non-homogeneous distribution. The papers were therefore analyzed only in the middle areas, which were found to be relatively homogeneous.

Advantage of purchased XRF calibration standards

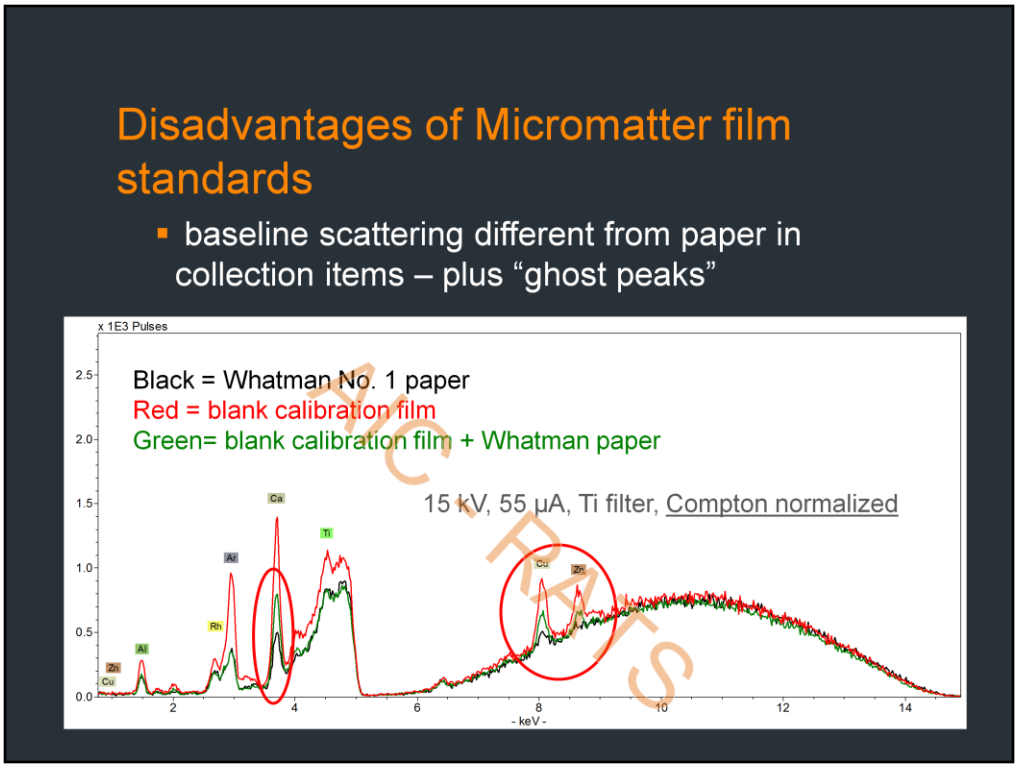
- pre-certified for concentration
- many metals and concentrations available and convenient to use



Micromatter standards: 6.3 µ Mylar films mounted in 36 mm rings with deposited metal salts

Alice Han, Jr. Fellow (from St. Mary's College of MD), 2011

The Micromatter standard films have the obvious advantage of pre-certified concentrations. These were recommended for use by Dr. Michael Glascock.

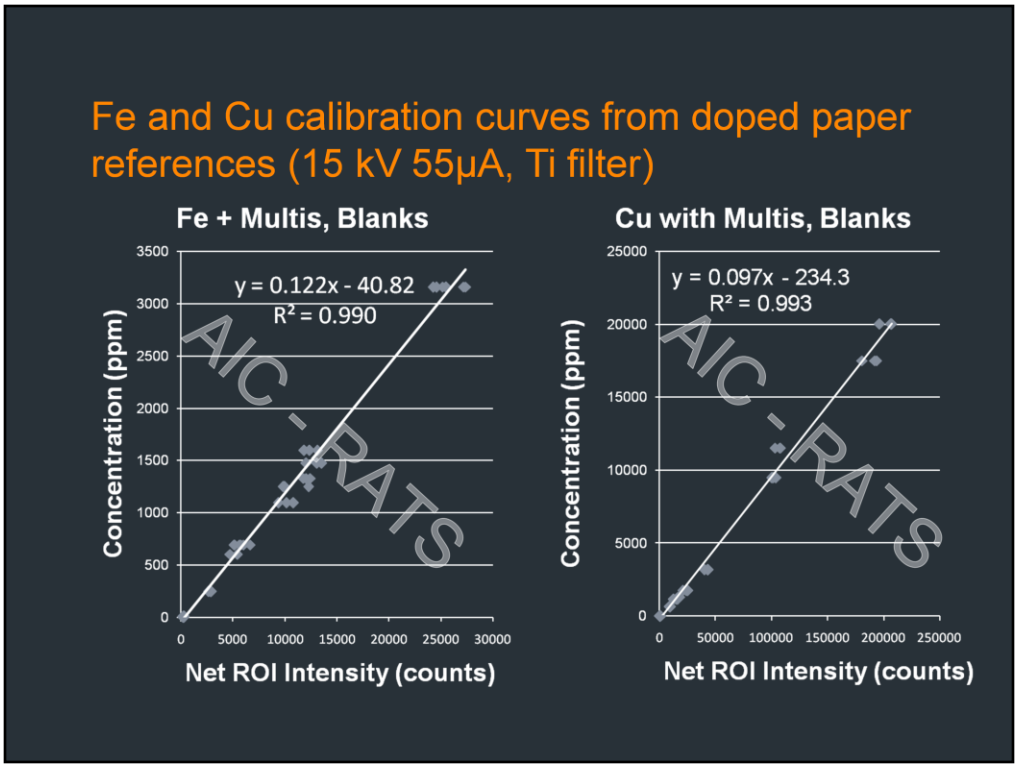


The blank Micromatter films have a serious disadvantage for use as paper calibration standards due to significant scattering and intensification of peaks, presumably arising from the Mylar (red spectrum). As shown in comparison to the blank Whatman paper spectrum (black), intensification of peaks associated with the instrument materials (Ti, Ca, Cu and Zn) leaves artifacts after Compton normalization. Slightly better matrix matching can be achieved by placing a piece of blank Whatman filter paper onto the films, with the film lying closer to the detector (green spectrum). The filter paper appears to dampen, but not completely diminish, the scattering effects, as seen in the circled areas and the Ti peaks. An additional disadvantage of the films is that repeated use can lead to abrasion, so that certified values will eventually be incorrect.

Processing of data (creation of calibration curves)

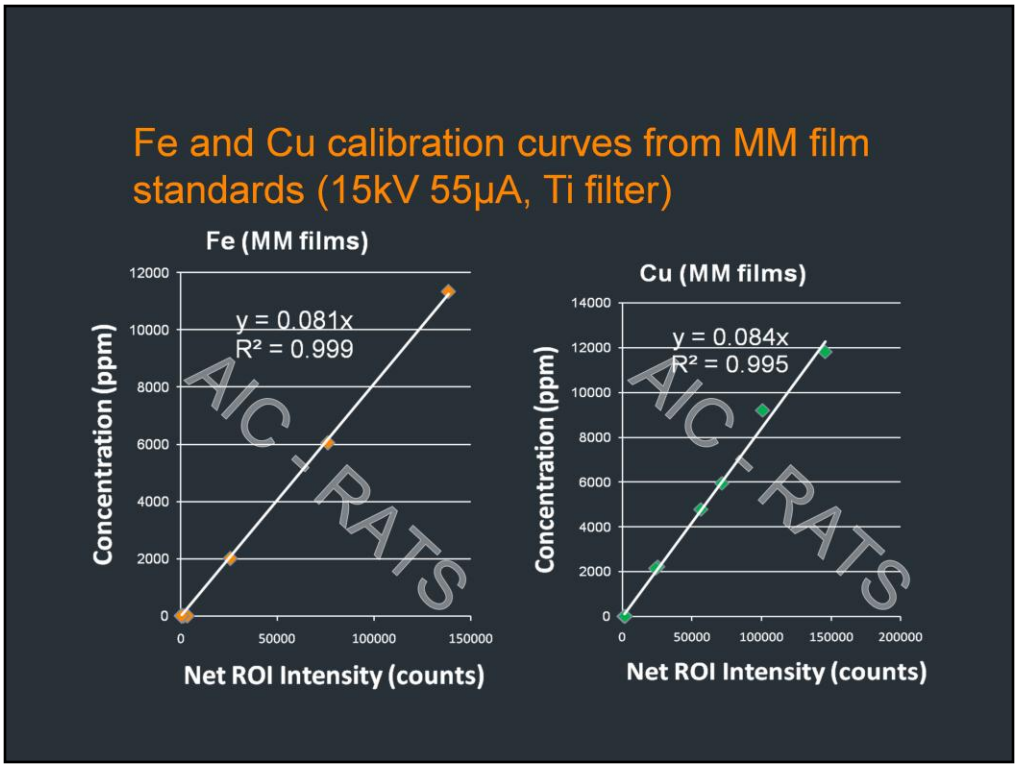
- Advantage of Calprocess: can be used conveniently in S1 PXRF
- Disadvantage of Calprocess: complicated to use and cannot see the curves created
- Advantage of using ROI (Artax)/Excel method: easy and can evaluate every aspect of curves created
- Disadvantage of ROI/Excel: somewhat laborious and can make mistakes

The XRF spectrum of a multi-element doped paper sample (filled) is shown overlaid with that of a blank Whatman filter paper (black line), using Artax software (Bruker, Inc.). This software allows definition of regions of interest (ROIs), shown by wide areas superimposed on elemental peaks. The elemental table at the lower right lists potential interferences in any ROI and helps define appropriate start and end energies, as shown for Fe. The area of each ROI under any selected elemental peak is given for both gross and net counts after background (blue line) subtraction; the table (bottom left) can be copied and pasted into a spreadsheet. In this method, reference and sample spectra have been normalized as a group to the Compton peak of the blank Whatman paper or blank film + Whatman paper, and net counts have been used.

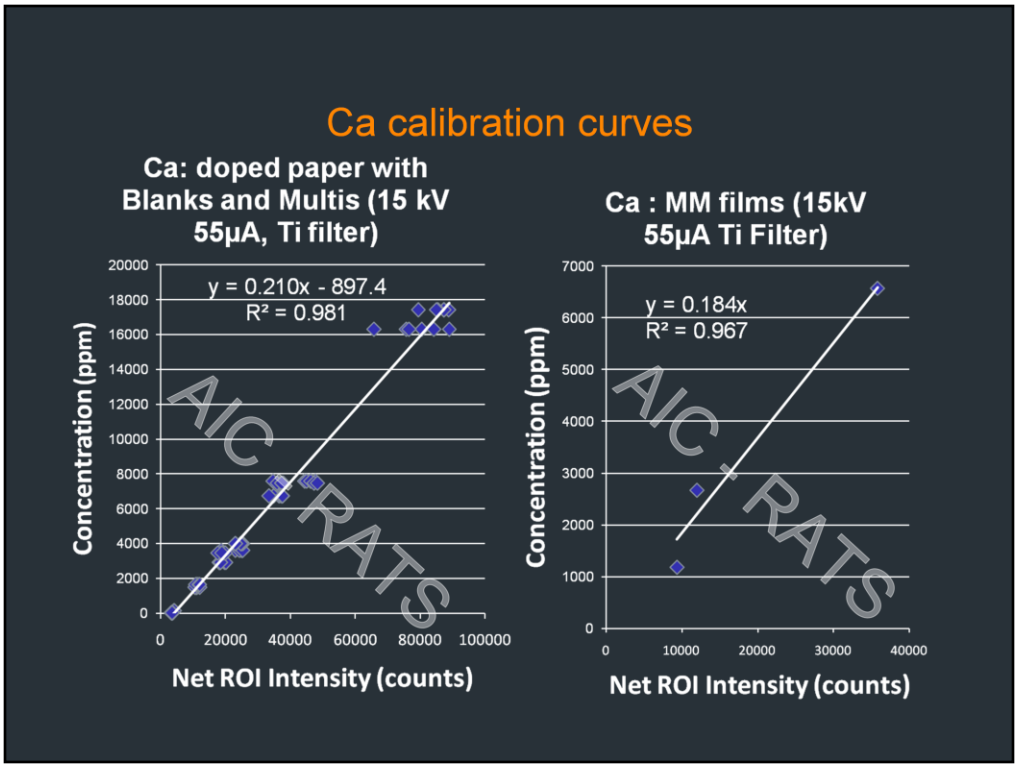


This slide shows two resulting calibration curves, where concentration is determined by ICP-MS and net ROI intensity values are given by Artax ROI definitions after background subtraction, as outlined in the previous slide. The curves are quite linear *in these concentration ranges*. It is important to limit the concentration ranges to those applicable to collection (i.e., sample) items, since a linear relationship may not be maintained at higher concentrations. Of the elements calibrated in this work, only potassium showed a second order relationship, rather than a linear one. The spread observed here in each concentration region represents both reading error, which is relatively small (as seen at low concentrations), and non-homogeneity in reference sample set, which is relatively large at high concentrations. As previously mentioned, these reference samples are not a final set. Production of better-quality samples in the future will tighten up clustering on the curves and the resulting precision. Additional validation of concentrations by other analytical techniques will correct slope accuracy.

Note that the curves are not forced through zero in order to account for the small Fe peak that is present due to steel parts in the instrument. Note also that the curves include data from multi-element samples, which fit nicely, indicating that any inter-element effects on Fe and Cu are low or negligible at these concentrations.

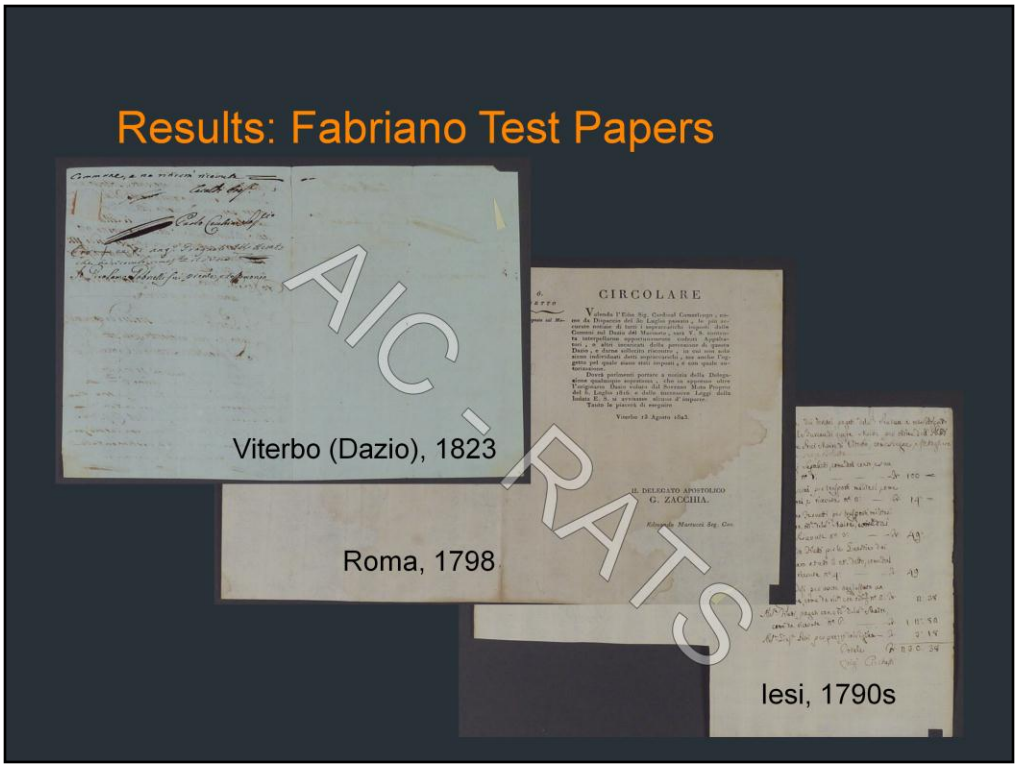


Initial Fe and Cu curves produced from the Micromatter films (with Whatman paper backing) show excellent correlation when forced through zero, which appears to partly compensate for scattering artifacts in these regions, as previously described. However, the total contribution of the film scattering effect is not well understood. Note that the limited data set shown here is a result of keeping readings for each film to a minimum, since reference films can easily be abraded through use.



Calibration of Ca using the doped papers (left) shows a linear relationship in the limited concentration range represented; this range is appropriate to historic materials encountered in collections. Note the spread of values at higher concentrations again, most likely arising from non-homogeneity in the reference samples. In addition, note that ICP-MS validation was only conducted on one set of samples, so that further validation both of more samples and in another laboratory is necessary for good accuracy in this case.

The initial Ca Micromatter (with Whatman paper backing) curve, in contrast, appears problematic, as is easily seen. Curves for Micromatter films of all elements produced using 40 kV and 20 µA appeared even worse, probably due to magnification of Ti, Rh, and other artifacts that occur at this higher power setting.



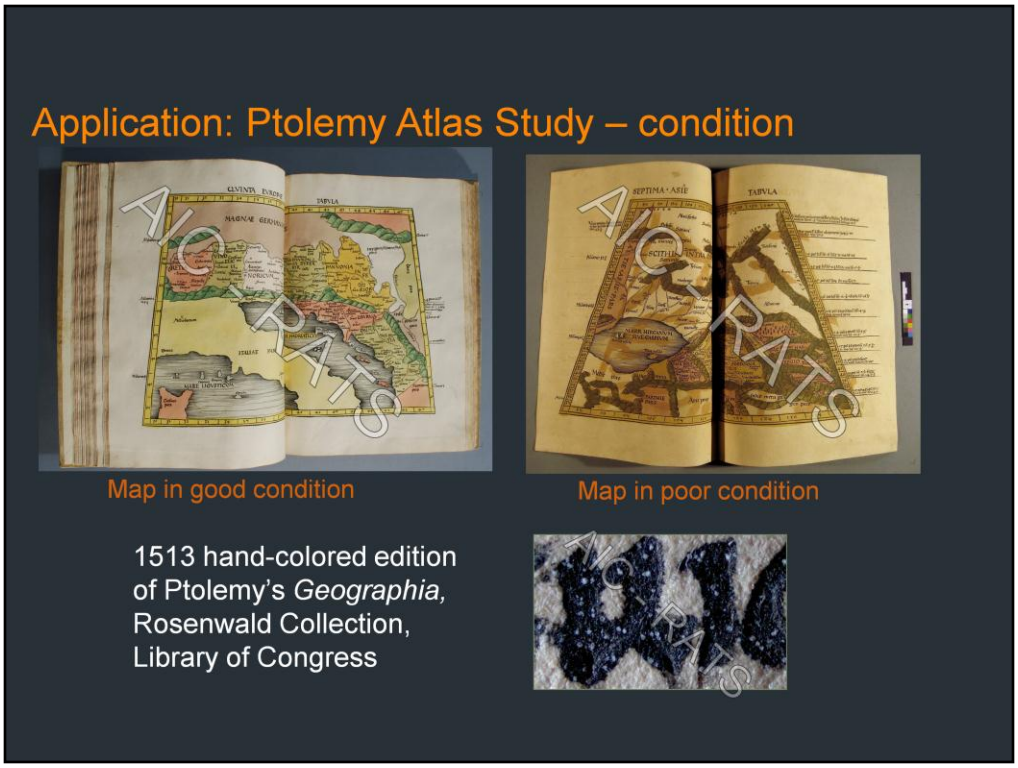
The papers shown are from a set of test papers used to see how well different calibration curves predict metal concentrations, which were determined for K, Ca, Fe, Cu, Zn and Pb by ICP-MS.
These papers were collected by Sylvia Albro for her research into the history of papermaking in Fabriano, Italy from the 17th – 19th C. They are not part of the LC collections and can therefore be cut up.

Comparative Results: Fabriano Papers (15kV 55μA Ti filter)

Sample	K ppm	K error	Ca ppm	Ca error	Fe ppm	Fe error	Cu ppm	Cu error	Zn ppm	Zn error
Doped Papers/Calprocess										
Multi-element #11*	2900	19%	1600	0%	660	9%	2000	13%	210	12%
Multi-element #12*	1100	9%	2900	1%	1400	12%	660	6%	140	0%
Viterbo (Dazio) 1823	700	15%	4300	1%	220	14%	<LOD	192%	<LOD	988%
Iesi 1790s	690	35%	3300	3%	110	15%	340	39%	<LOD	745%
Viterbo 1876	280	22%	3100	17%	51	67%	<LOD	210%	1100	46%
Doped Papers/ROI-Excel										
Multi-element #11*	3700	1%	1400	11%	620	2%	2100	19%	170	8%
Multi-element #12*	1400	15%	2700	6%	1200	3%	700	13%	140	0%
Viterbo (Dazio) 1823	500	17%	3700	13%	240	7%	<LOD	49%	<LOD	983%
Iesi 1790s	530	4%	2900	15%	150	9%	230	4%	<LOD	819%
Viterbo 1876	290	21%	5400	46%	190	21%	<LOD	101%	2000	2%
Micromatter Films										
Multi-element #11	2200	40%	1400	12%	520	13%	1800	1%	300	56%
Multi-element #12	840	32%	2300	20%	1100	13%	670	7%	100	27%
Viterbo (Dazio) 1823	410	33%	2200	49%	200	21%	<LOD	176%	<LOD	670%
Iesi 1790s	440	15%	1800	46%	130	3%	340	38%	<LOD	977%
Viterbo 1876	140	62%	1700	55%	85	44%	<LOD	91%	1600	22%

*calculated from curves that omit these doped samples

This table shows concentrations calculated from different methods for select samples; in the case of multi-element doped papers, results are calculated from curves that were produced without those individual samples. The Fabriano paper results (Viterbo and Iesi papers) are produced from one reading only on each paper, so that the margin of error may be much greater here due to likely uneven distribution of the metals. Nevertheless, these initial results overall look quite good when calculated by the top two methods, as shown by error (percent difference from ICP-MS value) that is generally <20% above detection limits (LOD-see slide 23), with some exceptions. The most notable exception is the Viterbo 1876 paper, which shows error that is relatively high across the board by all three methods. This is due to altered scattering in the matrix caused by relatively large amounts of Zn, and is a good warning against trying to quantify results for any sample that is not well matrix matched to the calibration standards. The altered scattering is easily observed in the baseline of the raw spectrum of this sample (not shown). Note also that the Calprocess method utilized here benefited greatly from calibration curves that were plotted out in Excel from ROIs defined in Artax (the second method), which showed whether curves were linear or second order and therefore gave guidance for manipulations allowed in Calprocess.

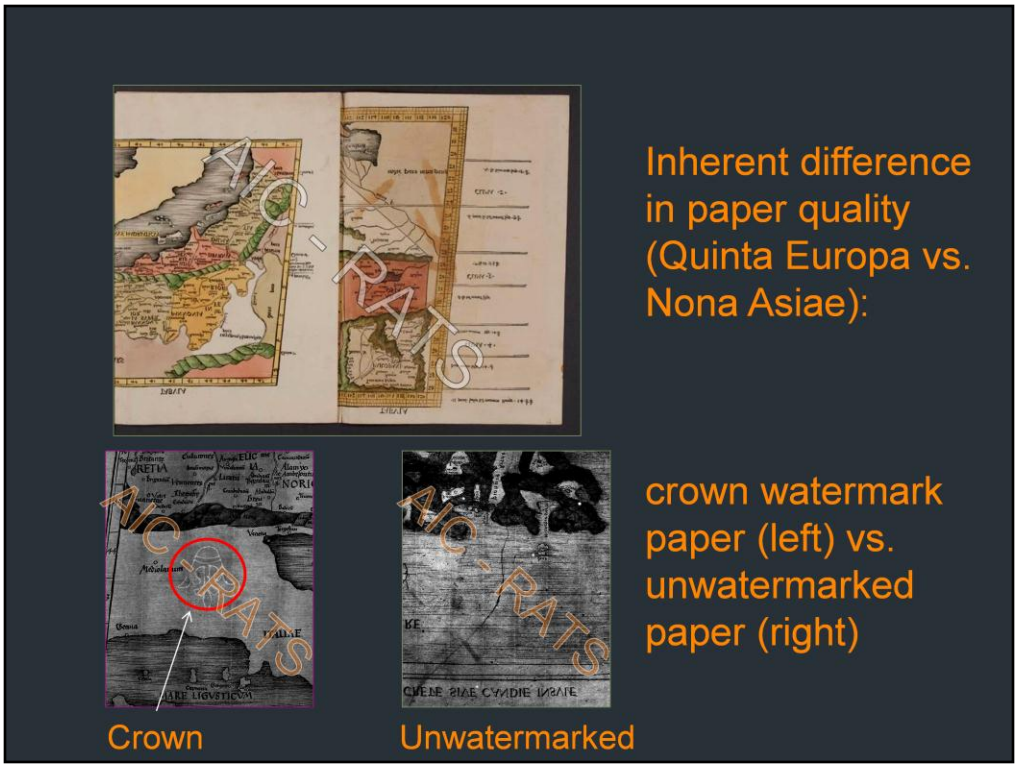


Two papers were presented about the Ptolemy *Geographia* technical study at 2011 AIC meeting, and have also been published in the AIC's Book and Paper Annual:

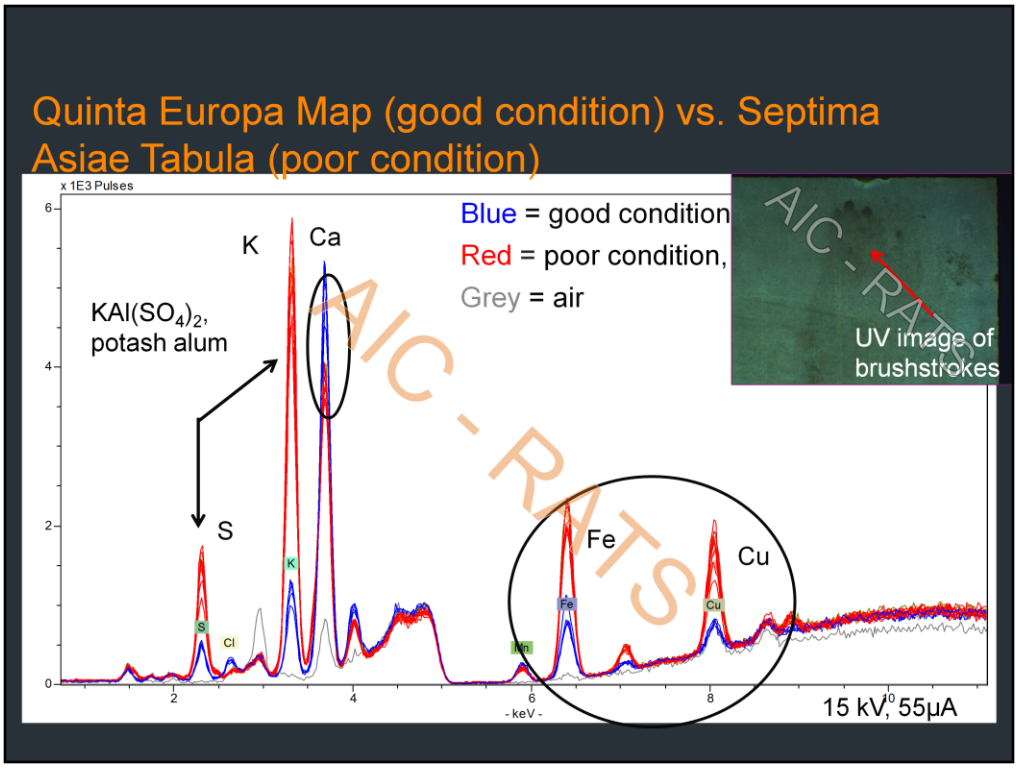
Brostoff, Lynn, Sylvia Albro, John Bertonaschi and Eliza Spaulding, The Relationship between Inherent Material Evidence in Cultural Heritage and Preservation Treatment Planning: Solving the Ptolemy Puzzle, Part II, *Book and Paper Annual 30* (2011): 29-33.

Albro, Sylvia, John Bertonaschi, Lynn Brostoff, Daniel De Simone, Fenella France, and Eliza Spaulding. Solving the Ptolemy Puzzle. *Book and Paper Annual* (2011): 5-8.

A central aim of this study seeks to explain why only 7 out of 47 hand-colored maps in the Ptolemy Atlas, all containing verdigris pigment, are in poor condition. Note that identification of verdigris was confirmed by polarizing light microscopy and other means. For example, the Quinta Europa Map (left) is cream colored and in good condition. In contrast, the Septima Asiae Tabula (right) has verdigris pigment-induced offset and discoloration, and is now medium brown and in fairly poor condition. In addition, as shown in lower right inset, white accretion/particles are observable on this and other maps in poor condition.



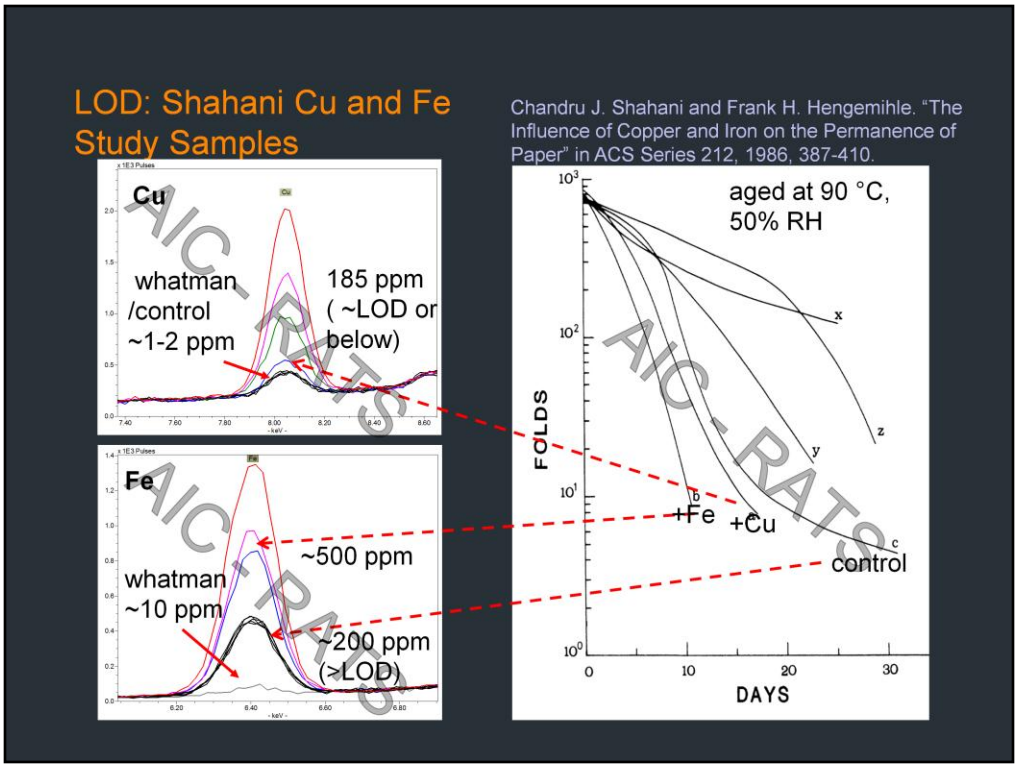
Further inspection revealed that there are three types of paper in the volume in terms of watermark. Two of the three different types of paper in the volume are shown here in visible and transmitted light. The maps printed and colored on laid paper with a crown watermark (upper and lower left) are generally in very good condition and exhibit expert papermaking qualities: even fiber distribution and mould lines. In contrast, maps and text on the unwatermarked paper (upper and lower right) appear inferior in terms of condition, flexibility, fiber distribution and mould line regularity. This is described in more detail in: Albro, Sylvia, John Bertonaschi, Lynn Brostoff, Daniel De Simone, Fenella France, and Eliza Spaulding. Solving the Ptolemy Puzzle, *Book and Paper Annual* (2011): 5-8.



XRF analysis of maps in varying condition revealed distinct differences in elemental profiles that appear to correspond to these different papers and their respective conditions. As exemplified by overlaid spectra from multiple spots on the paper substrates (away from colorants) of the Quinta Europa and Septima Asiae maps, poor condition substrates are characterized by relatively larger amounts of S, K, Fe and Cu (red spectra) and good condition substrates are characterized by relatively higher levels of Ca (blue spectra).

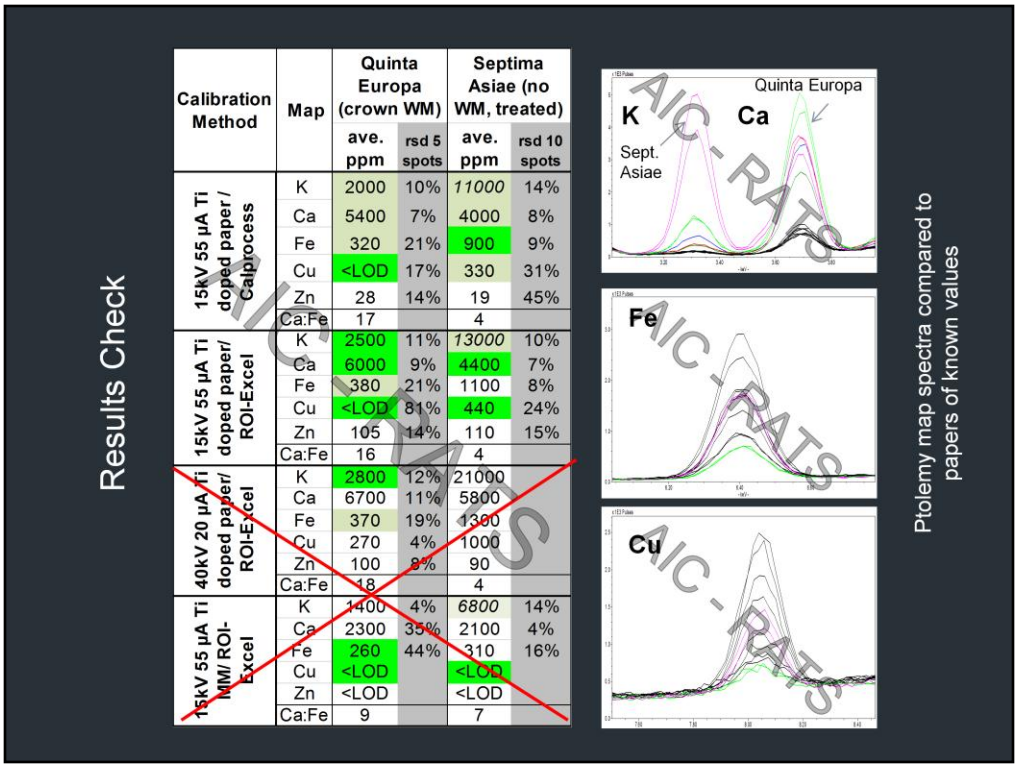
Detection of K and S here suggests the presence of K-alum, which was also confirmed by Raman and FT-IR spectroscopy. Note that these elements are also present in the map in good condition, but at much lower levels, such as may be expected from K-alum that is added to harden gelatin sizing. However, UV imaging (upper right inset) and FT-IR analysis (not shown) strongly suggest that the quite high levels of K alum detected on this and the other six maps in poor condition are the result of a gelatin solution having being brushed onto their surfaces. The red spectra here also show relatively greater amounts of Fe and Cu, the latter possibly as a result of brushing the alum solution over the Cu-containing pigmented areas, thereby spreading Cu ions in the paper.

This example raises the question of whether the concentration of various elements affects longevity in the paper substrate. In this case, *quantitative* XRF data was applied as an aid to understand the condition of the artifact.



Quantitative XRF also allows us to define the limit of detection (LOD) in an XRF experiment, so that we understand what lack of detection for any element means. In this illustration, LOD is defined for Fe and Cu at 15 kV, 55 µA and with a Ti filter from samples of known concentration that were produced for a former LC study on the effect of trace metals on paper longevity conducted by C. Shahani (reference above), selected results of which are shown at right. For Cu (upper left inset), XRF spectra of a blank Whatman paper and the Shahani study control paper show indistinguishable peak intensity; i.e., 1-2 ppm Cu is <LOD. In the case of 185 ppm Cu, the peak intensity is near LOD, within experimental error. On the other hand, Shahani study control paper show that 200 ppm Fe (below left inset) is easily distinguishable from a Whatman blank paper containing about 10 ppm Fe.

In relation to paper longevity and condition as described by the Shahani study, quantitative XRF thus allows a simple means of identifying artifacts on paper that contain levels of Fe and Cu that may be expected to compromise their aging behavior.



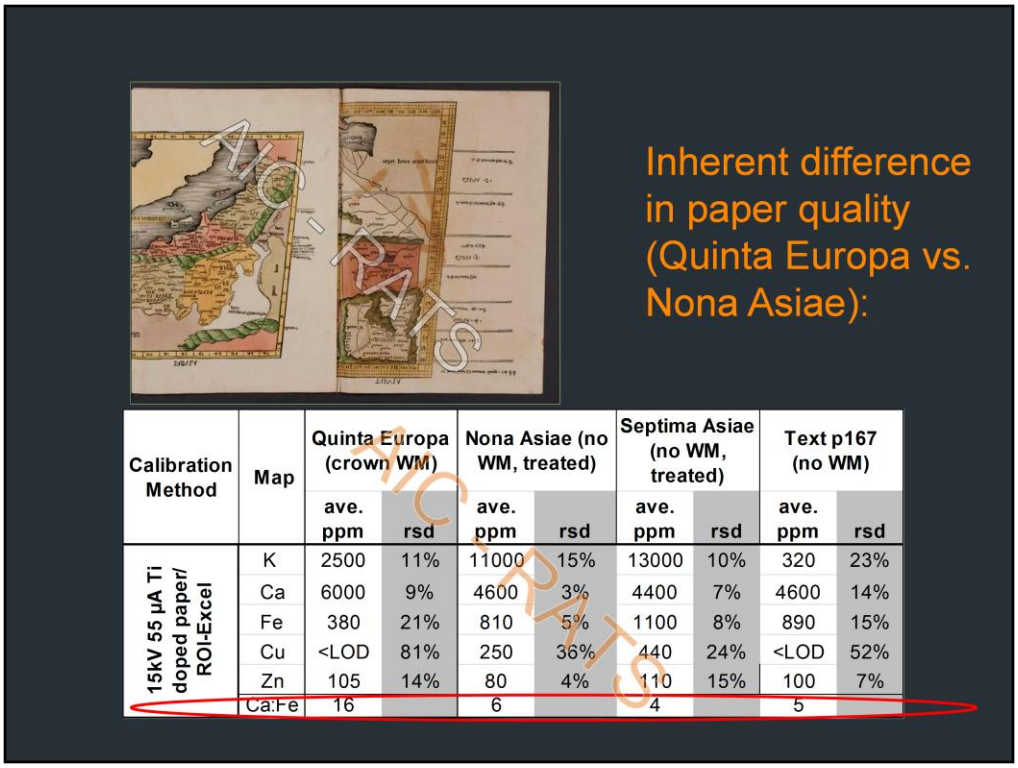
Calibration Method	Map	Quinta Europa (crown WM) ave. ppm	Quinta Europa (crown WM) rsd 5 spots	Septima Asiae (no WM, treated) ave. ppm	Septima Asiae (no WM, treated) rsd 10 spots
15kV 55 µA Ti doped paper / Calprocess	K	2000	10%	*11000*	14%
	Ca	5400	7%	4000	8%
	Fe	320	21%	900	9%
	Cu	<LOD	17%	330	31%
	Zn	28	14%	19	45%
	Ca:Fe	17		4	
15kV 55 µA Ti doped paper/ ROI-Excel	K	2500	11%	*13000*	10%
	Ca	6000	9%	4400	7%
	Fe	380	21%	1100	8%
	Cu	<LOD	81%	440	24%
	Zn	105	14%	110	15%
	Ca:Fe	16		4	
40kV 20 µA Ti doped paper/ ROI-Excel	K	2800	12%	21000	
	Ca	6700	11%	5800	
	Fe	370	19%	1300	
	Cu	270	4%	1000	
	Zn	100	8%	90	
	Ca:Fe	18		4	
15kV 55 µA Ti NM/ ROI-Excel	K	1400	4%	*6800*	14%
	Ca	2300	35%	2100	4%
	Fe	260	44%	310	16%
	Cu	<LOD		<LOD	
	Zn	<LOD		<LOD	
	Ca:Fe	9		7	

This table shows calculated concentrations of different elements by different calibration methods for the paper background in the same two maps from the Ptolemy Atlas. The relative standard deviation (RSD) shown is the variation of this element as detected in different spots on the sample.

In order to get some idea of the calculated concentration accuracy, we obviously cannot conduct destructive ICP-MS analysis here, but we can visually compare peak intensities in different regions that have a linear concentration relationship to papers of known concentration (normalized), as shown (insets on right), where: black = Whatman No. 1 and Shahani Cu-doped papers; purple-pink is Ptolemy Septima Asiae and lime green is Ptolemy Quinta Europa; blue is Fabriano paper Montefiascone; red is Fabriano paper Viterbo (Dazio); and green is Fabriano paper Iesi.

Results of visual inspection of the overlaid, normalized spectra indicate that Cu concentration in the selected maps should be <LOD (less than 60 ppm) in the Quinta Europa map and about 400-800 ppm in the Septima Asiae map. Fe concentration should be about 200 ppm or less in the Quinta Europa map and about 800 ppm in the Septima Asiae. K concentration is hard to judge visually, especially since it was shown not to be a linear function. Nevertheless, since the Montefiacone paper is known to contain 1227 ppm of K, it is not unreasonable that Quinta Europa could contain about half of this quantity and Septima Asiae could contain about 1/10 of this quantity. The Ca concentration in the Quinta Europa map should be quite a bit higher than the Viterbo (Dazio) paper, which is known to be 4300 ppm, and in the Septima Asiae map should be about the same as this value. Reasonable calculated values are marked in green or, when more speculative, in italics.

These visual comparisons indicate that the ROI-Excel calibration method, as well as the Calprocess method, appear to be reasonable methods for quantification of most of these elements at the stated instrumental settings. It is not clear, however, why the calculated values for Fe are somewhat high other than the non-homogeneous distribution of Fe in the paper substrates.



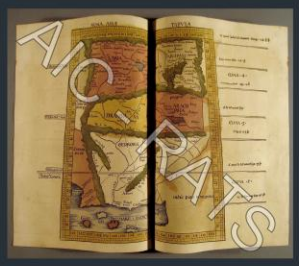
Calibration Method	Map	Quinta Europa (crown WM)		Nona Asiae (no WM, treated)		Septima Asiae (no WM, treated)		Text p167 (no WM)	
		ave. ppm	rsd	ave. ppm	rsd	ave. ppm	rsd	ave. ppm	rsd
15kV 55 µA Ti doped paper/ ROI-Excel	K	2500	11%	11000	15%	13000	10%	320	23%
	Ca	6000	9%	4600	3%	4400	7%	4600	14%
	Fe	380	21%	810	5%	1100	8%	890	15%
	Cu	<LOD	81%	250	36%	440	24%	<LOD	52%
	Zn	105	14%	80	4%	110	15%	100	7%
	Ca:Fe	16		6		4		5	

Quantitative XRF results for maps and text on different quality papers are shown above. We may conclude the following from these results:

1. Calculated Cu values appear fairly accurate, since visual comparison to known papers shows that the Text p.167 and Quinta Europa have Cu levels at about or below the Shahani control paper, which is 3 ppm, and the other papers are in between the Shahani Cu-doped IV and V study papers, i.e., between about 400 and 200 ppm. These values are close to those reported above and calculated by the ROI-Excel Method. In the Shahani study, the latter levels of Cu were shown to markedly compromise paper longevity. Therefore, we can conclude that the treatment intervention not only spread Cu around in the paper substrate, but contributed directly to acceleration of the paper's aging behavior.
2. Nona Asiae, as well as Septima Asiae and Text p. 167, have Fe concentrations at about the same level as in the Shahani Fe-doped IV paper, i.e., closer to 500 ppm. Calculated Fe concentration for the Quinta Europa should be about 200 ppm Fe when compared visually with the Shahani papers. This difference in relative amounts of Fe appears to be another indicator of differences in inherent paper quality.
3. K and Ca: Text p167 should have K and Ca levels at about the same as in the Fabriano Roma and so are calculated approximately correctly. The comparison of Ca:Fe ratios lends support here for inherent differences in the original paper quality between the crown watermarked and unwatermarked papers, which could explain differences in condition apart from the evident treatment intervention at a later date.

Note that the Ca:Fe ratios may be best indicators for paper condition, in combination with the absolute values for Fe and Cu.

Treatment Monitoring



Map	Nona Asiae (no WM, treated) ave. ppm	variation (rsd)	Nona Asiae (blotter washed) ave. ppm	variation (rsd)
K	11000	15%	7100	43%
Ca	4600	3%	4400	6%
Fe	810	5%	750	21%
Zn	*80*	*4%*	*140*	*11%*
Ca:Fe	6		6	

The application of this quantitative XRF analysis method has proved very useful for treatment planning and monitoring. This table shows elemental profiles in the paper substrates before and after blotter washing of Nona Asiae Tabula (after disbinding) with a 50:50 mixture of ethanol: water. Results show a diminishment of K after treatment, implying only partial removal of the K-alum coating. Since K levels in the Quinta Europa are about 2500 ppm, possibly due to added sizing before application of colorants, and these levels appear relatively benign in terms of an affect on the map condition, the decision was made to continue treatment to further reduce K to about that level. Note that the levels of Ca and Fe are essentially unchanged after blotter washing. Note also the apparent increase in RSD of K after treatment, which indicates that the treatment resulted in a non-uniform distribution of K.

Summary

- Quantification of trace elements in paper is not impossible, just difficult
- Evaluation of scattering and matrix effects essential for any quantification
- The preferred method found so far for K, Ca, Fe, Cu and Zn calibration is use of lab-made doped Whatman filter paper and processing curves with ROI-Excel method – can achieve ≤ 20% accuracy

Future Work

- Workshop(s) to make improved set of reference papers to share with colleagues
- Reference standardization through multiple analyses for improved accuracy
- Calibration of more elements (S & Pb, Mn & Cl, photo-related)
- Application of quantification to routine analysis and treatment monitoring
- Evaluation of statistical-based processing methods

Acknowledgments

- Jennifer Wade, former PRTD scientist
- The Ptolemy Group: John Bertonaschi, CD, and Dan De Simone, RBSCD
- Fenella France, Mark Sweeney and Roberta Shaffer, LS