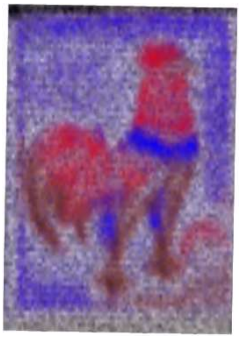
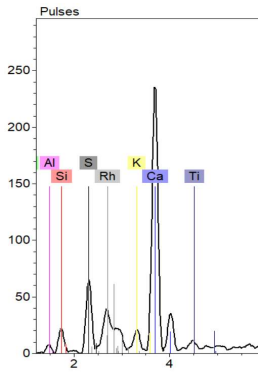
Handheld Macro-XRF scanning: Development of Collimators for Sub-mm Resolution

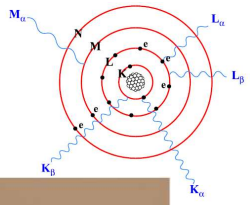
4th International Symposium on Analytical Philately

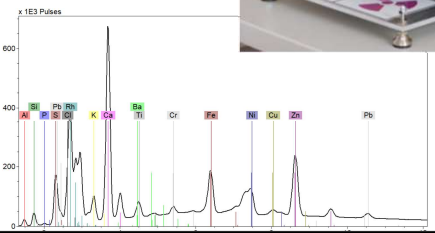
Aaron Shugar, PhD
Andrew W. Mellon Professor of Conservation Science
Art Conservation Department, SUNY Buffalo State College

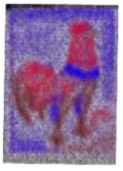
BUFFALO STATE
The State University of New York

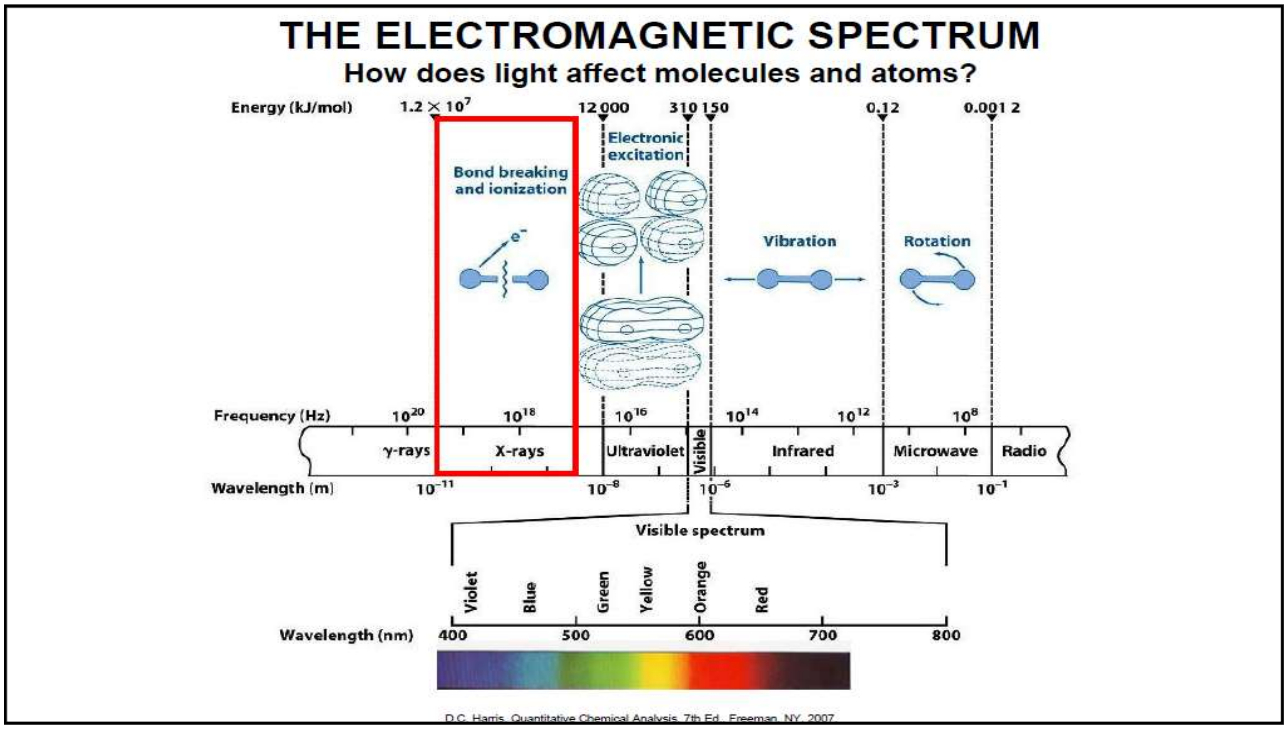
Overview of the Talk

- Basics introduction
- Collimators
- Macro scanning history
- Examples of scans and resulting data
- Summary and suggestion

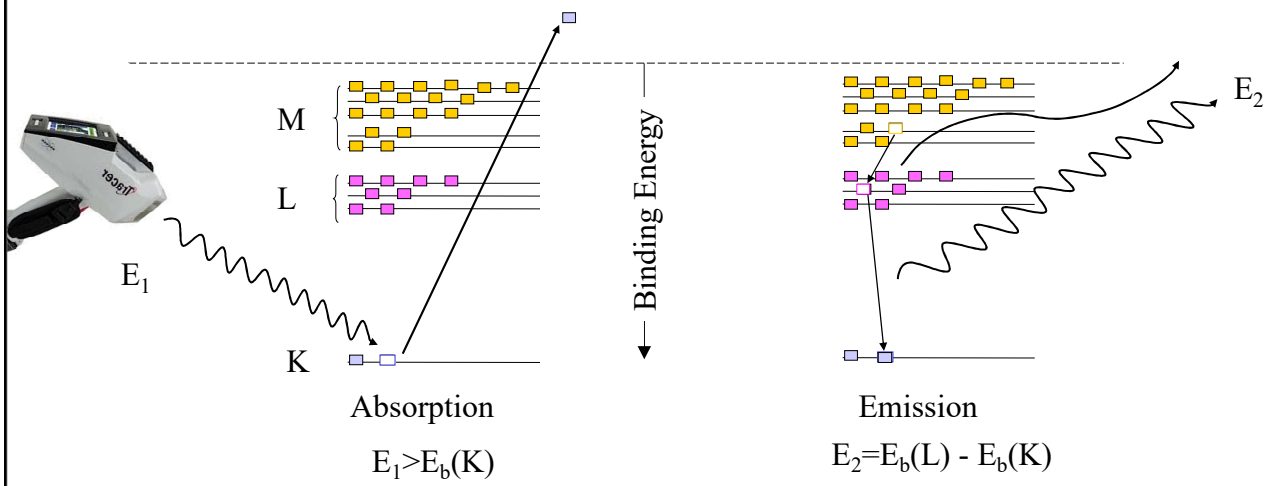








Electrons, the Photoelectric Effect and Fluorescence



Theory: X-ray identification (open architecture)

- **"Organic"** elements are not identified in spectrum (absorbed by air)
- **Low Z** elements only show **K lines** (L lines too low to be detected)
- **Medium Z** elements show **both K and L lines**
- **High Z** elements show **L and some M lines** (K can't be excited)

Bruker Tracer 5g
Can see F with He flush

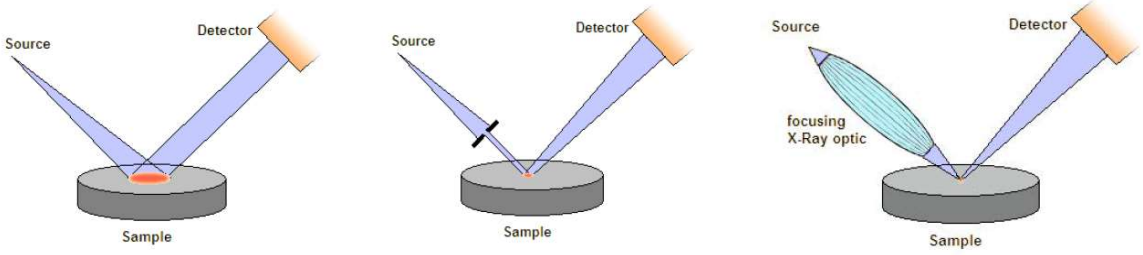
Na can be identified with special instrumentation setup or with Tracer 5g

1 H																2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114				

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Instruments: Source Optics - details

Conventional XRF | **μ-XRF with collimator** | **μ-XRF with optics**



Typical spot sizes and analytical tasks

20 – 60 mm	(50 μm) 0.1 – 8.0 mm	25 – 100 μm
Large areas	Small areas	Smallest spot
Homogeneous material	Position sensitive analysis for jewelry and coatings	Small particles and inclusions, distributions

restrict X-ray beam to small spot
restriction lowers source intensity

New Bruker Tracer 5i (g)

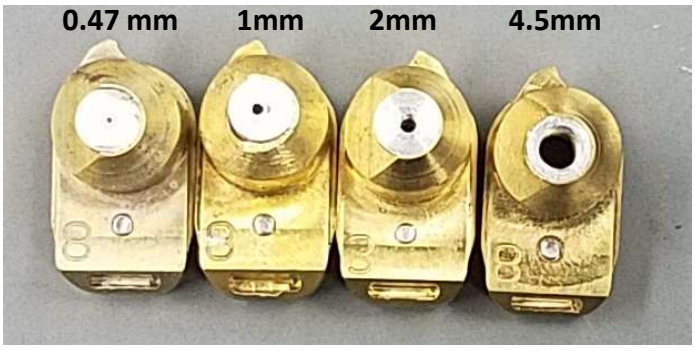
- 40mm^2 SDD detector; Typical resolution < 140eV @ 250,000cps Mn Kα
- Comes with 8mm and 3mm spot size interchangeable collimators.

8mm **4.5mm bore**

3mm **2mm bore**

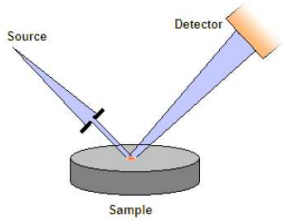
Making smaller collimators

- Remove larger collimator plug.
- Machine replacement with smaller bore diameter.
- Several made of different size for different application.



Collimator bore sizes.

µ-XRF with collimator

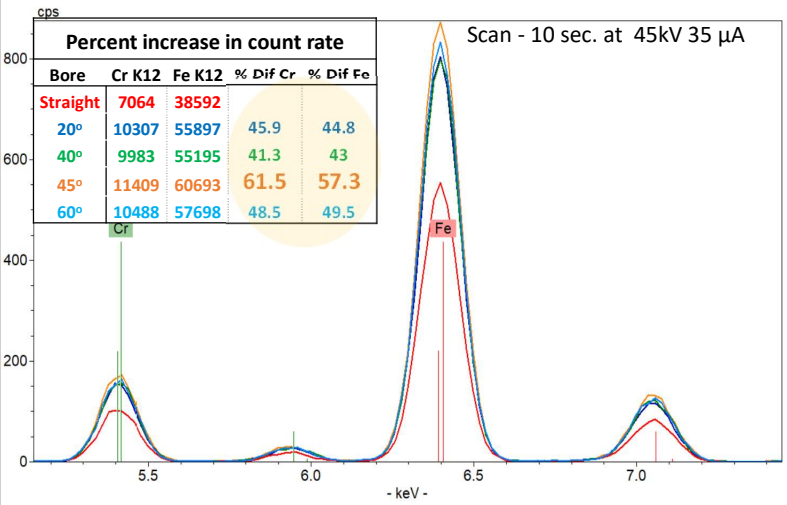


analytical tasks

(50 µm) 0.1 - 8.0 mm
Small areas
Position sensitive analysis for jewelry and coatings

restrict X-ray beam to small spot
restriction lowers source intensity

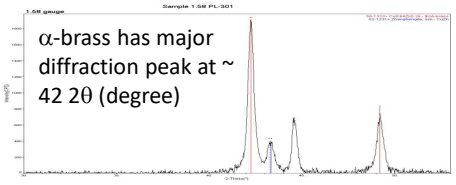
Increasing photon flux using Diffraction effects



Percent increase in count rate

Bore	Cr K12	Fe K12	% Dif Cr	% Dif Fe
Straight	7064	38592		
20°	10307	55897	45.9	44.8
40°	9983	55195	41.3	43
45°	11409	60693	61.5	57.3
60°	10488	57698	48.5	49.5

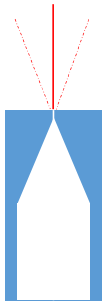
Scan - 10 sec. at 45kV 35 µA



α-brass has major diffraction peak at ~ 42 2θ (degree)

0.47mm hole drilled in brass. 20, 40, 45, or 60 degree cone cut to leave a 2mm straight end feed.

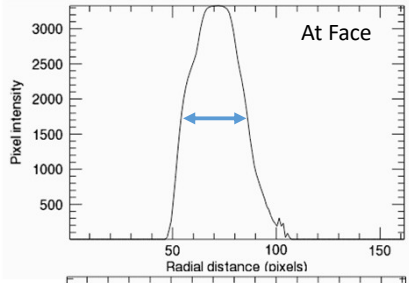
Testing for Beam 'Tightness'

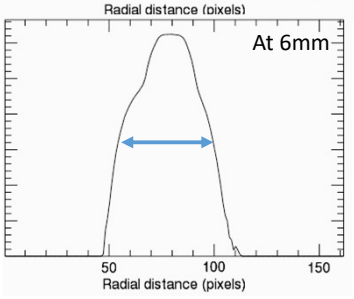


Potential for beam spread

2mm straight bore at end

Collimator Bore (mm)	cone angle	distance from nose (mm)	1/2 height diameter	top peak diameter
0.47	0	0	1.6	0.4
0.47	0	6	2.2	0.6
0.47	45	0	1.7	0.4
0.47	45	6	2.3	0.6

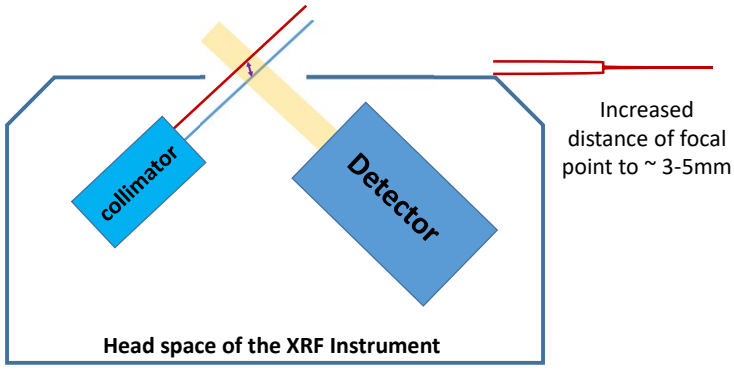




Radial distance of 45° coned 0.47 mm collimator from the radiograph at XRF face and at 6 mm distance. Similar results were found for all collimators. Each pixel is equal to 50um.

Adjusting Focal Point for Offset Analysis

By shifting the bore hole by 1 mm we are able to reposition the focal point of the X-ray beam/Detector.

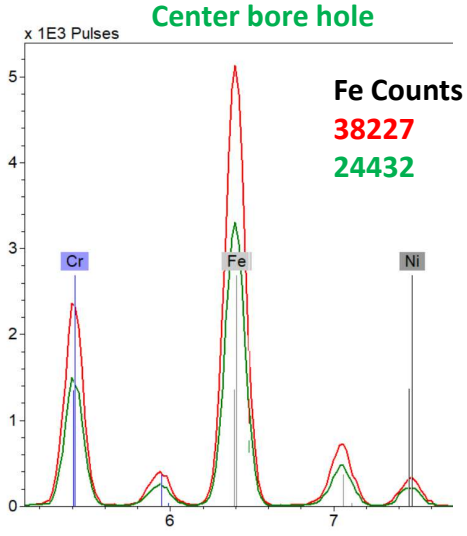


Increased distance of focal point to ~ 3-5mm

~5mm from instrument face

1 mm offset Bore

Center bore hole

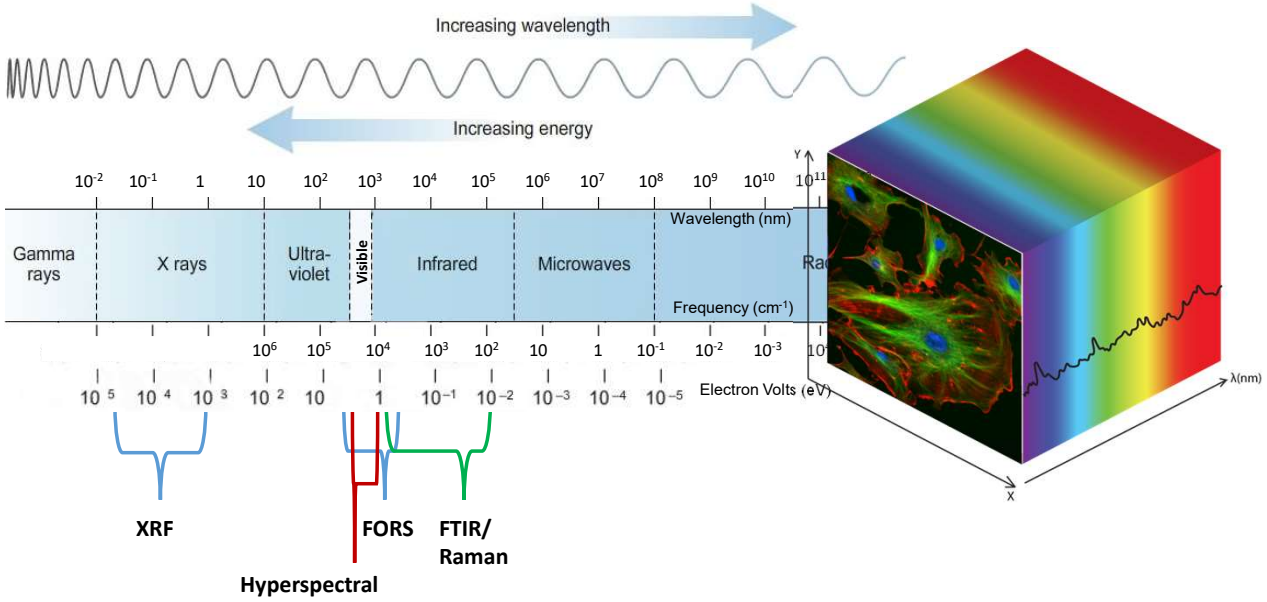


Fe Counts

38227

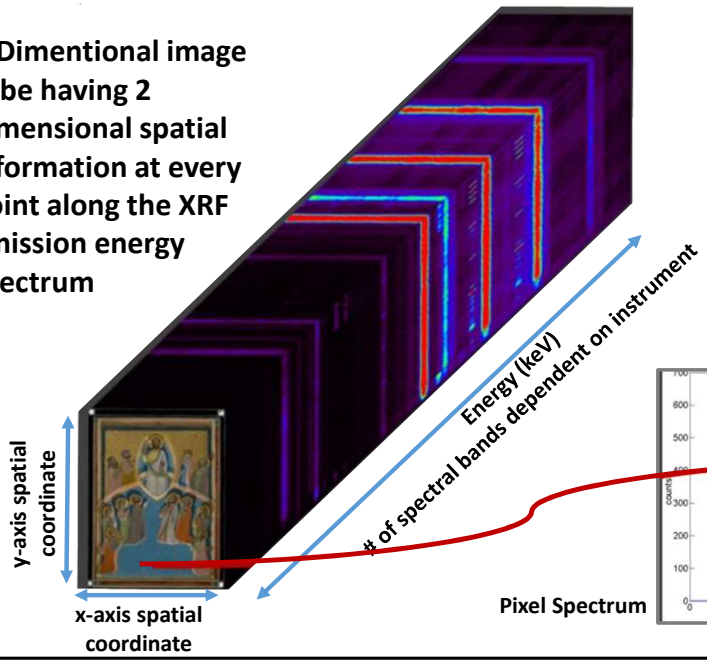
24432

Combining mapping techniques to gain more information



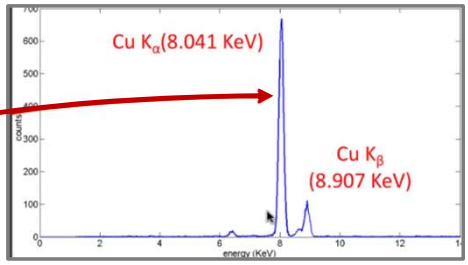
Elemental X-ray Fluorescence Imaging

3-Dimentional image cube having 2 dimensional spatial information at every point along the XRF emission energy spectrum



Elemental Copper (Cu) Map

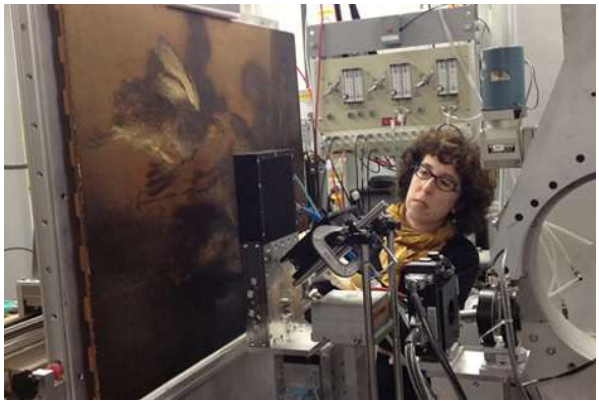
Pixel Spectrum



Information courtesy of Dr. J. Delaney

Large area MA-XRF scanning

- Synchrotron – pencil beam 0.5 x 0.5 mm spot size 2 s/pixel for the Van Gogh.
- CHESS G line – beam as low as 30µm spot size



Dr. Jennifer Mass aligning a Studio of Rembrandt painting on panel for synchrotron scanning at CHESS using the Maia Detector

Dik et al, *Analytical Chemistry* **2008** *80* (16), 6436-6442

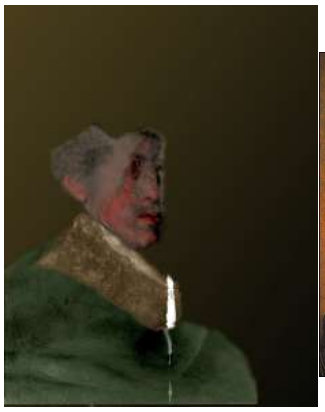
Large area MA-XRF scanning

- M6-Jetstream – Polycap Artax tube – Spot size 100 – 540 um – 30 or 60 mm^2 detector. Variable collection time as low as ~6ms/pixels.
- ~ price = + $300k

Rembrandt's An Old Man in Military Costume: the underlying image re-examined

An Old Man in Military Costume by Rembrandt van Rijn

Pb-L$_\alpha$ element map, rotated 180 to better show face and cloak of underlying man



Tentative color reconstruction of underlying figure

MacLennan, Douglas, et al. "Rembrandt's An Old Man in Military Costume: Combining hyperspectral and MA-XRF imaging to understand how two paintings were painted on a single panel." *Journal of the American Institute for Conservation* 58.1-2 (2019): 54-68.

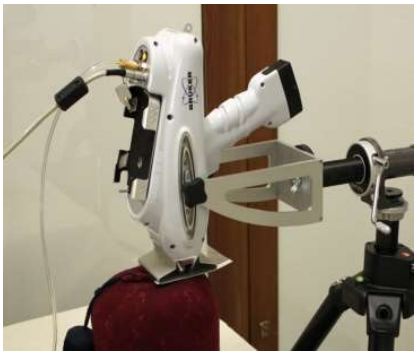
Smaller area MA-XRF scanning Units

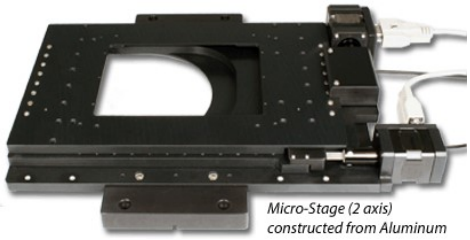
- Bruker M4 – Polycap Artax tube – Spot size as low as 25 um – 30 mm^2 detector. Variable collection time as low as ~6ms/pixels.
- ~ price = $200k

Hidden painting under paper cover

Handheld XRF scanning

- Early development attempted to use Tracer handheld for 'mapping' but was more of a controlled point scanner[1].
- XRF held stationary, motorized microscope stage used to move sample.
- Analysis local linked to image capture on microscope at magnification identical to spot size (~4x6mm).



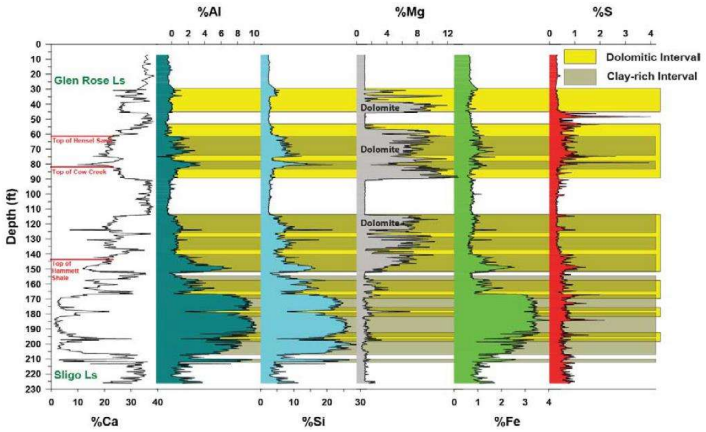


Micro-Stage (2 axis) constructed from Aluminum

1. Research performed by Ralph Wiegandt at the George Eastman House – Rochester, NY for the analysis of photographic images

Handheld XRF scanning

- System quickly evolved and was developed for the mining industry as a core scanner.
- Mainly used for 'line scanning' not imaging.



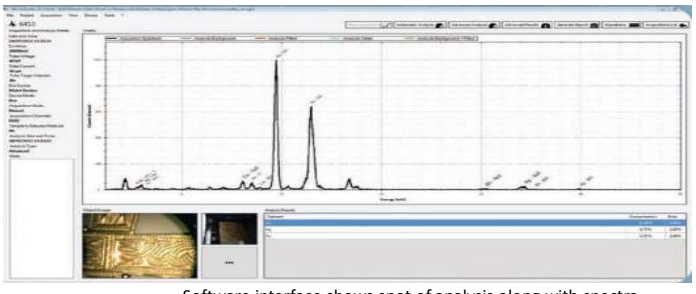
Rowe, Harry, Robert Loucks, and Charles Kerans. "Core Chemostratigraphy and Elemental Geochemistry Along a Dip-Section, Pearsall Formation, Lower Cretaceous, Central to South Texas." Unconventional Resources Technology Conference (URTEC), 2015.

MCS-1000E manufactured by DeWitt Systems Incorporated

Advancement in Handheld XRF Scanning of Art

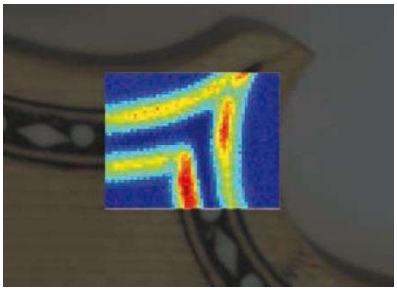
- Bruker (XGLab) Elio portable XRF scanning system improved resolution by offering 10 x 10 cm scan size integrating scan with internal camera.
- First use of 1mm collimator for collection, but limited in speed based on low count rate/sec (~1.5k/sec).

https://cosmosmagazine.com/archaeology/the-elements-of-art-high-tech-scan-reveals-secrets-of-an-ancient-painting



Software interface shows spot of analysis along with spectra

https://www.xglab.it/index.shtml

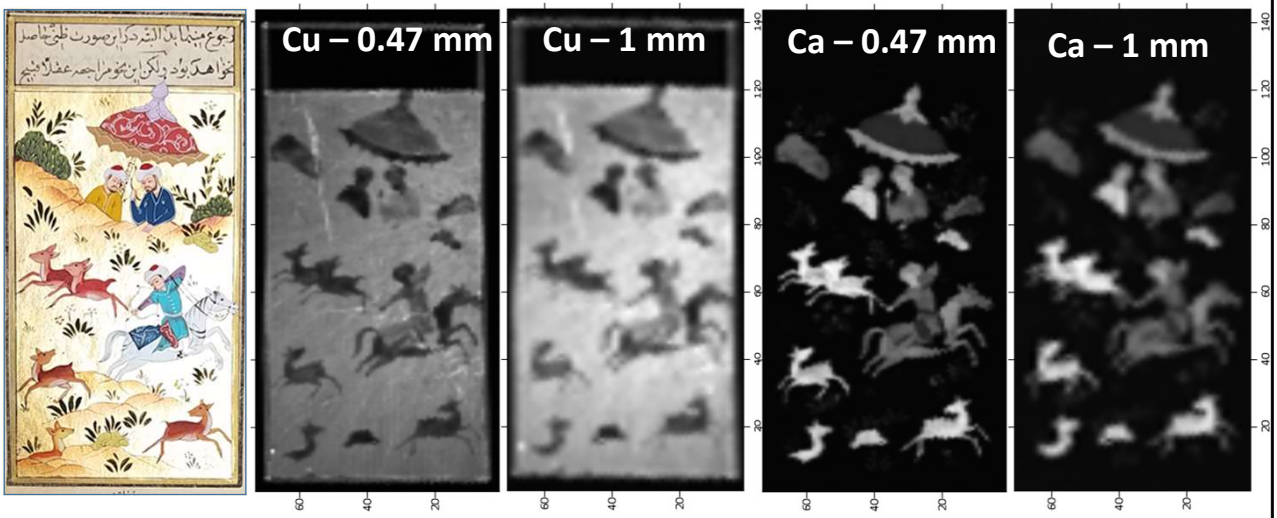


Fe-Ka XRF map, 55px x 43px, 1s/px, spot size 1mm, step size 0.5mm.

DeWitt MS-150E Scanning Bed for Tracer 5i(g)

- Interchangeable collimators
- ~ 148 x 148 mm scanning bed
- Travel as low as 0.1mm/sec.
- Integrated software.
- Collected data is deconvoluted in Bruker Artax software in preparation for mapping

Difference in image resolution using different collimators

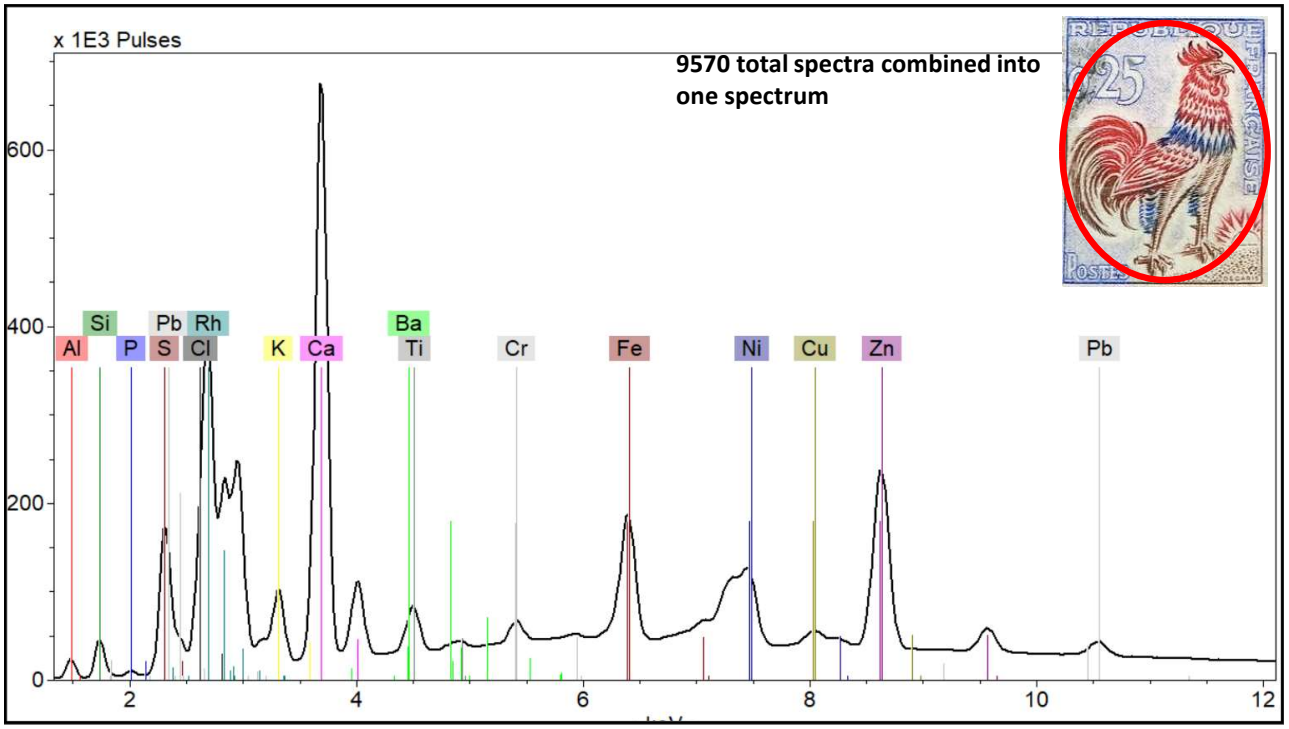


Illuminated Manuscript (72mm x 142mm) scanned with 1mm and 0.47 mm bore collimators. The 1mm scan has a pixel size at 1mm (X) x 2mm (Y) at 1mm/sec and the 0.47mm scan has a pixel size at 0.5mm (X) x 1mm (Y) at 0.5mm/sec. The scan shows that artifacts smaller than 0.5mm are resolvable.

Scanning Examples

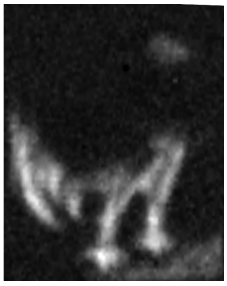
French .25 F. Gallic Rooster stamp designed by Albert Decaris, initially printed in 1962.

3¢ Oleander Bermuda Colonial stamp from the Island Flora Flowers stamp collection from 1970.

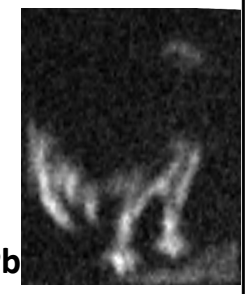


Resulting XRF Elemental Maps

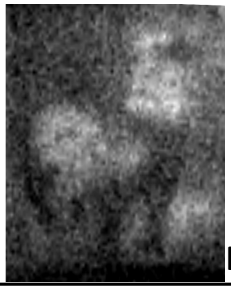

Ca

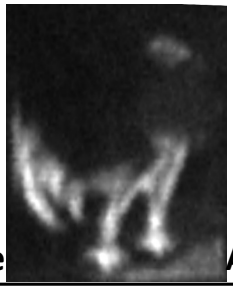

Cr

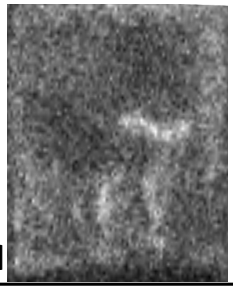

S

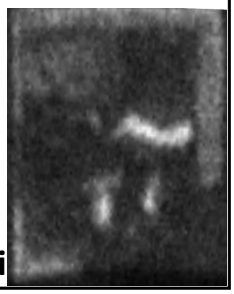

Pb

0.47 mm collimator
0.2x0.3mm step size


Cl

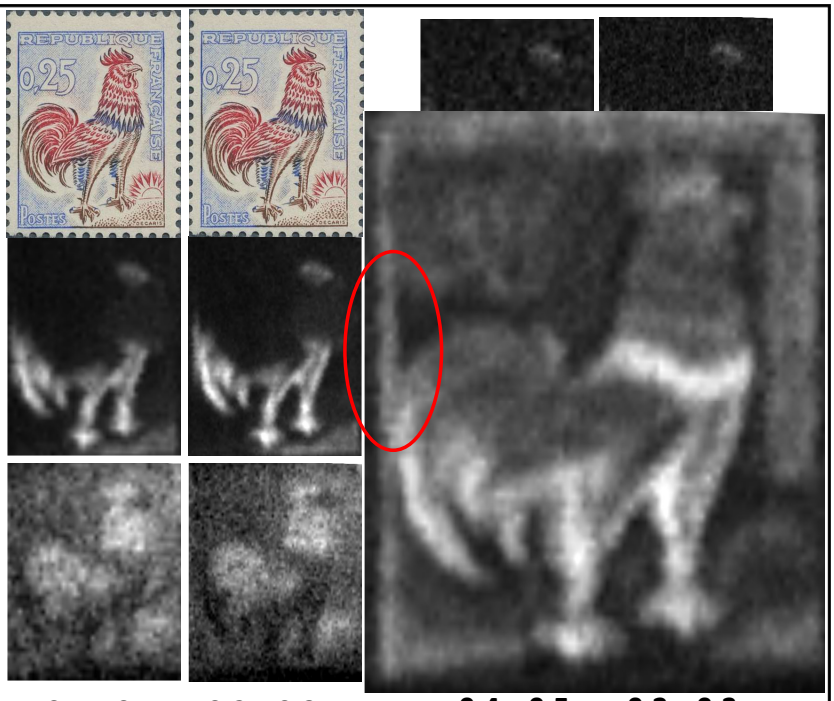

Fe


Al

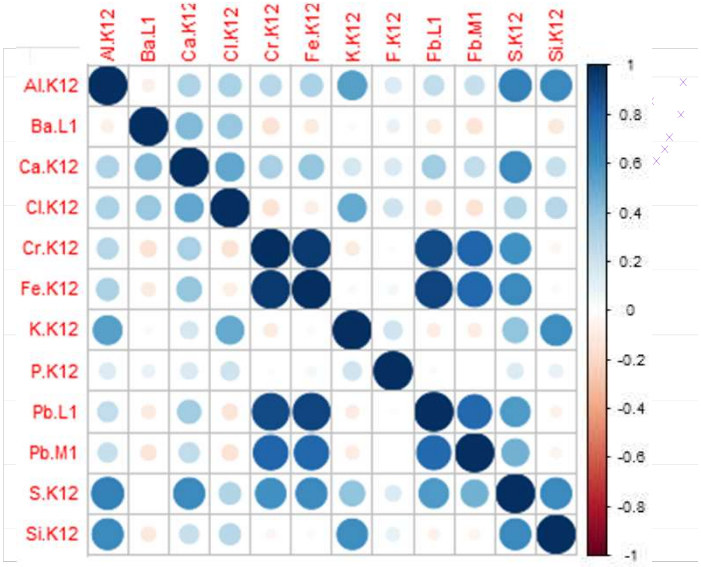

Si

Testing Resolution

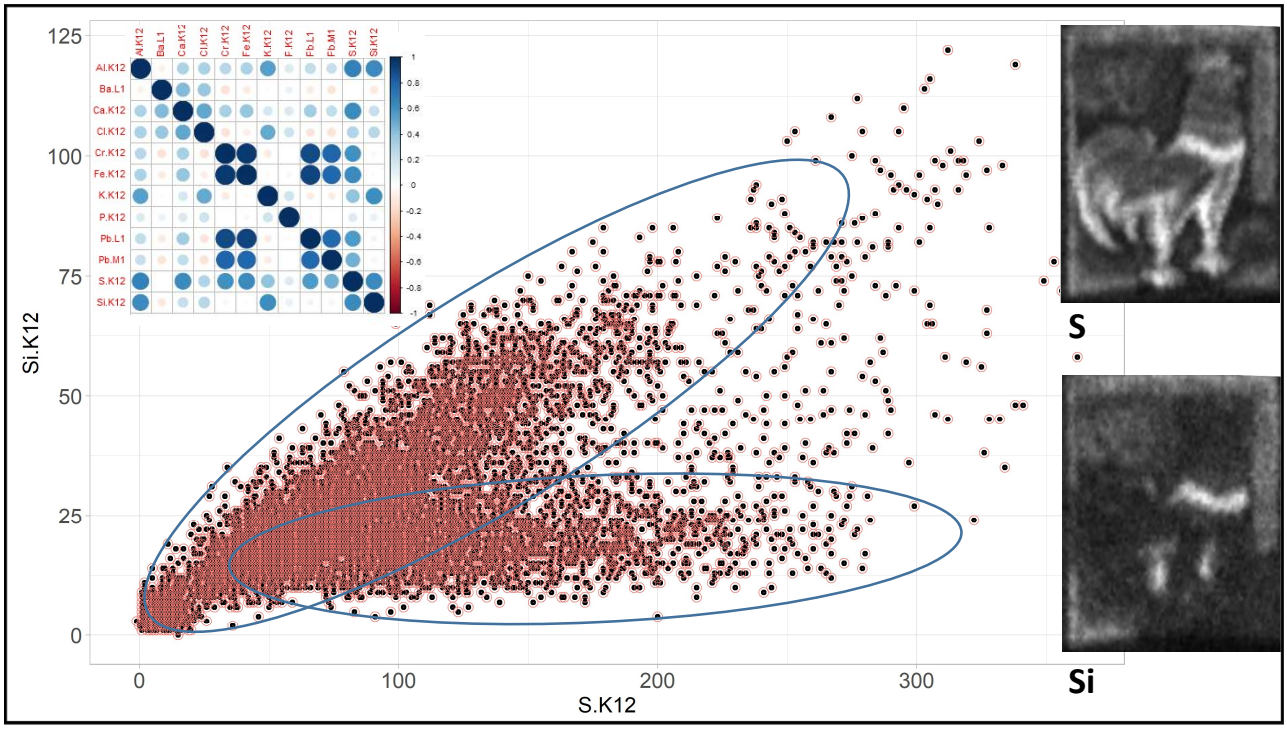
- 0.47mm collimator
- Scans run at
  - 0.2x0.3mm = ~ 2.6 hours
  - 0.3x0.4mm = ~ 1 hour
- Is it worth it for extra scan time?
- Resolution does improve and can resolve lines as small as 0.25 mm

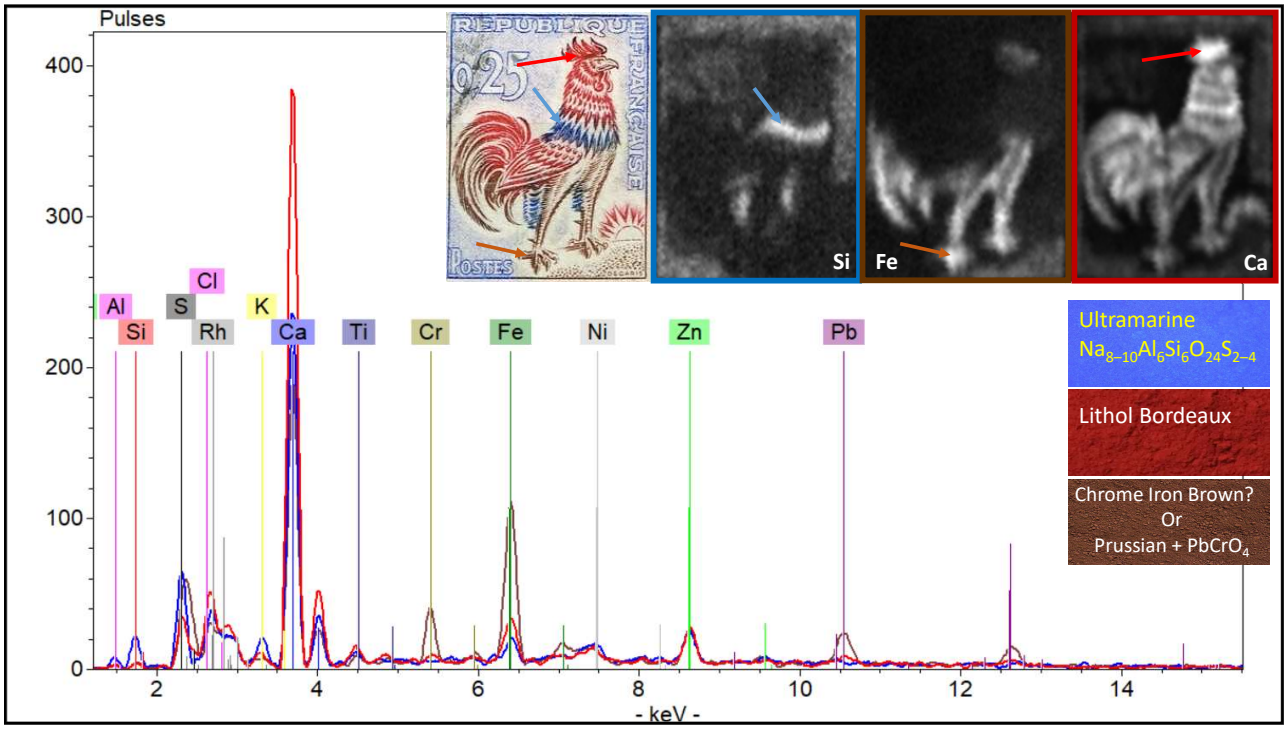


Assessment of data cube

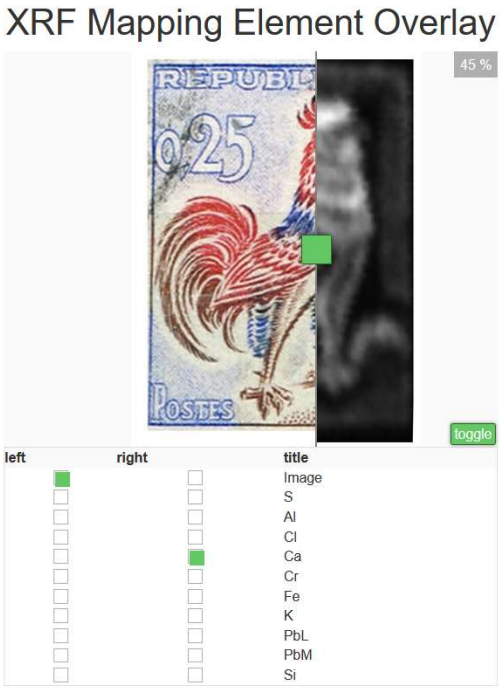


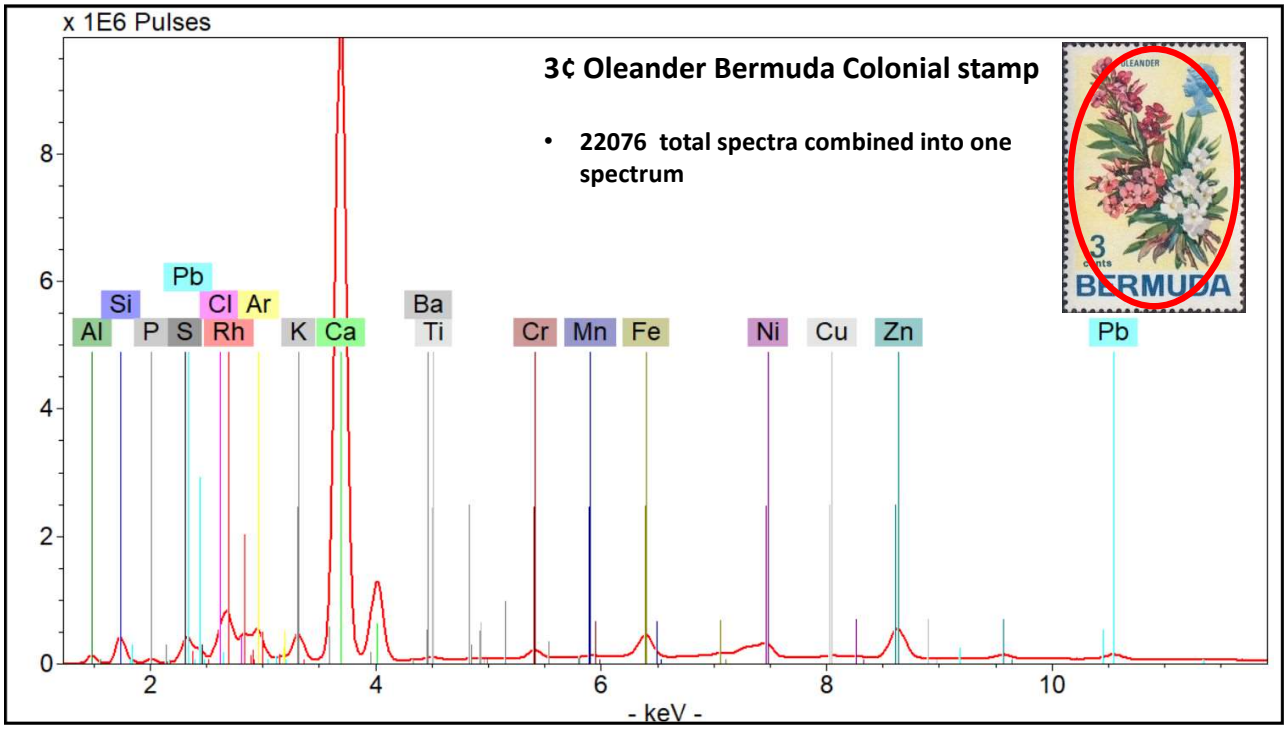
Correlation Table



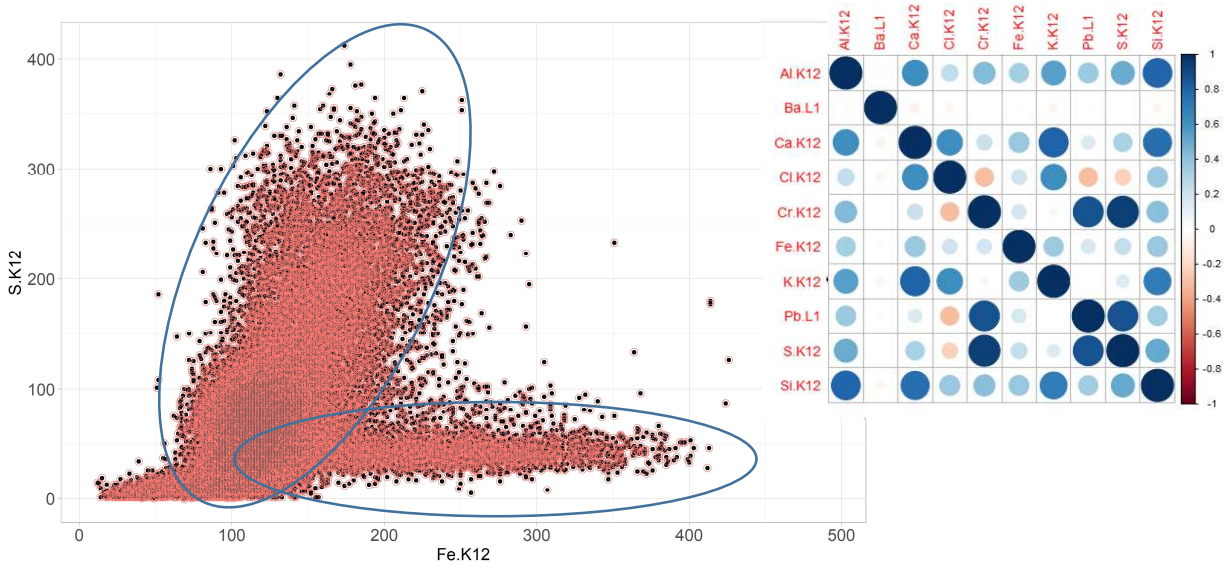


Maps can be imported into a web based slider program to compare the elements to the image and to each other



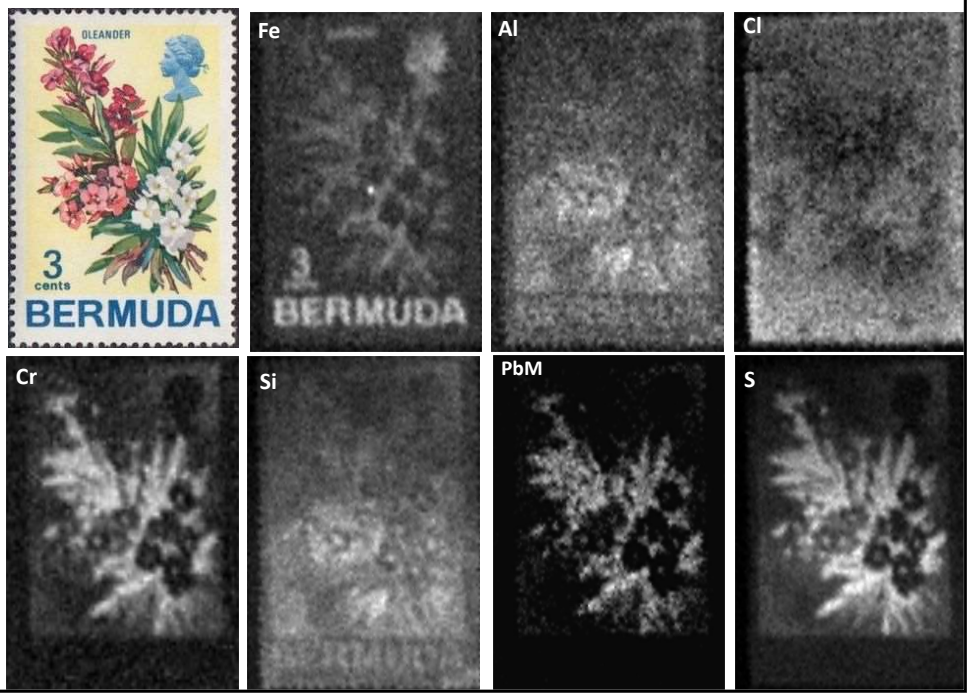


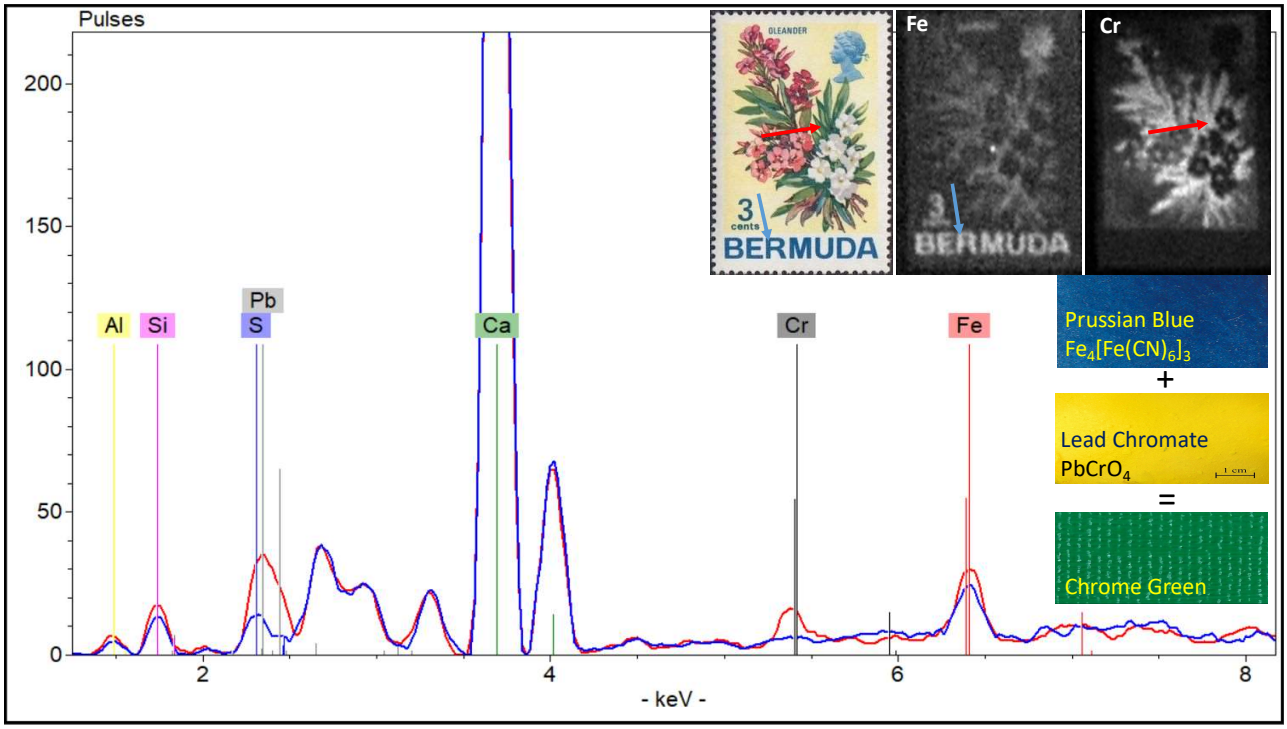
Scatterplot of S vs Fe (22076 spectral data points)



Resulting XRF Elemental Maps

Scanned at 0.3 x 0.4mm





Summary

- XRF Scanning more ideal for multi-colored stamps
- Benefits from collecting thousands of data point in a data cube
- Able to easily visualize element /pigment location
- Resolution possible down to ~0.25mm
- Cheaper using handheld XRF with scanning base rather than expensive polycap instruments.
- Most powerful when used in conjunction with other analytical techniques (i.e. FTIR, Raman, SEM)

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