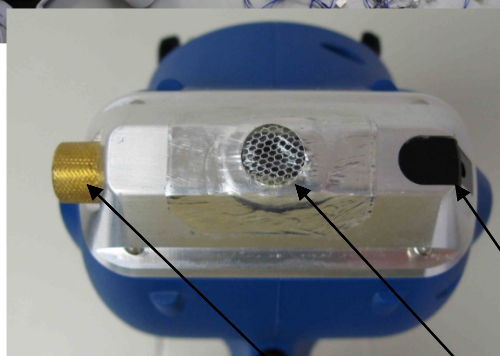
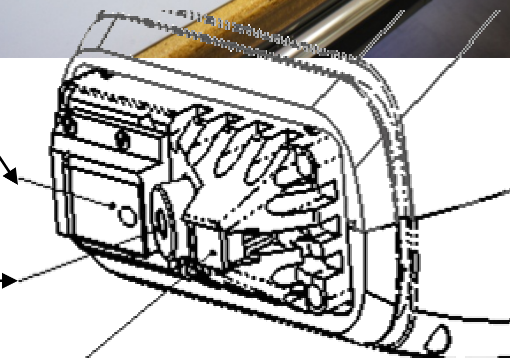
National Postal Museum Announces the First International Symposium on Analytical Methods in Philately

The Flashlight – The Basics



- Fluorescent Bulb, Rh
- Up to 45kV Photons
- 140eV Resolution Si-Drift Detector
- 13μ Be Detector Window
- IR Safety Sensor
- Vacuum window
- User selectable filter/target



How it Works – What is fluorescence?

In the most basic terms, fluorescence is the process in which:

- a **photon** is emitted from an flashlight
- The emitted **photon** interacts with the electrons in the atoms in the sample
- In some cases, this higher energy photon is absorbed by an electron causes that electron to leave the atom
- When an electron leaves an inner shell, the atom wants to fill the vacancy, so an electron from a higher shell drops down to fill that vacancy
- When an electron drops from a higher to a lower shell, the energy difference between the shells is released in the form of another **photon**, which is characteristic not only to each element, but to each shell transition; this is fluorescence
- In fluorescence instruments, a detector (eye) is used to pick up the emitted photons as well as those reflected

We'll get into further details of elemental fluorescence once we further explore photons.

Good news: you already know a lot about photons!

How it Works – Photons

What is a photon?

While nobody knows exactly what a photon is, we do know:

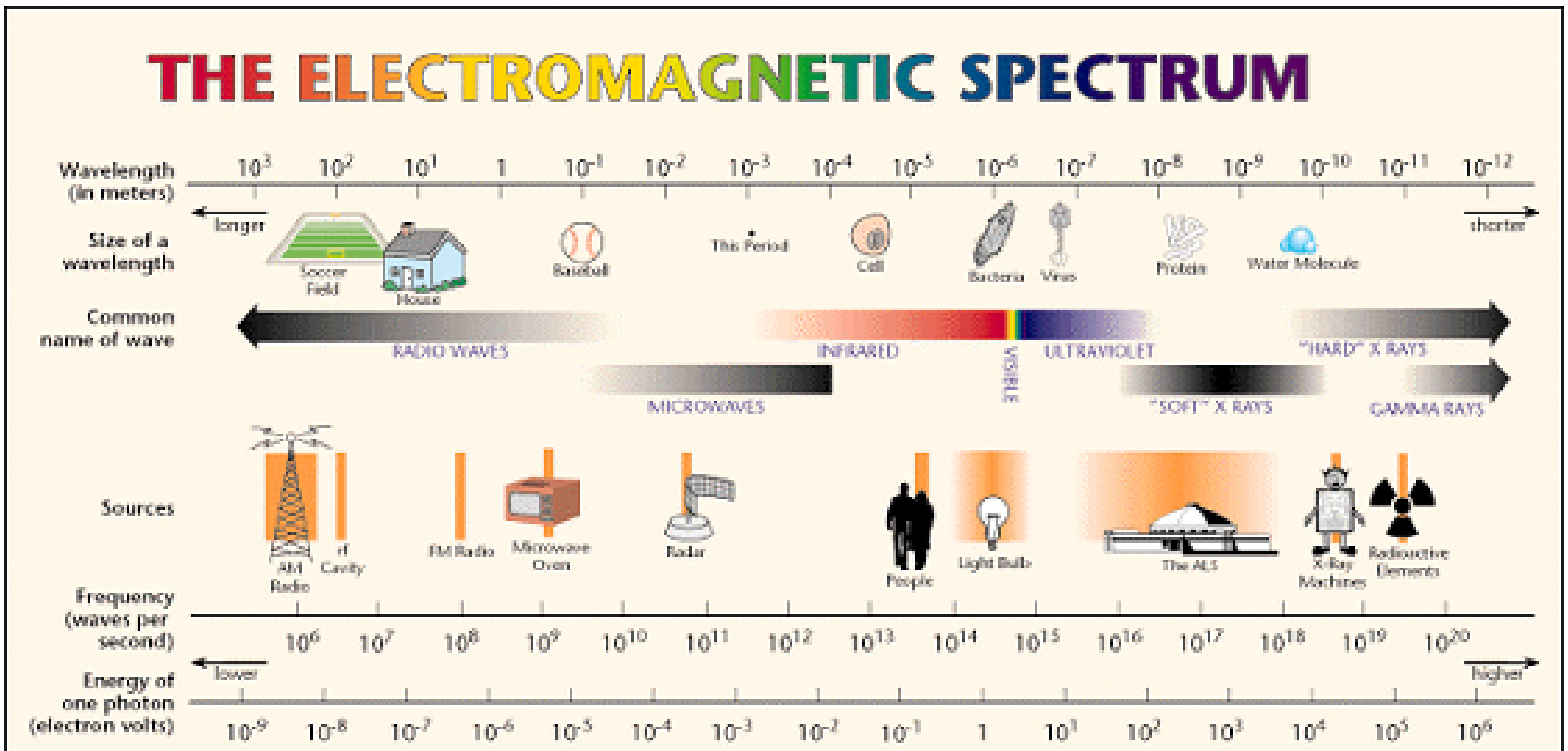
- "Discrete packets of electromagnetic radiation"
- Force carriers
- Sometimes they exhibit the characteristics of a wave, sometimes the characteristics of a particle
- Have no mass
- Have electromagnetic energy
- Have momentum
- In free space it is thought they always move at the speed of light, *c*, and consequently in our frame of reference they are infinitely short; i.e. they have no length in the direction they travel
- Appear to be "slowed down" when moving through matter, or absorbed completely

What happened to the good news? Here it comes…

Remember : $E=mc^2$

How it Works – Photons

Luckily, you already have a great deal of experience with and use photons every day of your life. You see using photon interactions which are very similar to the photon interactions in x-ray fluorescence.
Light hits the things you see, and is absorbed at certain energies based on molecular structure of the thing in question, and your eye is the detector for those energy ranges!



How it Works – Photons We Know (Visible Light)

- We see color because our eyes are excellent detectors of 1-3 eV photons.
  - Atoms and molecules can absorb light (= energy).
  - To understand how, let’s think on the level of one single atom, which is made up of neutrons, protons (in the nucleus) and electrons (in orbit around the nucleus). How many of each of these there are in an atom determines what element that atom is.
  - Electrons are bound to the nucleus at of any particular atom at specific energies, which are unique to each element. Think of it as gravity. The nucleus is like a planet, and depending on the “size” (energy) of a nucleus, it can hold “moons” (electrons) in various “orbits” (energy levels, binding energies) around it at specific distances.
  - When a beam of light hits the atom, some photons from that beam of light have just the right amount to knock the electrons out of it’s orbit. The binding energy of that electron is joined by the energy of the photon that knocked it from it’s orbit, that is, the photon is **absorbed**.

How it Works – Photons We Know (Visible Light)

- The energies which are not absorbed are reflected, and therefore detected by your eye.
- In other words, something that appears blue **absorbs** all photons other than those that have an energy of approximately 3eV. Only the light waves that appear as the observed color are reflected back to your eye, and the others are absorbed.
- This pattern of absorptions (or emissions) is unique to each element, molecule, etc.

How it Works – Photons We Know (Fill in the Blanks)

- When a murder is committed on CSI, detectives use ___________ light to look for blood stains that are not visible to the naked eye.
- When ultraviolet light hits a blood-stained carpet, the outer valence electrons in the protein molecules that make up blood become “excited” (UV fluorescence).
- When the electrons move back to the unexcited state they emit photons in the 3 eV range, the color of which is __________, an energy the human eye can see.
- Thus we can detect (see) traces of blood on a carpet. In this case we are indeed dealing with individual photons that are the result of valence electrons moving around in the protein molecule in the blood. These resulting photon energies give us molecular information.

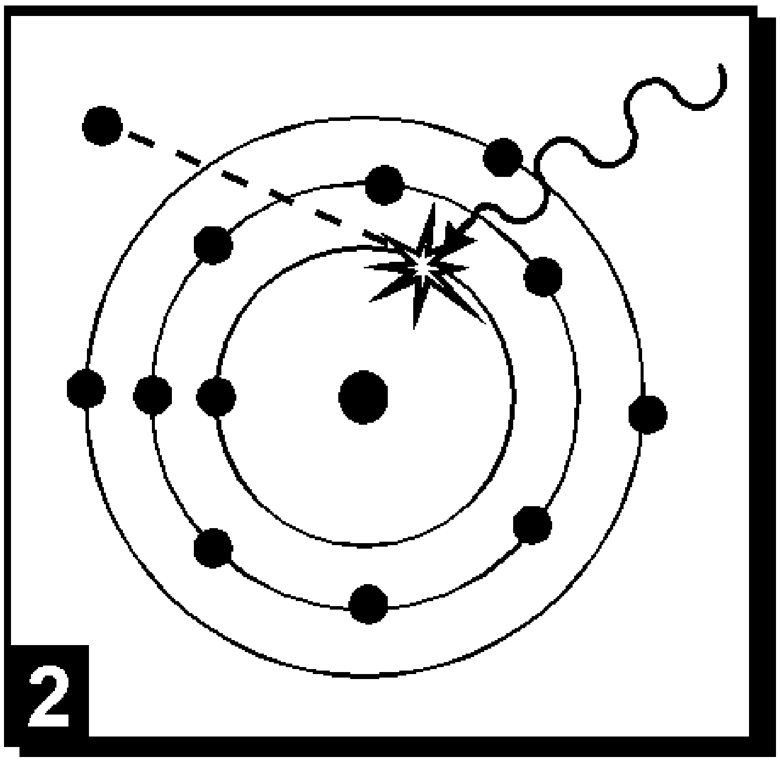
How it Works – Electrons

- How an electron functions in atomic and molecular structure is vital to the properties of that matter.
- The photon/electron interaction is what most influences what we can "measure" when using any beam of photons incident on our object and detecting the photons coming back from that object.
- Electrons are described as a particle, with 1 negative charge, 1/2 spin, rest mass of 0.511 keV and are fundamental to the structure of every atom. They exist in atomic structure in very defined quantum energy states controlled by the number of protons in the atomic nucleus.
- To add energy to an electron **bound in an atom** you have it absorb a photon, and for an electron to lose energy when in an atom or a molecule when moves from and outer shell to an inner shell it emits a photon equivalent to the energy difference between those atomic levels.
- Unlike protons and neutrons, which make up the nucleus of the atom, we find free electrons outside the atoms and molecules in large quantities, moving from atom to atom or molecule to molecule

How it Works – So what about those photons and electrons?

- The principles of fluorescence —and its uses in measurement—are based entirely in photon-electron interactions, just like light. **The Tracer instrument is, in essence, an expensive flashlight!**
- In the process used to create photons in the range of 1 keV to 250 keV (x rays) in an x-ray tube, electrons are accelerated to, say, 40kV and then slammed into at solid material, for instance Rh. In this case the highest energy photon you can make is 40 keV.
- The rapid slowing down of the electrons by colliding with the Rh atomic structure causes the electrons to radiate photons between 0 and 40 keV. The technical name given to this process is called *bremsstrahlung* and is used in the sense of radiation emitted from electrons stopping in matter.
- Higher energy light photons, like X-rays, tend to want to plow through more matter before they get absorbed. (Hence, their use in medical imaging: they can pass through your "soft" tissue, but are more readily absorbed in your bones, which are denser.)

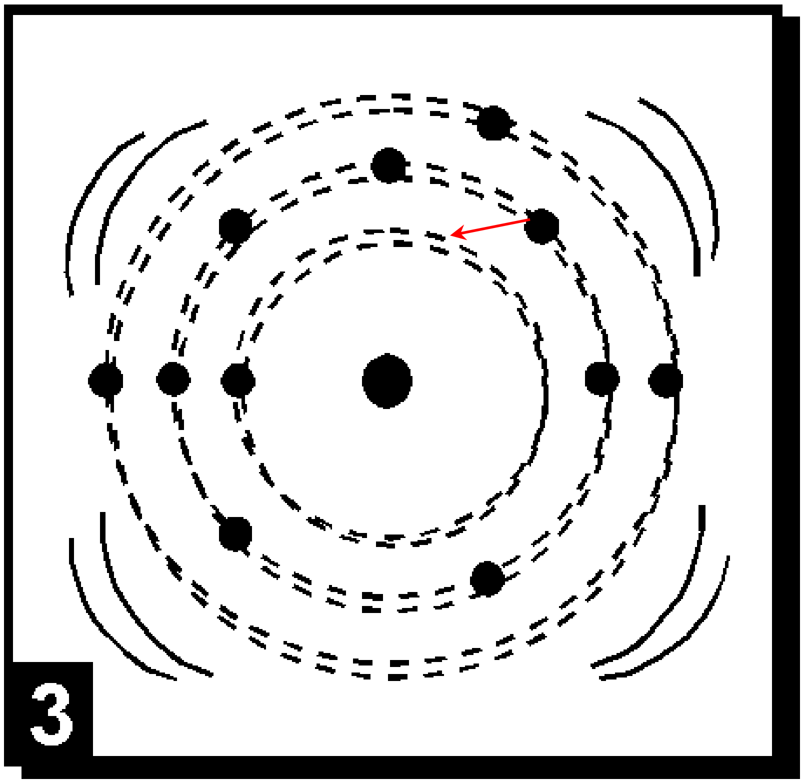
How it Works – XRF (x-ray fluorescence)



When the switch is pulled, activating the Analyzer's x-ray tube, the x-rays strike the inner shell electron of the atoms in the sample and it is ejected from the atom.*

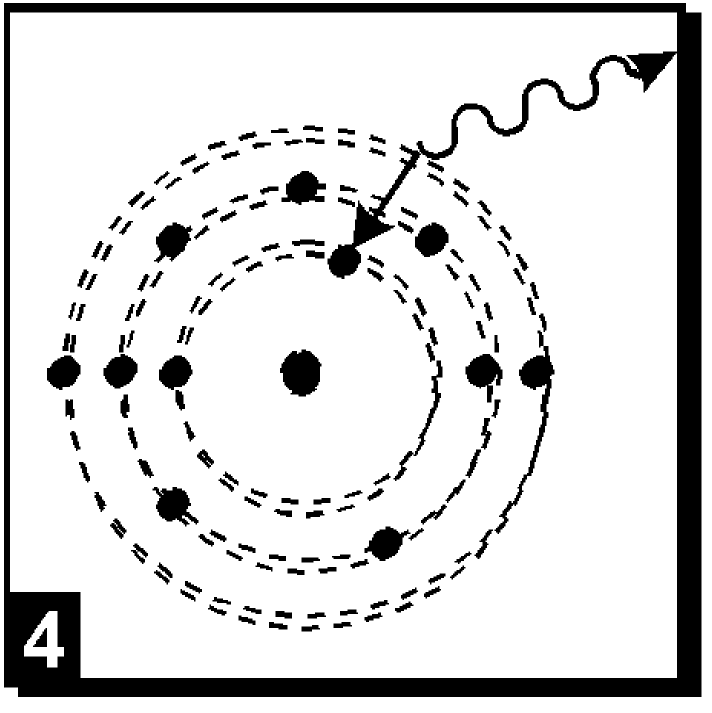
*** X-ray energy must be higher than absorption edge of the element.***

How it Works – XRF (x-ray fluorescence)



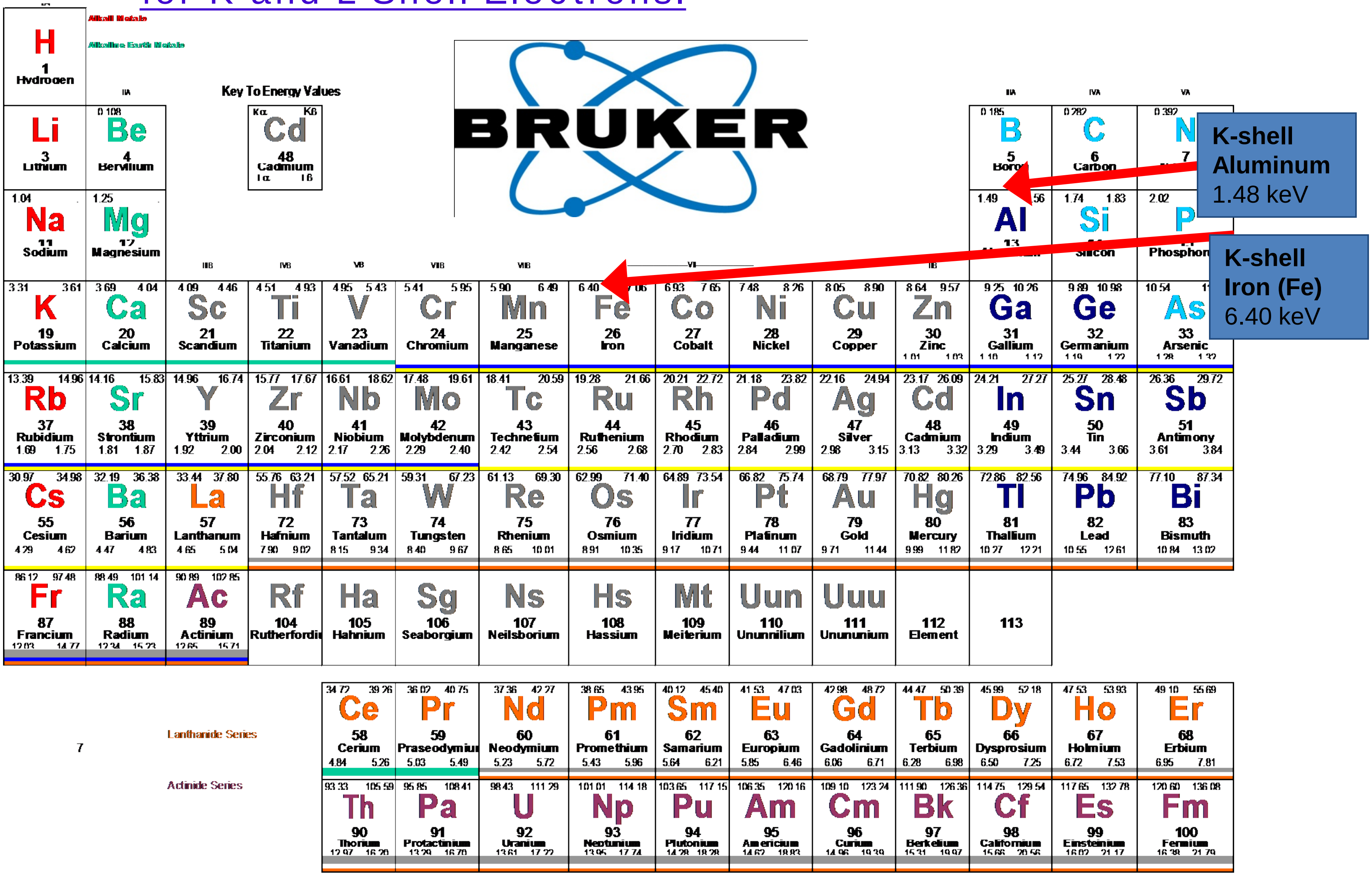
Next, an electron from an outer shell moves to fill the vacancy in the inner shell.

How it Works – XRF (x-ray fluorescence)

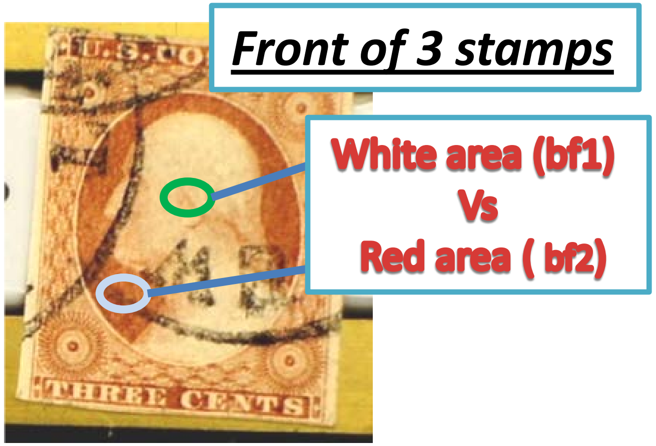


An *X-ray photon* is released and hits the analyzer's SiPIN detector. (This photon's energy is unique to the element it came from-- e.g., Aluminum K-shell energy is 1.47 keV)

Note: Each Element has its Own Signature Energy for K and L-Shell Electrons.



Front of 3 stamps



Number of photons per element detected in 500 sec from the **front** of the stamps at position 1 vs 2

Comparison of stamps 5004, 5011 and 5013 front (White to Red area):

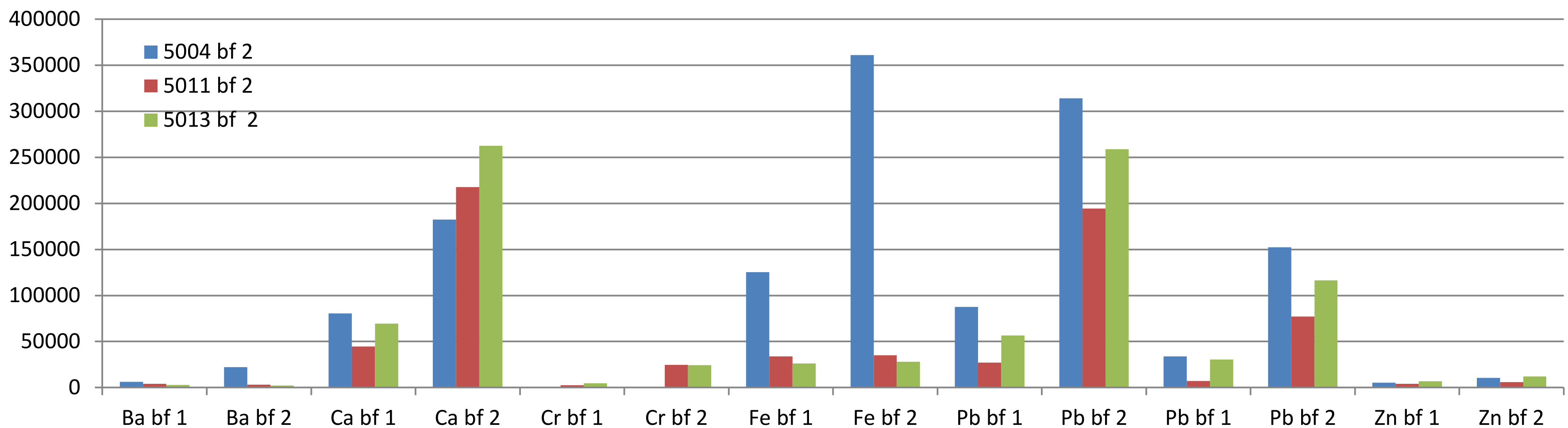
Looking at number of photons from each element, from the front of the 3 stamps in the white and the Red area it is clear that 5004 is very different; it contains Ba, less Ca , no Cr, large amounts of Fe, more Pb and the same Zn.

5011 and 5013 based on the elemental analysis are very similar in elemental content with small shifts the concentration of the elements Ca , Fe, Pb and Zn. The relative amounts of these shifts can be seen in the table and the plots.

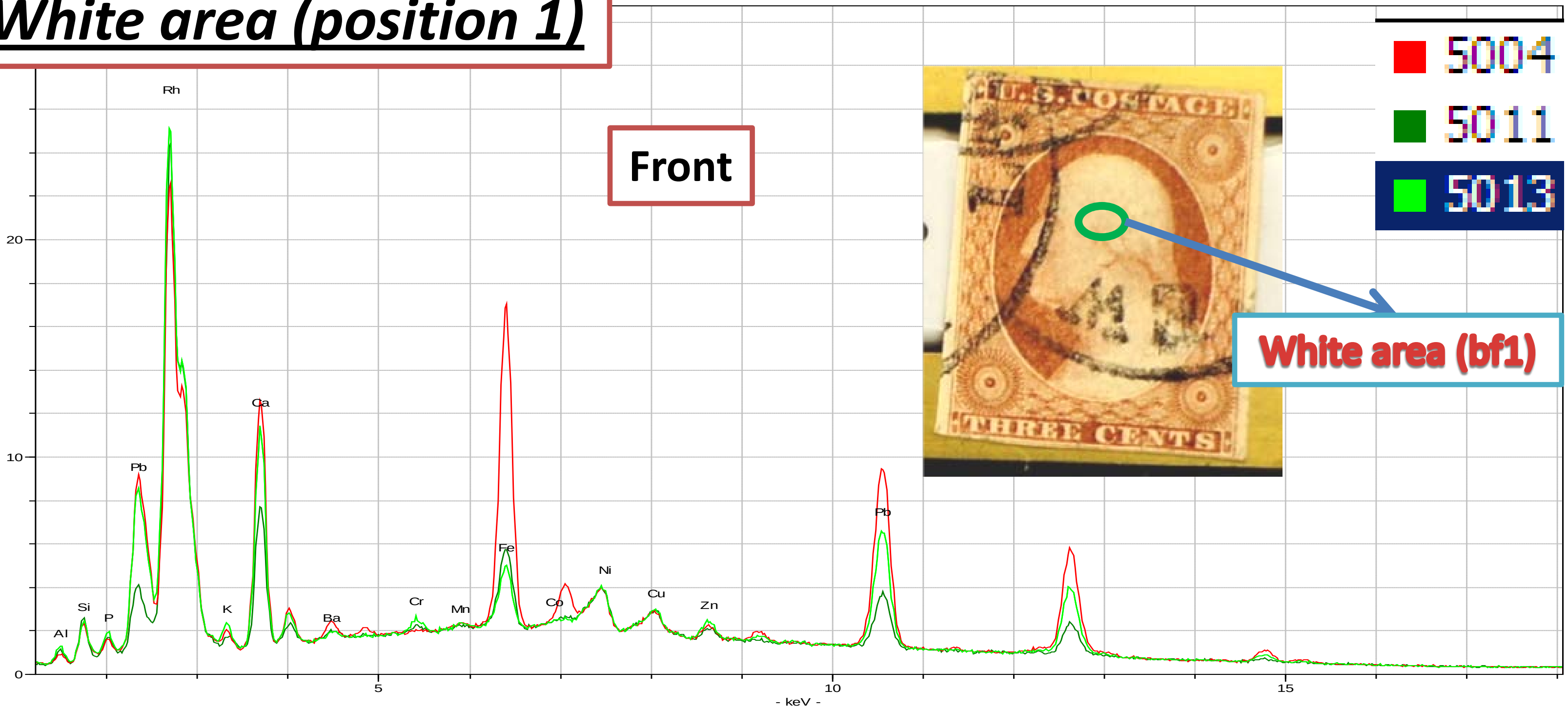
Looking at the white versus red data one sees that there is a little of the same ink used in the white portion of the image on all 3 stamps, as the same elements are detected in both the red and white areas. However the white area has much less of those elements.

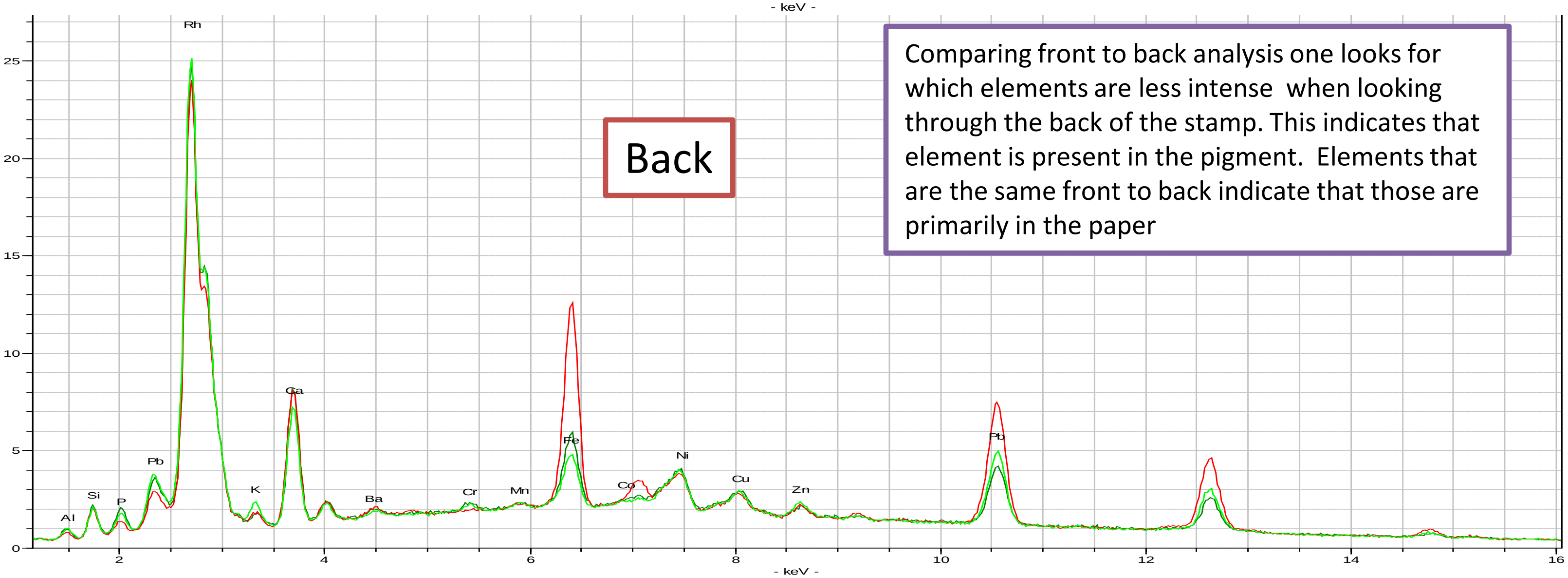
Also this is a way to detect which elements are in the paper and not the pigment when the intensity shows up the same in both pigments. For instance it appears there is both Ca in the pigment and the paper, for all 3 stamps. Fe does not appear in the pigment of 5011 and 5013. Zn does not appear in any of the pigments.. Pb appears in all 3 pigments. Ba occurs only in the pigment of 5004 and Cr appears only in the pigment of 5011 and 5013.

	Ba bf 1	Ba bf 2	Ca bf 1	Ca bf 2	Cr bf 1	Cr bf 2	Fe bf 1	Fe bf 2	Pb bf 1	Pb bf 2	Pb bf 1	Pb bf 2	Zn bf 1	Zn bf 2
5004	6331	22115	80586	182271	401	298	125295	360912	87605	314158	33970	152192	5193	10666
5011	4074	3056	44499	217690	2668	24783	33792	35145	27043	194390	7150	77105	4131	6035
5013	2817	2355	69412	262589	4812	24346	26348	28087	56661	258836	30484	116354	6759	12054

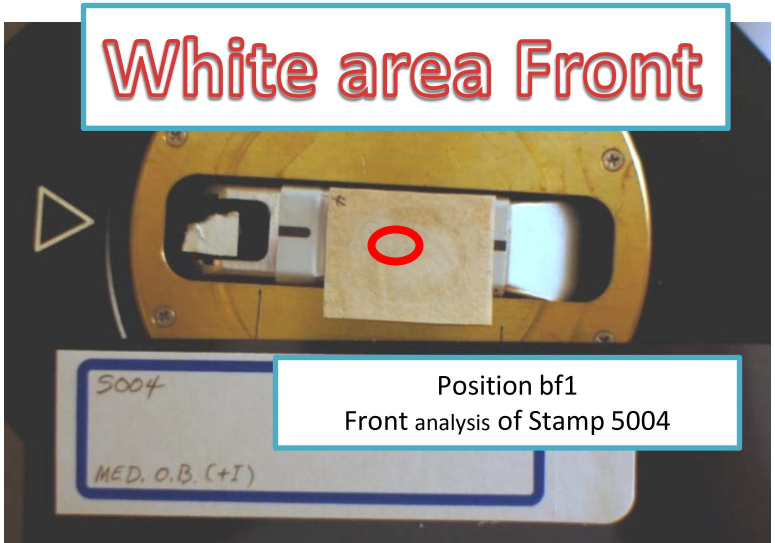


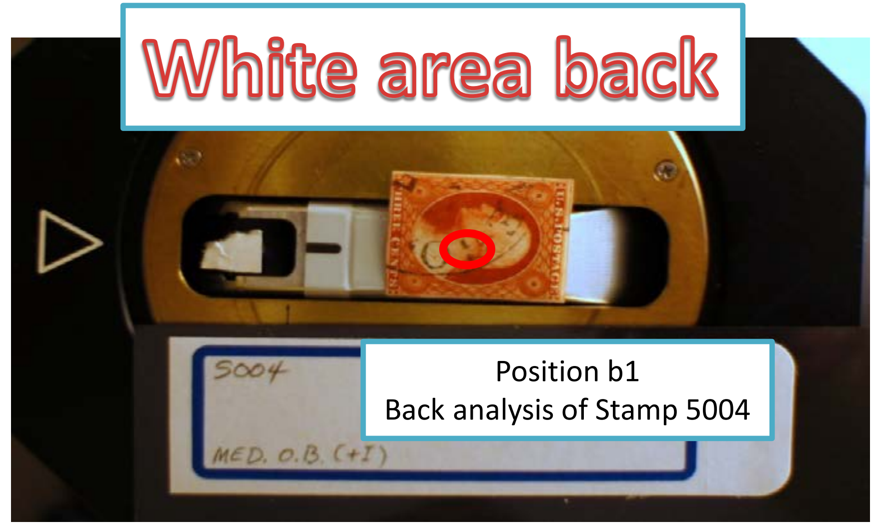
White area (position 1)





Comparing front to back analysis one looks for which elements are less intense when looking through the back of the stamp. This indicates that element is present in the pigment. Elements that are the same front to back indicate that those are primarily in the paper



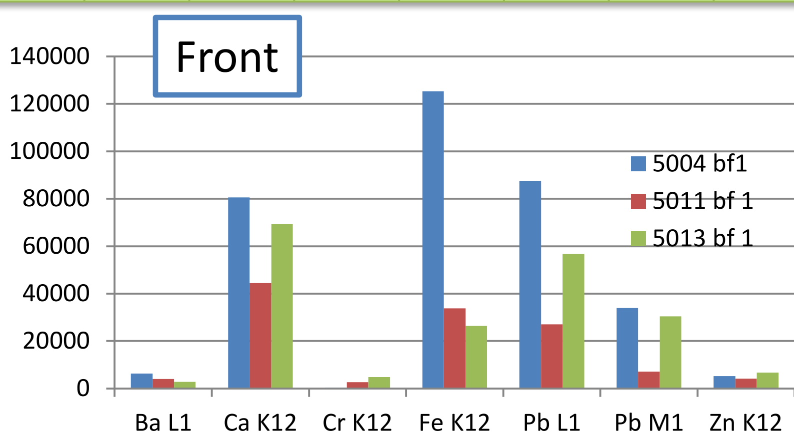


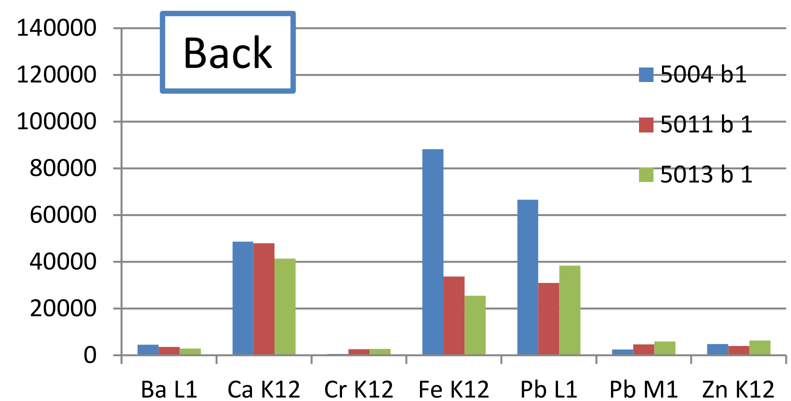
Looking at number of photons from each element in the white area, from the front of the 3 stamps it is clear some of the red pigment is present all though at a much lower concentration as the Red pigment is displayed on a scale maximum scale of 400000 versus 140000 shown below.

Comparing the front to back analysis the elements present in the pigments show lower concentration in the back analysis. Note that front to back 5011 shows very little change indicating its white area has very little pigment present on the front.

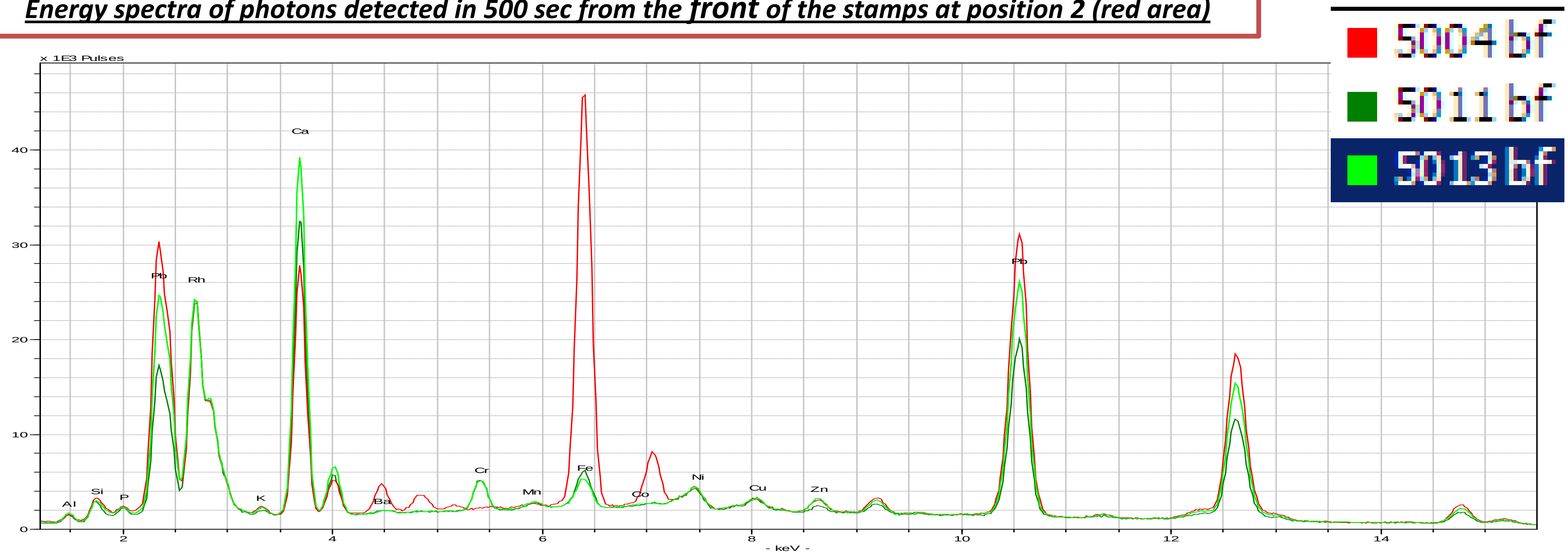
	Ba L1	Ca K12	Cr K12	Fe K12	Pb L1	Pb M1	Zn K12
5004 bf1	6331	80586	401	125295	87605	33970	5193
5011 bf 1	4074	44499	2668	33792	27043	7150	4131
5013 bf 1	2817	69412	4812	26348	56661	30484	6759

	Ba L1	Ca K12	Cr K12	Fe K12	Pb L1	Pb M1	Zn K12
5004 b1	4521	48619	581	88186	66652	2479	4824
5011 b 1	3596	47997	2677	33697	31016	4774	4041
5013 b 1	2964	41356	2790	25488	38384	5887	6365

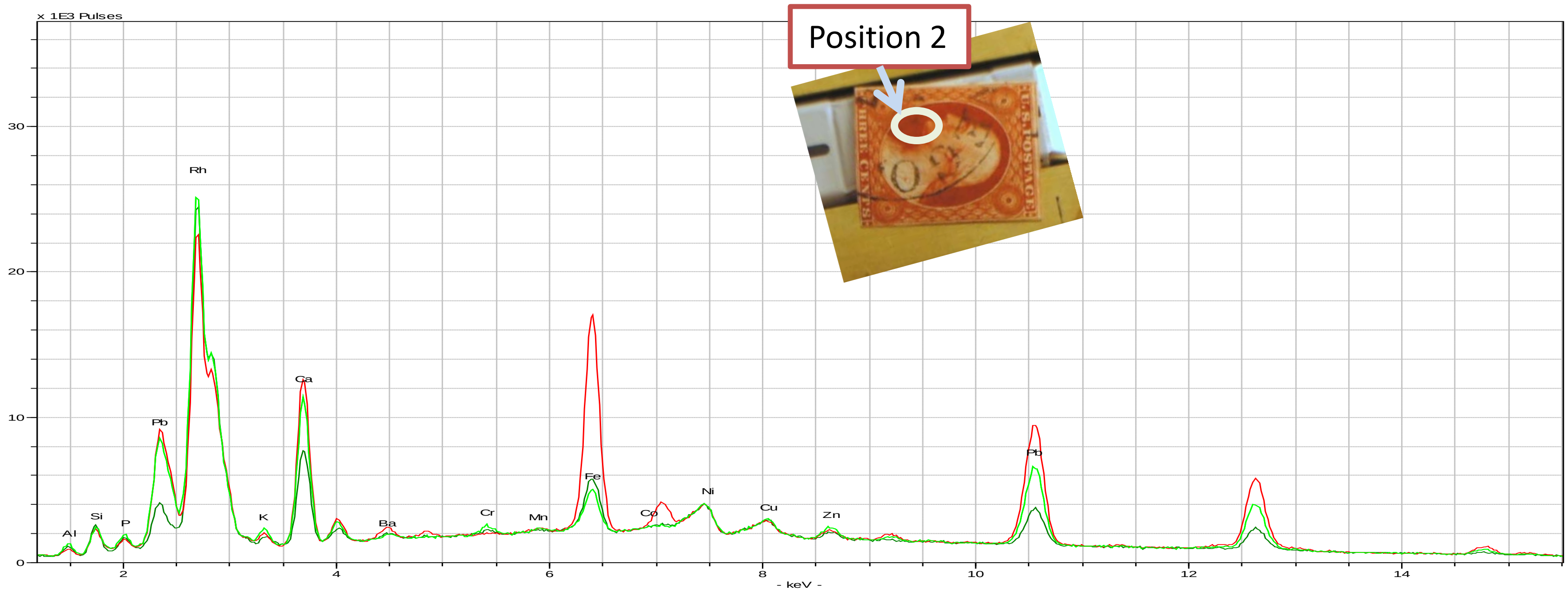




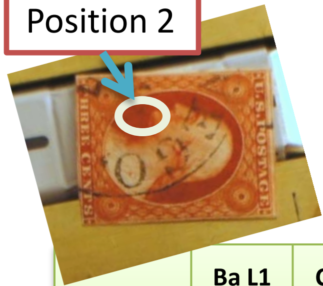
Energy spectra of photons detected in 500 sec from the front of the stamps at position 2 (red area)



Energy spectra of photons detected in 500 sec from the back of the stamps at position 2 (red area)



Position 2



Front and back of Red area (bf2) on all 3 stamps

Number of photons per element detected in 500 sec from the **front** of the stamps at position 2

	Ba L1	Ca K12	Cr K12	Fe K12	Pb L1	Pb M1	Zn K12
5004 bf 2	22115	182271	298	360912	314158	152192	10666
5011 bf 2	3056	217690	24783	35145	194390	77105	6035
5013 bf 2	2355	262589	24346	28087	258836	116354	12054

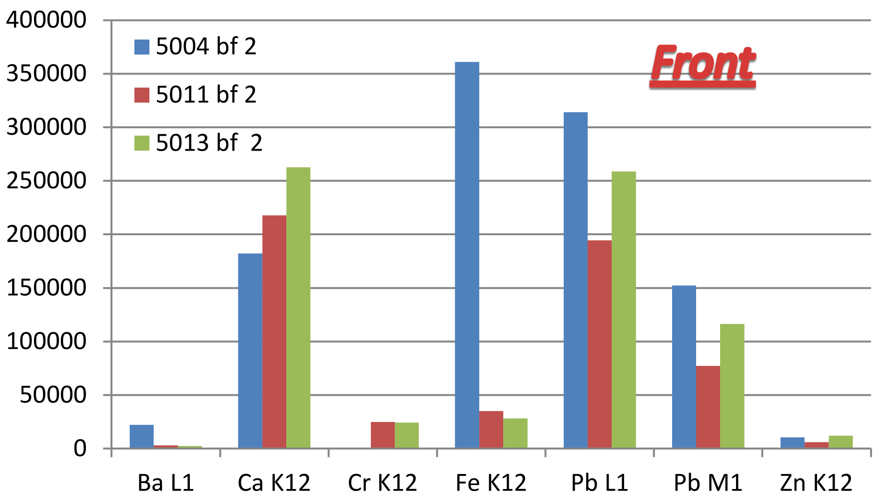
Number of photons per element detected in 500 sec from the **back** of the stamps at position 2

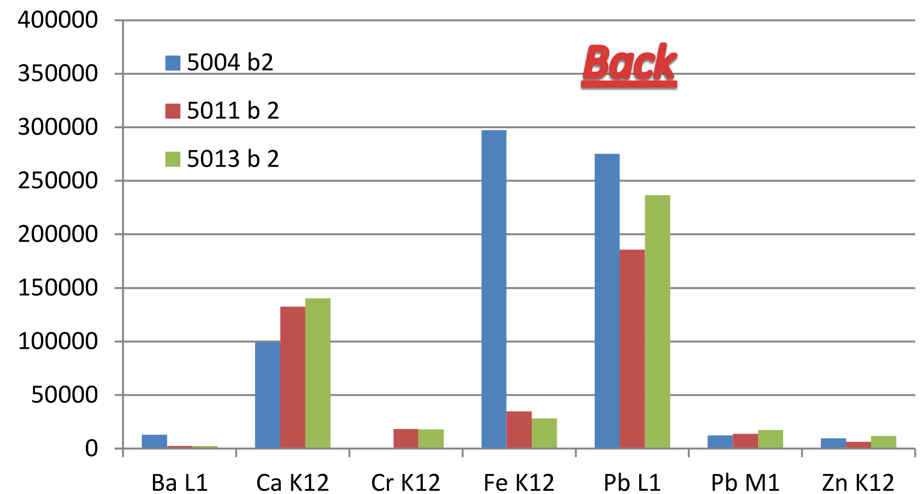
	Ba L1	Ca K12	Cr K12	Fe K12	Pb L1	Pb M1	Zn K12
5004 b2	13046	99375	405	297374	275176	12361	9661
5011 b 2	2505	132668	18288	34906	185646	13954	6222
5013 b 2	2524	140214	18101	28141	236698	17425	11631

Looking at number of photons from each element, from the front of the 3 stamps it is clear that 5004 is very different; it contains Ba, 30% less Ca , no Cr, 90% more Fe, 20% more Pb.

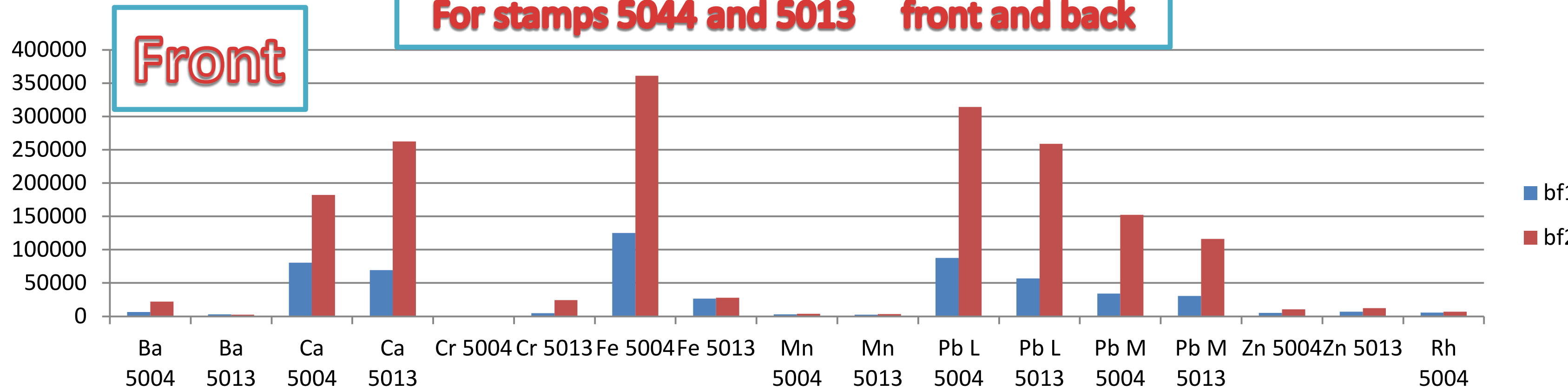
5011 and 5013 are very similar in elemental content with shifts in the concentration of the elements. They contain Ca, Cr, Pb the relative amounts of these can be seen in the plots.

Comparing the front to back analysis it is clear that all the elements show lower concentration from the back except for Fe and Zn, that appear to be in the paper since they are the same front to back.

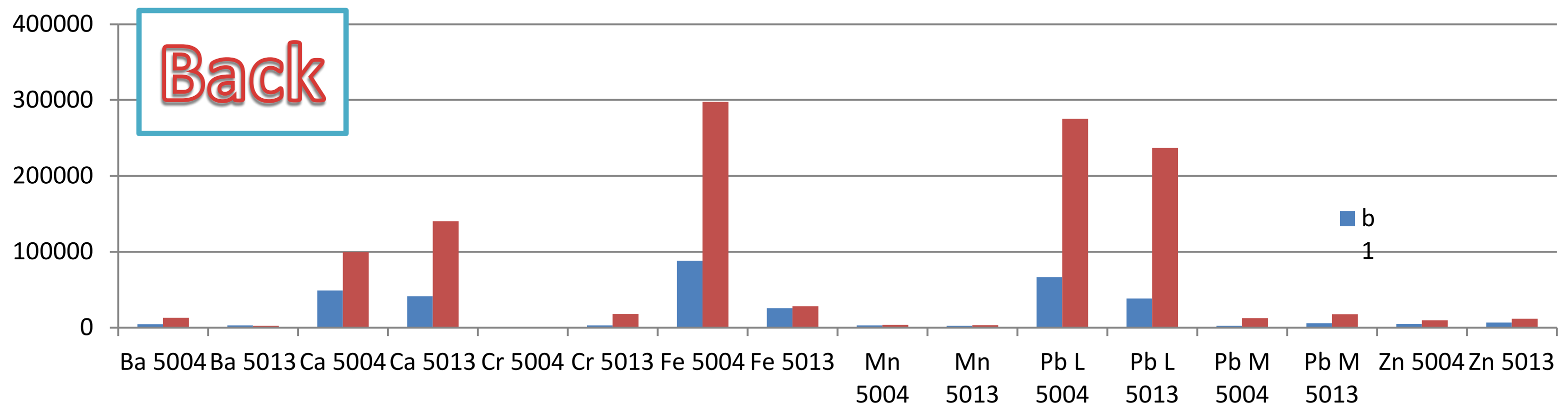




White area (bf1) Vs Red area (bf2)
For stamps 5044 and 5013 front and back



	Ba 5004	Ba 5013	Ca 5004	Ca 5013	Cr 5004	Cr 5013	Fe 5004	Fe 5013	Mn 5004	Mn 5013	Pb L 5004	Pb L 5013	Pb M 5004	Pb M 5013	Zn 5004	Zn 5013
bf1	6331	2817	80586	69412	401	4812	125295	26348	2861	2334	87605	56661	34184	30484	5193	6759
bf2	22115	2355	182271	262589	298	24346	360912	28087	3869	3281	314158	258836	152408	116354	10666	12054



	Ba 5004	Ba 5013	Ca 5004	Ca 5013	Cr 5004	Cr 5013	Fe 5004	Fe 5013	Mn 5004	Mn 5013	Pb L 5004	Pb L 5013	Pb M 5004	Pb M 5013	Zn 5004	Zn 5013
b1	**4521**	**2964**	**48619**	**41356**	**581**	**2790**	**88186**	**25488**	**2730**	**2536**	**66652**	**38384**	**2479**	**5887**	**4824**	**6365**
b2	**13046**	**2524**	**99375**	**140214**	**405**	**18101**	**297374**	**28141**	**3620**	**3187**	**275176**	**236698**	**12361**	**17425**	**9661**	**11631**

See next page for discussion

Comparison of stamps 5004 and 5013 front and back (White to Red area):

Looking at number of photons from each element, from the front of the 2 stamps in the white and the Red area it is clear that 5004 is very different; it contains Ba, less Ca , no Cr, large amounts of Fe, more Pb and the same Mn and Zn.

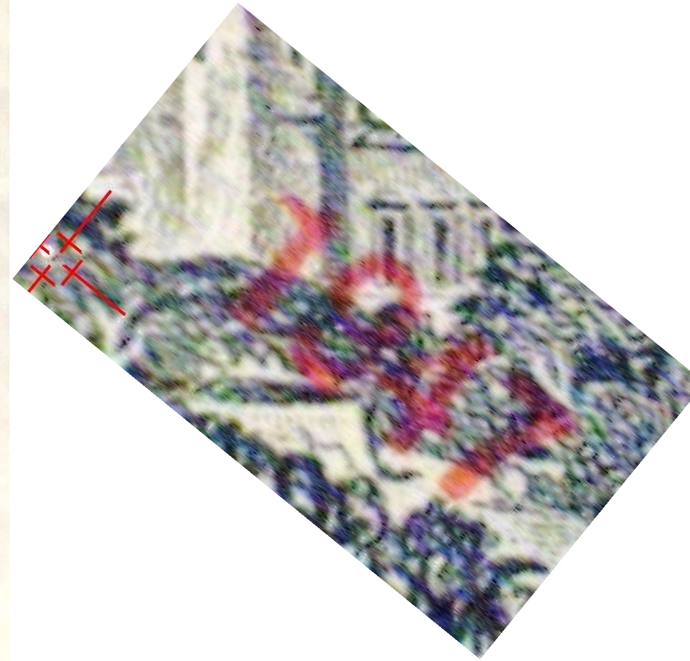
5011 and 5013 based on the elemental analysis are very similar in elemental content as was seen above and so 5011was not analyzed here.

Looking at the white versus red data one sees that there is a little of the same ink used in the white portion of the image on the stamps, as the same elements are detected in both the red and white areas. However the white area has much less of those elements.

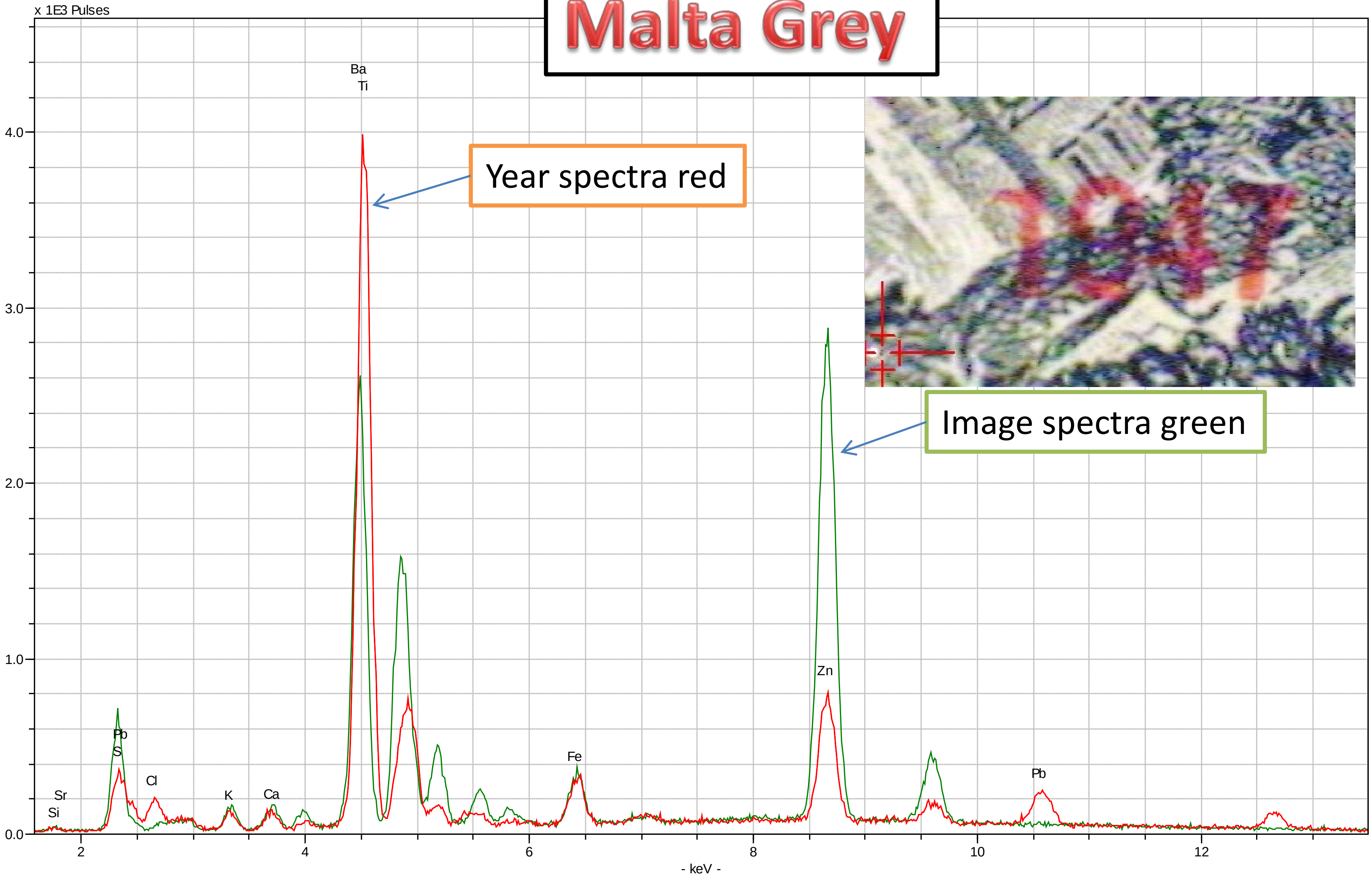
Also this is a way to detect which elements are in the paper and not the pigment when the intensity shows up the same in both pigments. For instance it appears there is both Ca in the pigment and the paper, for all 3 stamps. Fe does not appear in the pigment of 5011 and 5013. Mn and Zn does not appear in any of the pigments.. Pb appears in all 3 pigments. Ba occurs only in the pigment of 5004 and Cr appears only in the pigment of 5011 and 5013.

Malta Stamps Elemental scan

Malta Grey



Malta Grey



x 1E3 Pulses
4.0
3.0
2.0
1.0
0.0
Ba
Ti
Year spectra red
Image spectra green
Sr
Si
Pb
S
Cl
K
Ca
Fe
Zn
Pb
2
4
6
8
10
12
- keV -

Malta Grey

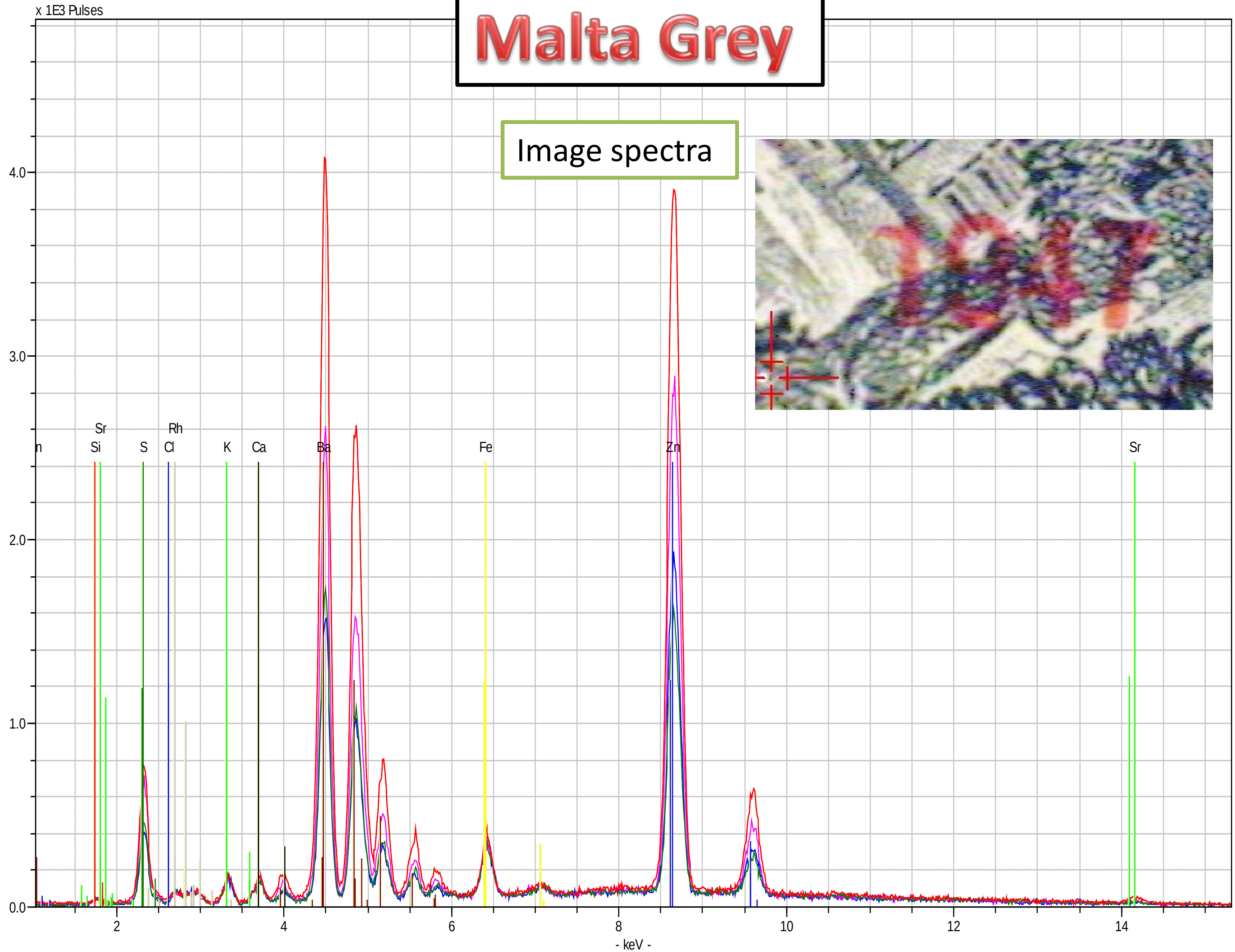
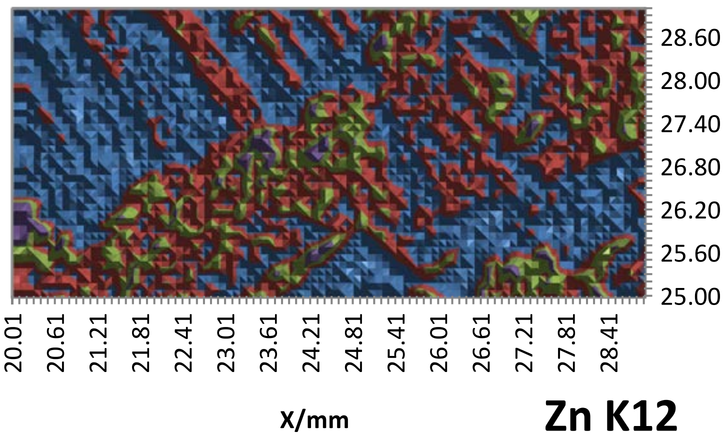


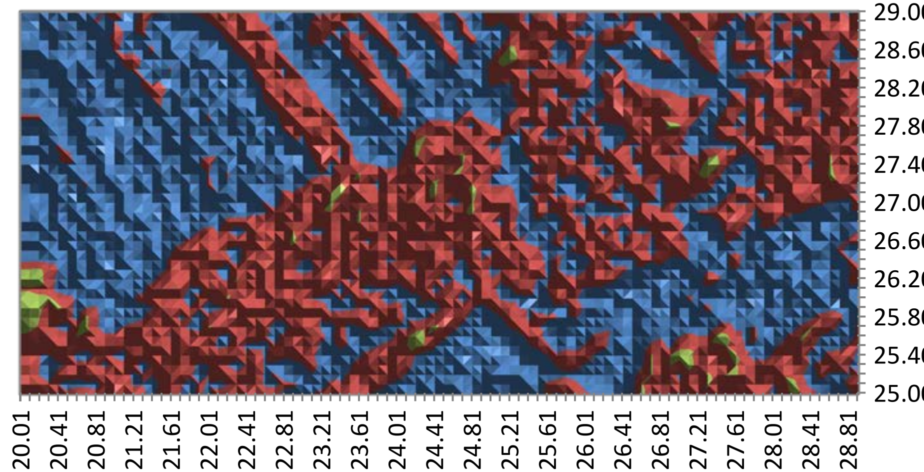
Image spectra
x 1E3 Pulses
4.0
3.0
2.0
1.0
0.0
Sr
Rh
n
Si
S
Cl
K
Ca
Ba
Fe
Zn
Sr
2
4
6
8
10
12
14
- keV -

Malta Grey stamp Elemental scan

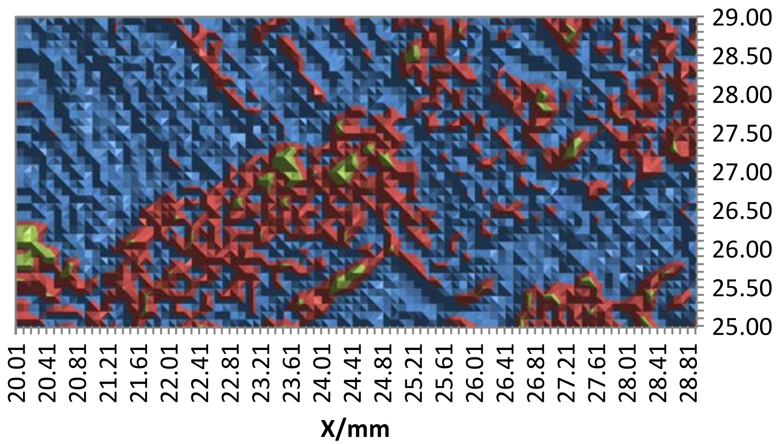
Ba L1

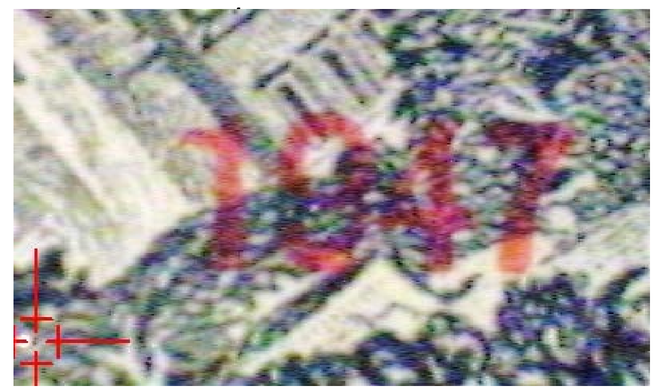


S K12



Zn K12

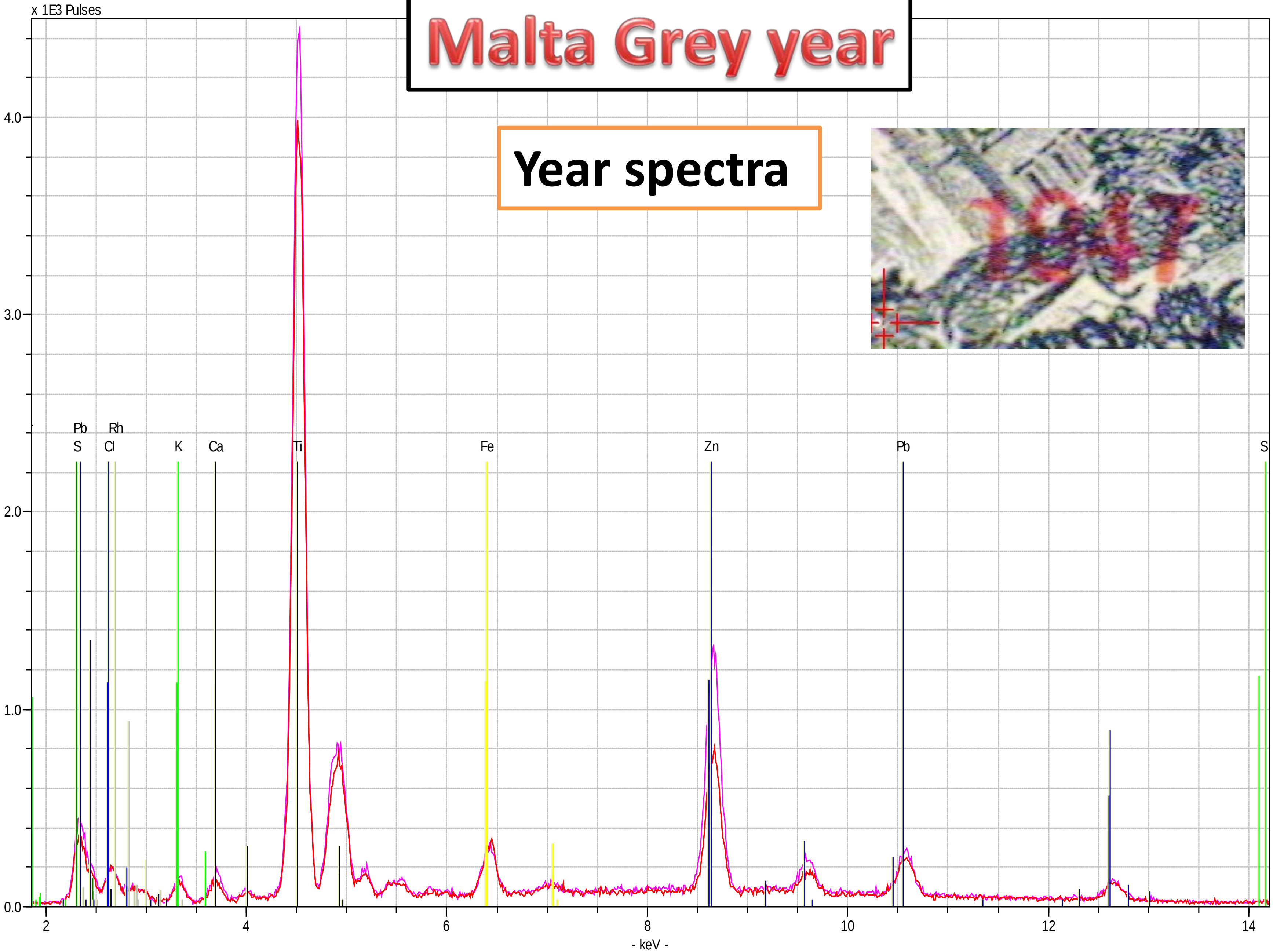




- 150000-200000
- 100000-150000
- 50000-100000
- 0-50000

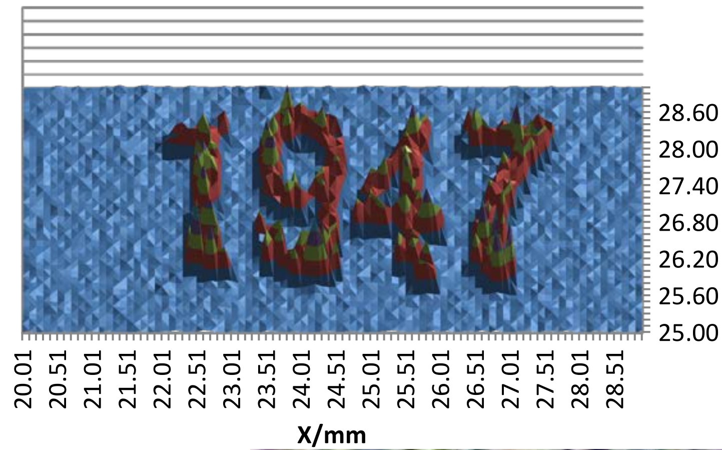
Malta Grey year

Year spectra

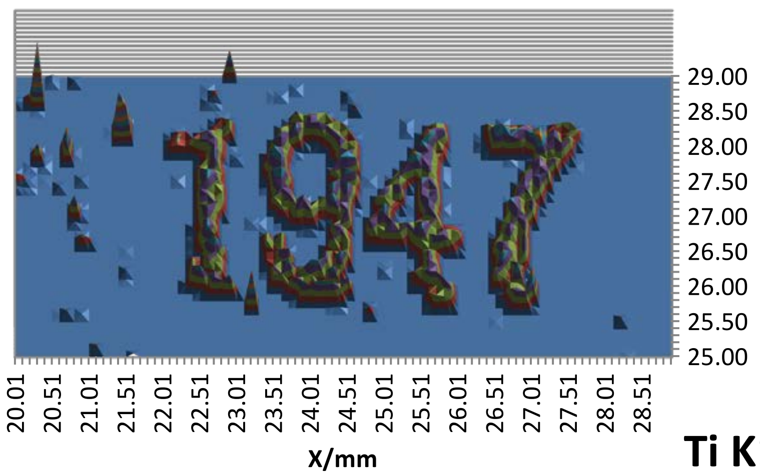


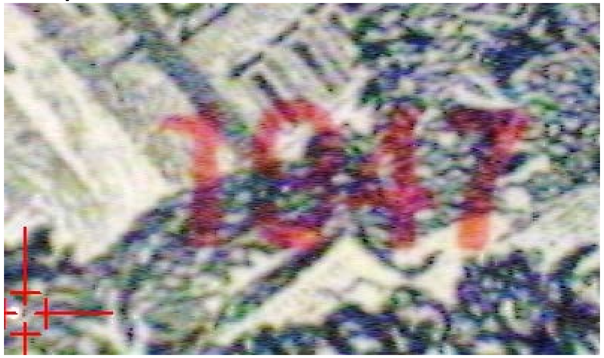
Malta Grey stamp Elemental scan

Pb L1

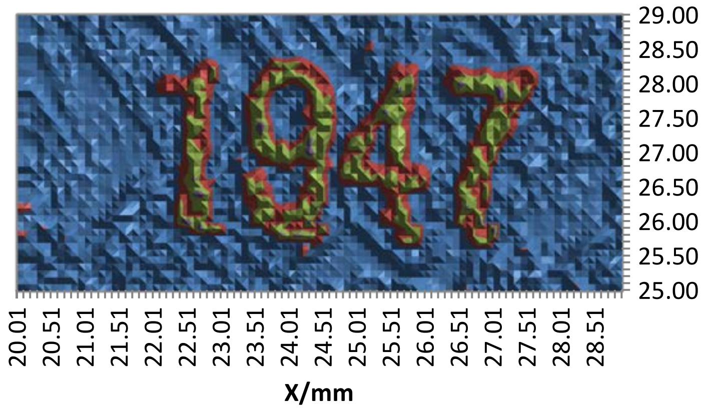


Cl K12



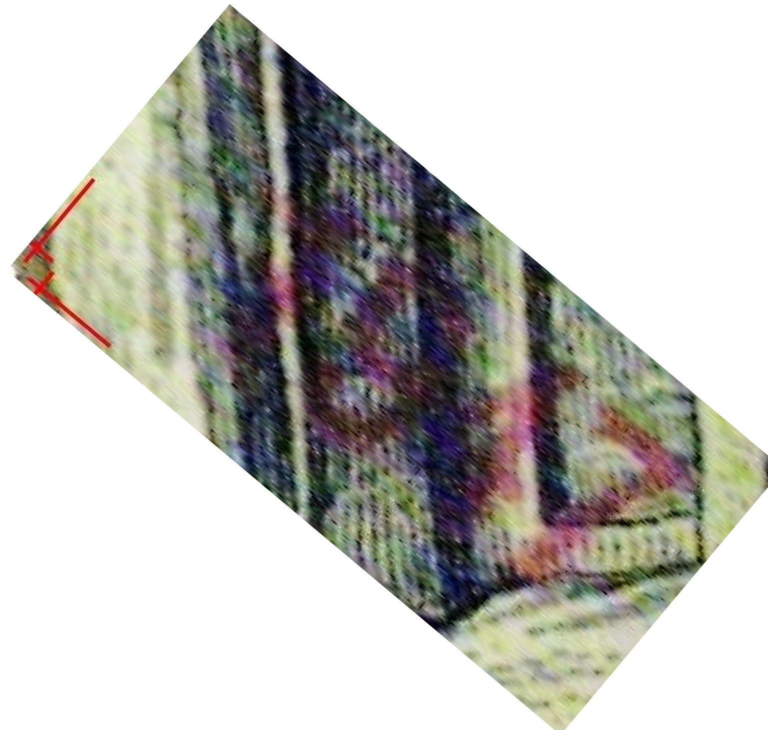


Ti K12

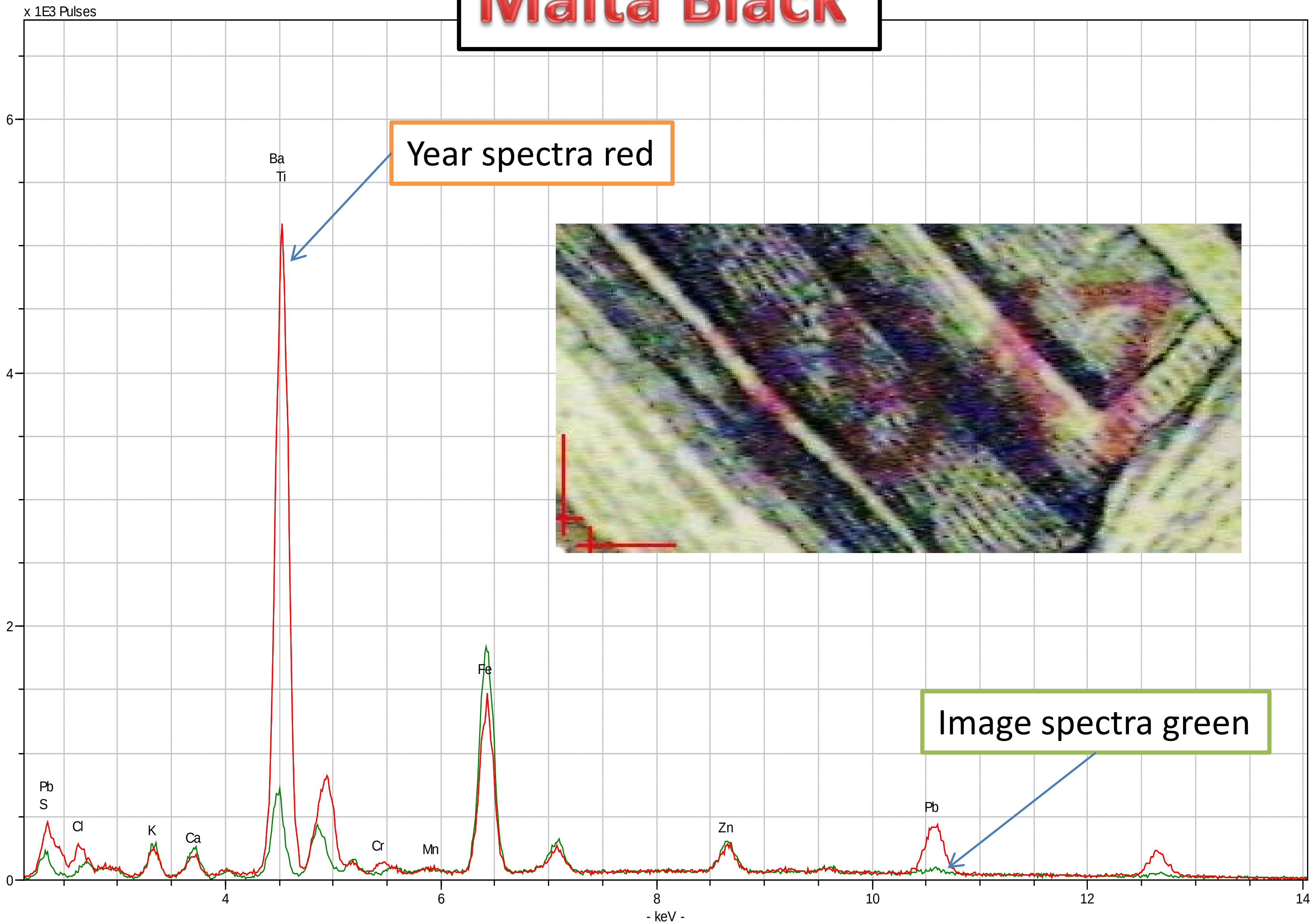


- 80000-100000
- 60000-80000
- 40000-60000
- 20000-40000
- 0-20000

Malta Black



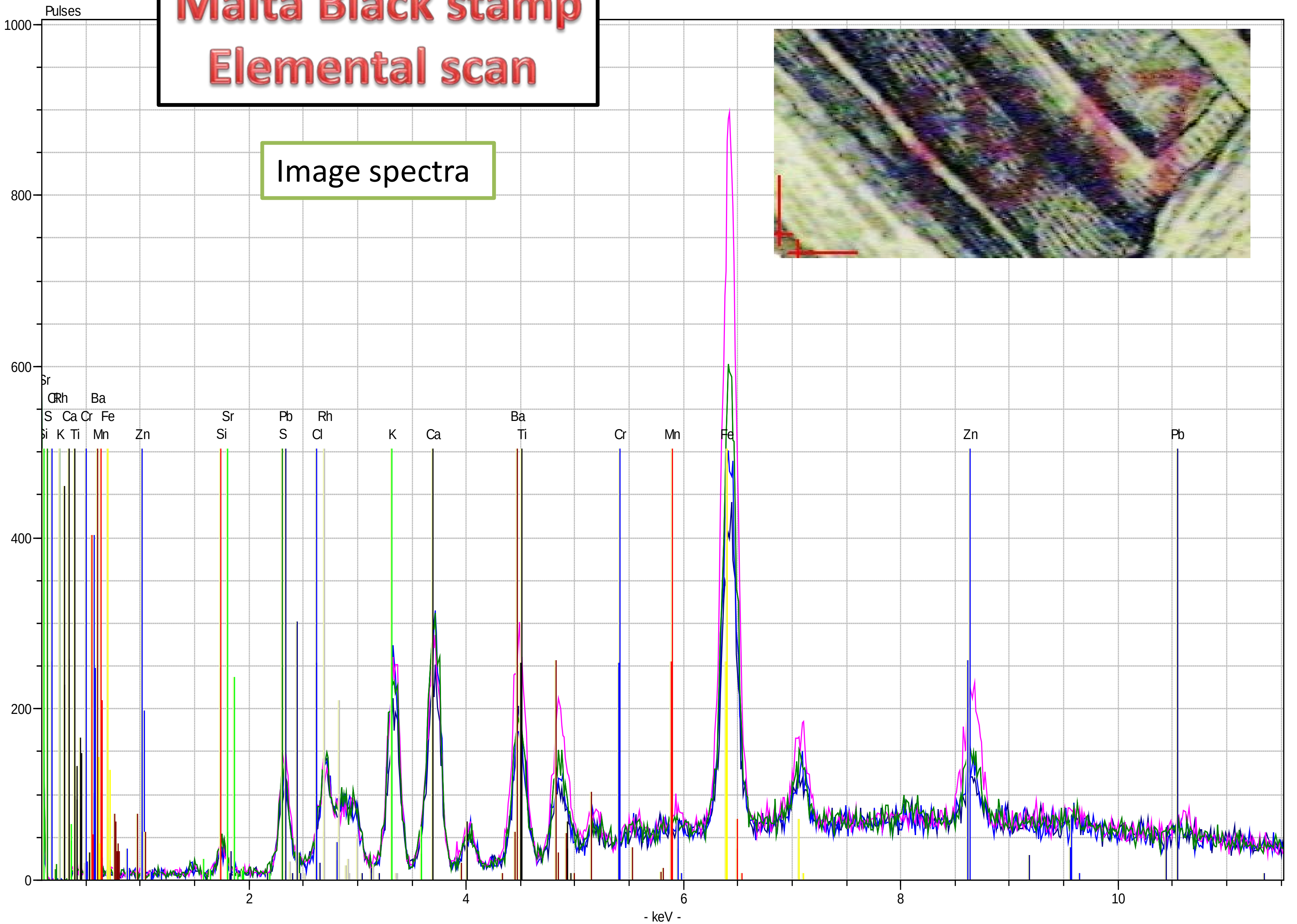
Malta Black



x 1E3 Pulses
Year spectra red
Image spectra green
Ba
Ti
Fe
Pb
S
Cl
K
Ca
Cr
Mn
Zn
Pb
0
2
4
6
4
6
8
10
12
14
- keV -

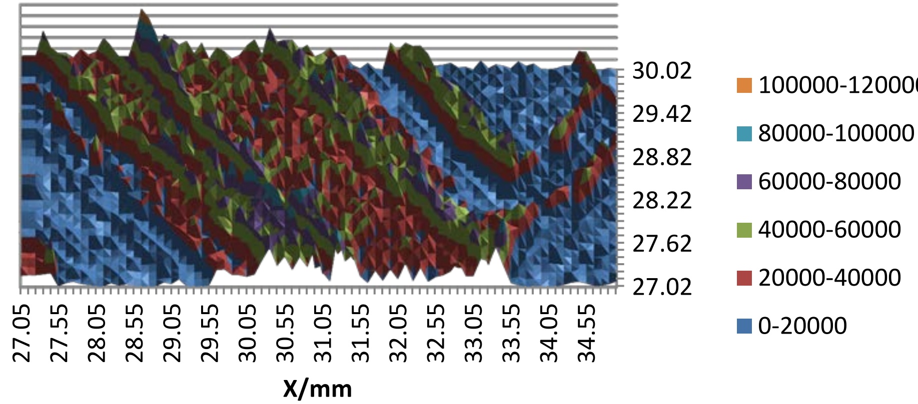
Malta Black stamp Elemental scan

Image spectra

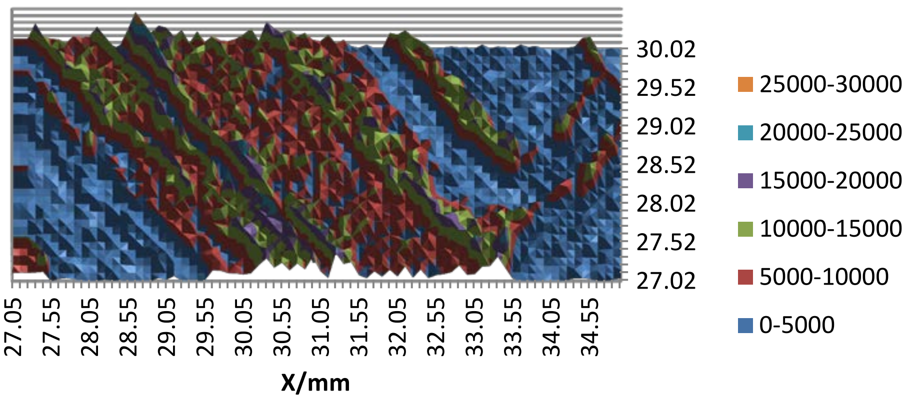


Malta Black stamp Elemental scan

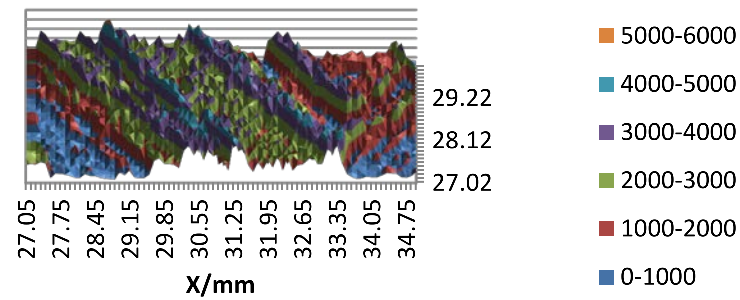
Fe K12



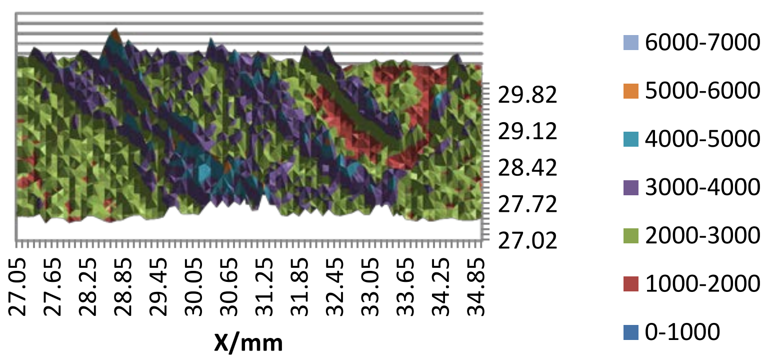
Ba L1

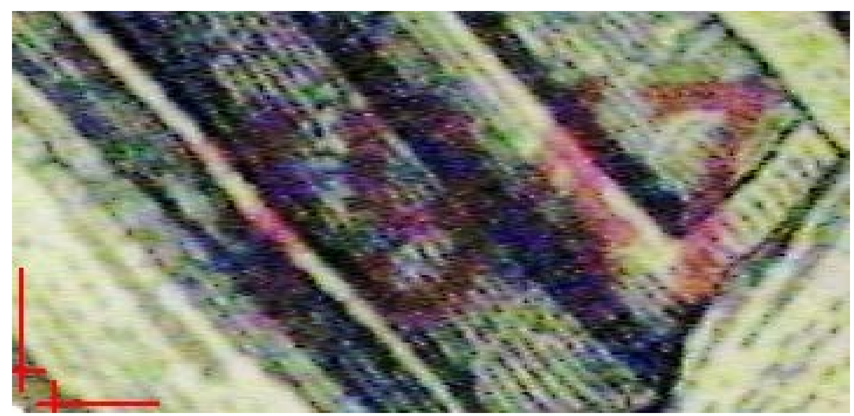


S K12



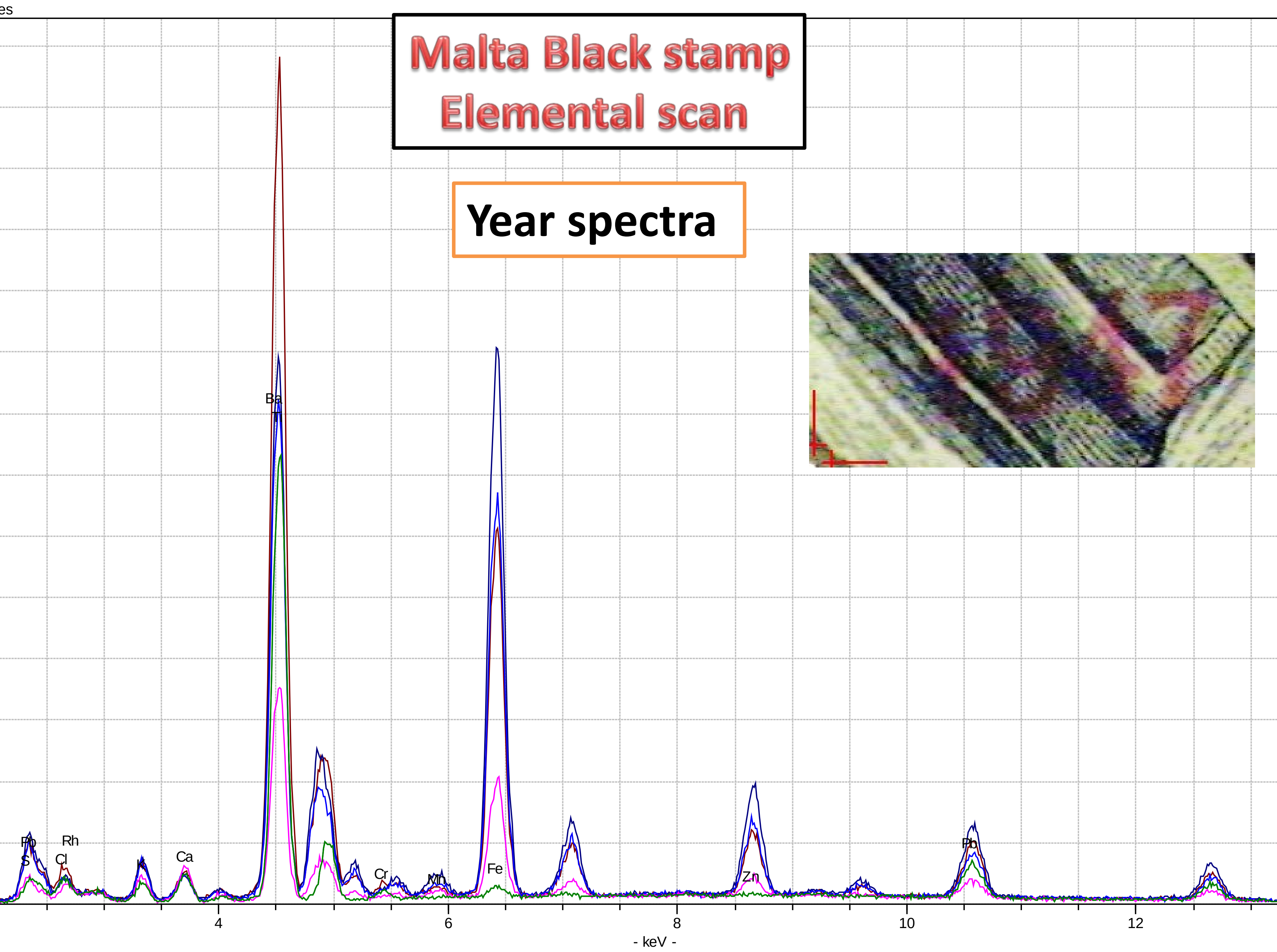
K K12





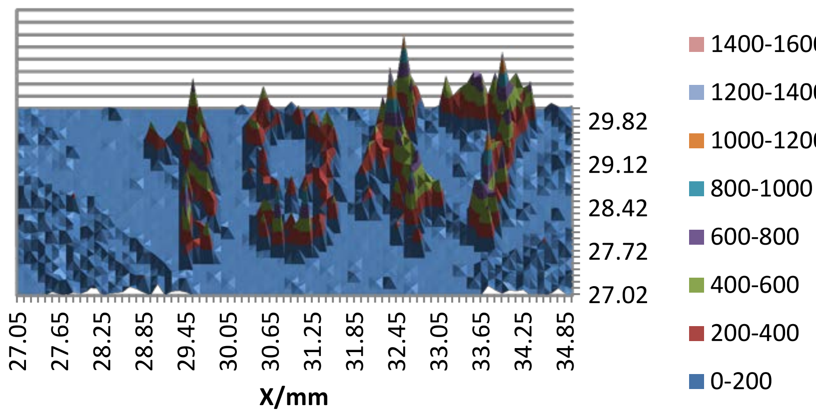
Malta Black stamp Elemental scan

Year spectra

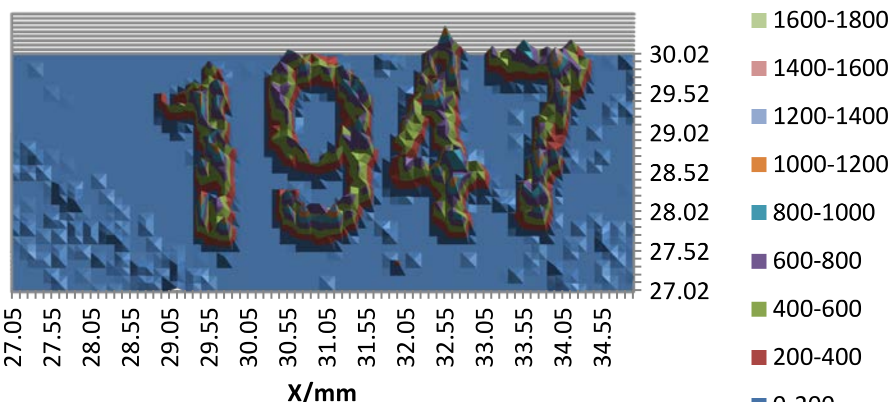


Malta Black stamp Elemental scan

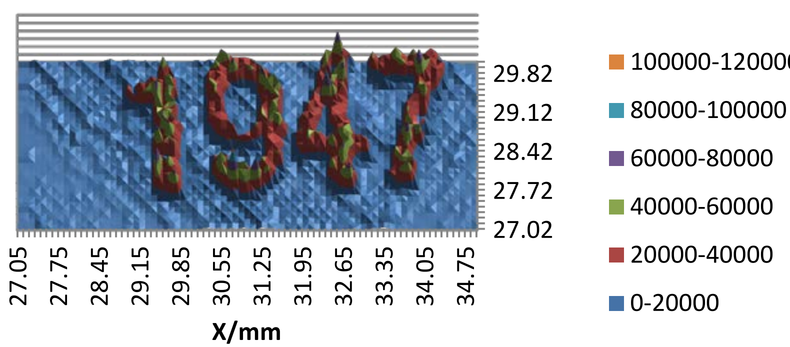
Cr K12



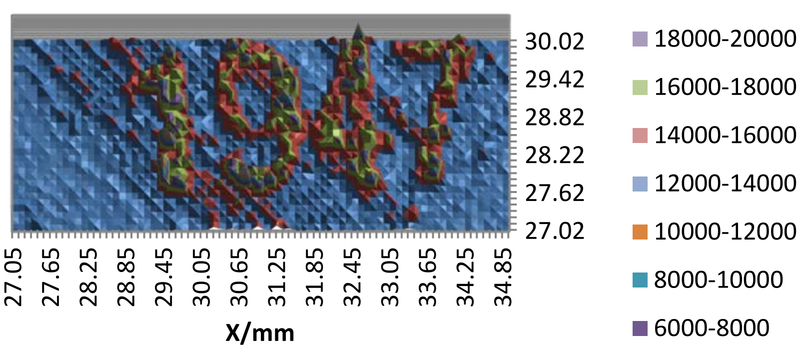
Cl K12

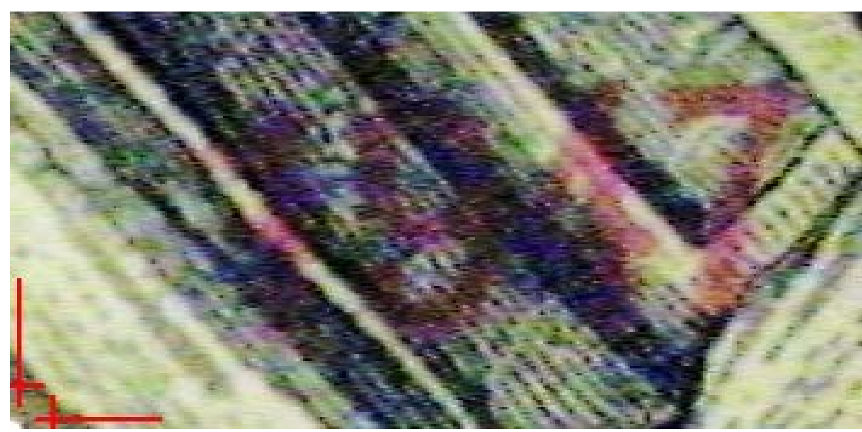


Ti K12

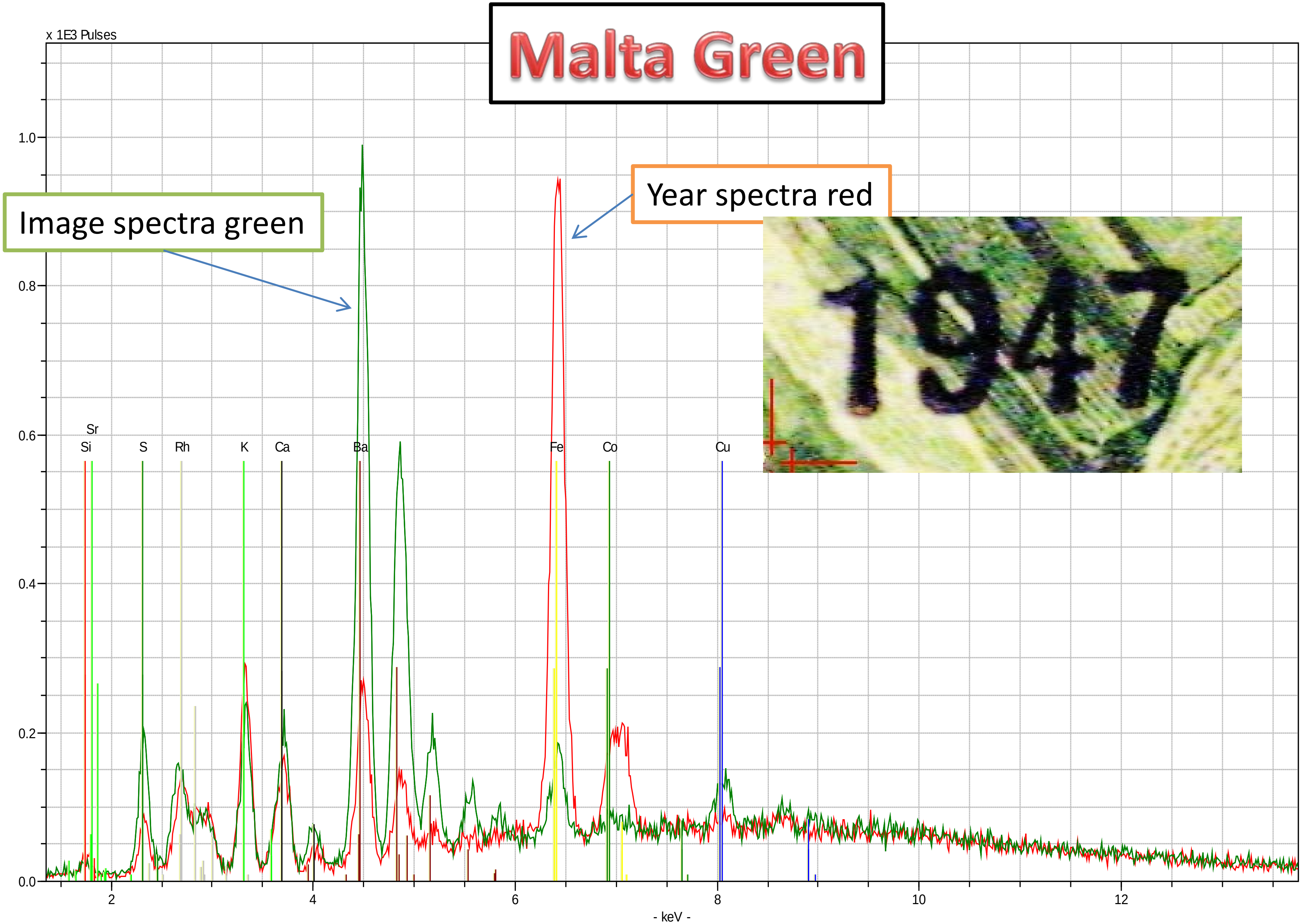


Pb L1





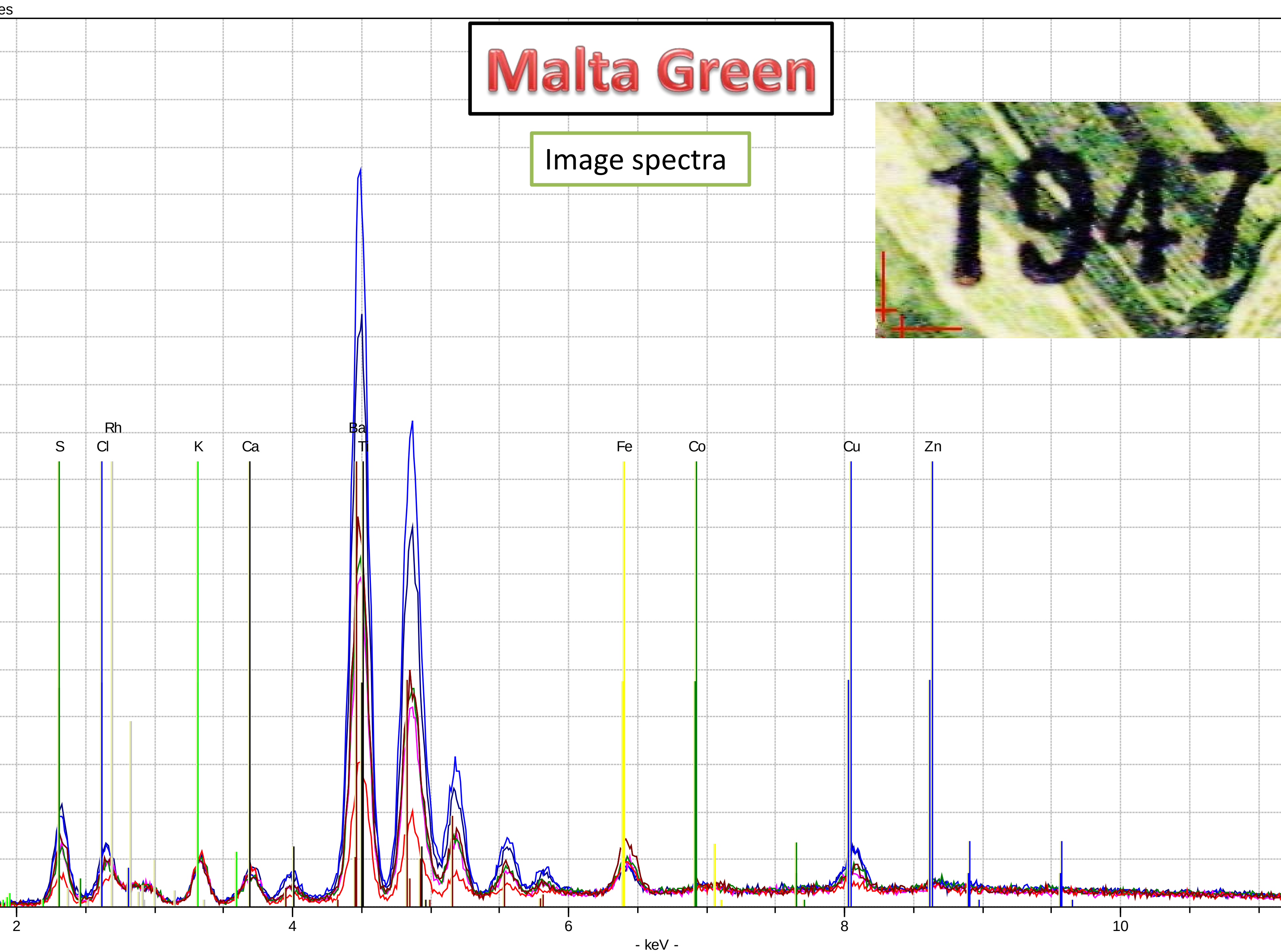
Malta Green

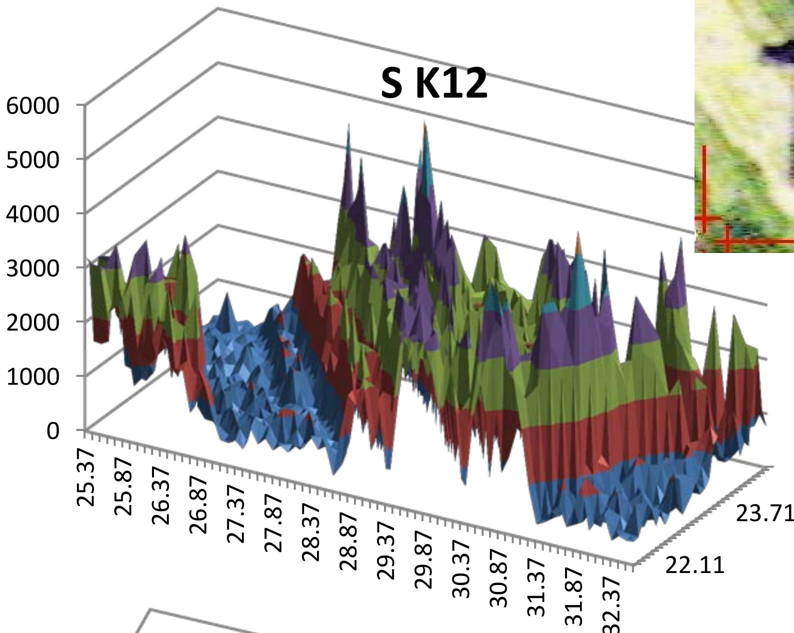


Malta Green
x 1E3 Pulses
Image spectra green
Year spectra red
Sr
Si
S
Rh
K
Ca
Ba
Fe
Co
Cu
1947
1.0
0.8
0.6
0.4
0.2
0.0
2
4
6
8
10
12
- keV -

Malta Green

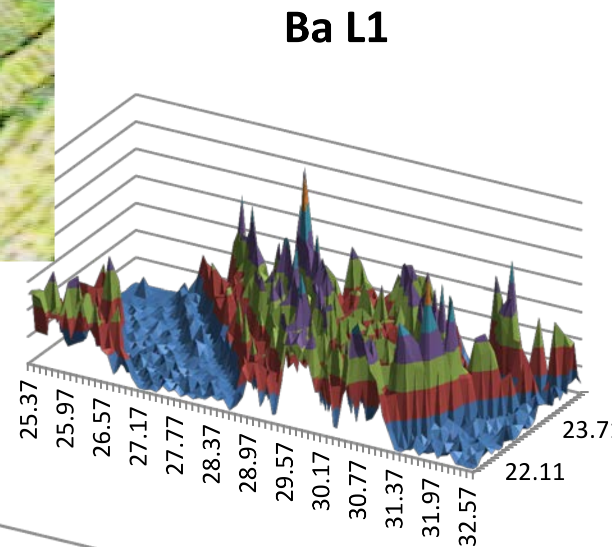
Image spectra



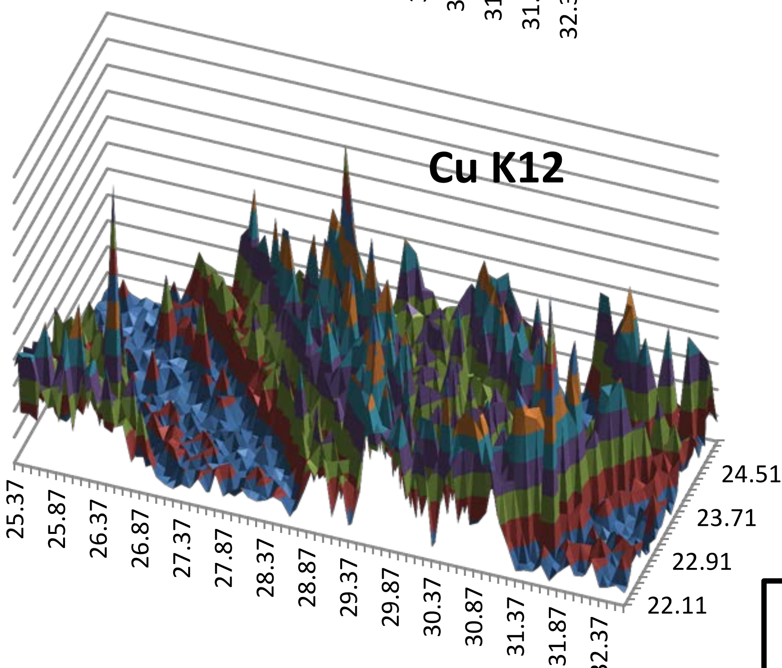


S K12
6000
5000
4000
3000
2000
1000
0
25.37
25.87
26.37
26.87
27.37
27.87
28.37
28.87
29.37
29.87
30.37
30.87
31.37
31.87
32.37
23.71
22.11

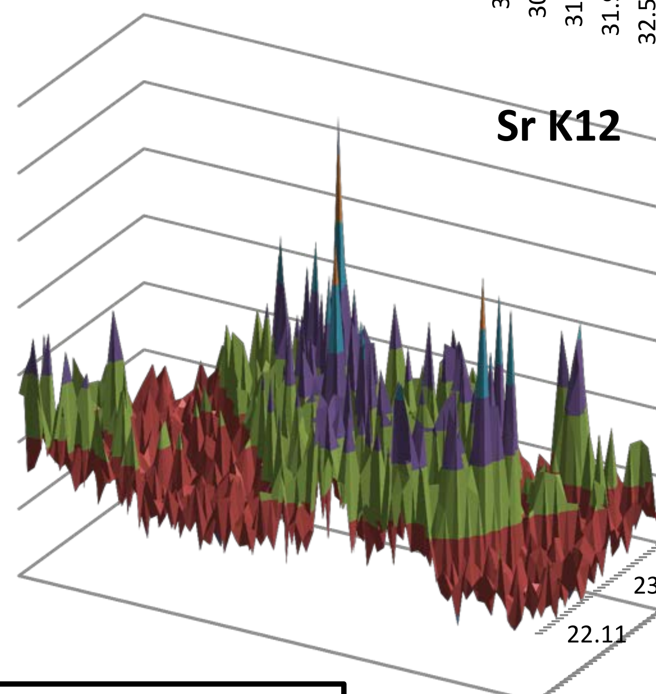
1947



Ba L1
25.37
25.97
26.57
27.17
27.77
28.37
28.97
29.57
30.17
30.77
31.37
31.97
32.57
23.71
22.11



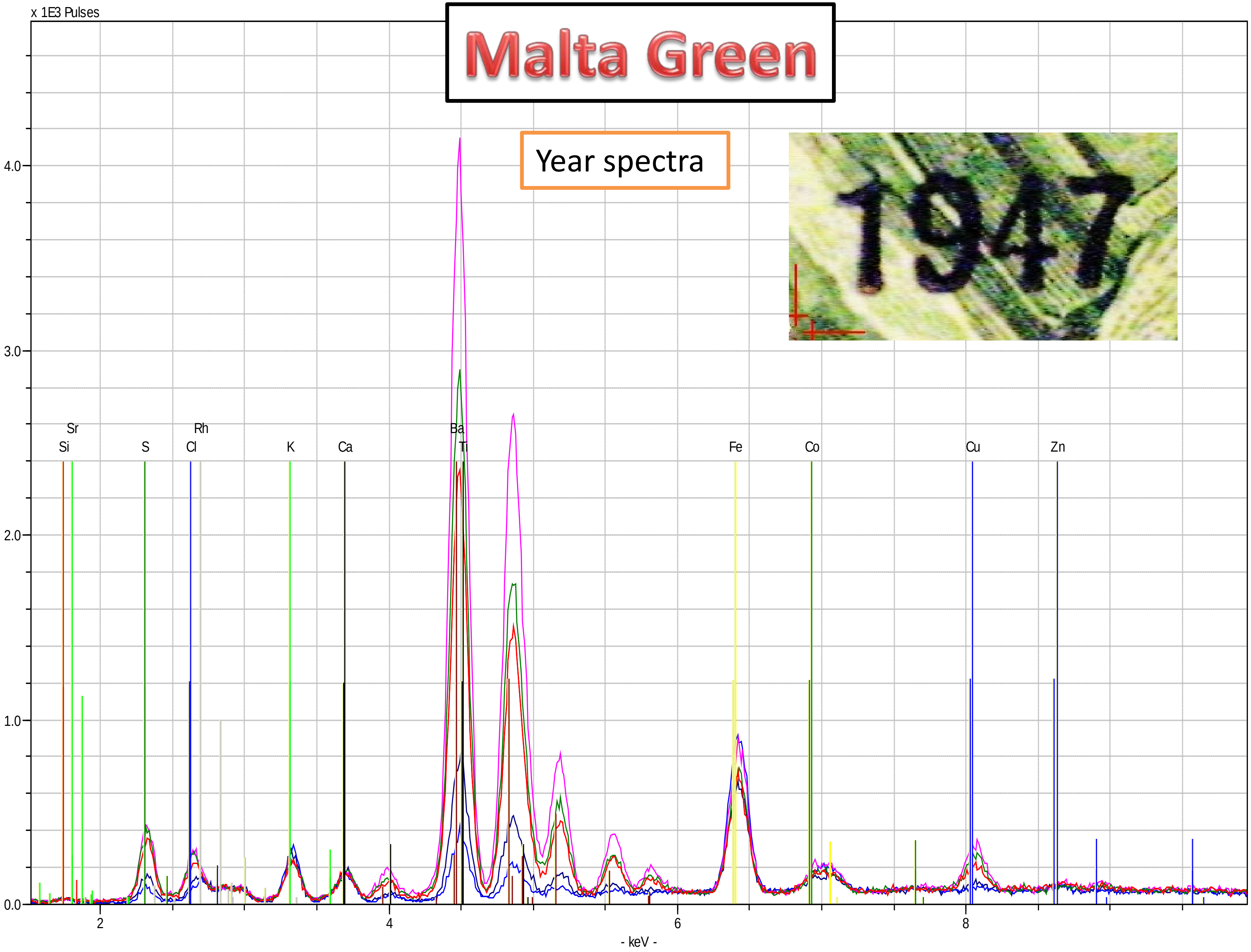
Cu K12
25.37
25.87
26.37
26.87
27.37
27.87
28.37
28.87
29.37
29.87
30.37
30.87
31.37
31.87
32.37
24.51
23.71
22.91
22.11

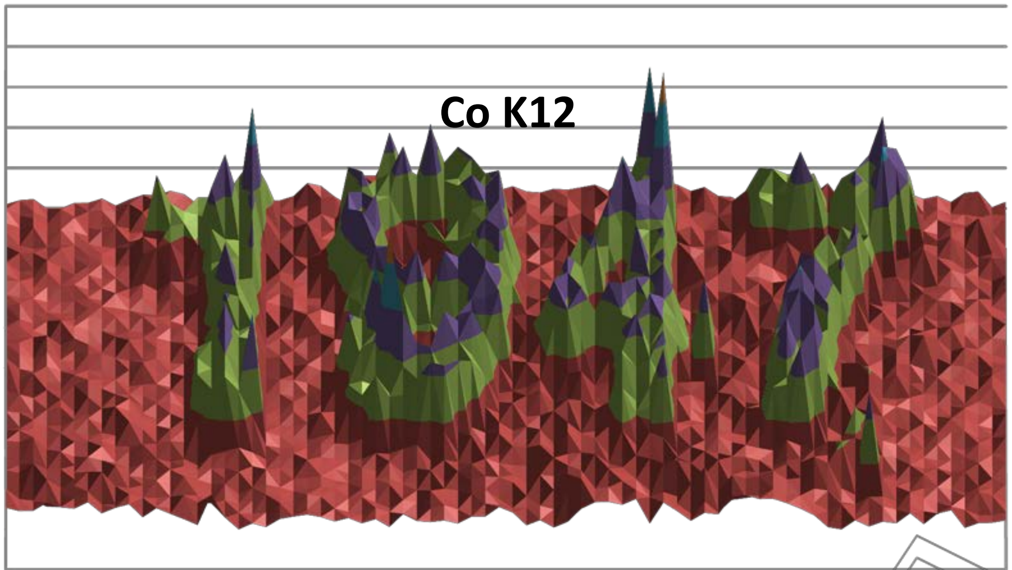


Sr K12
23.71
22.11

Malta Green

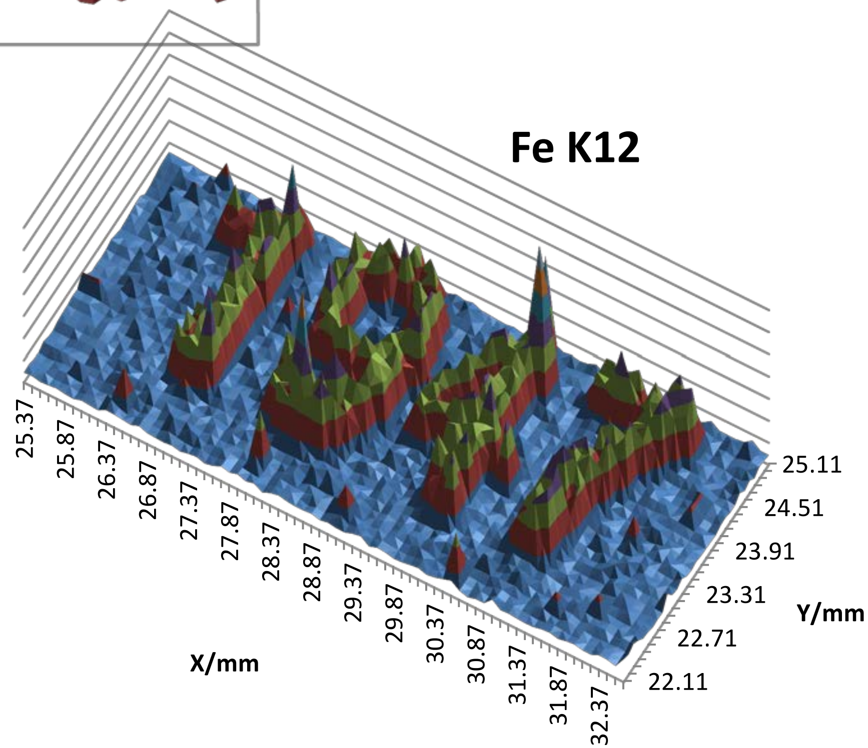
Malta Green


Year spectra
x 1E3 Pulses
4.0
3.0
2.0
1.0
0.0
Sr
Si
S
Rh
Cl
K
Ca
Ba
Ti
Fe
Co
Cu
Zn
2
4
6
8
- keV -
1947

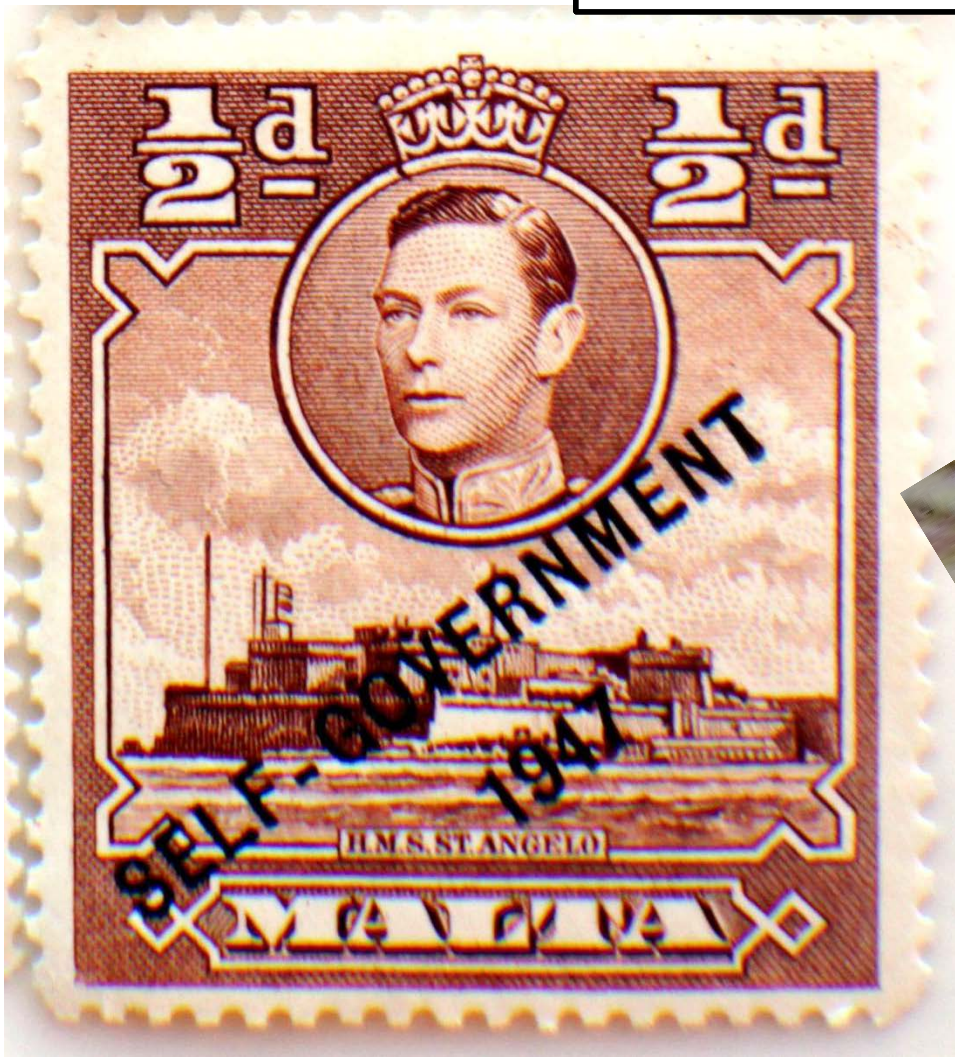

Co K12

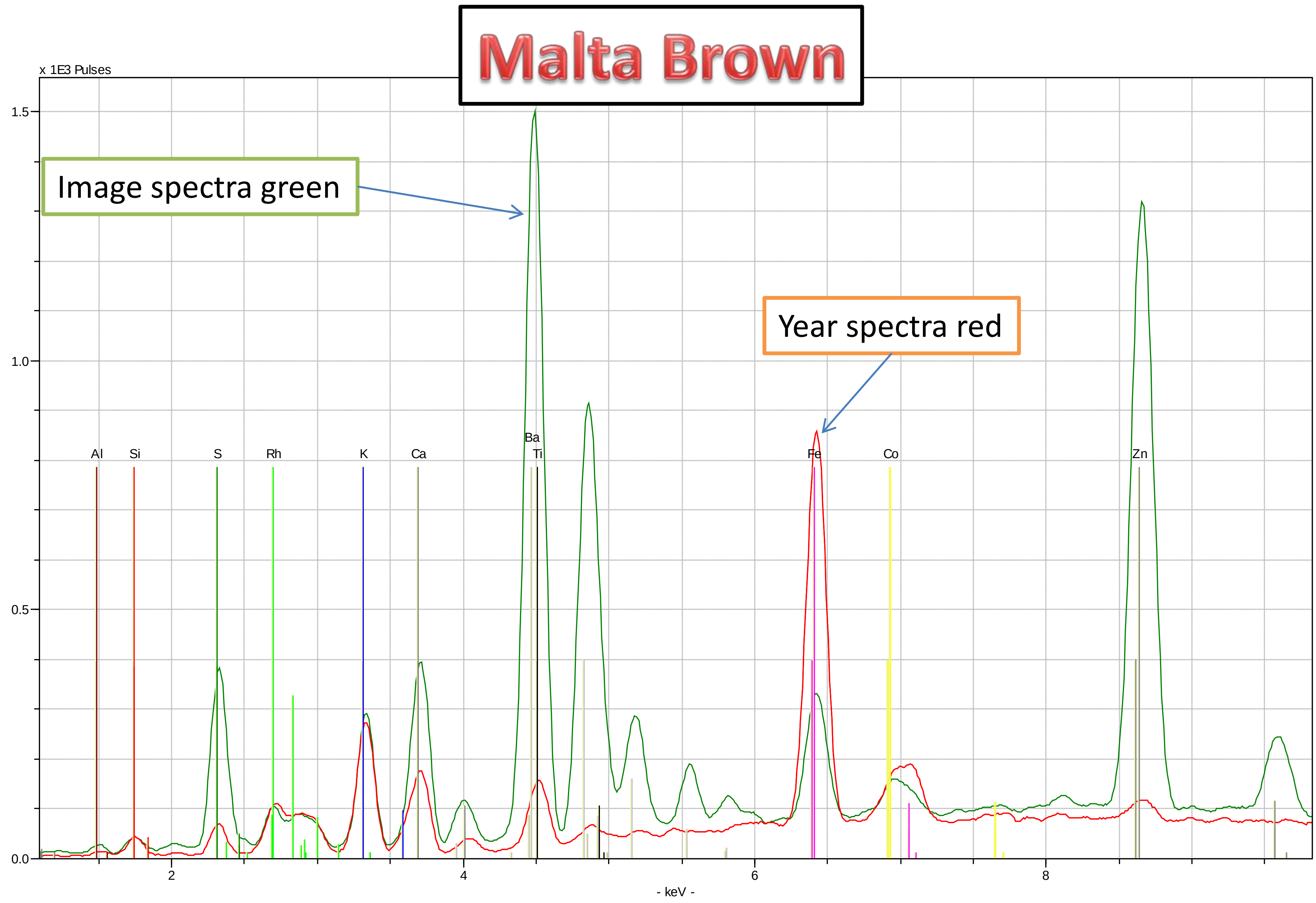
Malta Green


1947


Fe K12
25.37
25.87
26.37
26.87
27.37
27.87
28.37
28.87
29.37
29.87
30.37
30.87
31.37
31.87
32.37
X/mm
25.11
24.51
23.91
23.31
22.71
22.11
Y/mm

Malta Brown

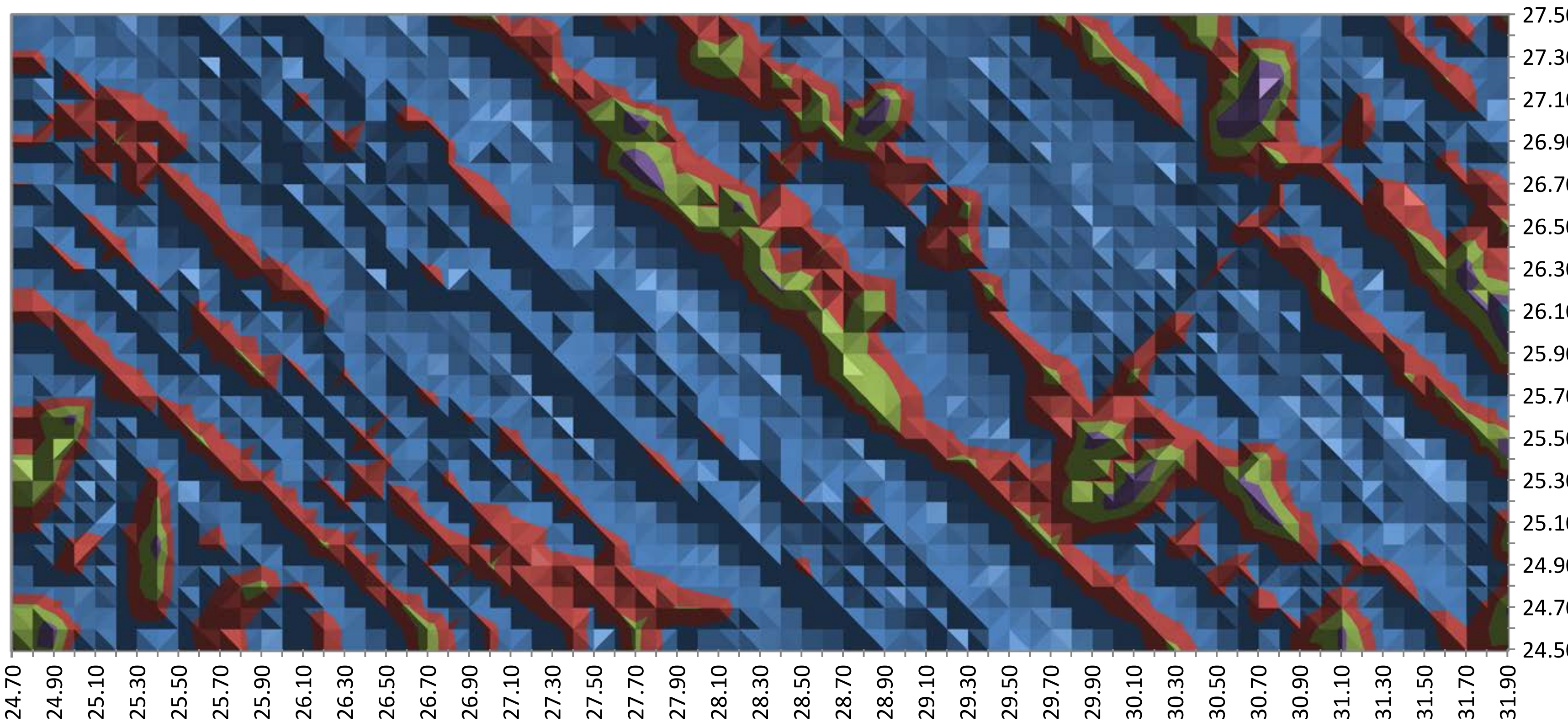


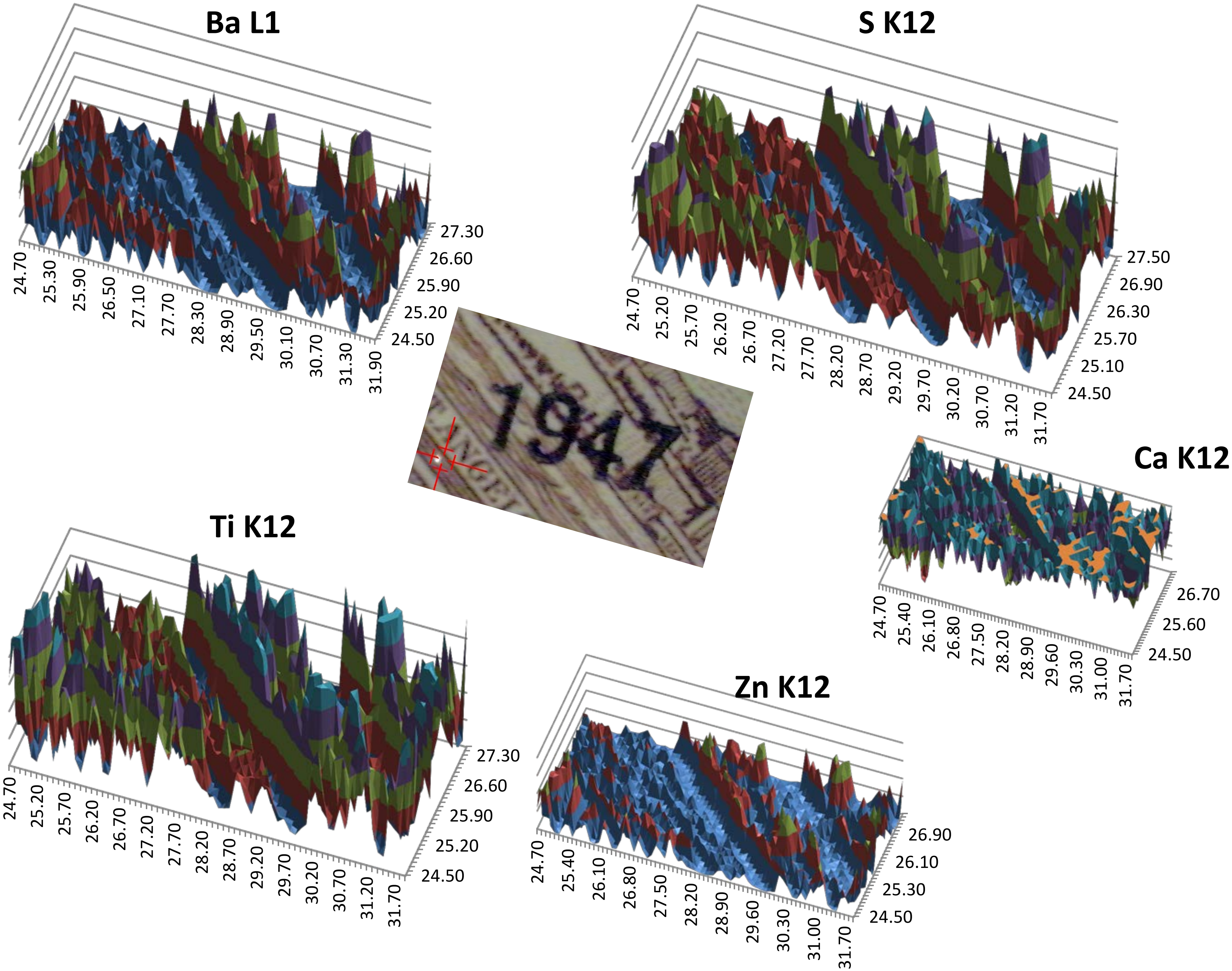


Malta Brown
x 1E3 Pulses
1.5
1.0
0.5
0.0
Image spectra green
Year spectra red
Al
Si
S
Rh
K
Ca
Ba
Ti
Fe
Co
Zn
2
4
6
8
- keV -


1947

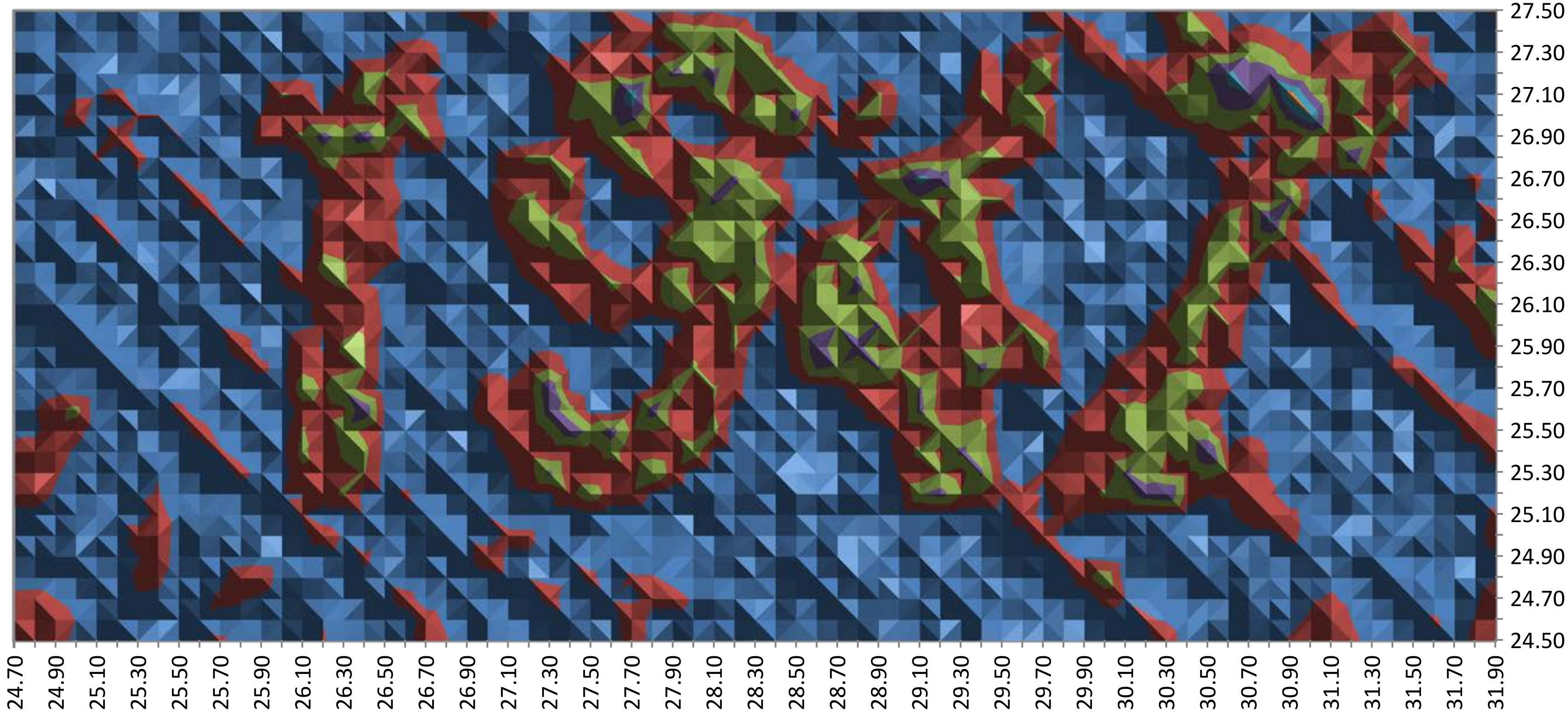
Ba L1

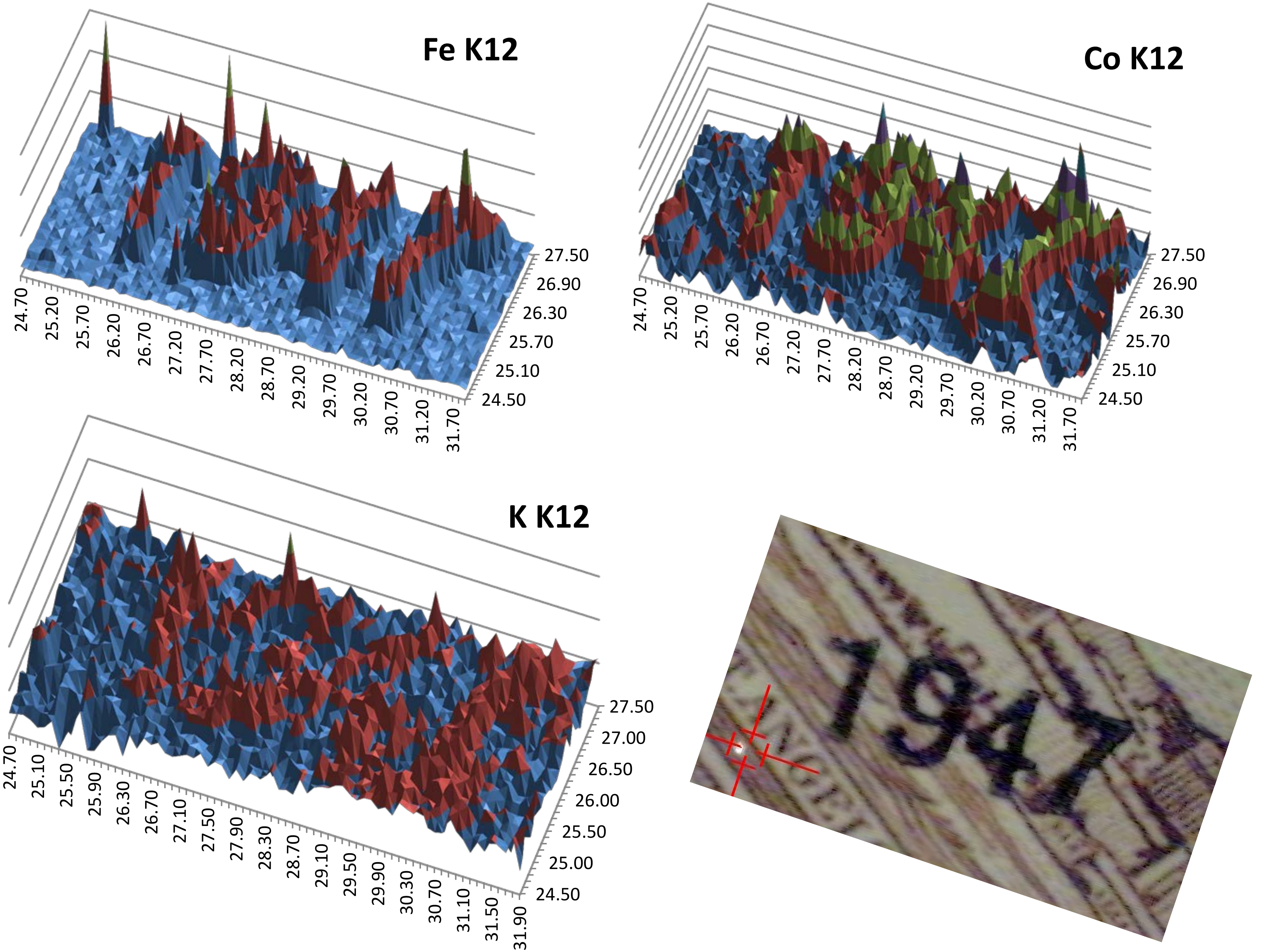

27.50
27.30
27.10
26.90
26.70
26.50
26.30
26.10
25.90
25.70
25.50
25.30
25.10
24.90
24.70
24.50
24.70
24.90
25.10
25.30
25.50
25.70
25.90
26.10
26.30
26.50
26.70
26.90
27.10
27.30
27.50
27.70
27.90
28.10
28.30
28.50
28.70
28.90
29.10
29.30
29.50
29.70
29.90
30.10
30.30
30.50
30.70
30.90
31.10
31.30
31.50
31.70
31.90


Ba L1
24.70
25.30
25.90
26.50
27.10
27.70
28.30
28.90
29.50
30.10
30.70
31.30
31.90
27.30
26.60
25.90
25.20
24.50
S K12
24.70
25.20
25.70
26.20
26.70
27.20
27.70
28.20
28.70
29.20
29.70
30.20
30.70
31.20
31.70
27.50
26.90
26.30
25.70
25.10
24.50
1947
Ca K12
24.70
25.40
26.10
26.80
27.50
28.20
28.90
29.60
30.30
31.00
31.70
26.70
25.60
24.50
Ti K12
24.70
25.20
25.70
26.20
26.70
27.20
27.70
28.20
28.70
29.20
29.70
30.20
30.70
31.20
31.70
27.30
26.60
25.90
25.20
24.50
Zn K12
24.70
25.40
26.10
26.80
27.50
28.20
28.90
29.60
30.30
31.00
31.70
26.90
26.10
25.30
24.50


1947

Co K12


27.50
27.30
27.10
26.90
26.70
26.50
26.30
26.10
25.90
25.70
25.50
25.30
25.10
24.90
24.70
24.50
24.70
24.90
25.10
25.30
25.50
25.70
25.90
26.10
26.30
26.50
26.70
26.90
27.10
27.30
27.50
27.70
27.90
28.10
28.30
28.50
28.70
28.90
29.10
29.30
29.50
29.70
29.90
30.10
30.30
30.50
30.70
30.90
31.10
31.30
31.50
31.70
31.90


Fe K12
24.70 25.20 25.70 26.20 26.70 27.20 27.70 28.20 28.70 29.20 29.70 30.20 30.70 31.20 31.70
24.50 25.10 25.70 26.30 26.90 27.50
Co K12
24.70 25.20 25.70 26.20 26.70 27.20 27.70 28.20 28.70 29.20 29.70 30.20 30.70 31.20 31.70
24.50 25.10 25.70 26.30 26.90 27.50
K K12
24.70 25.10 25.50 25.90 26.30 26.70 27.10 27.50 27.90 28.30 28.70 29.10 29.50 29.90 30.30 30.70 31.10 31.50 31.90
24.50 25.00 25.50 26.00 26.50 27.00 27.50
1947