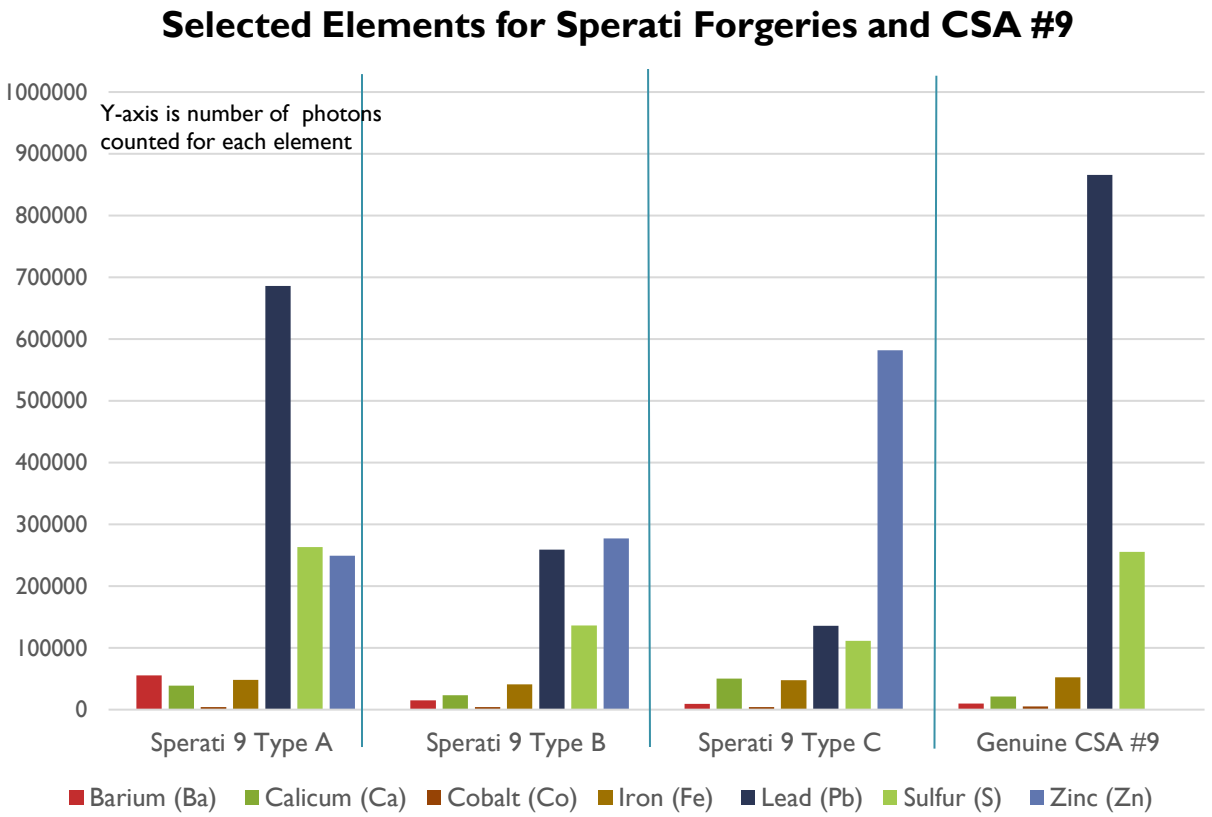
The Use of X-ray Fluorescence in Detecting Philatelic Forgeries

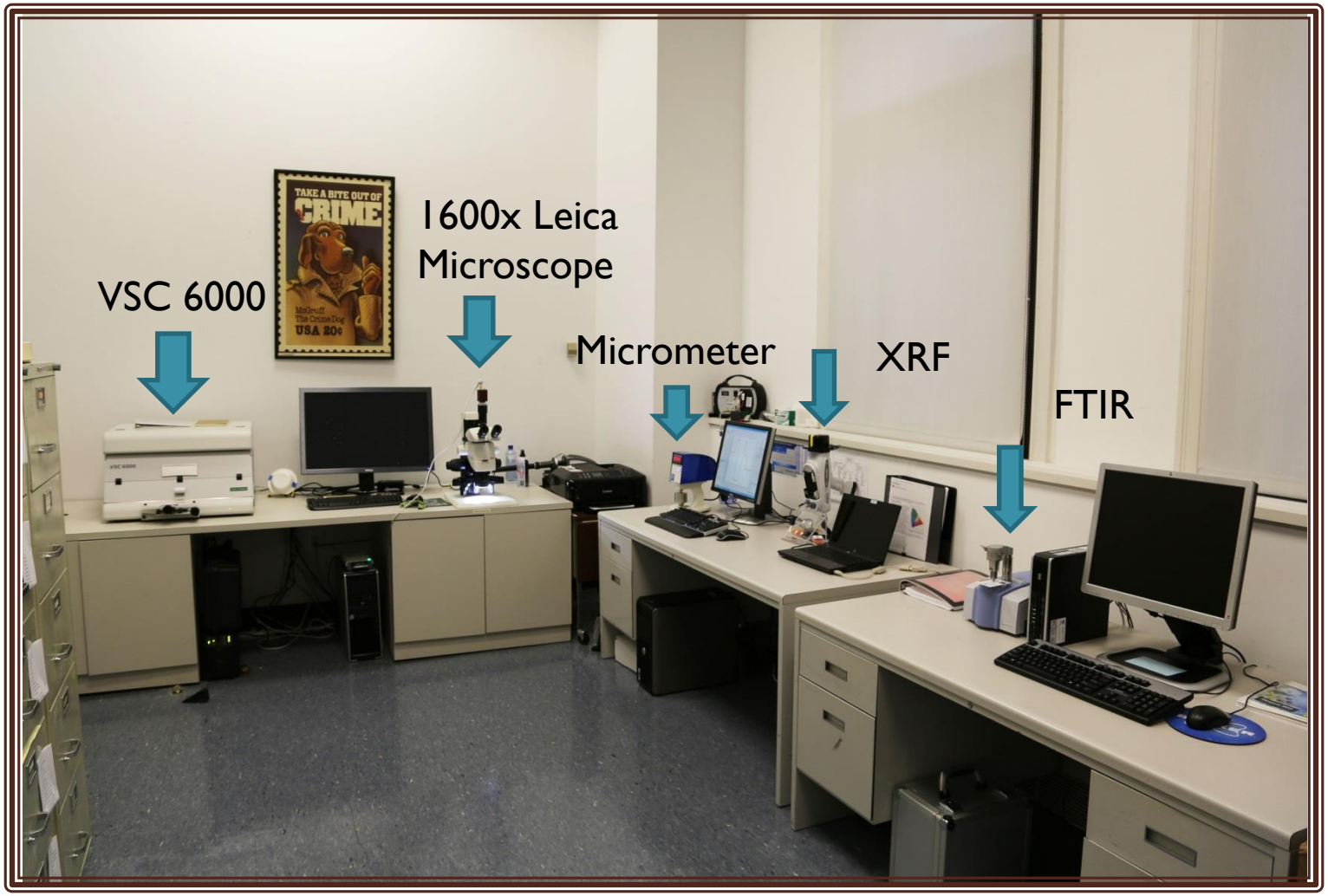


Thomas Lera, research chair - Emeritus

Second International Symposium on Analytical Methods in Philately – Itasca, IL 2015

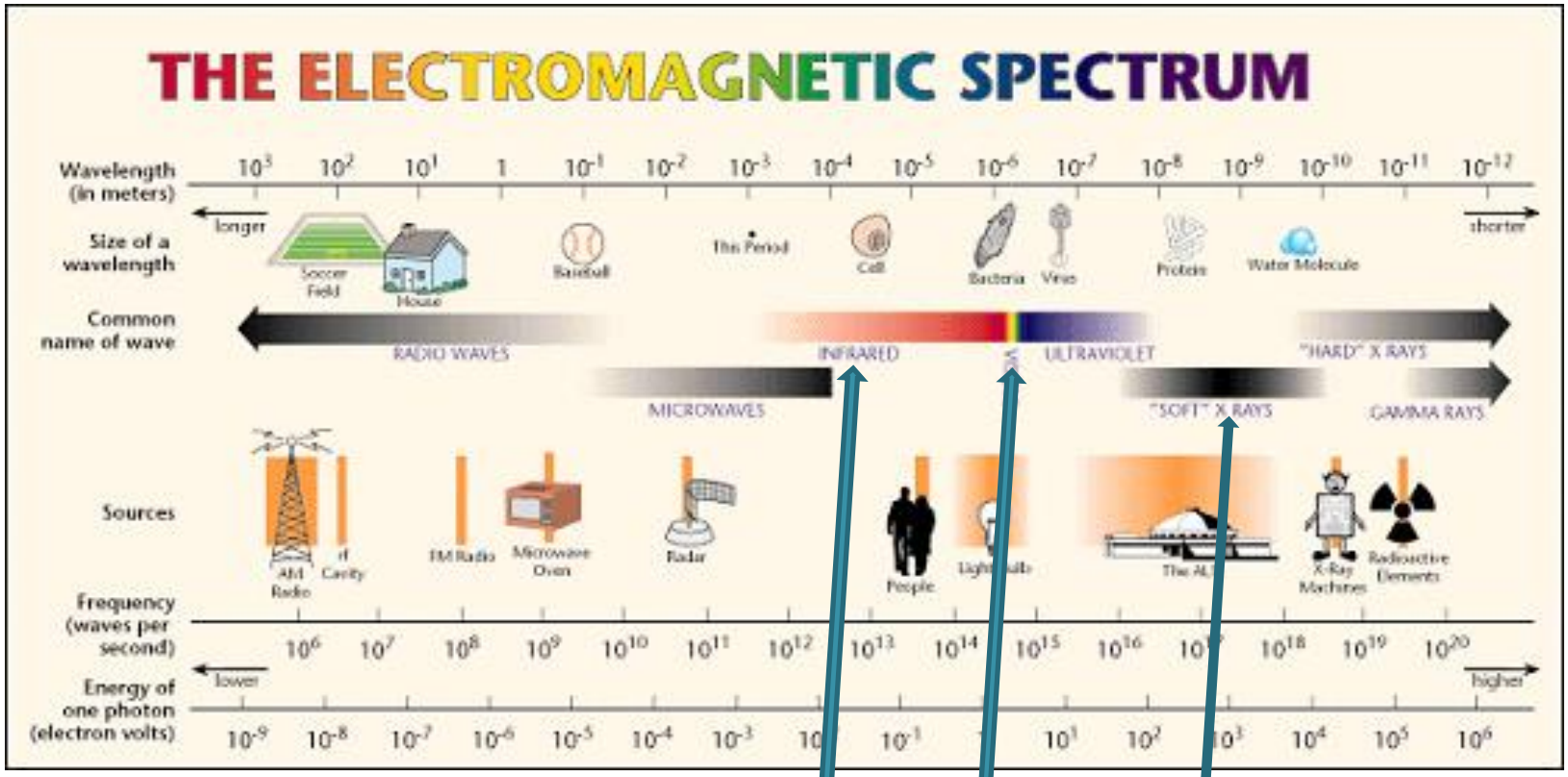
Smithsonian *National Postal Museum*

NPM Scientific Laboratory

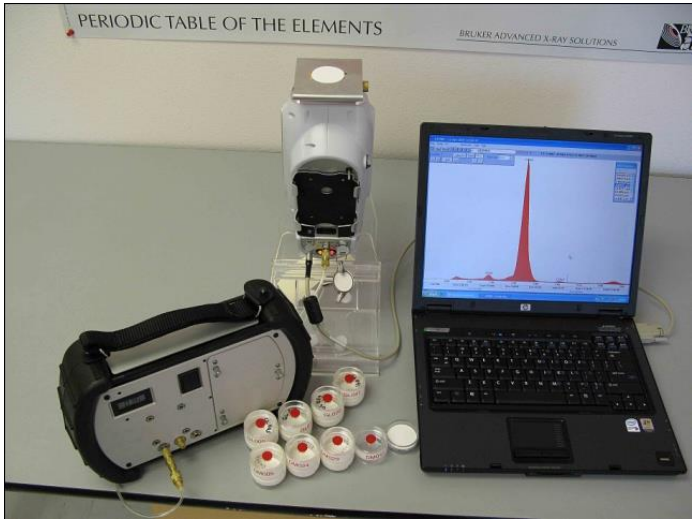


How it Works

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 - XRF



Very sensitive elemental analysis by anyone in seconds anywhere

The principles of XRF—and its uses in measurement—are based entirely in photon-electron interactions. **The XRF instrument is, in essence, an expensive flashlight!**

The signal passes from the instrument's detector, to the digital pulse processor, to the CPU where the data is transformed from counts per channel, to spectra and quantitative chemistries in seconds with *no* sampling.

How it Works – XRF (x-ray fluorescence)

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.

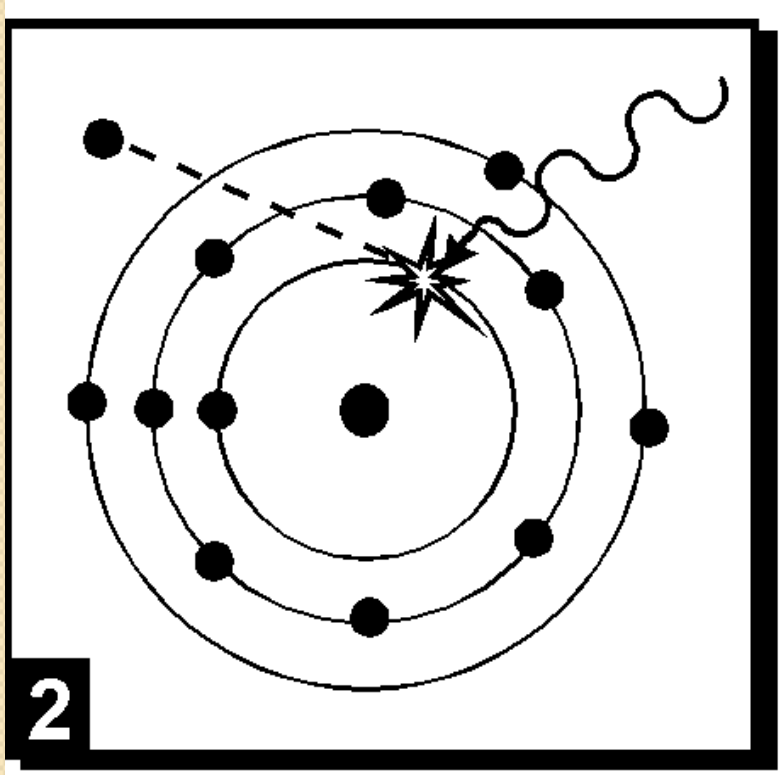
- Electrons are bound to the nucleus at of any particular atom at specific energies, which are unique to each element. Think of it as gravity. The nucleus is like a planet, and depending on the "size" (energy) of a nucleus, it can hold "moons" (electrons) in various "orbits" (energy levels, binding energies) 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**.

- 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.

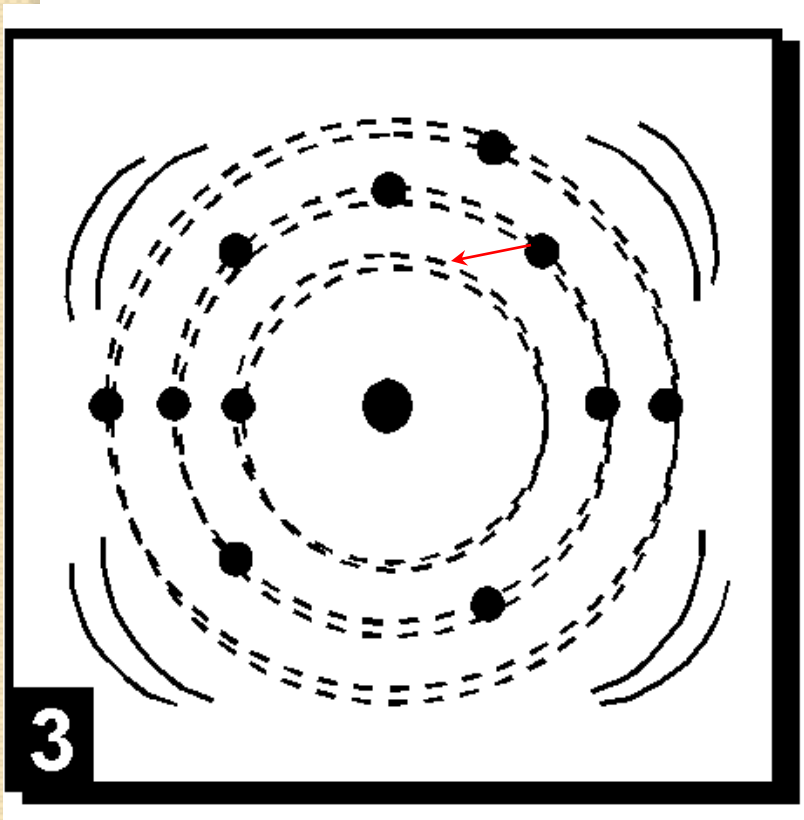
How it Works – XRF (x-ray fluorescence)



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.*

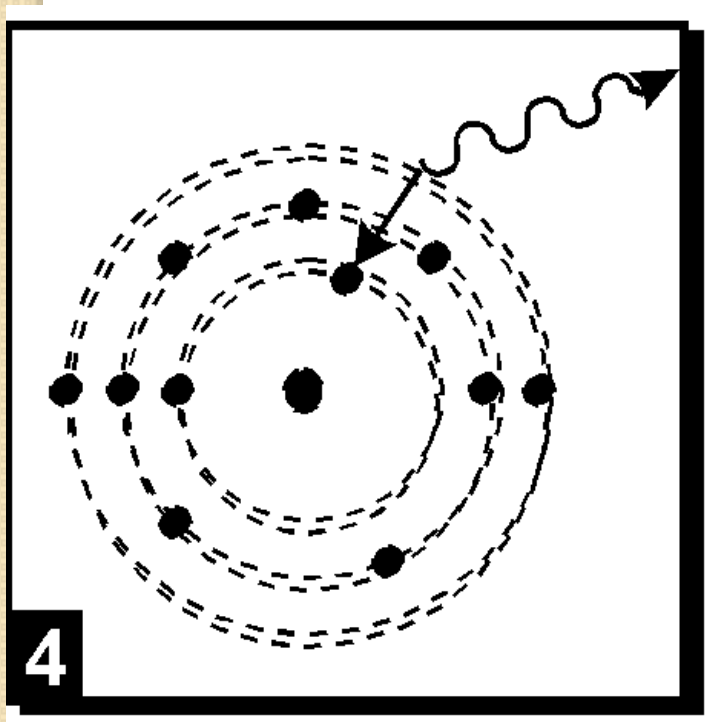
* *X-ray energy must be higher than absorption edge of the element.*

How it Works – XRF (x-ray fluorescence)



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

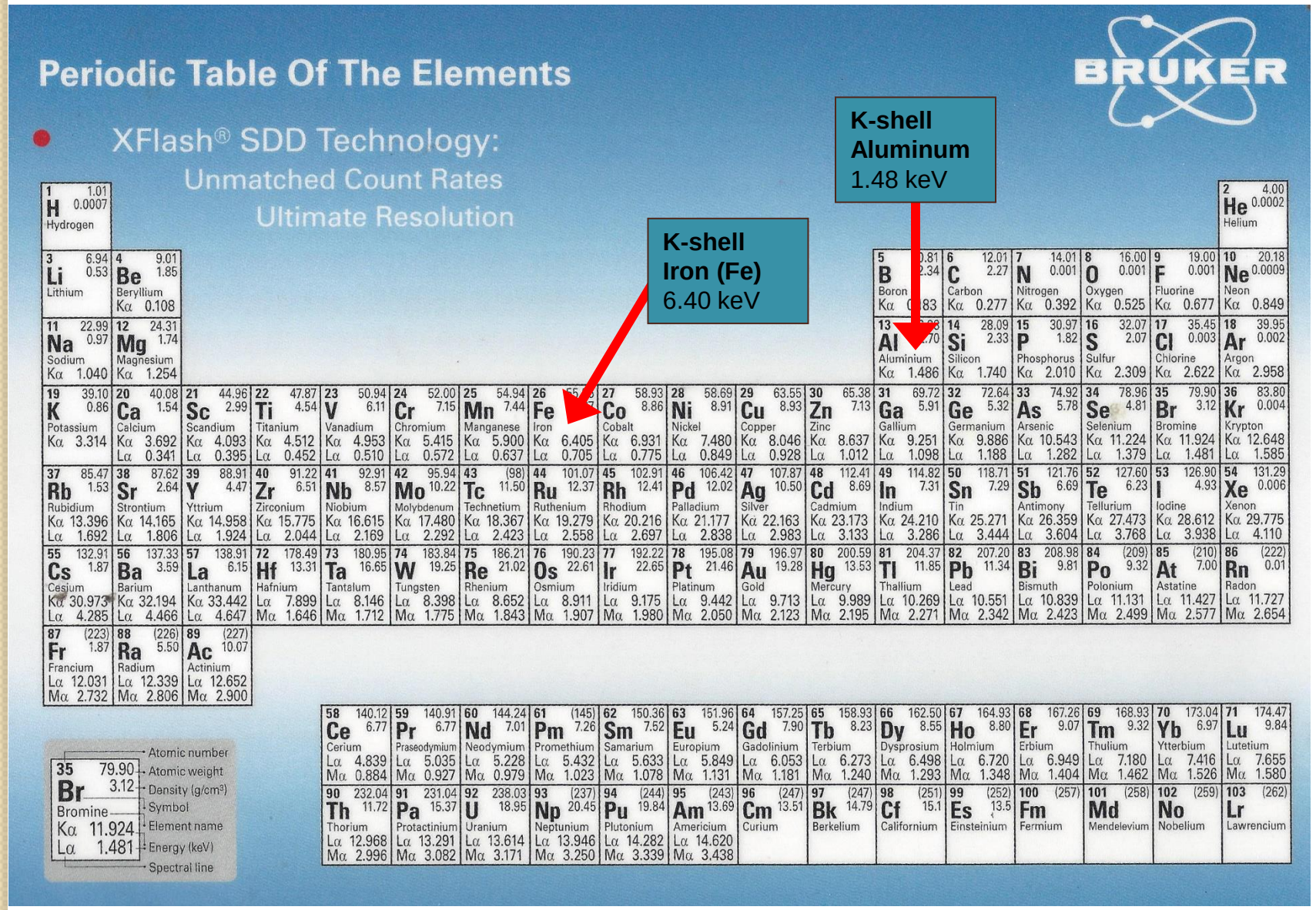
How it Works – XRF (x-ray fluorescence)



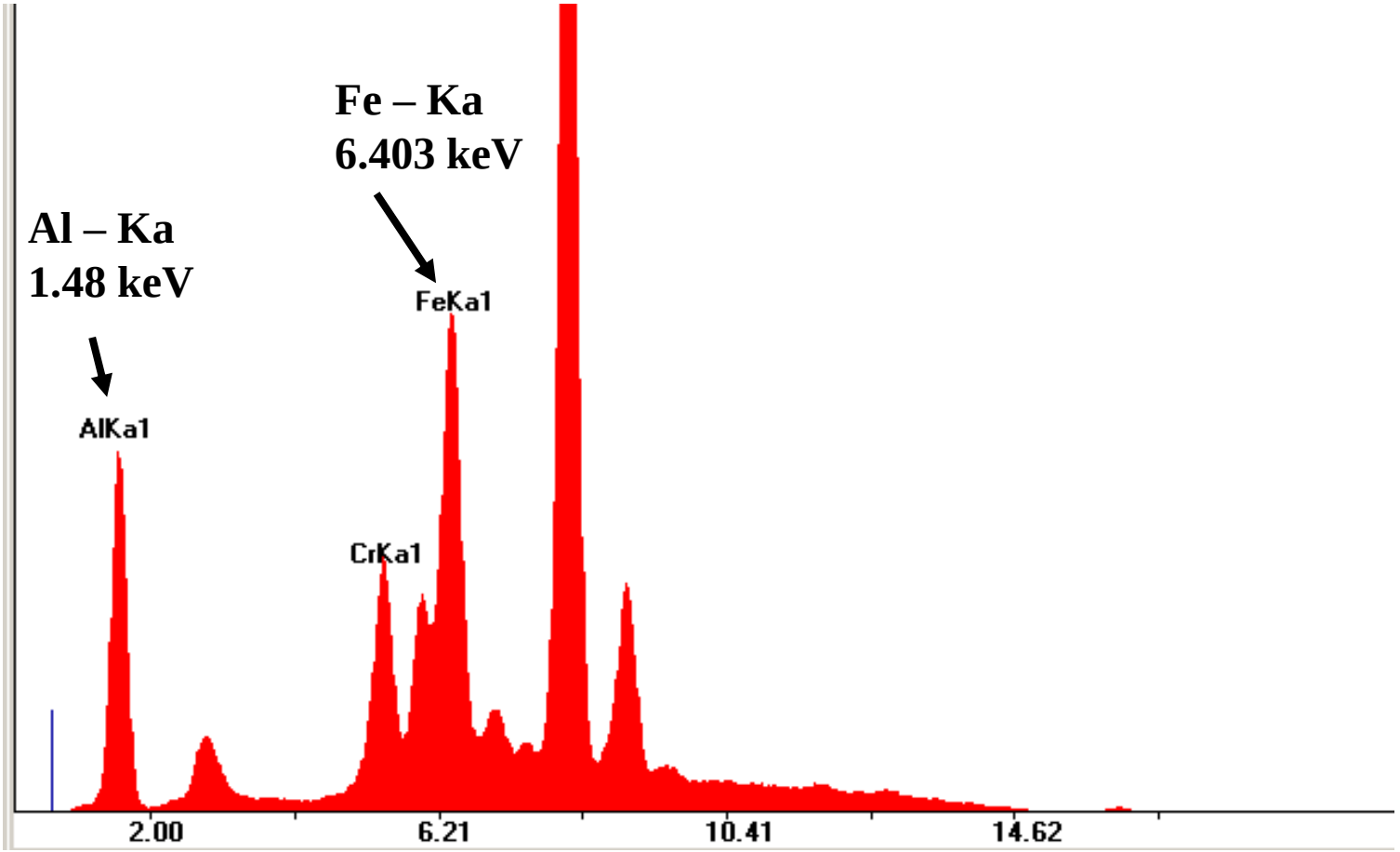
An *X-ray photon* is released and hits the analyzer's detector.

(This photon's energy is unique to the element it came from-- e.g., Aluminum K-shell energy is 1.47 keV)

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



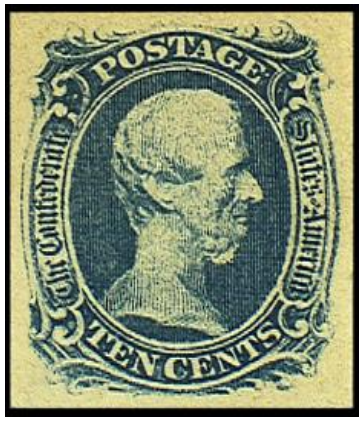
Each Element has its Own Signature Energy for K and L-Shell Electrons



A Simple XRF Application

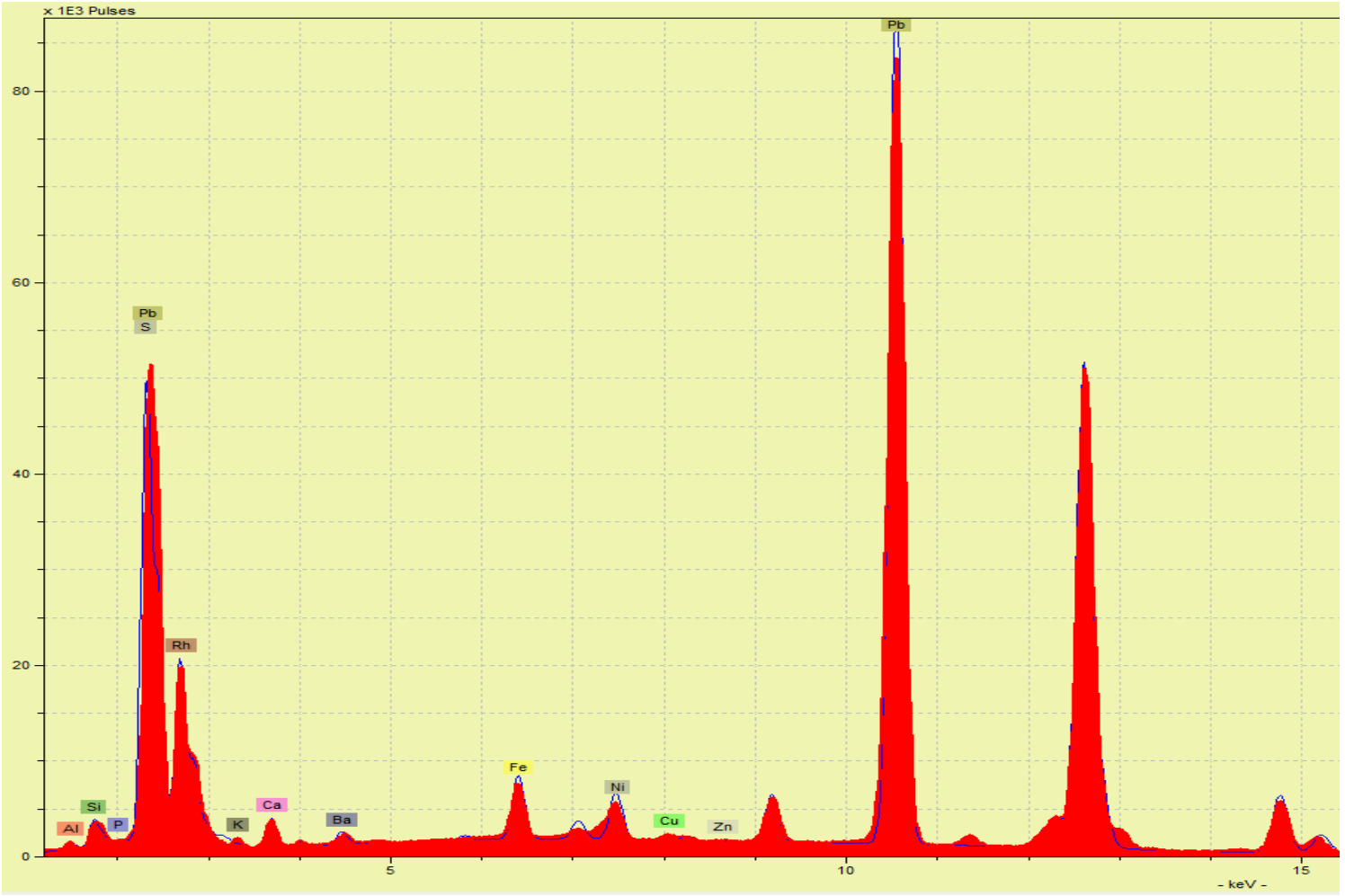
Target Stamps

Stamp A
Genuine



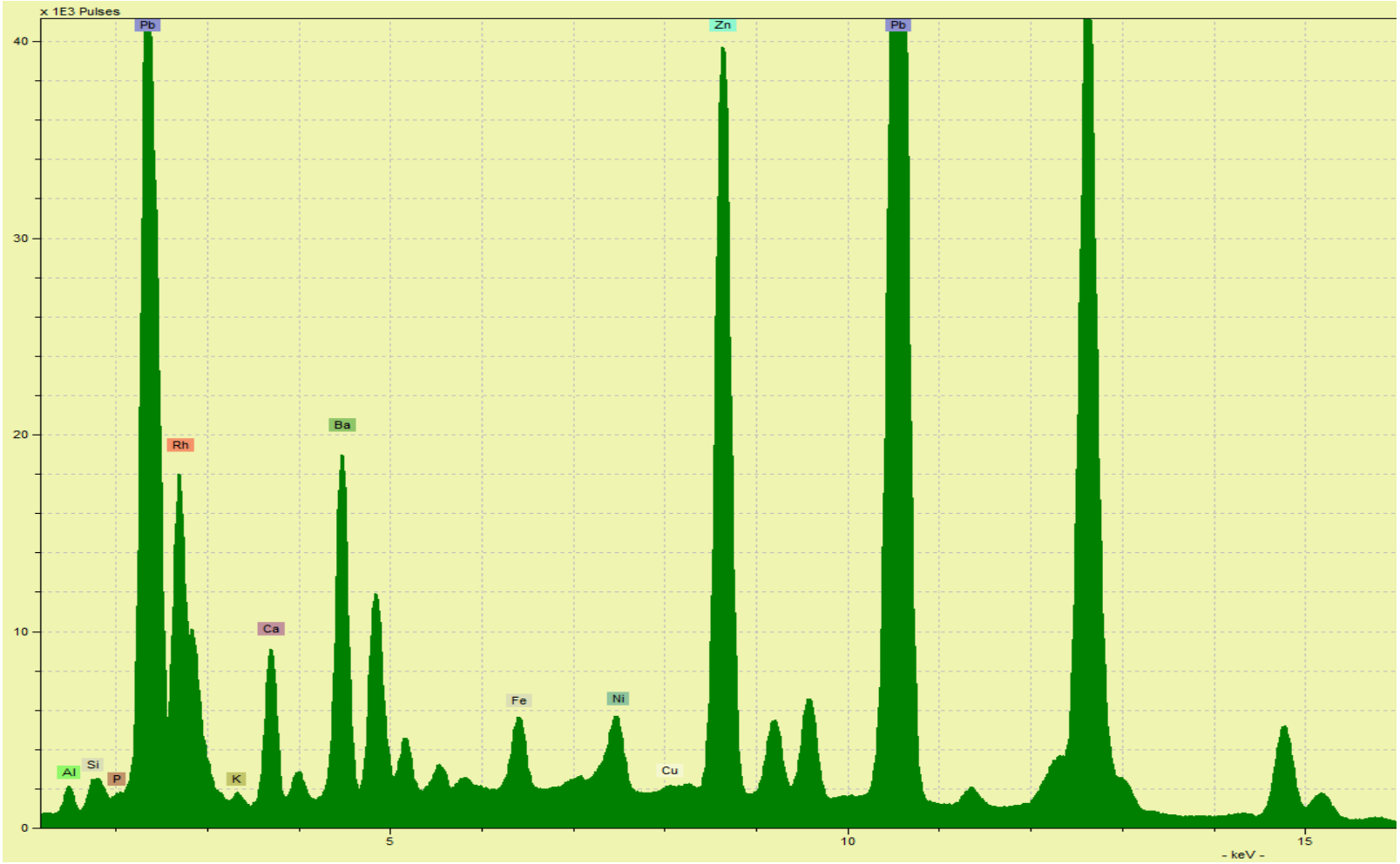
Stamp B
Forgery

Stamp "A" Ink Composition



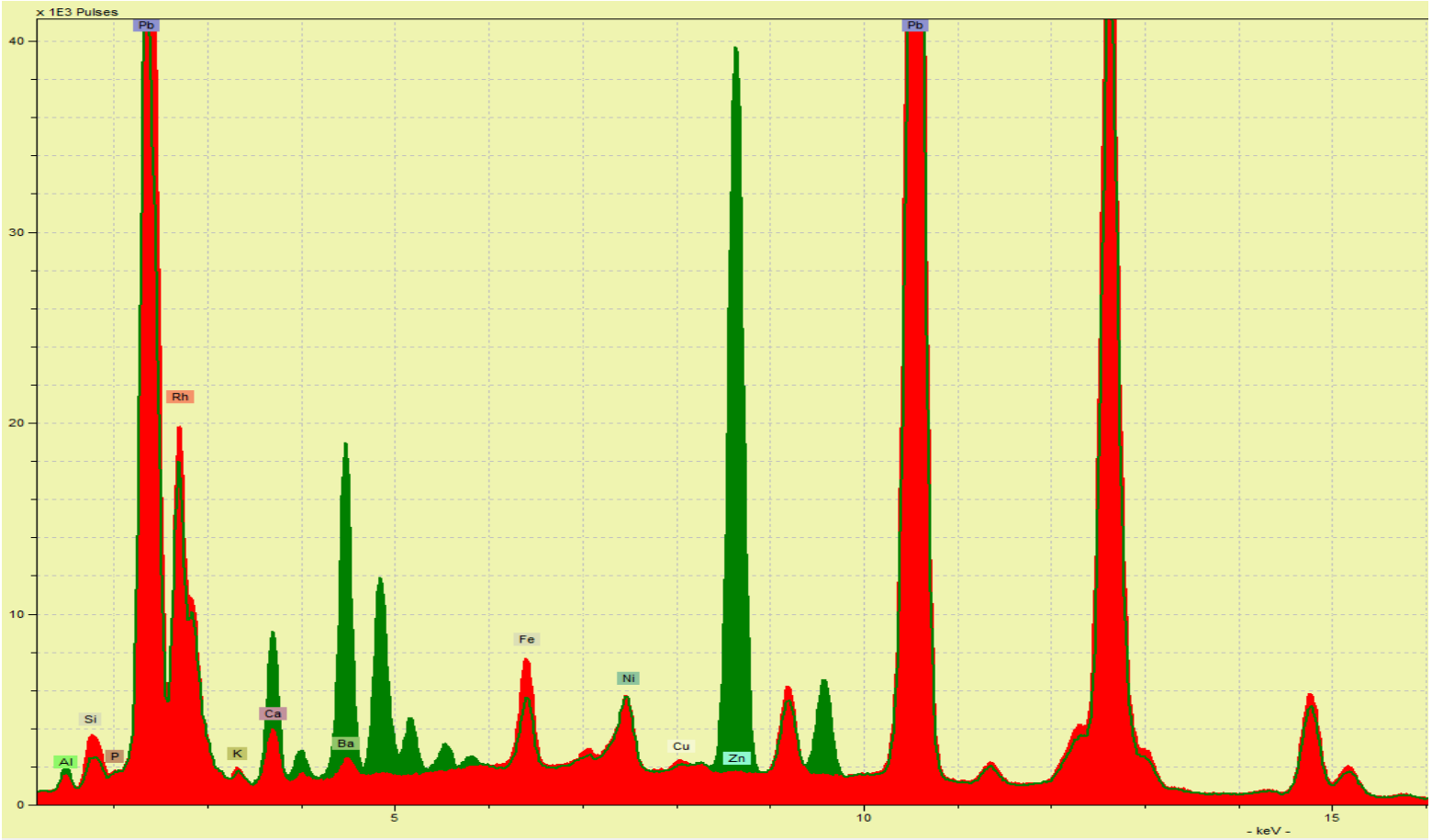
Energy (KeV)

Stamp "B" Ink Composition



Energy (KeV)

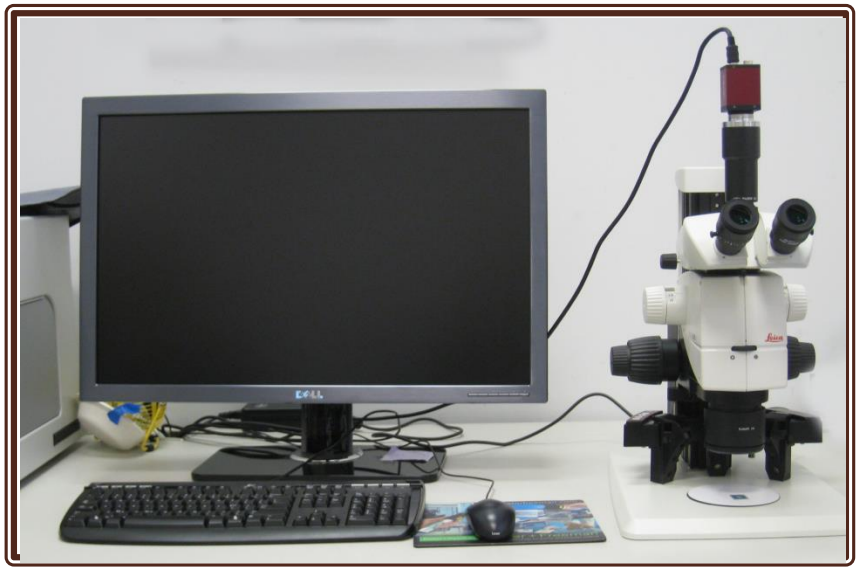
Comparison of Inks

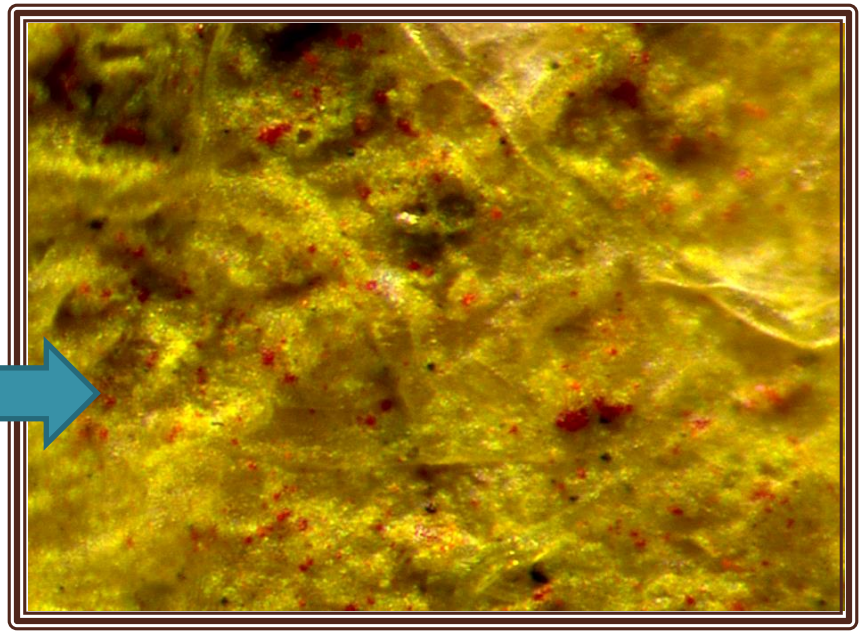


- **Red - Stamp "A" has much more Lead and no Zinc and little Calcium**
- **Green - Stamp "B" has much more Zinc, Barium and Calcium**

Microscopy

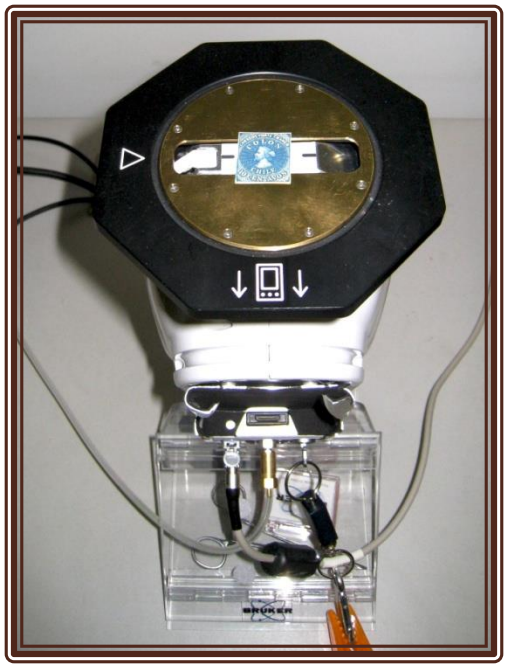
- Leica microscope
- Magnification range 78 to 1600x
- Can be used to record close examination details
- Image at right contains small bright red pigment particles in overall yellow-green ink.
- These particles are vermilion pigments (600x).

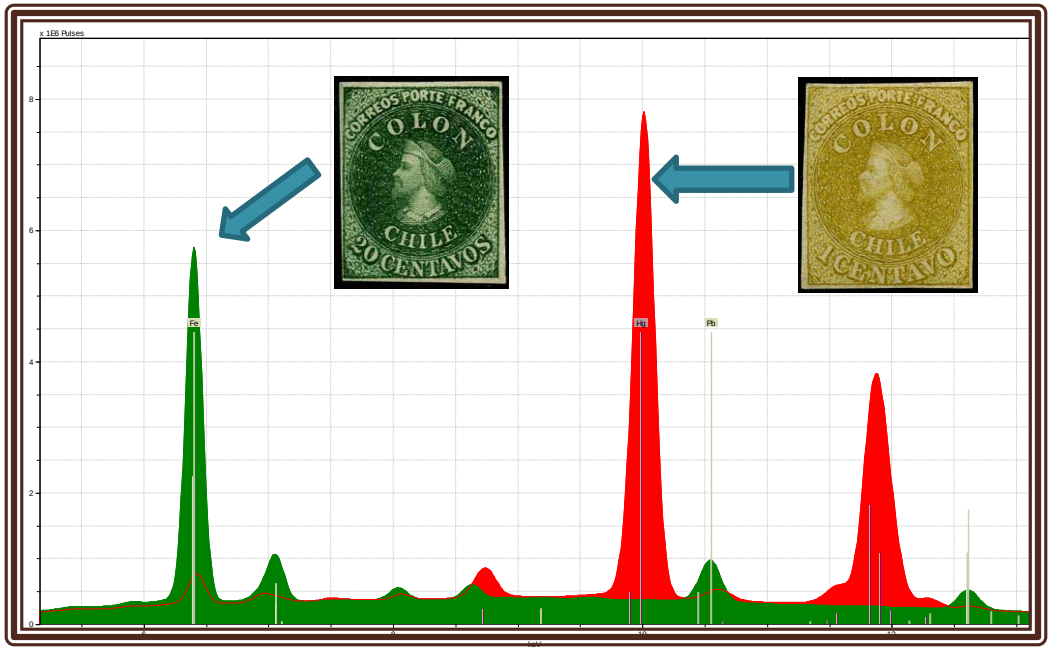




X-Ray Fluorescence (XRF) Tracer

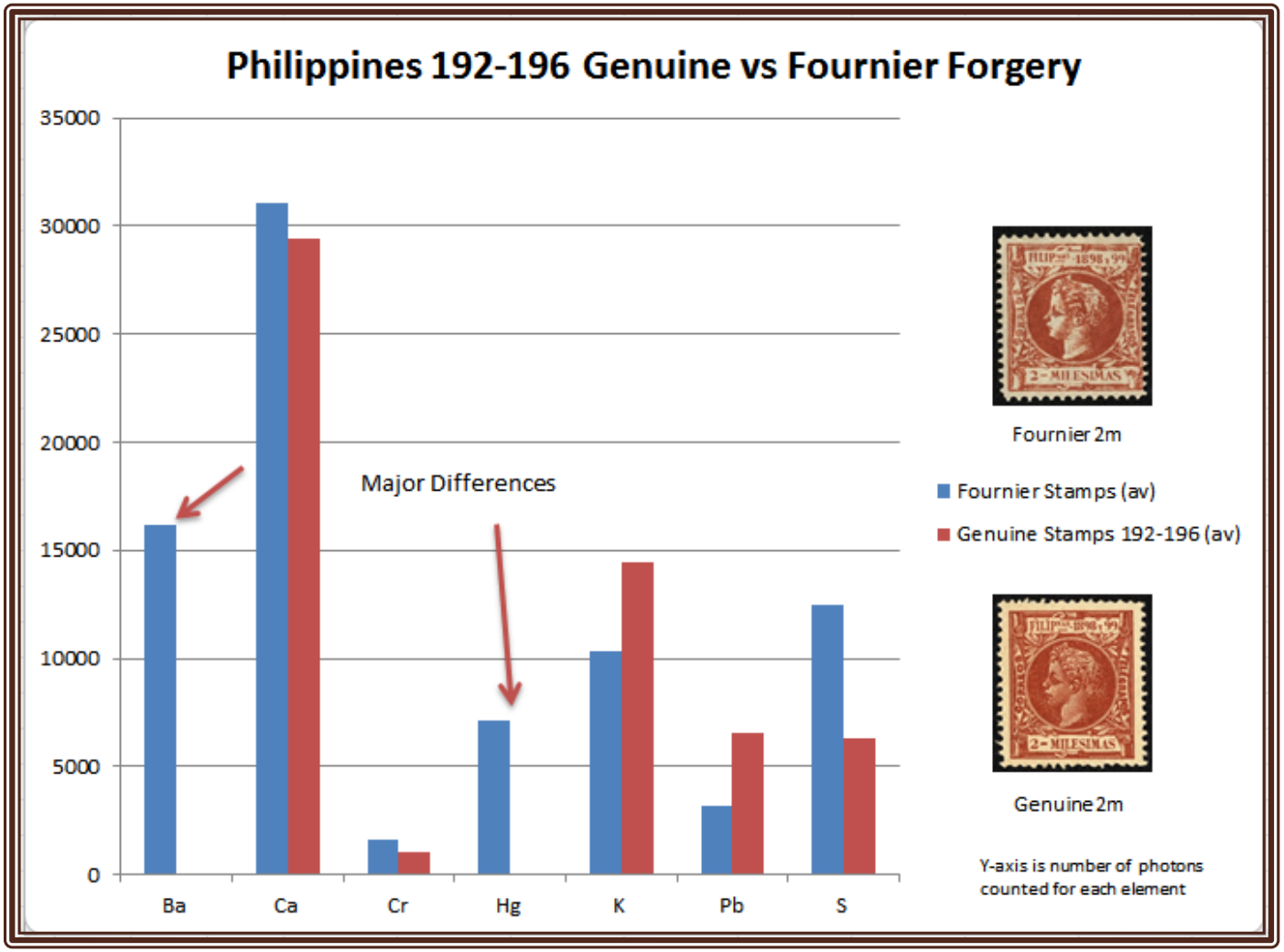
- Spot size is ~3 mm x 4 mm
- Vacuum available to identify lighter elements
- Identifies chemical elements not molecules
- Penetrates all layers of stamp
  - Affected by albums, envelopes, hinge residue etc.





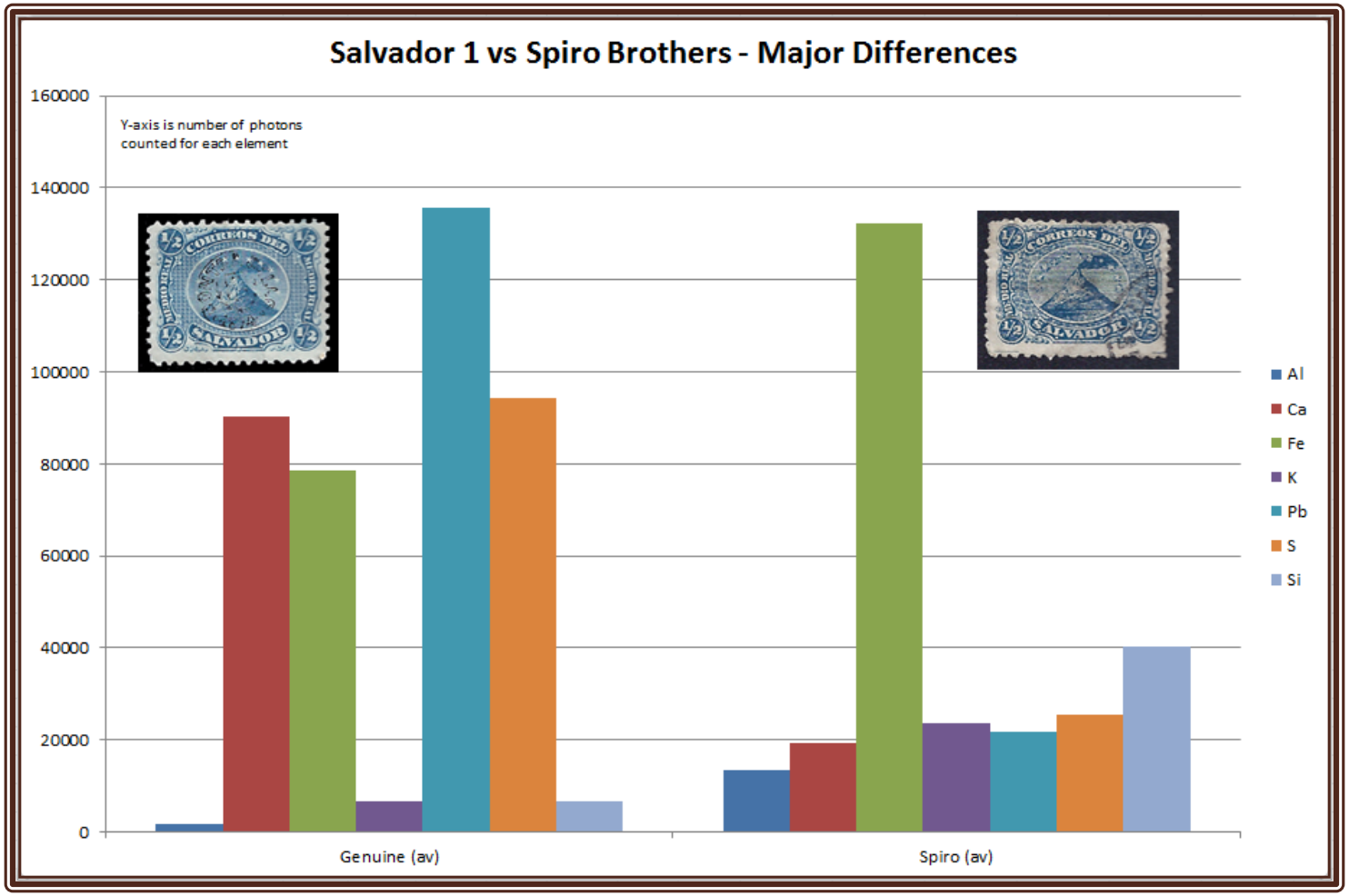
X-Ray Fluorescence (XRF) Analysis

Original ink (1898) versus Fournier Forgery Ink



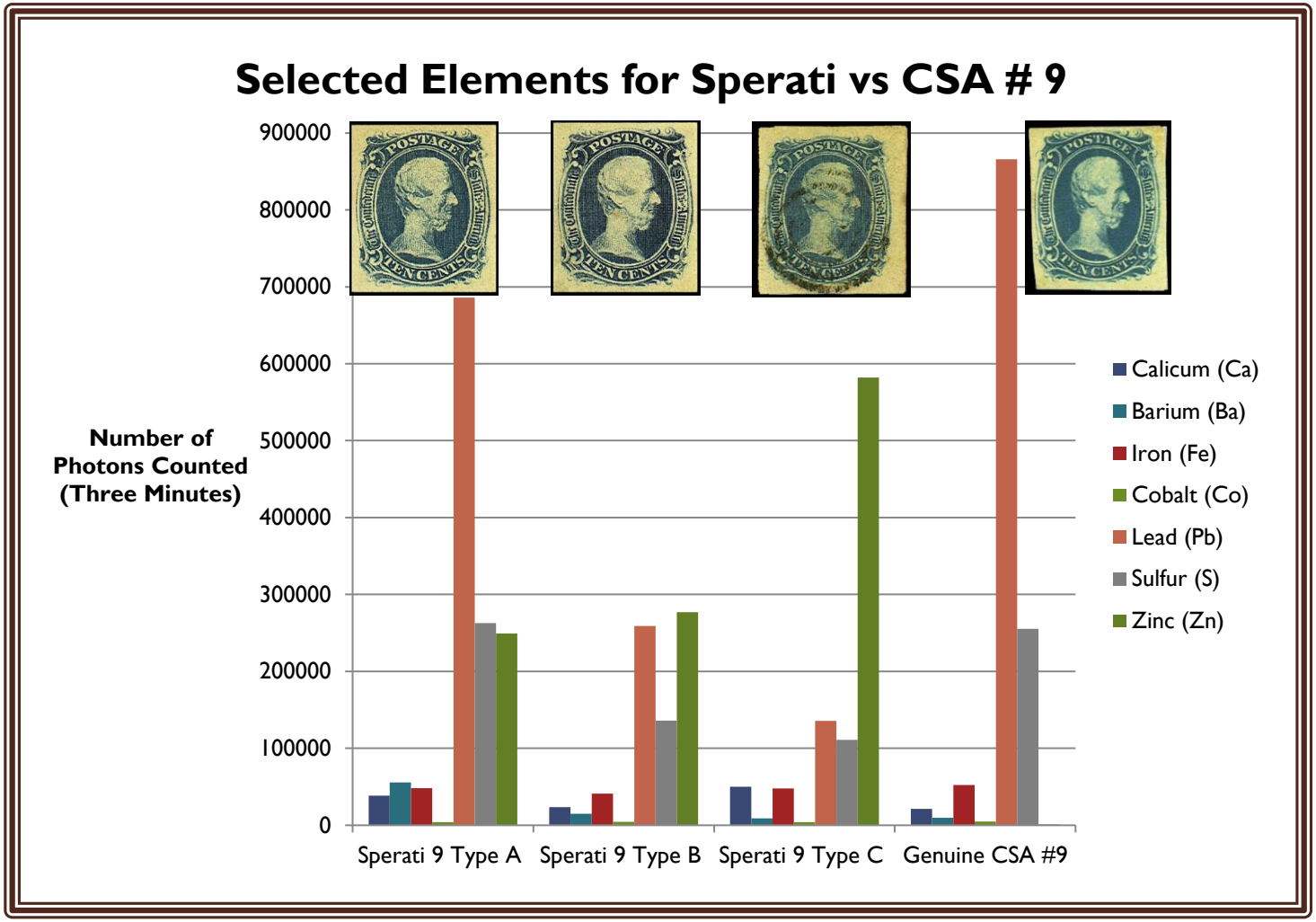
X-Ray Fluorescence (XRF) Analysis

Original ink (1867) versus Spiro Brothers Forgery Ink



X-Ray Fluorescence (XRF) Analysis

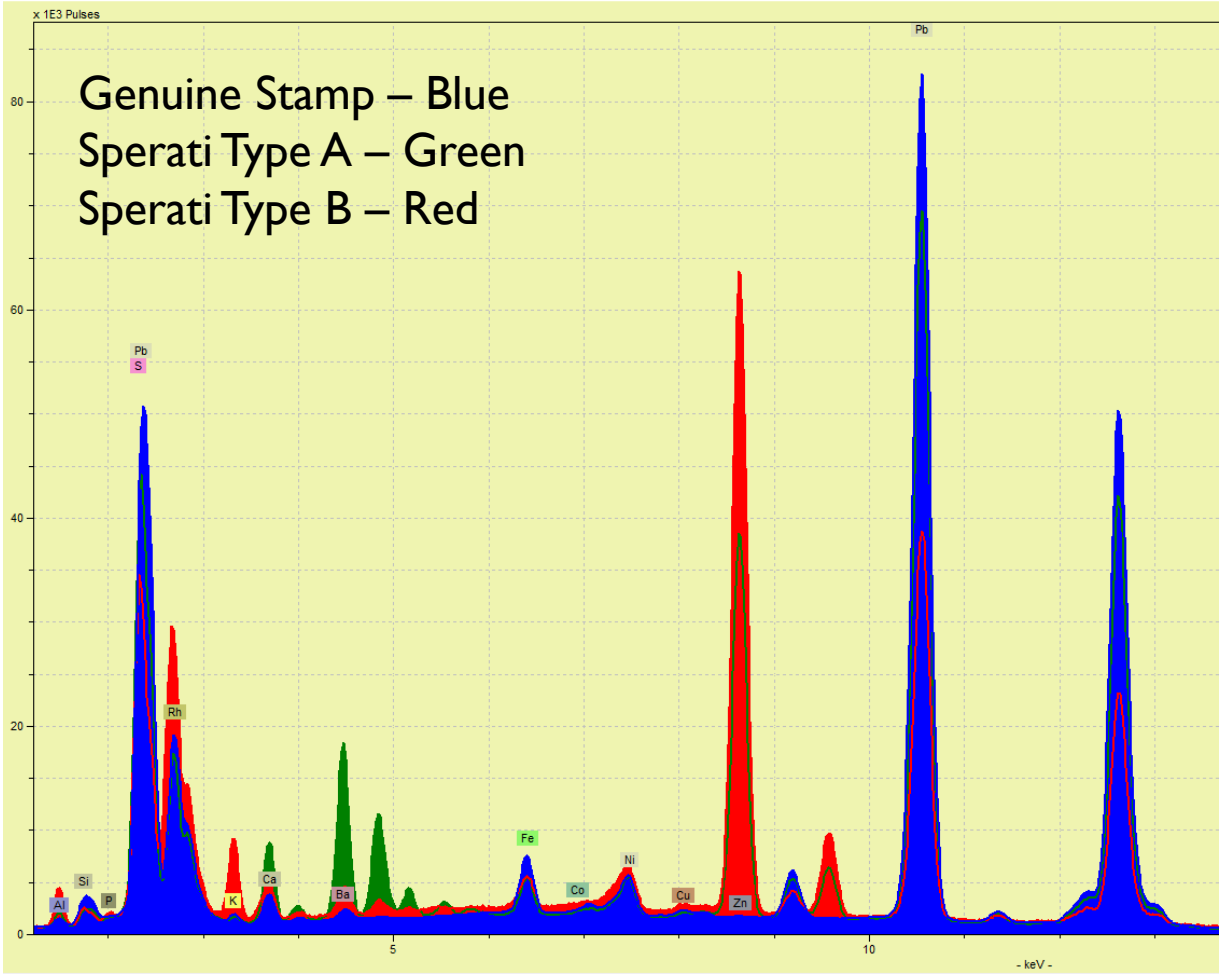
Original ink (1863) versus Sperati Forgery Ink



Sperati's Printing Press

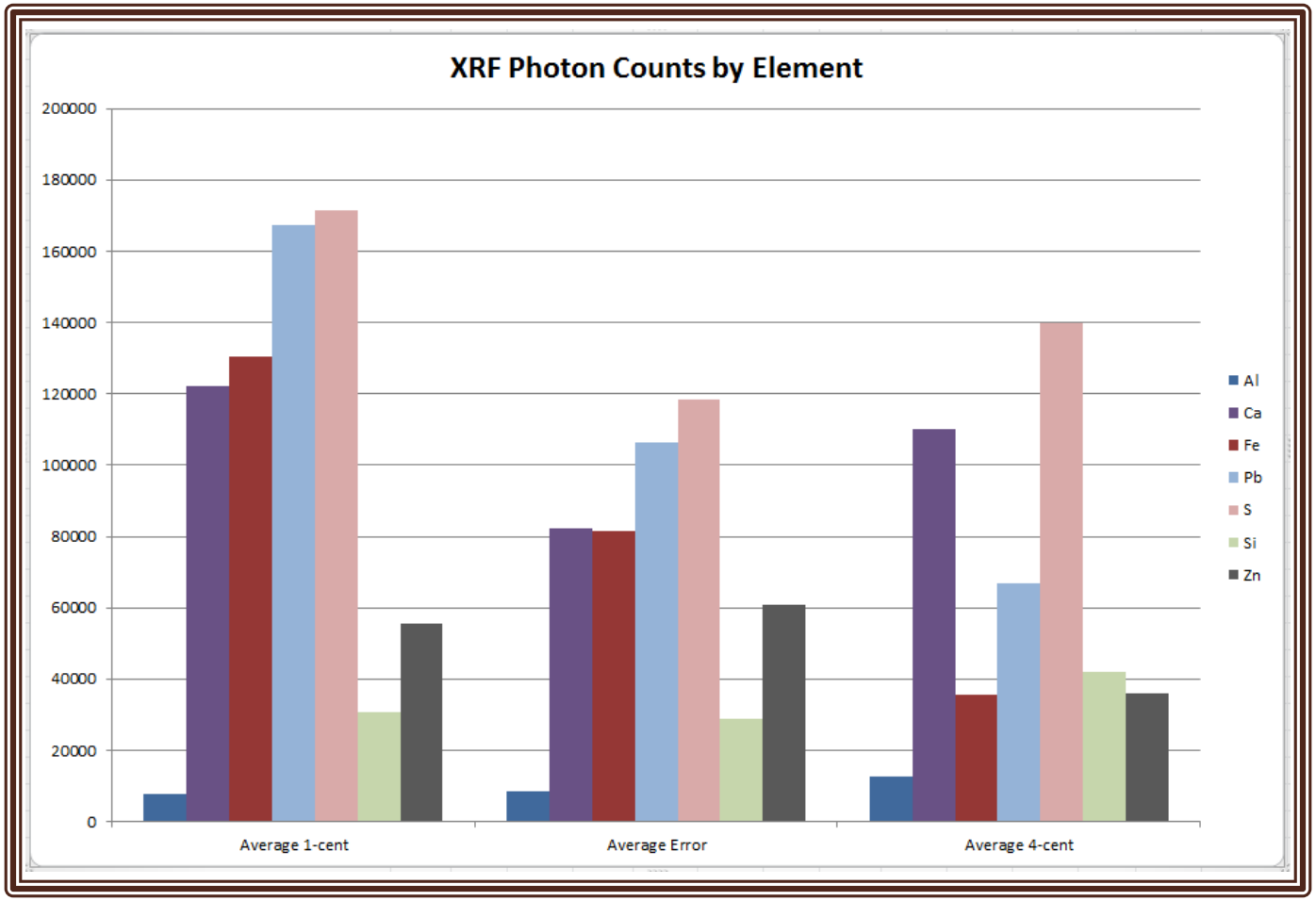
X-Ray Fluorescence (XRF) Analysis

Original ink (1863) versus Sperati Forgery Ink



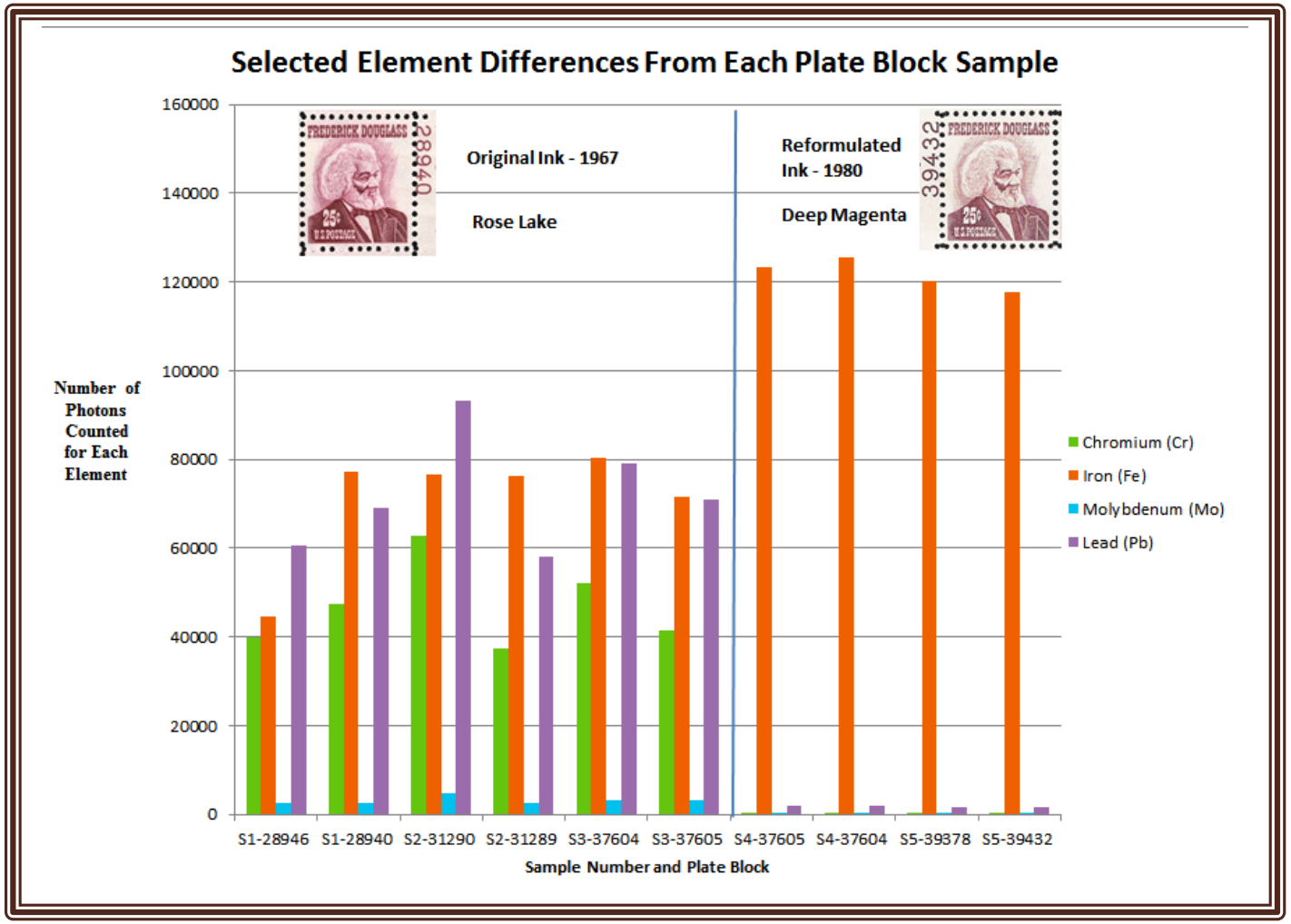
A different view of the previous data

Other uses of XRF:1893 1-cent, 4-cent and the 4-cent Colombian error



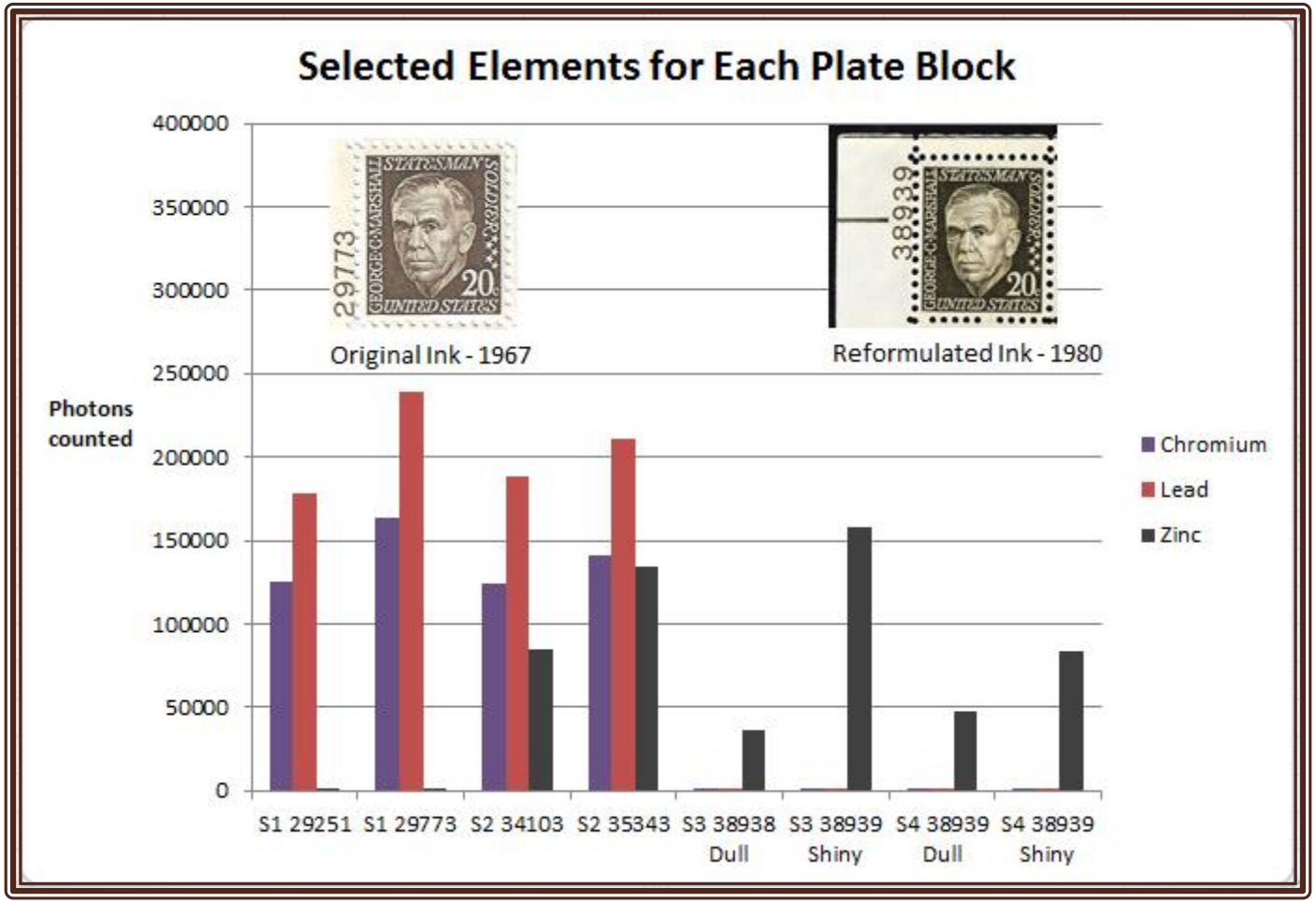
The 1-cent and 4-cent color error stamps have similar characteristics while the regular 4-cent stamp Scott 233 is different indicating two major pigments were used.

Other uses of XRF - color changes



Lead Molybdate Chrome Orange ($Pb(CrMoS)O_4$) pigment eliminated

Other uses of XRF - color changes



The principal tagging agent was a pigment using zinc silicate activated with small amounts of copper (Zn_2SiO_4[Cu]) developed by Sylvania Electric Products Company

Instrument Review

- Good visual inspection of forgeries is required.
- X-ray techniques penetrate all the way through the stamp.
- XRF identifies many elements but can't identify molecular composition.
- Standards for color matching were not yet developed.
- The forger concluded that the ink was "good enough for government work."

Science and Philately

I hope this presentation bridges the knowledge gap !

- It established analytical methods to validate the authenticity of stamps or covers (genuine or counterfeit)
- It shared knowledge by showing philatelists and organizations how to use the equipment and interpret the results

Scholarships and Research Grants

The Smithsonian National Postal Museum has scholarships available:

http://www.postalmuseum.si.edu/Scholarships or email Thomas Lera lerat@si.edu

The Institute for Analytical Philately can provide research grants

http://www.analyticalphilately.org/applyingforagrant.html

or email John Barwis jbarwis@charter.net

THE END