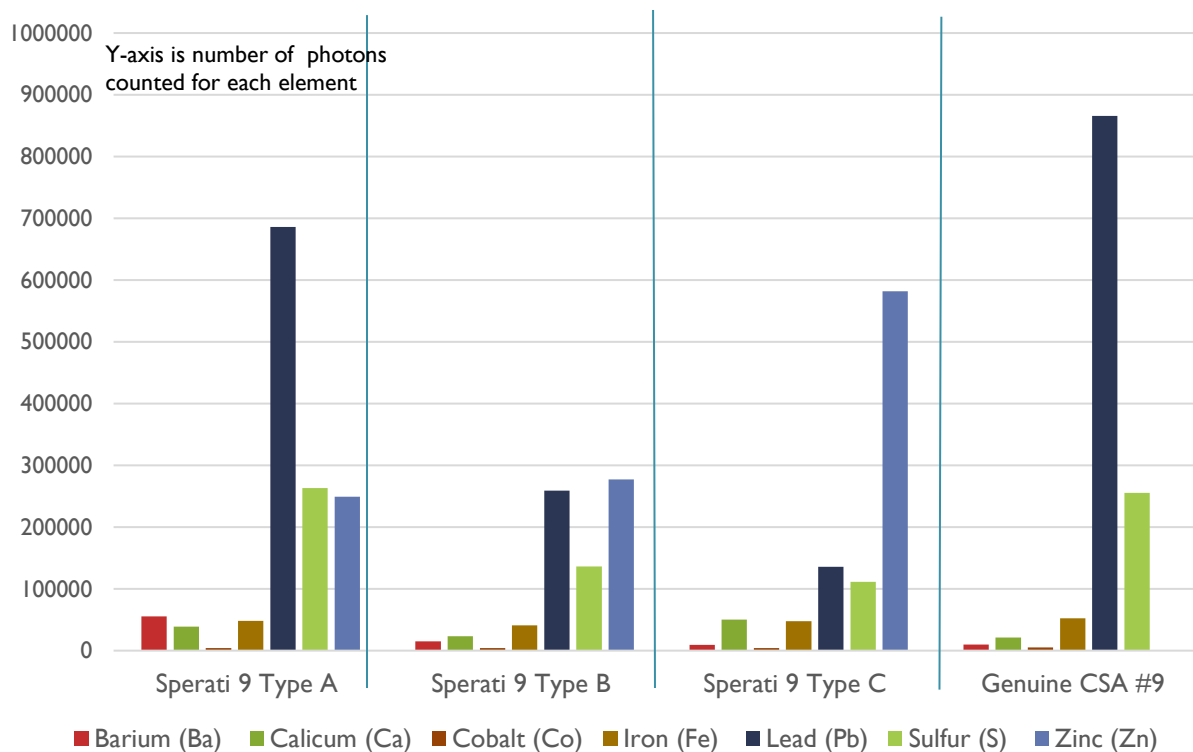


The Use of X-ray Fluorescence in Detecting Philatelic Forgeries

Selected Elements for Sperati Forgeries and CSA #9



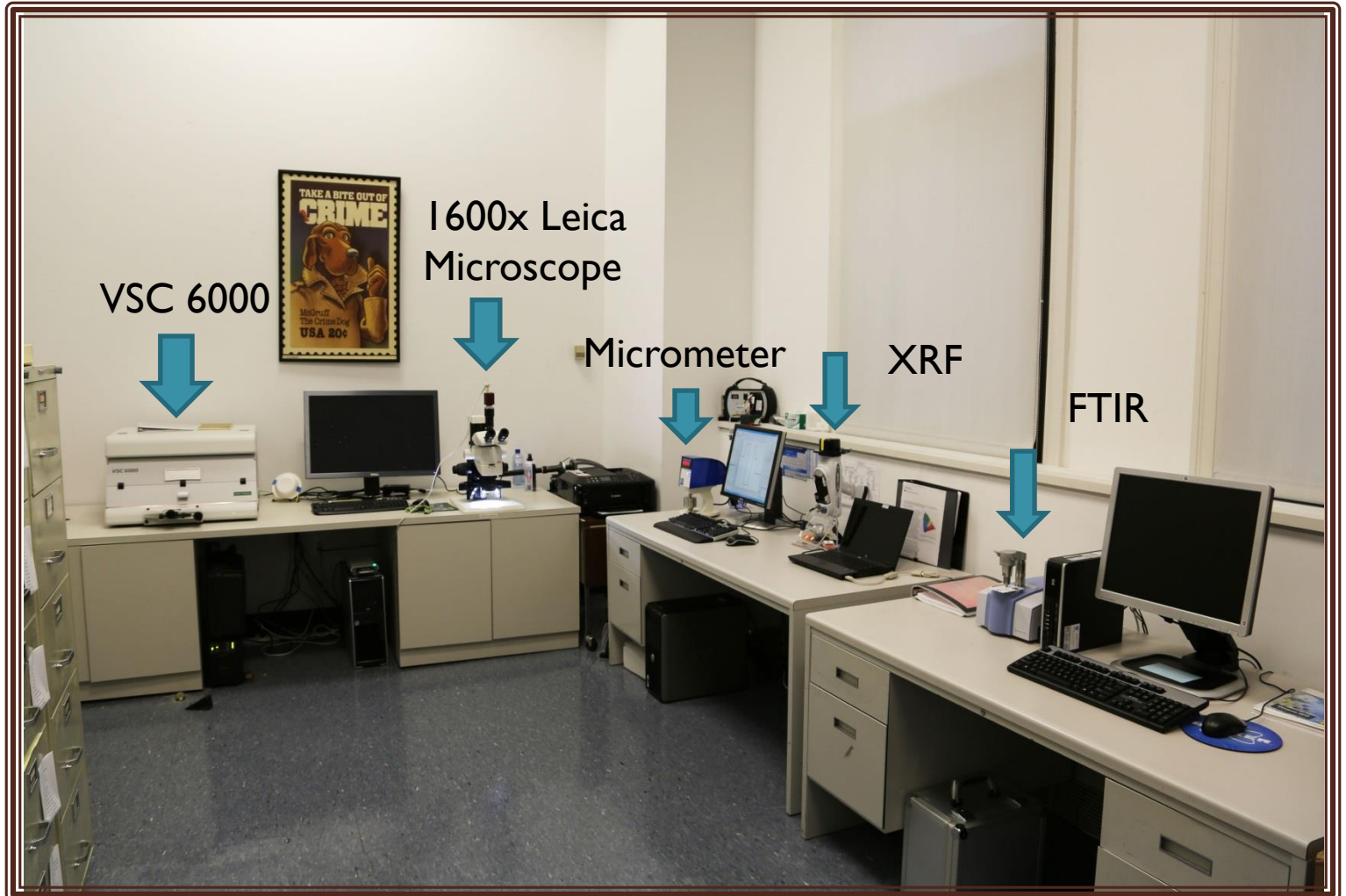
Thomas Lera, research chair - Emeritus

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



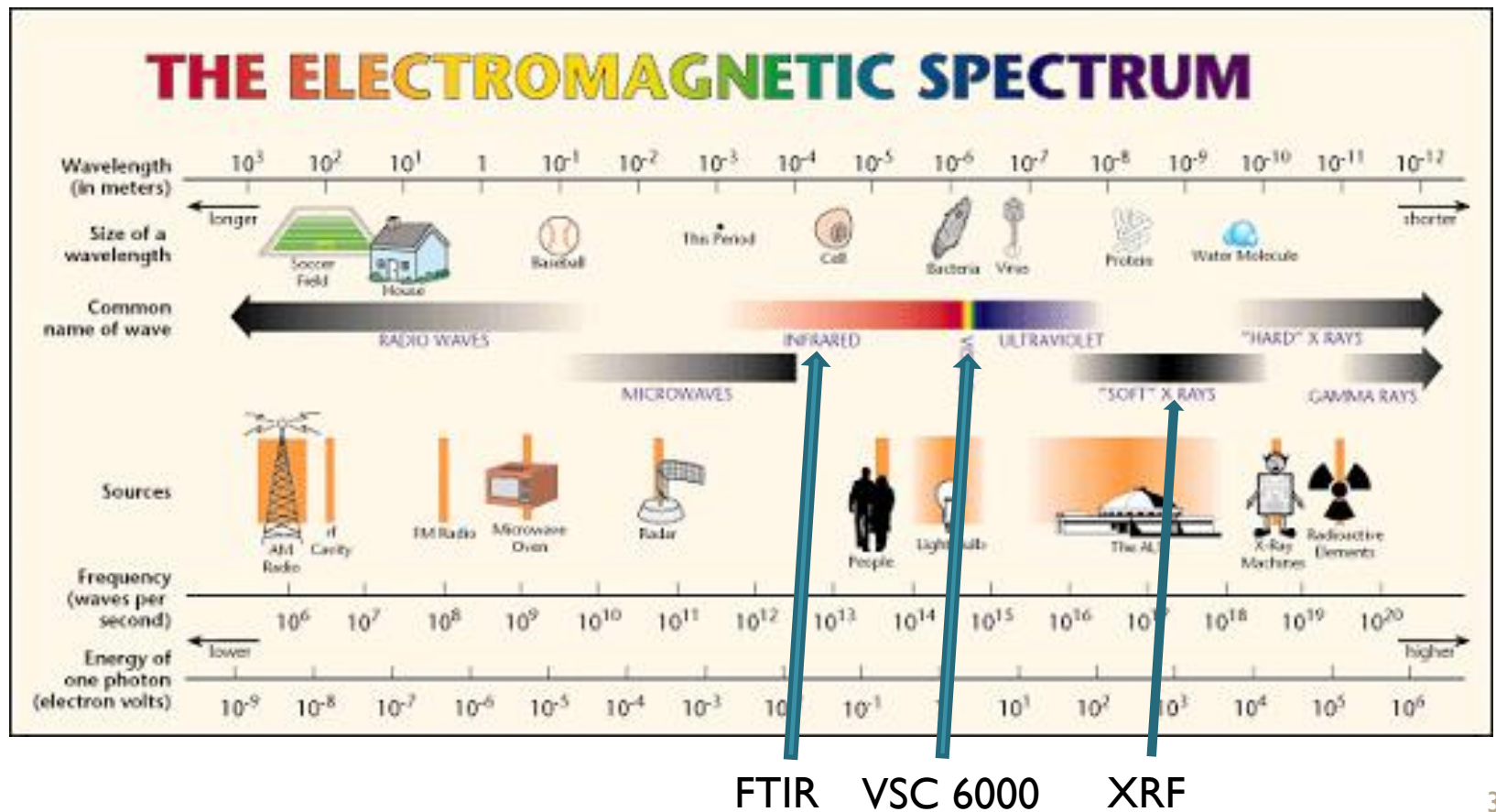
Smithsonian
National Postal Museum

NPM Scientific Laboratory

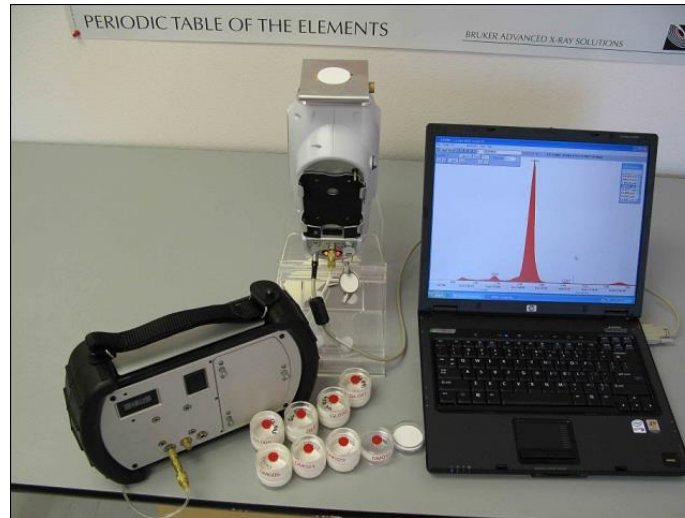


How it Works

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!**

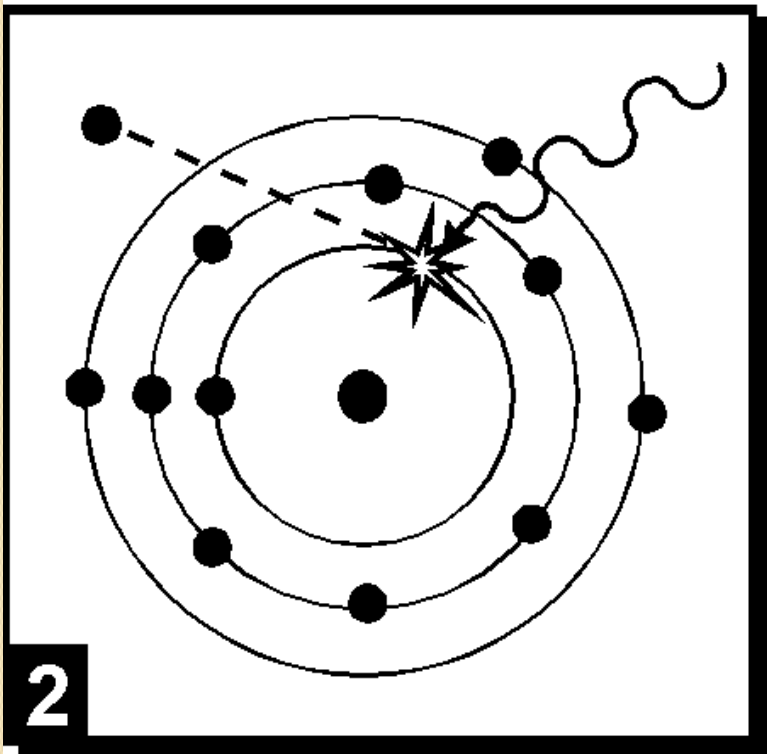
The signal passes from the instrument's detector, to the digital pulse processor, to the CPU where the data is transformed from counts per channel, to spectra and quantitative chemistries in seconds with no sampling.

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.

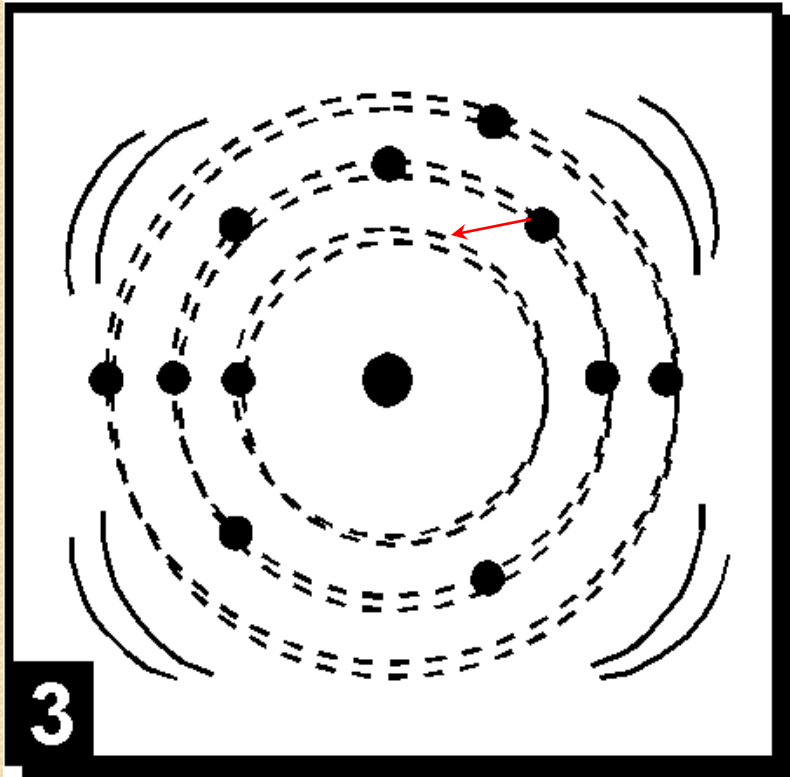
How it Works – XRF (x-ray fluorescence)



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.*

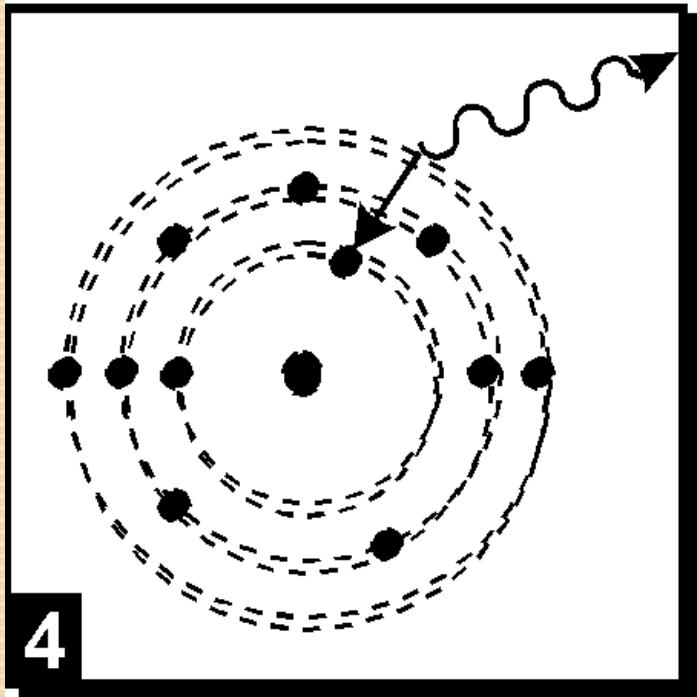
** X-ray energy must be higher than absorption edge of the element.*

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



Periodic Table Of The Elements

- XFlash® SDD Technology: Unmatched Count Rates Ultimate Resolution

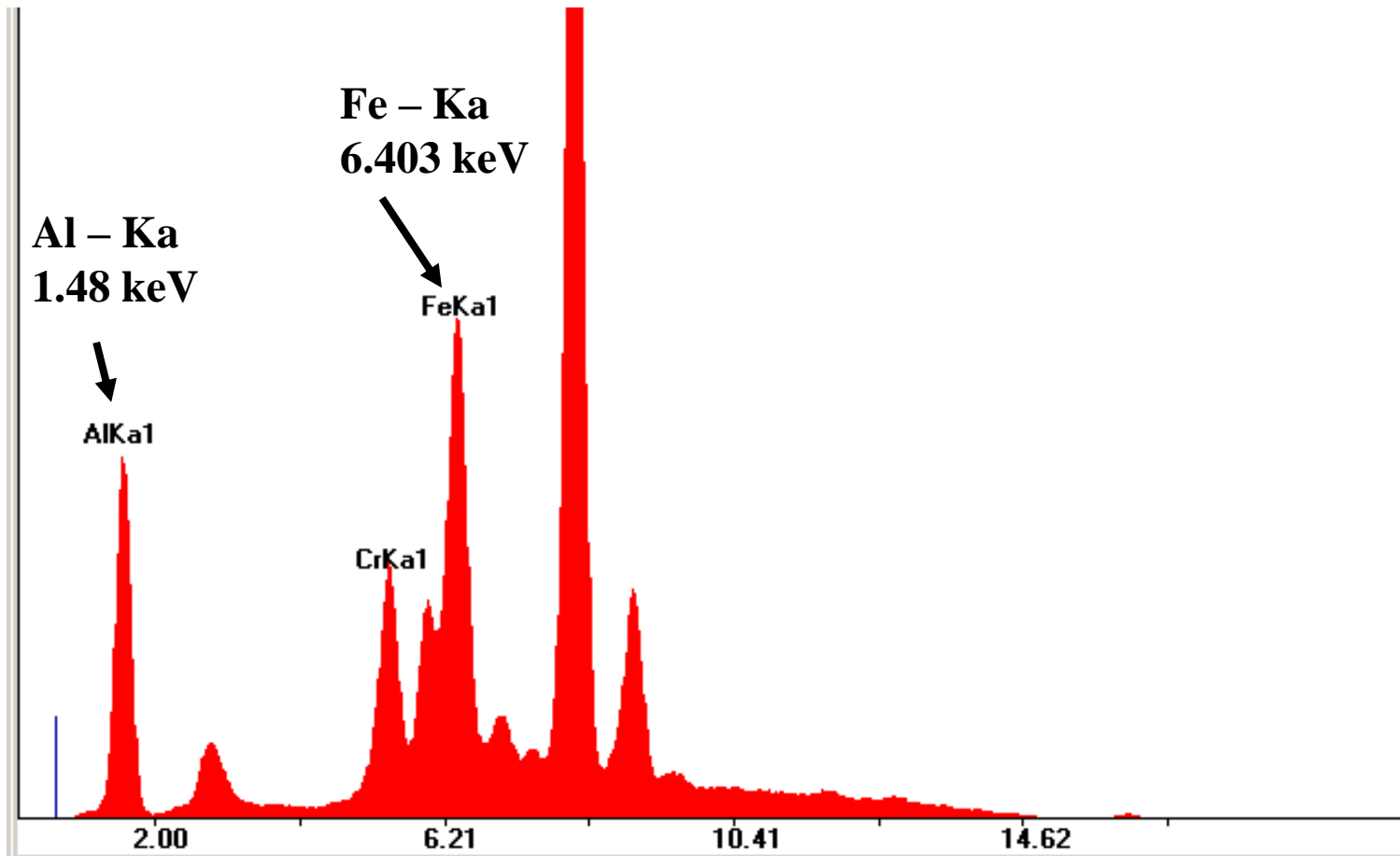
K-shell Aluminum
1.48 keV

K-shell Iron (Fe)
6.40 keV

1 H Hydrogen 1.01 0.0007																	2 He Helium 4.00 0.0002																												
3 Li Lithium 6.94 0.53	4 Be Beryllium 9.01 1.85 0.108																	5 B Boron 10.81 2.34 0.83	6 C Carbon 12.01 2.27 0.277	7 N Nitrogen 14.01 0.001 0.392	8 O Oxygen 16.00 0.001 0.525	9 F Fluorine 19.00 0.001 0.677	10 Ne Neon 20.18 0.0009 0.849																						
11 Na Sodium 22.99 0.97 1.040	12 Mg Magnesium 24.31 1.74 1.254																	13 Al Aluminum 26.98 1.70 1.486	14 Si Silicon 28.09 2.33 1.740	15 P Phosphorus 30.97 1.82 2.010	16 S Sulfur 32.07 2.07 2.309	17 Cl Chlorine 35.45 0.003 2.622	18 Ar Argon 39.95 0.002 2.958																						
19 K Potassium 39.10 0.86 3.314	20 Ca Calcium 40.08 1.54 3.692	21 Sc Scandium 44.96 2.99 4.093	22 Ti Titanium 47.87 4.54 4.512	23 V Vanadium 50.94 6.11 4.510	24 Cr Chromium 52.00 7.15 5.415	25 Mn Manganese 54.94 7.44 5.637	26 Fe Iron 55.85 7.5 6.405	27 Co Cobalt 58.93 8.86 6.931	28 Ni Nickel 58.69 8.91 7.480	29 Cu Copper 63.55 8.93 8.046	30 Zn Zinc 65.38 7.13 8.928	31 Ga Gallium 69.72 5.91 9.251	32 Ge Germanium 72.64 5.32 9.886	33 As Arsenic 74.92 5.78 10.543	34 Se Selenium 78.96 4.81 11.224	35 Br Bromine 79.90 3.12 11.924	36 Kr Krypton 83.80 0.004 12.648																												
37 Rb Rubidium 85.47 1.53 13.396	38 Sr Strontium 87.62 2.64 14.165	39 Y Yttrium 88.91 4.47 14.958	40 Zr Zirconium 91.22 6.51 15.775	41 Nb Niobium 92.91 8.57 16.615	42 Mo Molybdenum 95.94 10.22 17.480	43 Tc Technetium (98) 11.50 18.367	44 Ru Ruthenium 101.07 12.37 19.279	45 Rh Rhodium 102.91 12.41 20.216	46 Pd Palladium 106.42 12.02 21.177	47 Ag Silver 107.87 10.50 22.163	48 Cd Cadmium 112.41 8.69 23.173	49 In Indium 114.82 7.31 24.210	50 Sn Tin 118.71 7.29 25.271	51 Sb Antimony 121.76 6.69 26.359	52 Te Tellurium 127.60 6.23 27.473	53 I Iodine 126.90 4.93 28.612	54 Xe Xenon 131.29 0.006 29.775																												
55 Cs Cesium 132.91 1.87 30.973	56 Ba Barium 137.33 3.59 4.466	57 La Lanthanum 138.91 6.15 4.647	72 Hf Hafnium 178.49 13.31 7.899	73 Ta Tantalum 180.95 16.65 8.146	74 W Tungsten 183.84 19.25 8.398	75 Re Rhenium 186.21 21.02 8.652	76 Os Osmium 190.23 22.61 8.911	77 Ir Iridium 192.22 22.65 9.175	78 Pt Platinum 195.08 21.46 9.442	79 Au Gold 196.97 19.28 9.713	80 Hg Mercury 200.59 13.53 9.989	81 Tl Thallium 204.37 11.85 10.269	82 Pb Lead 207.20 11.34 10.551	83 Bi Bismuth 208.98 9.81 10.839	84 Po Polonium (209) 9.32 11.131	85 At Astatine (210) 7.00 11.427	86 Rn Radon (222) 0.01 11.727																												
87 Fr Francium (223) 1.87 12.031	88 Ra Radium (226) 5.50 12.339	89 Ac Actinium (227) 10.07 12.652																																											
<table border="1"> <tbody> <tr> <td>58 Ce Cerium 140.12 6.77 4.839</td> <td>59 Pr Praseodymium 140.91 6.77 5.035</td> <td>60 Nd Neodymium 144.24 7.01 5.228</td> <td>61 Pm Promethium (145) 7.26 5.432</td> <td>62 Sm Samarium 150.36 7.52 5.633</td> <td>63 Eu Europium 151.96 5.24 5.849</td> <td>64 Gd Gadolinium 157.25 7.90 6.053</td> <td>65 Tb Terbium 158.93 8.23 6.273</td> <td>66 Dy Dysprosium 162.50 8.55 6.498</td> <td>67 Ho Holmium 164.93 8.80 6.720</td> <td>68 Er Erbium 167.26 9.07 6.949</td> <td>69 Tm Thulium 168.93 9.32 7.180</td> <td>70 Yb Ytterbium 173.04 6.97 7.416</td> <td>71 Lu Lutetium 174.47 9.84 7.655</td> </tr> <tr> <td>90 Th Thorium 232.04 11.72 12.968</td> <td>91 Pa Protactinium 231.04 15.37 13.291</td> <td>92 U Uranium 238.03 18.95 13.614</td> <td>93 Np Neptunium (237) 20.45 13.946</td> <td>94 Pu Plutonium (244) 19.84 14.282</td> <td>95 Am Americium (243) 13.69 14.620</td> <td>96 Cm Curium (247) 13.51 14.79</td> <td>97 Bk Berkelium (247) 14.79</td> <td>98 Cf Californium (251) 15.1 13.5</td> <td>99 Es Einsteinium (252) 13.5</td> <td>100 Fm Fermium (257)</td> <td>101 Md Mendelevium (258)</td> <td>102 No Nobelium (259)</td> <td>103 Lr Lawrencium (262)</td> </tr> </tbody> </table>																		58 Ce Cerium 140.12 6.77 4.839	59 Pr Praseodymium 140.91 6.77 5.035	60 Nd Neodymium 144.24 7.01 5.228	61 Pm Promethium (145) 7.26 5.432	62 Sm Samarium 150.36 7.52 5.633	63 Eu Europium 151.96 5.24 5.849	64 Gd Gadolinium 157.25 7.90 6.053	65 Tb Terbium 158.93 8.23 6.273	66 Dy Dysprosium 162.50 8.55 6.498	67 Ho Holmium 164.93 8.80 6.720	68 Er Erbium 167.26 9.07 6.949	69 Tm Thulium 168.93 9.32 7.180	70 Yb Ytterbium 173.04 6.97 7.416	71 Lu Lutetium 174.47 9.84 7.655	90 Th Thorium 232.04 11.72 12.968	91 Pa Protactinium 231.04 15.37 13.291	92 U Uranium 238.03 18.95 13.614	93 Np Neptunium (237) 20.45 13.946	94 Pu Plutonium (244) 19.84 14.282	95 Am Americium (243) 13.69 14.620	96 Cm Curium (247) 13.51 14.79	97 Bk Berkelium (247) 14.79	98 Cf Californium (251) 15.1 13.5	99 Es Einsteinium (252) 13.5	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)
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35	79.90	Atomic number
Br	3.12	Atomic weight
Bromine		Density (g/cm ³)
K α 11.924		Symbol
L α 1.481		Element name
		Energy (keV)
		Spectral line

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



A Simple XRF Application

Target Stamps

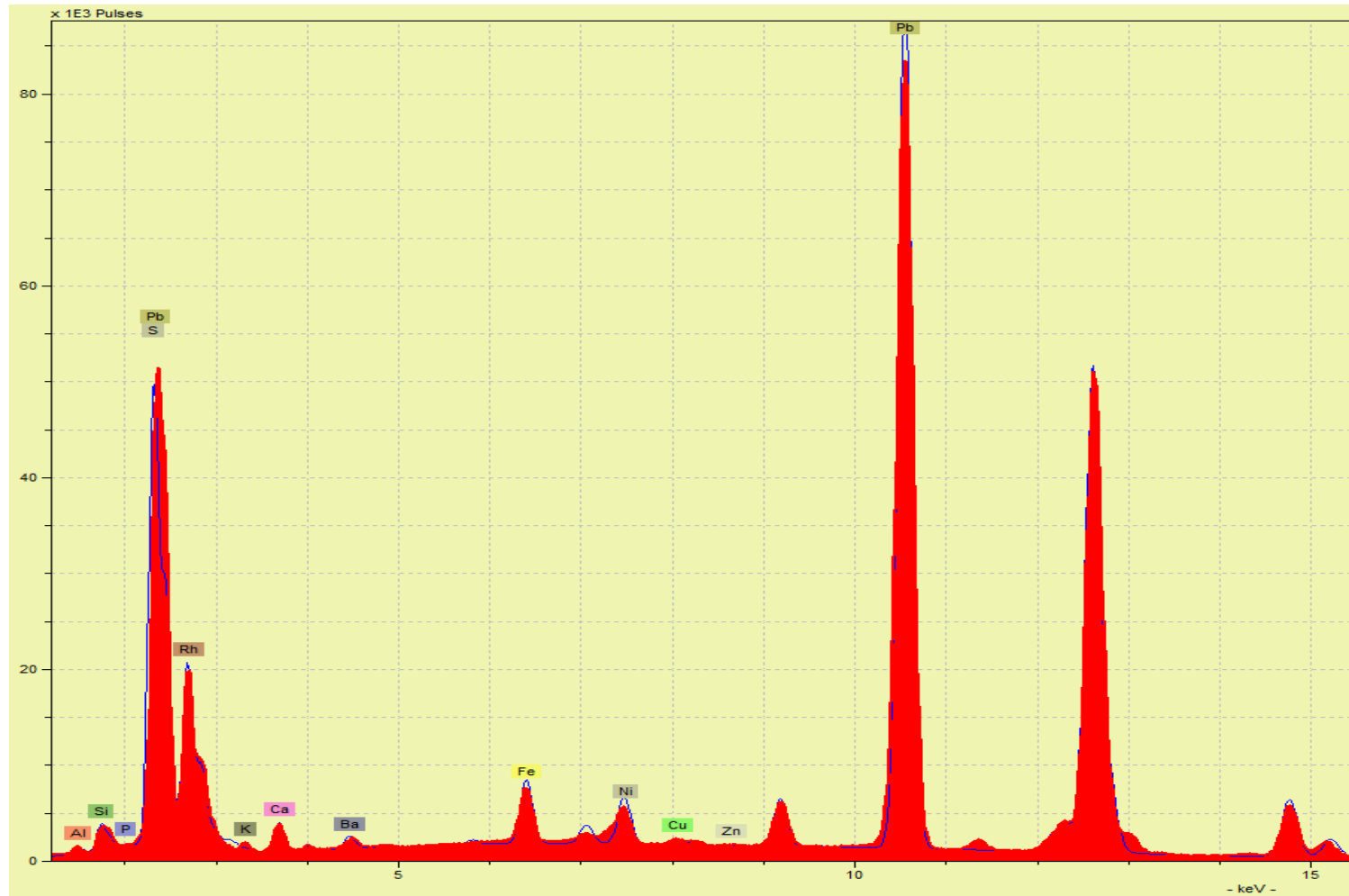


Stamp A
Genuine



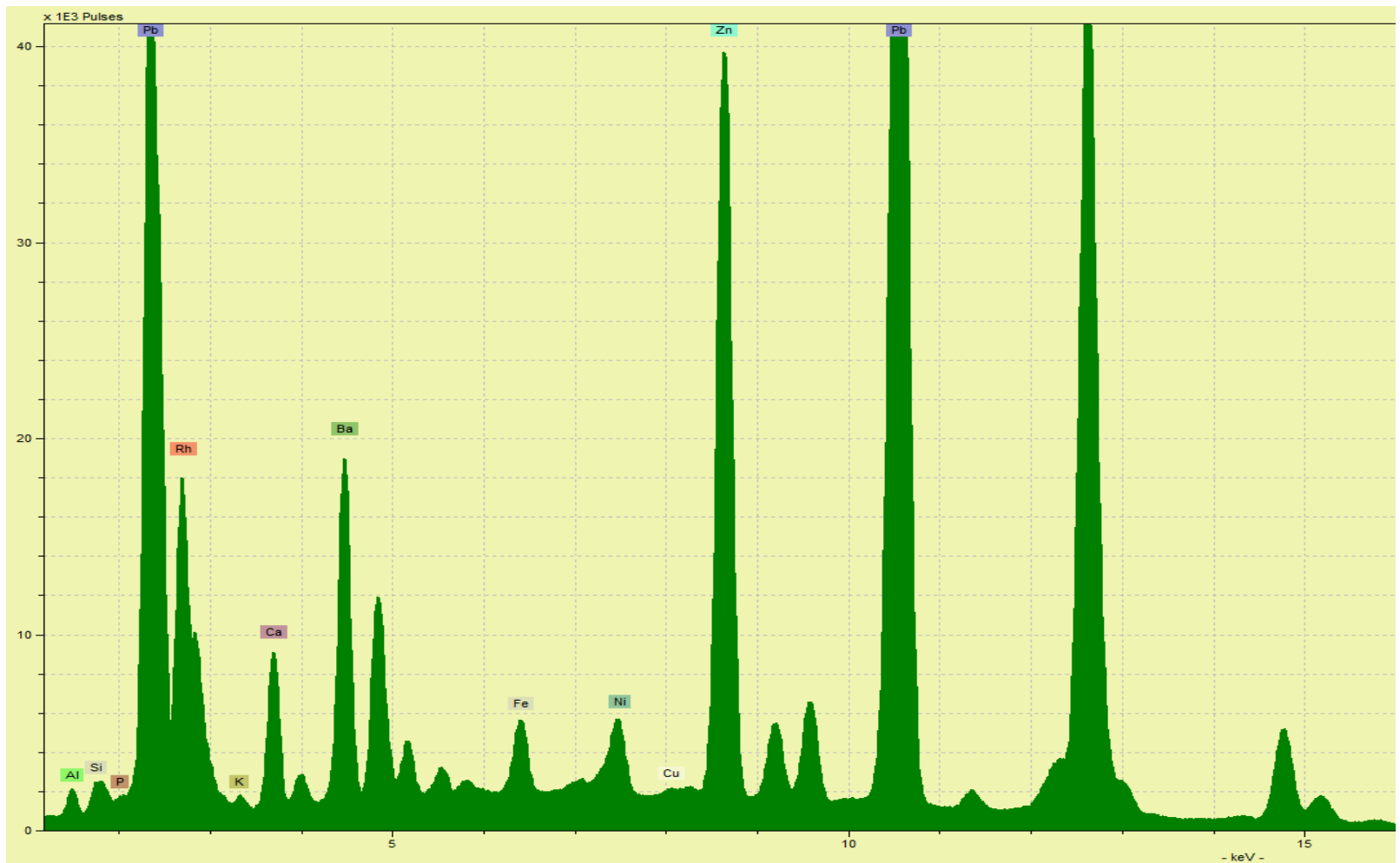
Stamp B
Forgery

Stamp "A" Ink Composition



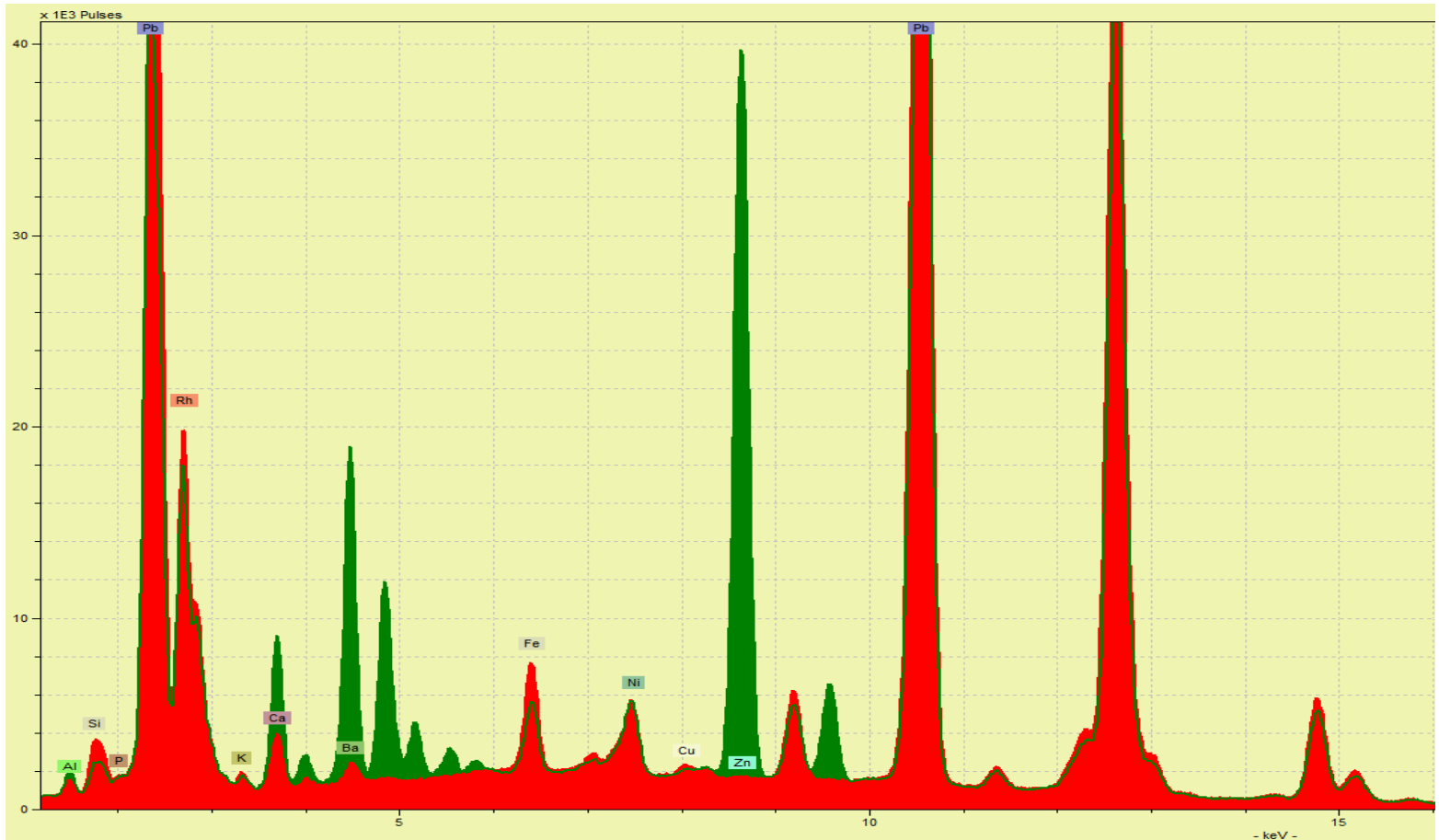
Energy (KeV)

Stamp "B" Ink Composition



Energy (KeV)

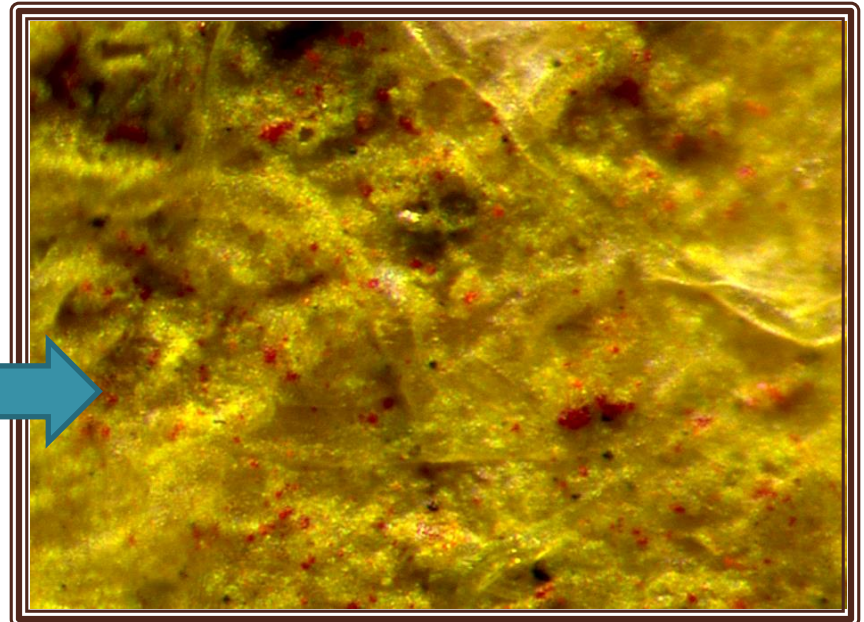
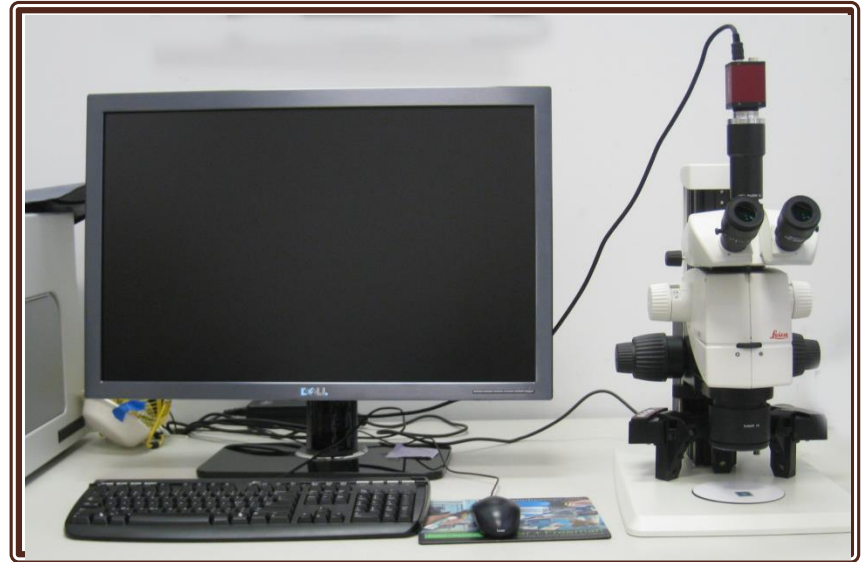
Comparison of Inks



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

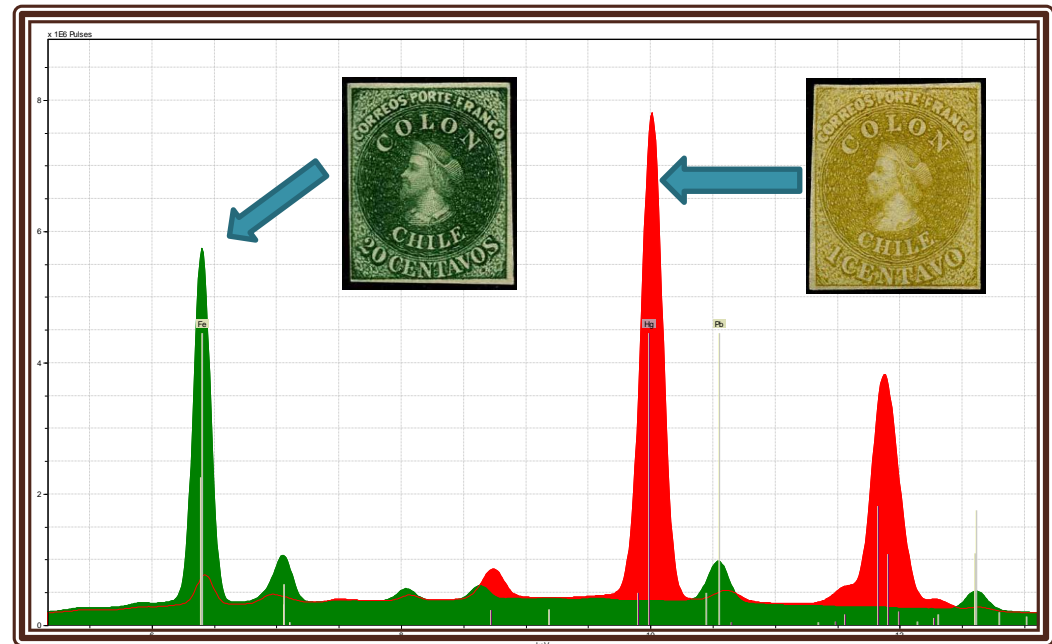
Microscopy

- 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).



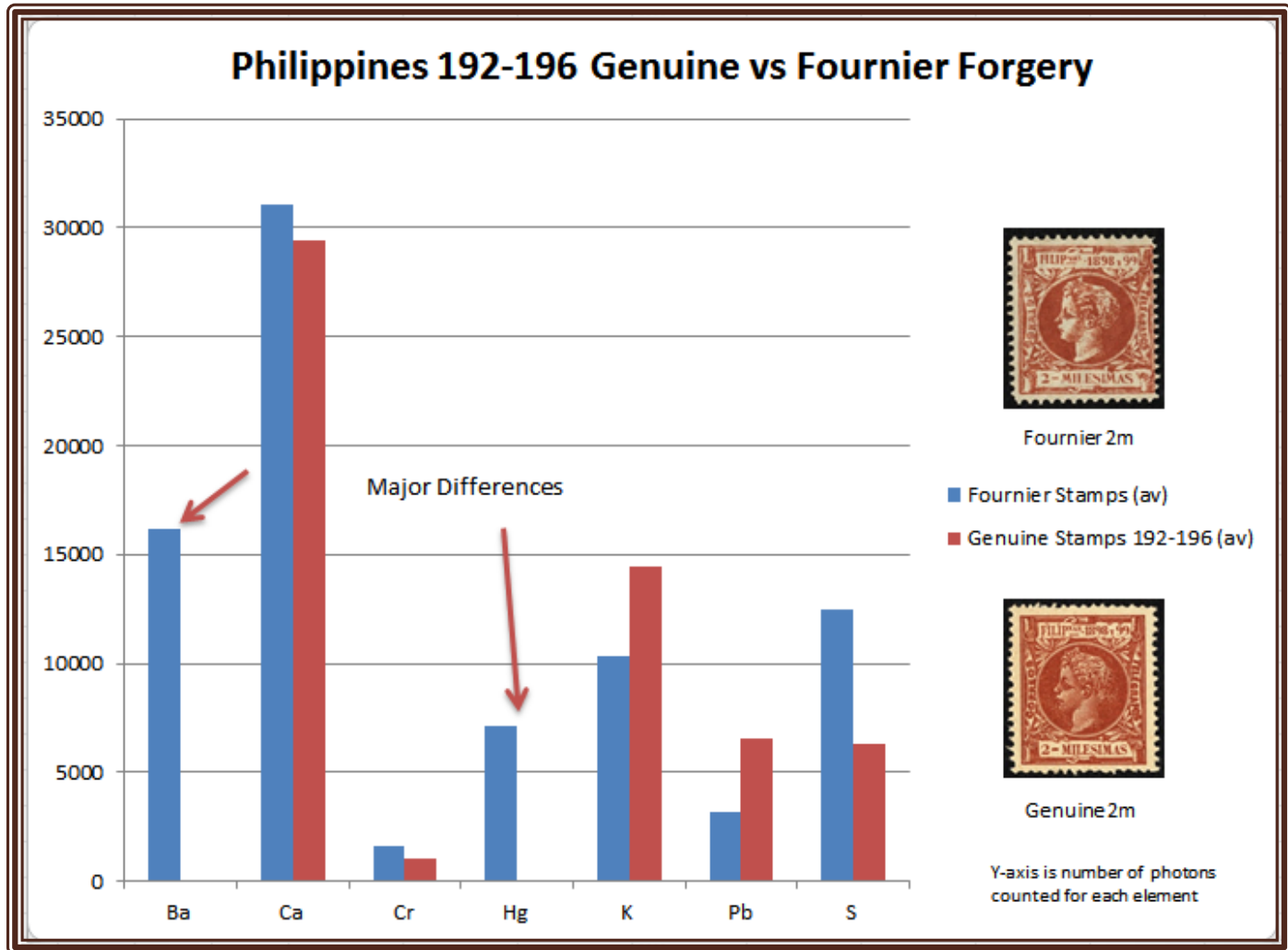
X-Ray Fluorescence (XRF) Tracer

- 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.



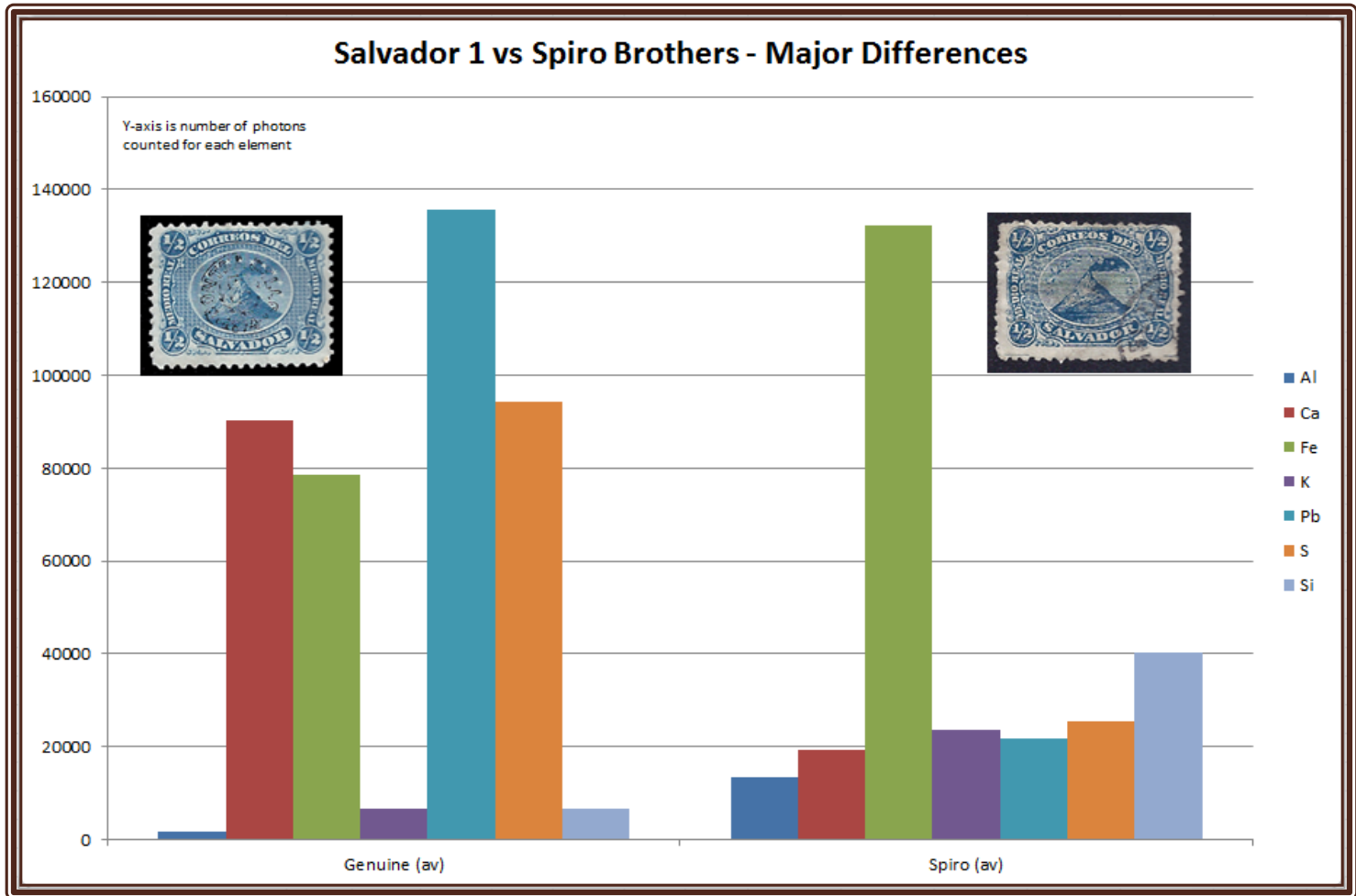
X-Ray Fluorescence (XRF) Analysis

Original ink (1898) versus Fournier Forgery Ink



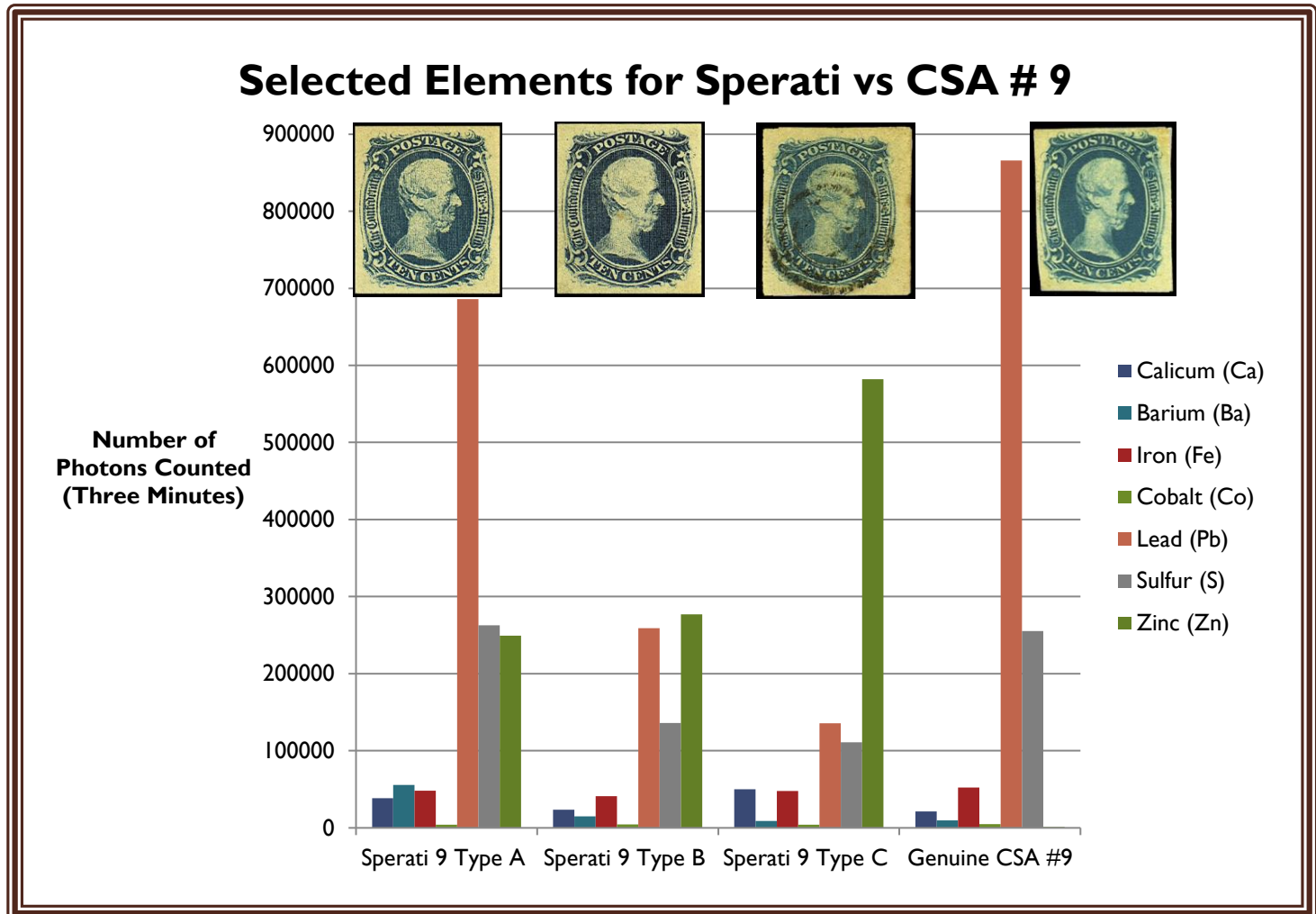
X-Ray Fluorescence (XRF) Analysis

Original ink (1867) versus Spiro Brothers Forgery Ink

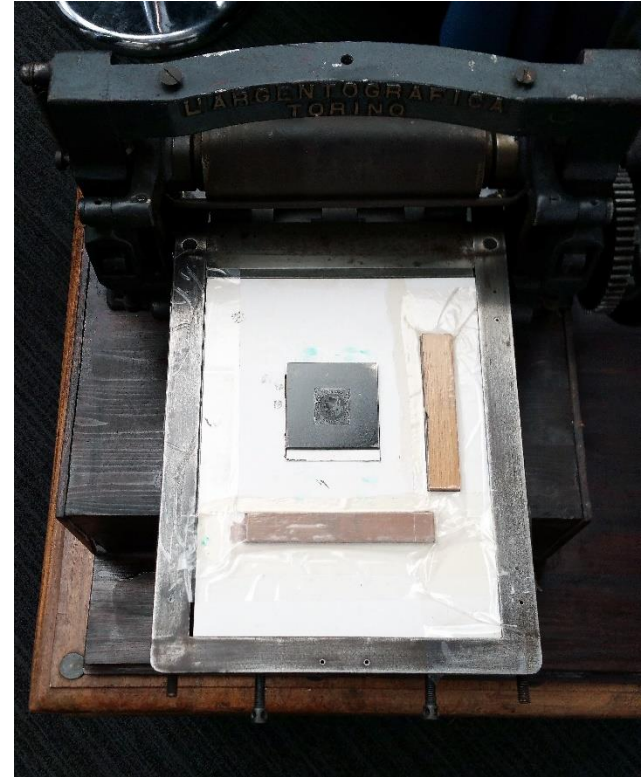


X-Ray Fluorescence (XRF) Analysis

Original ink (1863) versus Sperati Forgery Ink

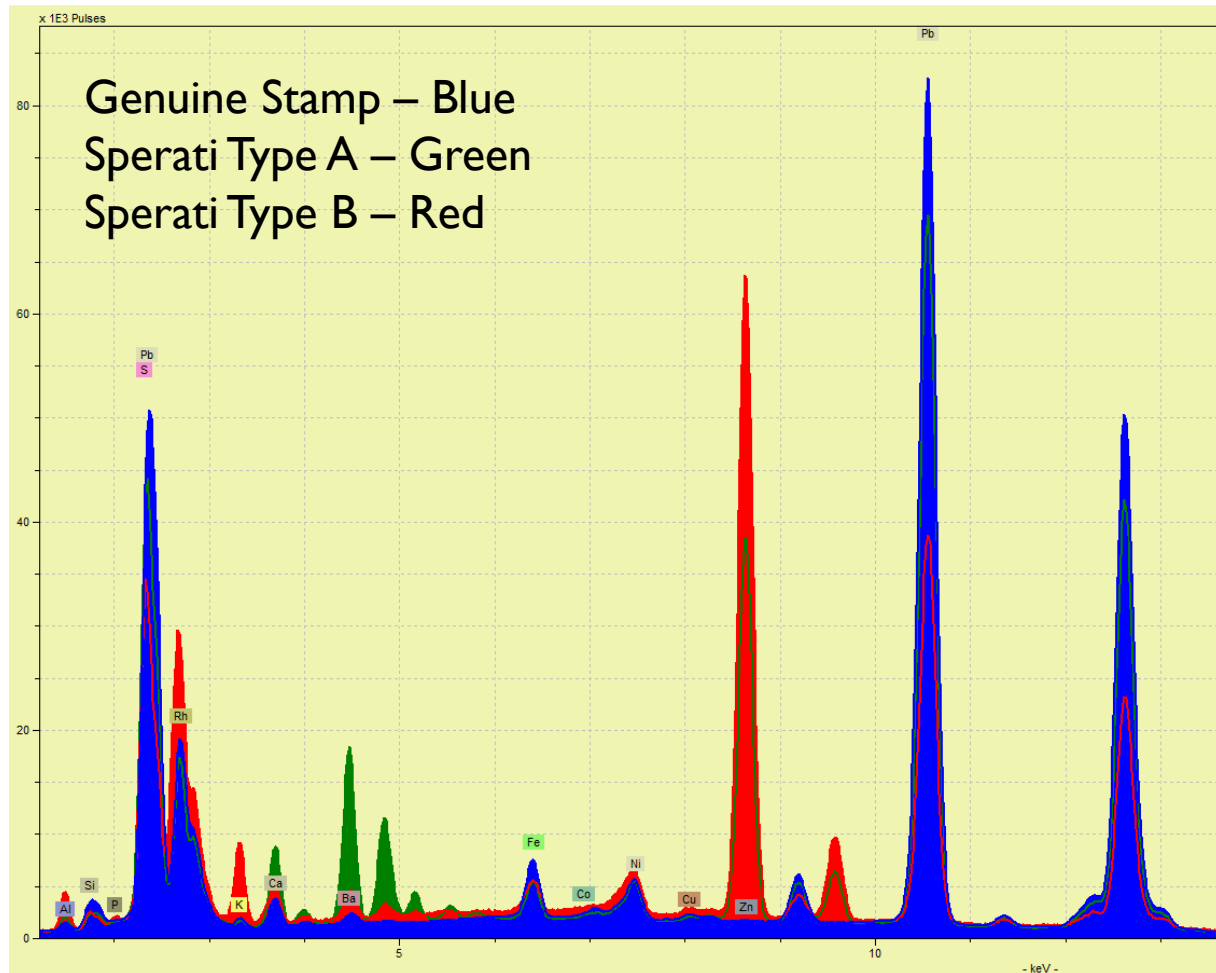


Sperati's Printing Press



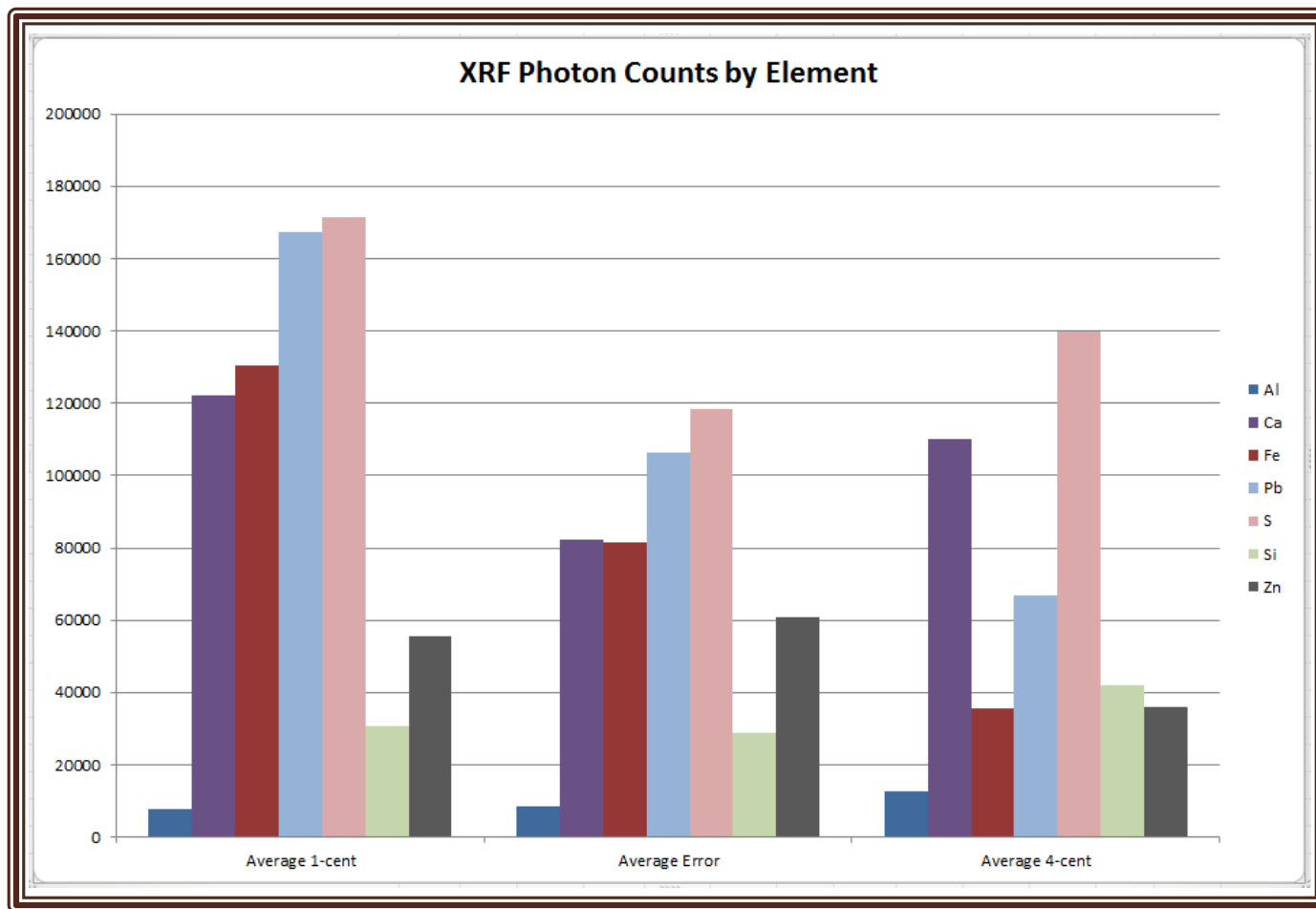
X-Ray Fluorescence (XRF) Analysis

Original ink (1863) versus Sperati Forgery Ink



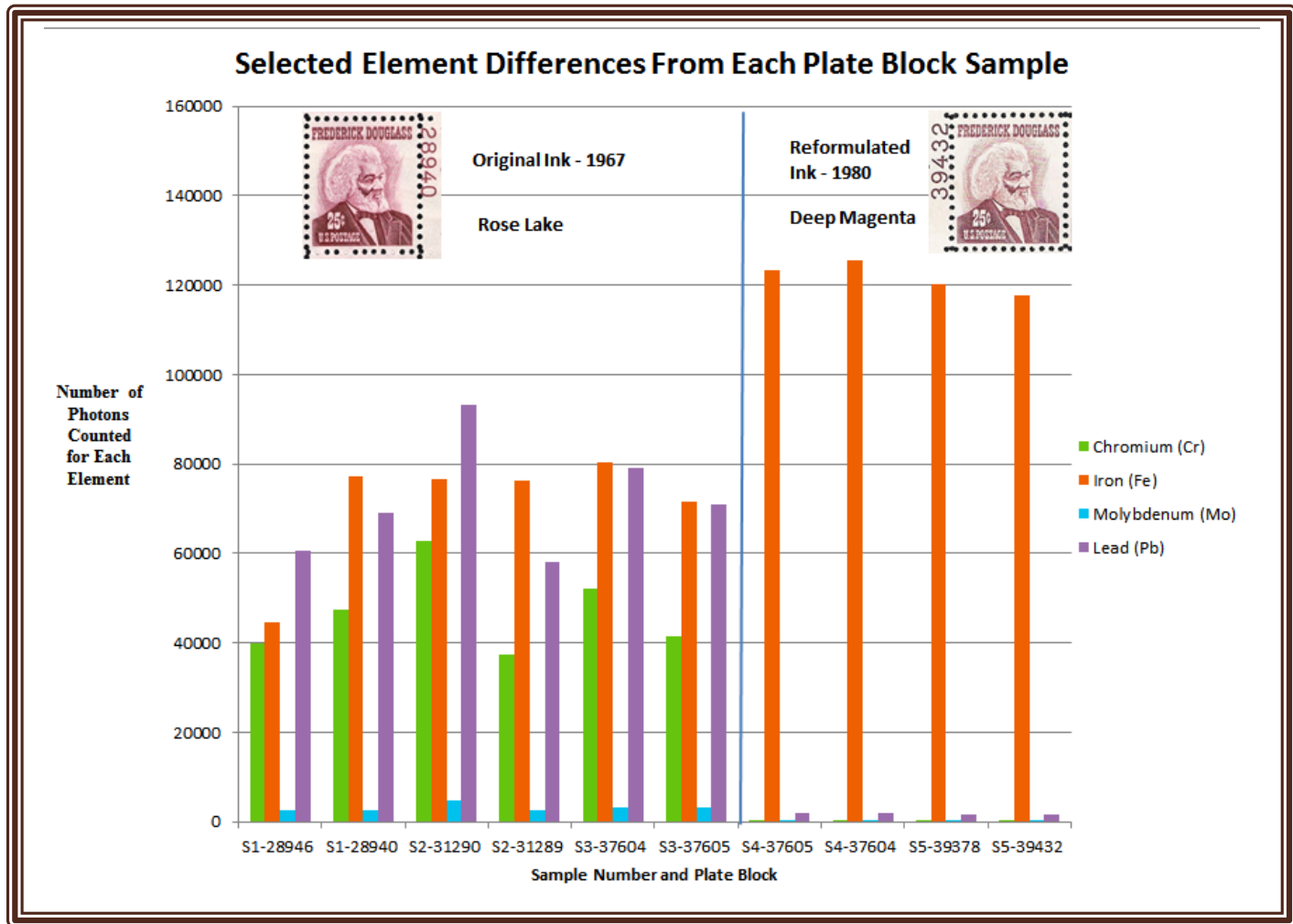
A different view of the previous data

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



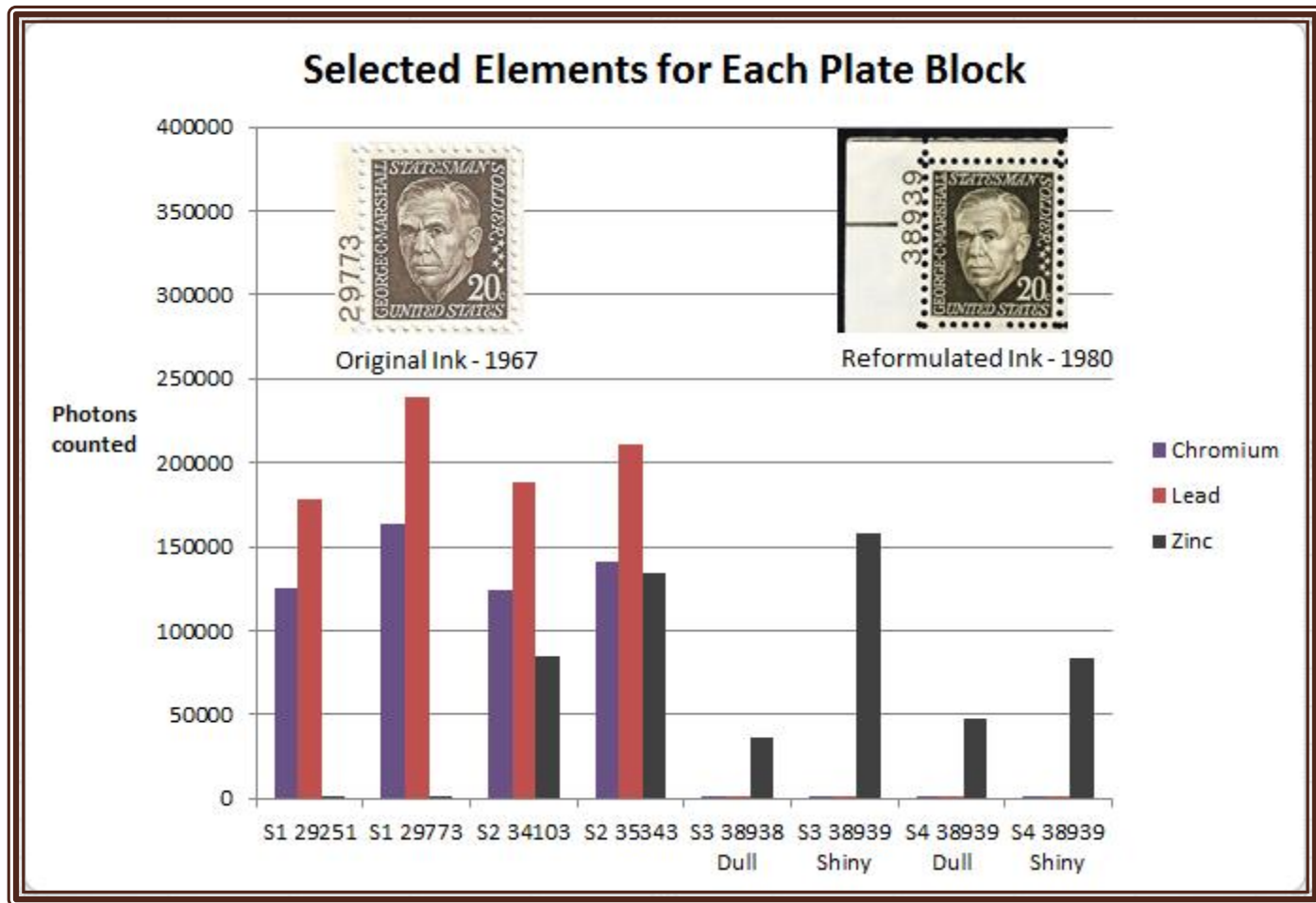
The 1-cent and 4-cent color error stamps have similar characteristics while the regular 4-cent stamp Scott 233 is different indicating two major pigments were used.

Other uses of XRF - color changes



Lead Molybdate Chrome Orange ($\text{Pb}(\text{CrMoS})\text{O}_4$) 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