The Devil is in the Details
Method and Rules of Engagement
for metal object
analysis using
1000 to 40000 eV Photons

<u>Material Conditions</u>
Remember that art and archaeological metal objects are NOT modern alloys.

The techniques use to fabricate them did not in general create objects of uniform content spatially or elementally. Almost every object has various surface layers which are either purposefully done like enameling, waxing, plating, patination, gilding etc. Or the surface variation is the result of the fabrication process, for instance when fabricating a sterling Ag object, the object is generally enriched in Ag at the expense of Cu on the surface as the result of the material properties of mixing Cu and Ag. Or enrichment occurs during the life of an environmentally exposed or buried metal alloy, causing surface composition changes which have taken place. In fact "surface depletion" might be a better term, since it seems likely that it is the leaching out of the less chemically stable elements which causes the surface composition to change.

Semi quantitative detailed xrf analysis of these complex surfaces can teach one much about the object and its relative elemental composition if the raw photon spectra is examined in every detail with the knowledge of how the photon physics creates such a spectrum. Quantitative analysis of these complex surfaces and relating to accurate bulk alloy compositions is an exercise in folly!

The reason for this is the 1000 to 40000 eV photons interact with all the various layers with various contributions from each layer to the final analysis as a function of the thickness of each layer in an exponential manner. Since the thickness of these layers vary widely from spot to spot on the object, and the layers thicknesses are unknown analysis in a quantitative manner is impossible.

This is all because 1000 to 40000 eV photons (XRF) only analyzes to a depth of 0.0034 cm to about 0.015 cm depending on the alloy!

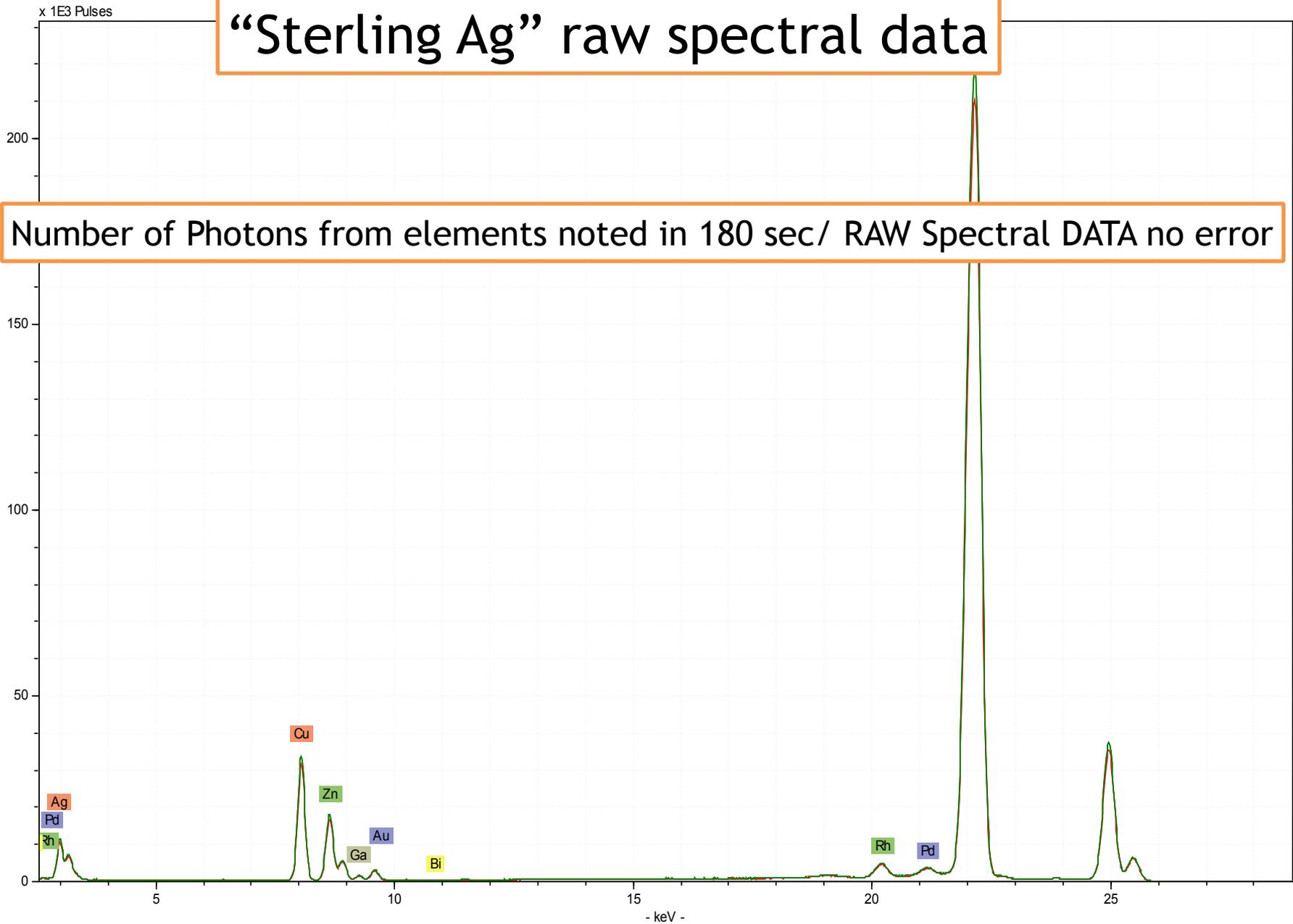# THE RULES of metal analysis in archaeology and museums:

1. The first step is when doing any alloy never ever believe any numbers unless you first look in detail at your raw photon spectra and make sure there is nothing in the raw spectral data that is a surprise. You must do this with every spectrum you take including standards and especially artifacts!
2. You must know the concentration range used in the calibration and the Elements included and always check your unknown spectra an make sure they fall within these limits before believing the numbers
3. Second step, alloys of precious metals are never uniform in concentration, so even if the visible photons (1 to3 eV) are registering in through your spectrometers (your eyes) that it very uniform do not believe them analyze your sample in several places and overlay all the spectra and make sure they are identical within the width of the line. If they are not then your samples are not uniform!
4. Third; if the visible photons (1 to3 eV) are registering in through your spectrometer's (your eyes) that it not uniform, believe them, it is non-uniform. Analyze your sample in several places. Your eyes are doing molecular analysis so if they see a difference in how 1 to 3 eV are interacting then there is a difference!
5. Fourth all analysis of precious alloys are to a depth of $t = 4.61/(70 \times 19.3) = 0.0034$ cm . In every artifact and handled (Touched with oily hands) standards there is a difference in the surface and the bulk. So if you want an accurate reading of the bulk material you must have a clean surface. In many cases that is not possible so just be aware that your measurement is an approximation of the bulk at best.
6. Many things are plated be very wary often you measure right through the plating, and your wt% results are then a joke but will look reasonable!
7. The raw photon spectra from the Tracer instrument is never wrong, if one spot to another gives you a different photon spectra on an object then there is a difference in the elemental content, spot to spot!
8. If you want to "see" ppm variations then you are going to need to analyze for at least 300 seconds.

I would suggest you print these items out and commit them to memory.

Sterling Ag?
many more elements
than just Cu and
Ag
Zn is a problem
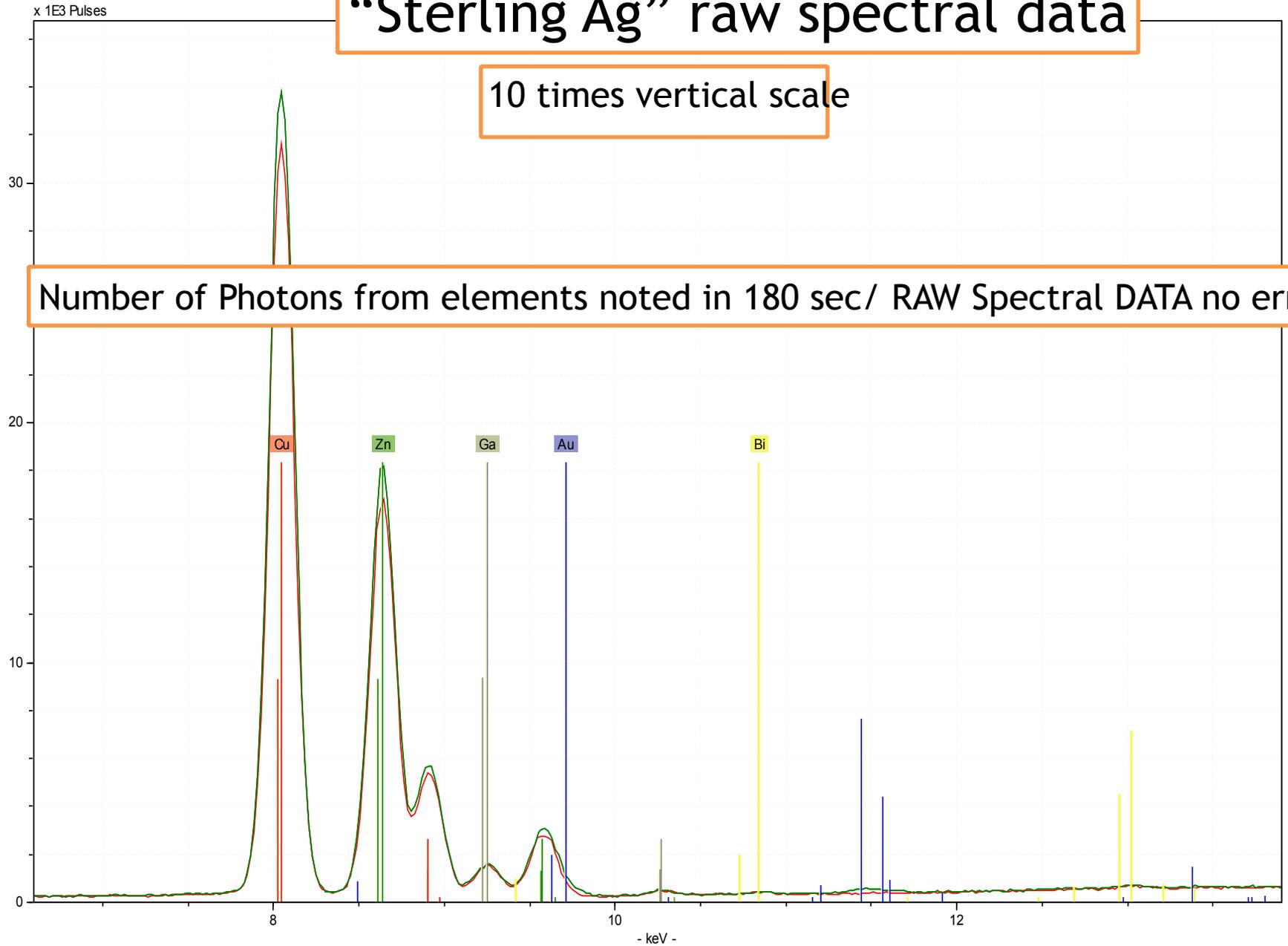
"Sterling Ag" raw spectral data

Number of Photons from elements noted in 180 sec/ RAW Spectral DATA no error
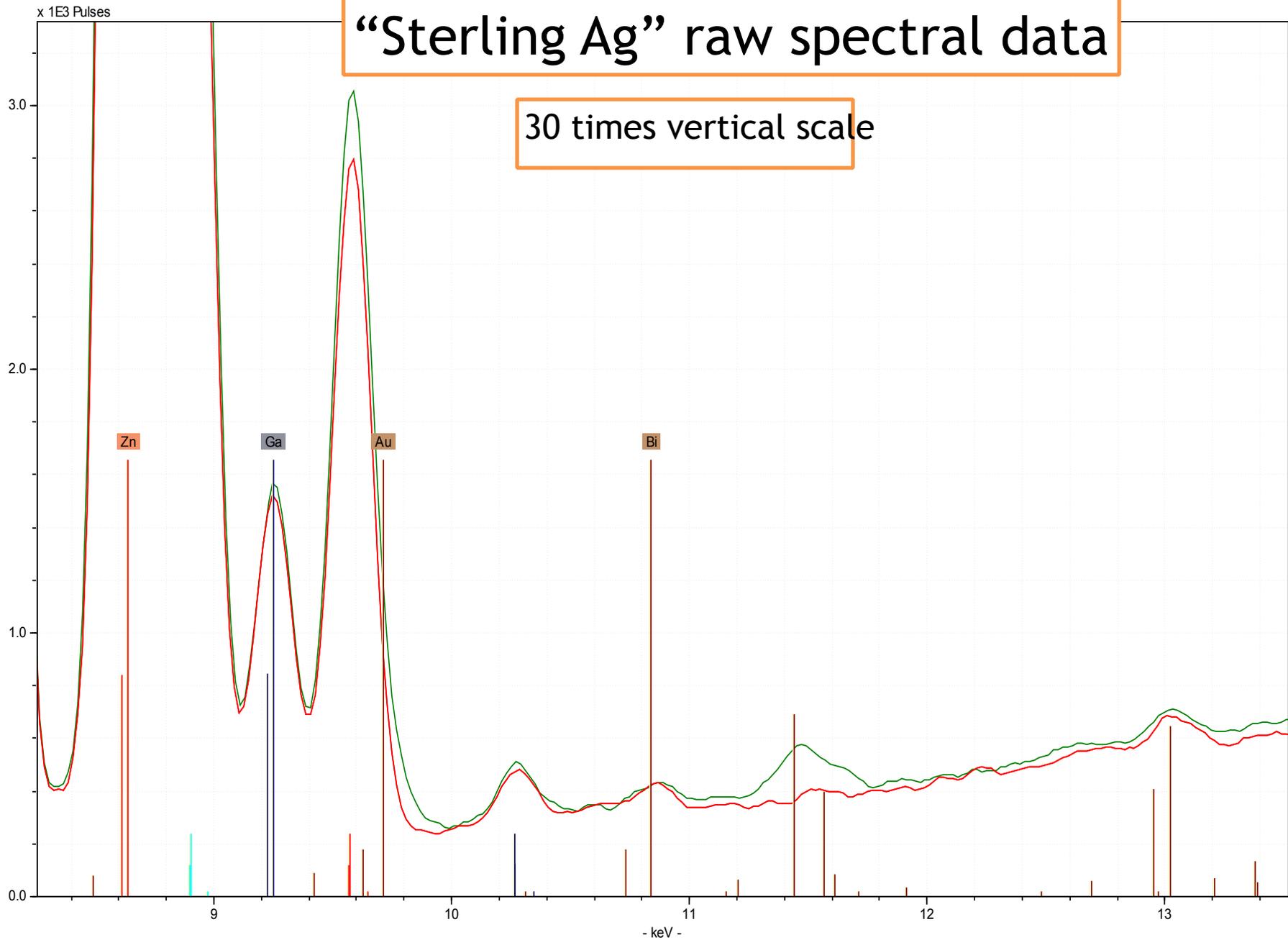
"Sterling Ag" raw spectral data

10 times vertical scale

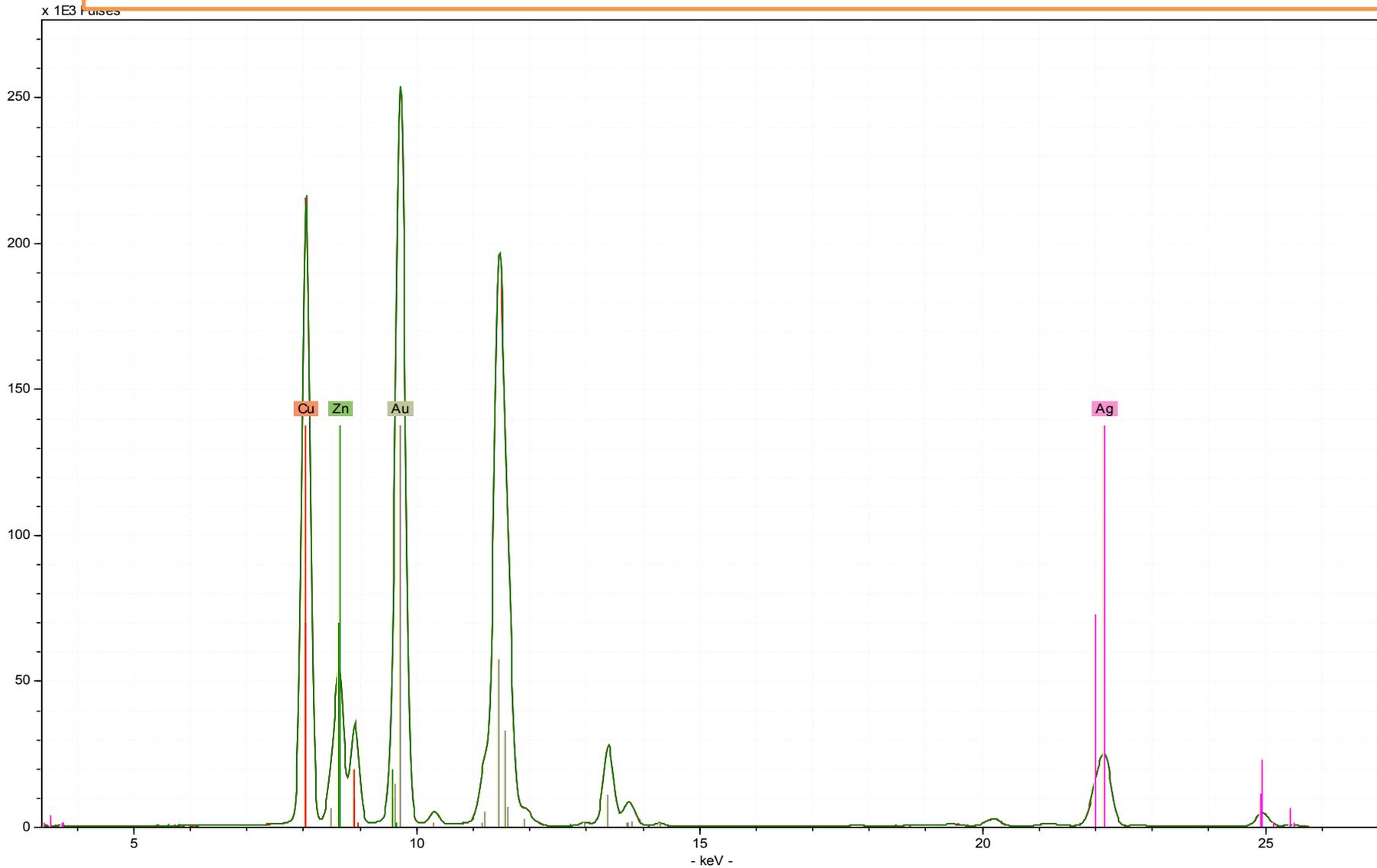Number of Photons from elements noted in 180 sec/ RAW Spectral DATA no error

"Sterling Ag" raw spectral data

30 times vertical scale

"Au STD" raw spectral data

Number of Photons from elements noted in 180 sec/ RAW Spectral DATA no error

STEPS REQUIRED TO DO SPECTRA ANALYSIS USING ARTAX SOFTWARE provided with the Tracer

CHANGING PDZ FILES TO TXT FILES FOR ARTAX
The Group Conversion option UNDER THE SETUP TAB IN S1PXRF allows the user to change the data format in an entire folder TO TXT FILES FOR ARTAX ANALYSIS.
To convert files, select Group Conversion from the Setup tab. Click the PDZ Name button (Figure 7) and then select the PDZ folder you wish to convert. Check the Output TXT (Artax) and Replace duration with livetime [adjust spectrum accordingly] checkboxes. This box executes a command to correct all spectrum data to the instrument live time rather than real time, allowing direct comparison of one spectrum to another in absolute terms. When this box is checked, the FWHM (Full Width Half Maximum) and ELin (Energy Line) fields will appear (Figure 8). Enter the correct information in the FWHM field (for PIN diode, the FWHM is typically 200 eV; for SDD systems, it is 150 eV). The ELin field may be left blank (the number is read from data stored with each spectrum file; however, it is typically 0.02 KeV for an SDD system, and 0.04 KeV for a PIN diode system). Click the Execute PDZ button to convert ALL spectra in the folder (the conversion will create files in the same folder with the identical name as the source file, but with a .txt extension). The .txt files can be analyzed using the Artax software, described in a separate user guide.
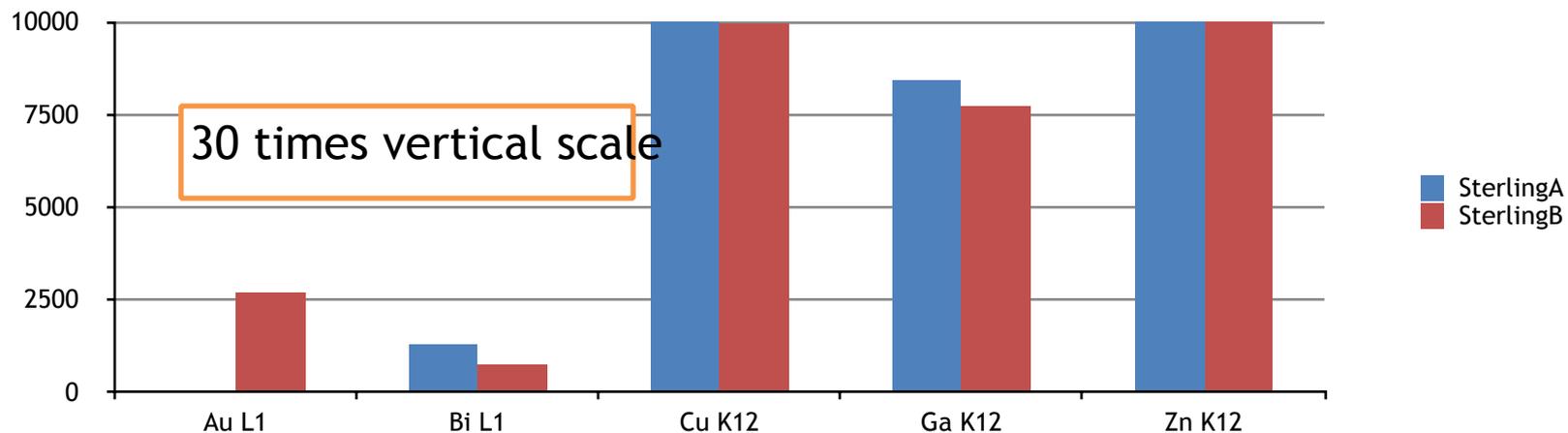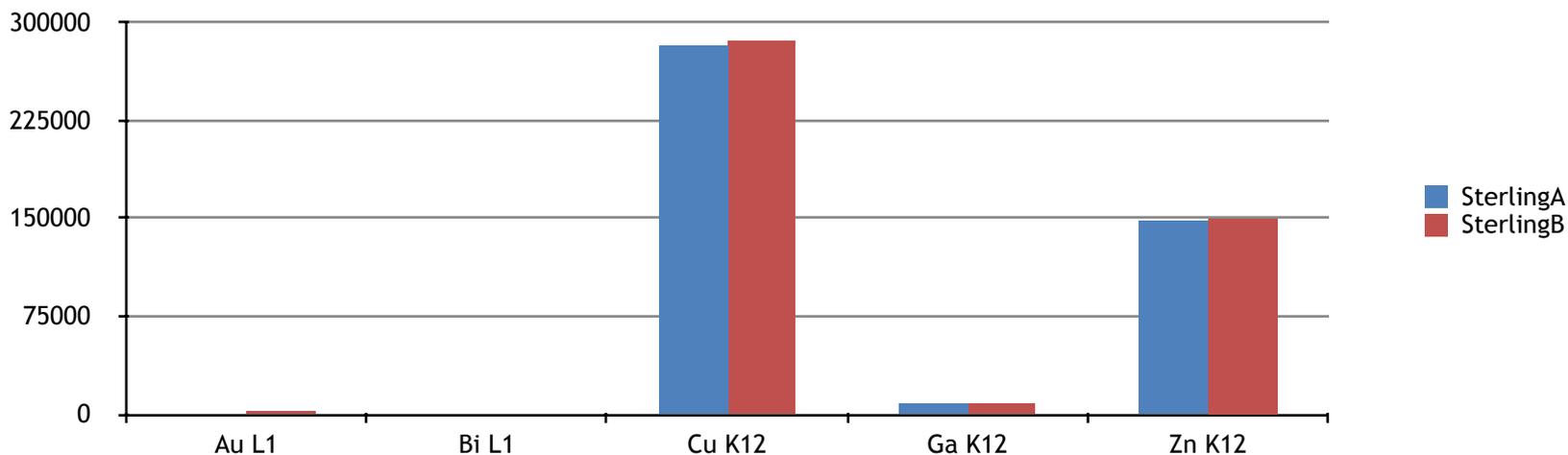
Net area analysis in Artax 7
1. In ARTAX, click on 'File', click on "open spectrum", file the folder that has all your txt spectrum files, highlight them all and click open
2. Click on "project", click on "new project", right click on "object", click on "add node", enter "Points" in name box. Highlight this folder.
3. Go back to "Project" tab. click on "Add spectrum".
4. Click on "File", click on "save project", give a name (.rtx), click on "save"
5. Click on "spectrum" tab
6. Go to method list and pick your method! See below
7. Highlight the Points folder
8. Click on "Analyze" and then on "Evaluate Results", a progress bar should appear as all the spectra are being evaluated with "your named method"
9. Then click on "Export" and then on" Results to Excel" Then a box will appear so you name the excel file and put it in a folder that you want the results to be in!
10. Now immediately resave your project file because it now contains your spectra and your results. Use the same name you did before and save on top of the old version of the rtx file.
11. Now go to the folder you saved your results in and open the file and got to the Points tab to see all your net area data. You then edit out the area that gives you no information.

Method Creation
•To create a method open a spectrum that is typical of the spectra you want to analysis, get the periodic table and LABEL ALL THE ELEMENTS THAT ARE IN THE SPECTRUM, YOU CAN NOT SKIP ONE JUST BECAUSE YOU ARE NOT INTERESTED IN IT, YOU MUST LABEL ALL THE ELEMENTS THAT THE SYSTEM HAS DETECTED IN YOUR SAMPLE.
•Then click on the Method editor that is to the left of the method name.
•Click on Identification and make sure the dot is in the Preset list option to the left of the periodic table
•Then click Get elements
•Then go to the Name box and type in whatever name you would like for your method
•Click on Corrections then set cycles at 9 and then pick your energy range for fitting, typically the range of analysis.
•Then click on add
Then click on ok at the bottom of the popup method editor window. Your method should now be in the method window at the top of the Artax screen

Artax analysis software analysis: Number of Photons from elements noted in 180 sec/ RAW DATA no error

	Ag K12	Au L1	Bi L1	Cu K12	Ga K12	Zn K12
SterlingA	3664608	0	1293	282163	8394	148296
SterlingB	3606493	2649	740	285317	7755	150480

30 times vertical scale

To calculate Wt % concentration

(**NOTE for Metal you must do all your unknown analysis using the yellow filter and 40 kV lowest micro amps setting**)

1. you just open s1pxrf
2. and click on setup and Select Coef and then select your CFZ file in your metal calibration folder , it is named GL1.CFZ
3. And then a CONC button will appear. NOTE you use the numbers in the pop up that are on the right of the box, the units are in Wt %

Elements and Wt % range of concentration used for the Quantitative calibration

	Ni	Cu	Zn	Au	Pb	Ag
40C11000-70B	0	1	0	0	0	0
40XXS10KW_900	0.1449	0.3072	0.1158	0.4206	0	0
40XXS14KY_UA1	0	0.282	0.0365	0.5843	0	0.0951
40XXS18KY_765	0	0.06	0.0075	0.7505	0	0.182
40XXS22KY_394	0	0.049	0.0016	0.9168	0	0.0325
Ag	0	0	0	0	0	1
Ag100Cu	0	1	0	0	0	0
Ag10Cu	0	0.1	0	0	0	0.9
Ag20Cu	0	0.2	0	0	0	0.8
Ag30Cu	0	0.3	0	0	0	0.7
Ag40Cu	0	0.4	0	0	0	0.6
Ag50Cu	0	0.5	0	0	0	0.5
Ag5Cu1Au1Pb	0	0.0503	0	0.0106	0.0105	0.9286
AG5Cu1Au1Pb-2	0	0.0503	0	0.0106	0.0105	0.9286
Ag5Cu5Au-2	0	0.05	0	0.05	0	0.9
Ag60Cu	0	0.6	0	0	0	0.4
Ag70Cu	0	0.7	0	0	0	0.3
Ag80Cu	0	0.8	0	0	0	0.2
Ag90Cu	0	0.9	0	0	0	0.1
AgSterling	0	0.075	0	0	0	0.925
AgSterling-2	0	0.075	0	0	0	0.925
Au0.25Cu	0	0.025	0	0.9975	0	0
Au0.25Cu-2	0	0.025	0	0.9975	0	0
Au41.5Cu	0	0.455	0	0.545	0	0
Au41.5Cu-2	0	0.455	0	0.545	0	0

Sample analysis given in wt%

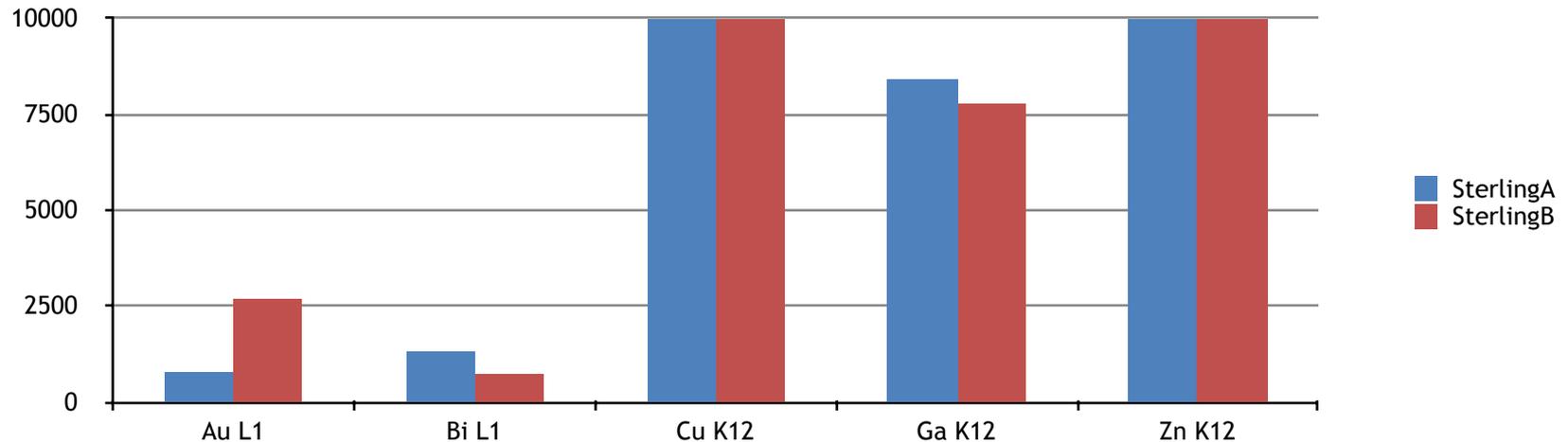|	SterlingA	SterlingB	Au STD_FP-42	Au STD_FP-43
NiKa1	-0.002	-0.002	-0.001	-0.001
CuKa1	0.060	0.061	0.249	0.248
ZnKa1	0.023	0.024	0.038	0.038
AuLa1	0.003	0.004	0.584	0.584
PbLb1	0.000	0.000	0.000	0.000
AgKa1	0.909	0.907	0.123	0.124
SUM	0.994	0.994	0.993	0.993

Certified analysis of Au STD:
1. Cu 24.6 wt% +/- 0.15%
2. Zn 3.9 wt% +/- 0.2%
3. Au 58.6 wt% +/- 0.2%
4. Ag 12.9 wt% +/-0.15%

The table above is the output of a calibration and the numbers are in weight percent. They even add up to 100% but the problem is the devil is in the details. This calibration is actually much more accurate than FP give you but did not include Bi and Ga.

The plot below is the Raw photon data and it is telling you have Ga and Bi in your samples. But Ga and Bi was not in the calibration so no numbers are given for them! And the Au the Weight percent numbers content is not the same as the raw photon numbers indicate. The number of photons show that there is much more Au in the sample B. Note the Raw spectrum is never wrong!

In ancient alloys often the critical information about the material is in the Trace elements. Not in the major alloy elements.
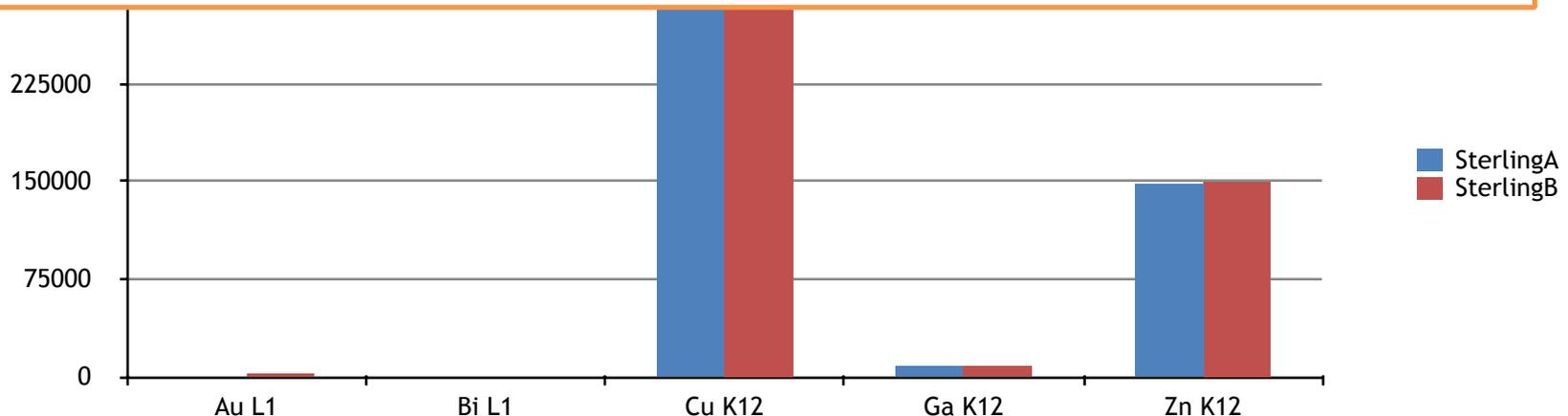
Sample analysis given in wt%

	SterlingA	SterlingB	Au STD_FP-42	Au STD_FP-43
NiKa1	-0.002	-0.002	-0.001	-0.001
CuKa1	0.060	0.061	0.249	0.248
ZnKa1	0.023	0.024	0.038	0.038
AuLa1	0.003	0.004	0.584	0.584
PbLb1	0.000	0.000	0.000	0.000
AgKa1	0.909	0.907	0.123	0.124
SUM	0.994	0.994	0.993	0.993

Certified analysis of Au STD:
1. Cu 24.6 wt% +/- 0.15%
2. Zn 3.9 wt% +/- 0.2%
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4. Ag 12.9 wt% +/-0.15%

There is another problem The Wt % numbers for Zn and Cu also do not match the relative photon intensity. Also it is very unusual to have Zn and Cu and Au and Bismuth in a "Sterling Ag" object. Indeed this is very likely not a Sterling Ag object but is Ag plated Brass. Which is actually then "pure" Ag plated on a Brass object. Which then means the wt% above are entirely fictional quantities for the Sterling Ag object, but real for the Au STD!

Conclusions:
1. It is very likely the "Sterling Ag" is Ag plated Brass
2. Further analysis of that object needs to be done
3. It is very important to look at the raw spectrum in every case in detail
4. The Quantitative calibration did not include all the elements detected in the object
5. The updated calibration works well on the Au std and is within the quoted tolerances.
6. But you must know the concentration range used in the calibration and the Elements included and always check your unknown spectra an make sure they fall within these limits before believing the numbers