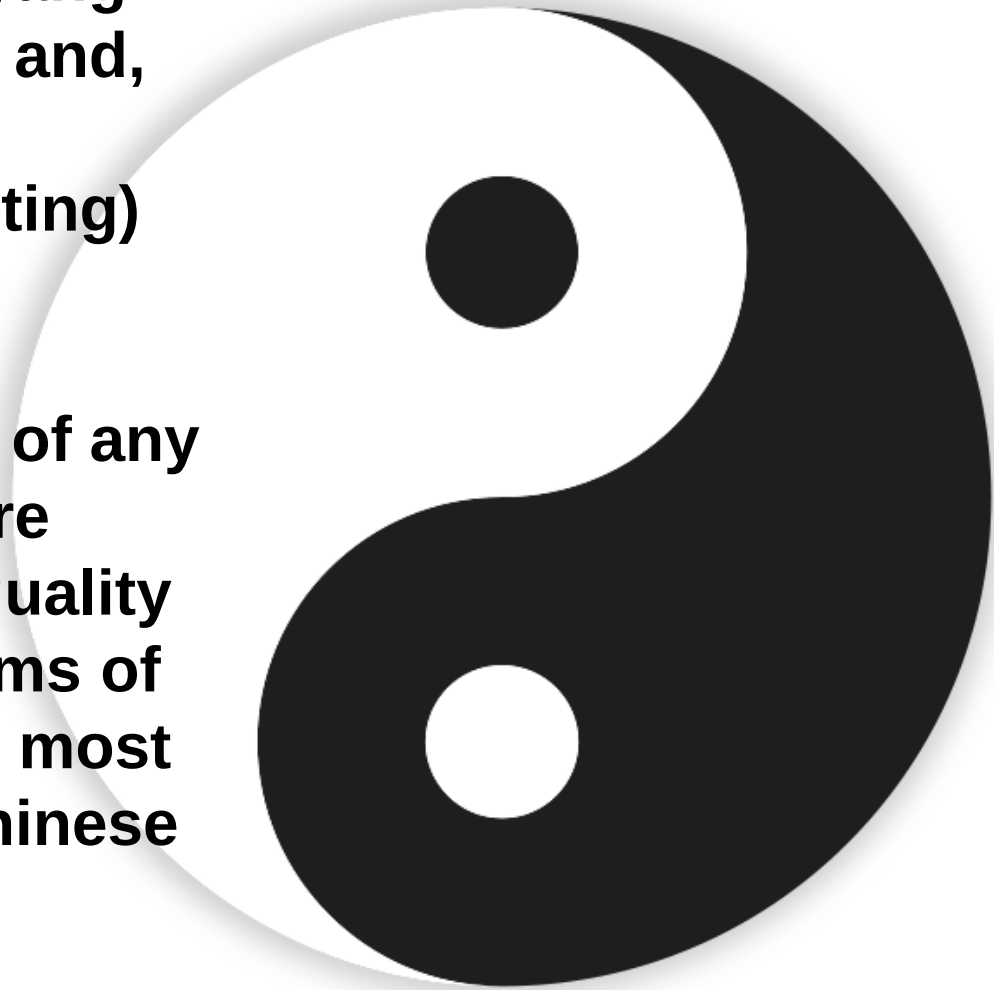


An aerial photograph of a vast, flat, arid landscape, likely a salt flat or desert. In the foreground, there are some low, rocky mounds and a small, dark, irregularly shaped area. The middle ground is a vast, flat expanse of light-colored ground, possibly salt or sand. In the background, there are several ranges of mountains, some with patches of snow or light-colored rock. The sky is a clear, deep blue.

*THE YIN AND YANG OF XRF ANALYSIS AS A TOOL IN
THE INVESTIGATION OF CULTURAL HERITAGE WORKS*

Dr. Bruce J. Kaiser
Chief Scientist
Bruker AXS

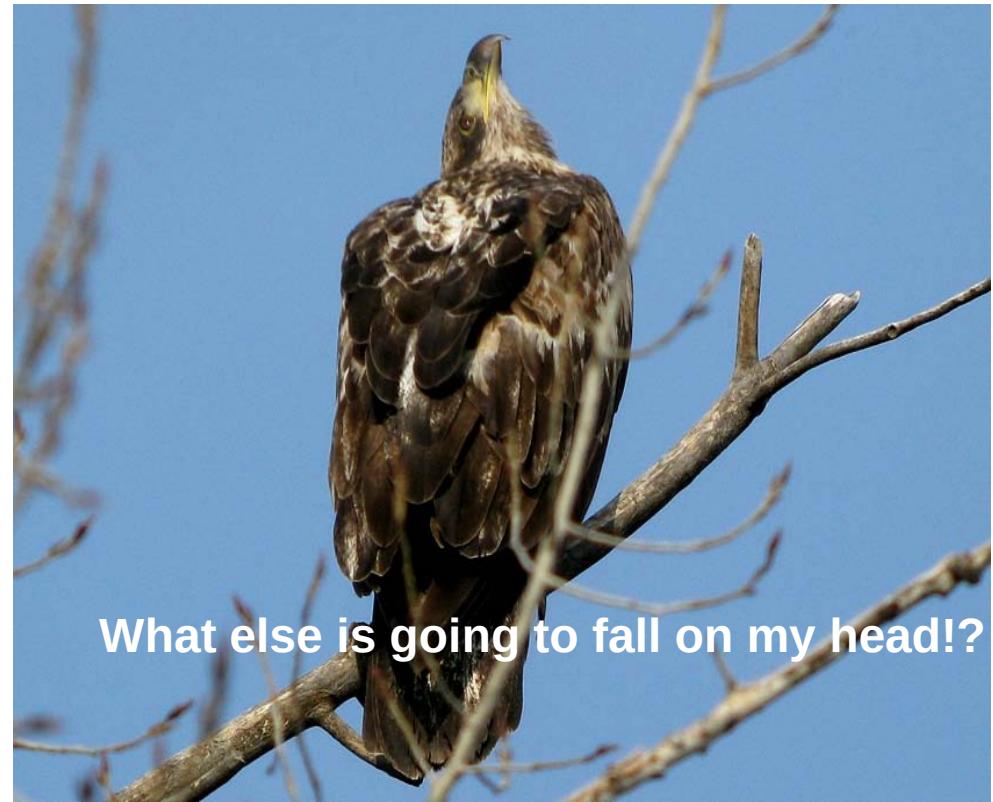
The concept of yin and yang describes two opposing and, at the same time, complementary (completing) aspects of any one phenomenon (object or process) or comparison of any two phenomena. They are universal standards of quality at the basis of the systems of correspondence seen in most branches of classical Chinese science and philosophy,



The YIN

Never **ever** believe numbers unless you know the physics and your sample atom by atom

- Answers vary as;
 - the inverse square of the distance to the element
 - Exponentially relative to matrix density
 - Exponentially relative to elemental X ray energy emission
 - Exponentially relative to element location in the sample matrix
 - Exponentially relative to beam filtering and energy
 - X ray beam distribution
 - Orders of magnitude relative to sample uniformity



And the Yang

- Always review the raw spectrum there are many treasures there in
- Use the Physics in the *Yin* to your advantage
 - Voltage
 - Current
 - Filter
 - Secondary target
 - Variations of the above 4
 - Subtraction
 - Normalization
 - Analysis locations
 - Front to back and Back to front
 - Transmission test or calculations
- Your instrument system must give you control over all these things
- You must have good visual real time access to the raw spectrum



So much for the **PROBLEM** hornet, I made him **LUNCH!**

Something to scratch one's head about?



Innovative XRF Setup and Analytical Approaches for 7 Specific Measurement Treasures

Using the Yin

Chlorine on Fe

Layered paint element location

Ppm analysis of elements in glass

Al analysis in Cu alloys

How deep am I measuring

Heavy metal poisons analysis on ethnographic collections

Measurement of toning agents on photographs



Focus gets you knowledge and lunch!

Chlorine on Fe or any Metal

It should be noted the Cl analysis is very much a SURFACE ANALYSIS when using xrf, as the Cl atom emits only a 2.7 keV x ray. This low an energy x ray is not able to escape the sample unless the atom is very near the surface.

Fabrication of thin film Chlorine References

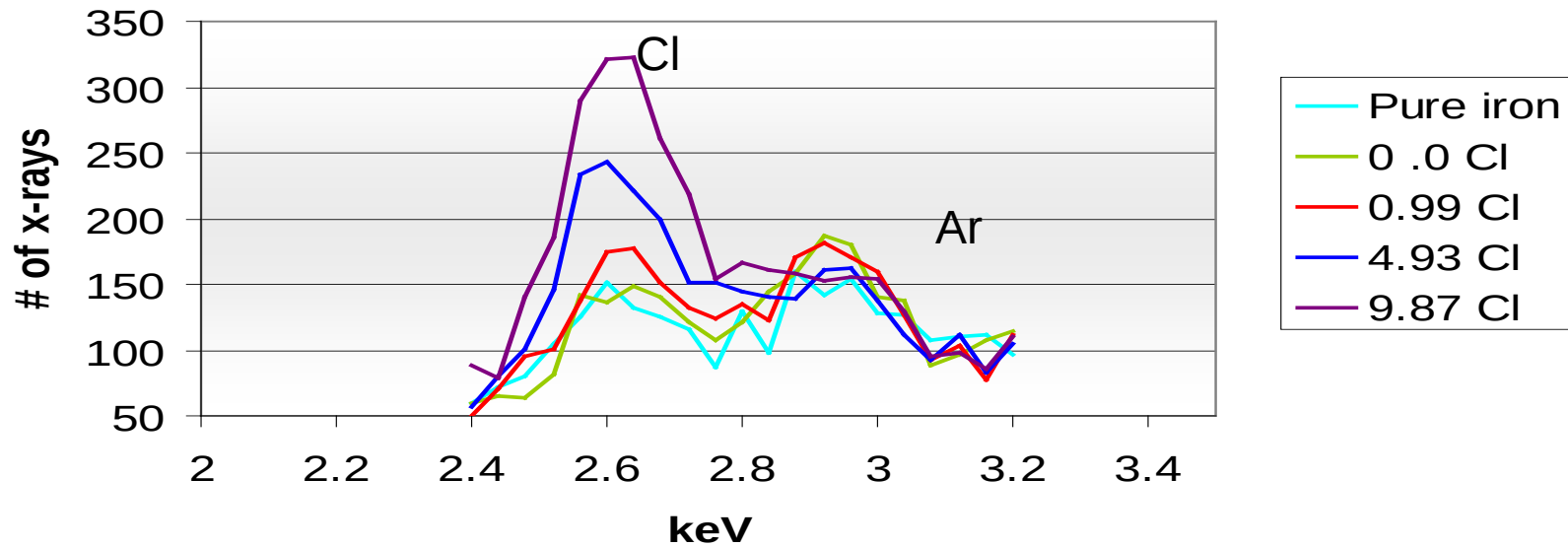
- 1.83 gms of Zirconium dichloride oxide ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was added to 100 ml of distilled water.
- Then various amounts were pipetted on to light weight paper circles 8.2 cm in diameter
- The paper was saturated with the solution in each case to assure that the solution distributed uniformly over the entire surface
- Each paper was then let dry on a plastic sheet for 1 hour
- The resulting microgram/cm values for Zr and Cl

Zr-ug/sq-cm	Cl-ug/sq-cm
0.000	0.000
1.269	0.987
6.347	4.933
12.693	9.866



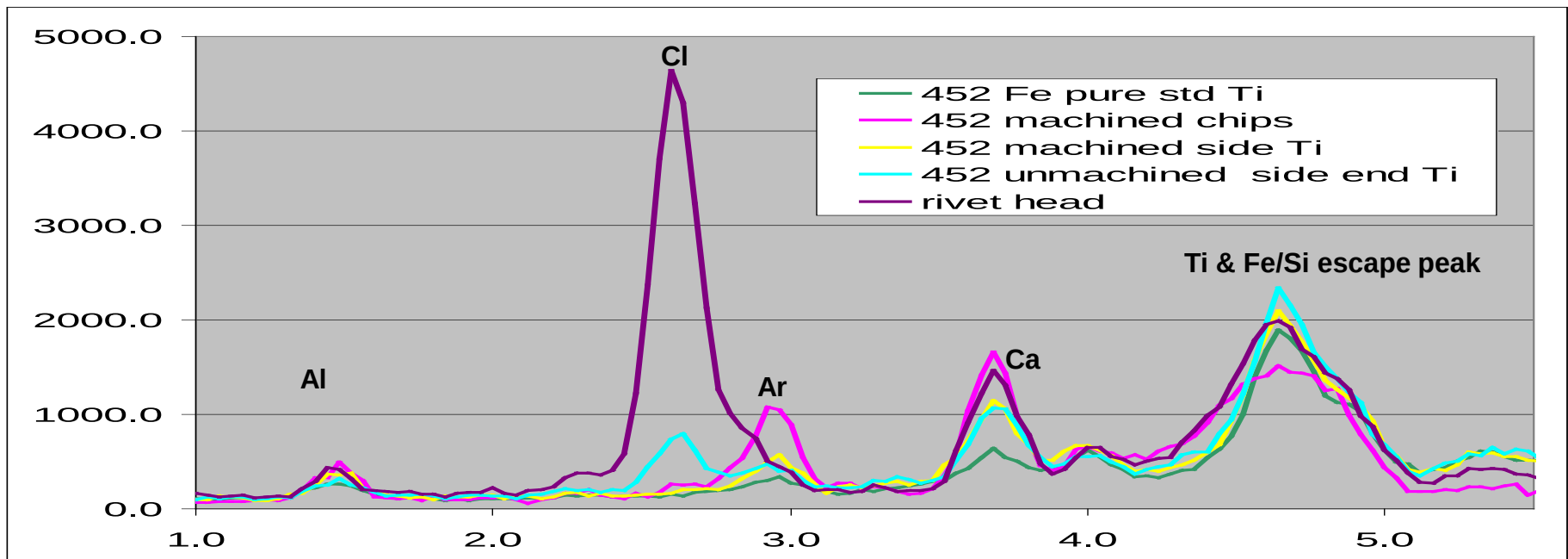
Man this is a lot of work for so little!

Cl sensitivity (ugm/square cm)



- .001" Ti foil to eliminate the Rh L lines and generate Ti x-rays to excite Cl
- Cl references were backed by pure Fe to mimic Cl corrosion on Fe.
- **spectra were taken**
 - 8 kV
 - 35 micro amps.
 - with Vacuum
- 2.6 keV is the Cl K x-ray.
- 2.95 keV is the Ar K x-ray which is in the air in the paper.

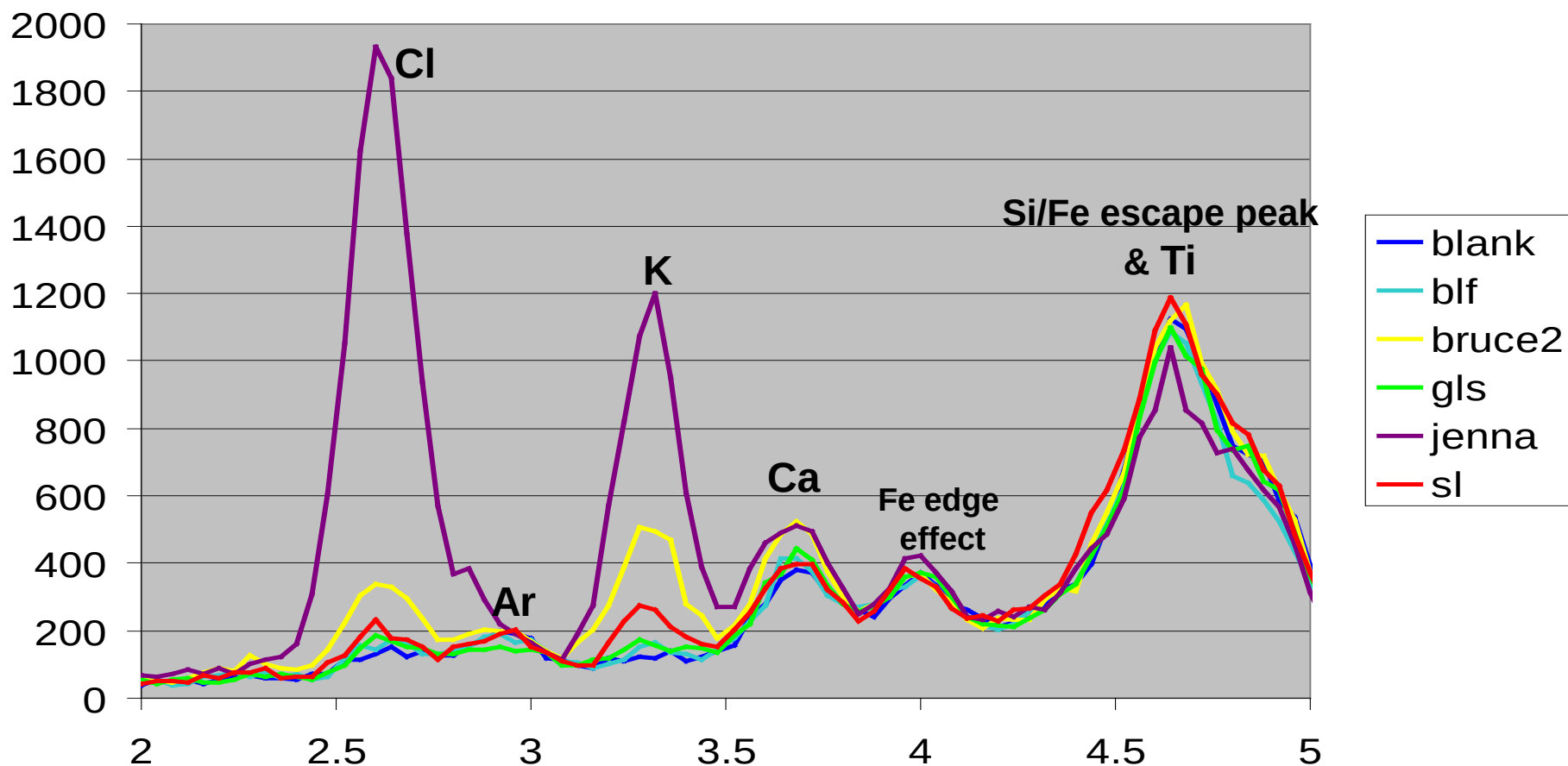




Rivet Analysis: The “**rivet head**” and “**unmachined side end**” both show Cl present on the side of the rivet. The “**unmachined side end**” was taken near the end of the rivet.

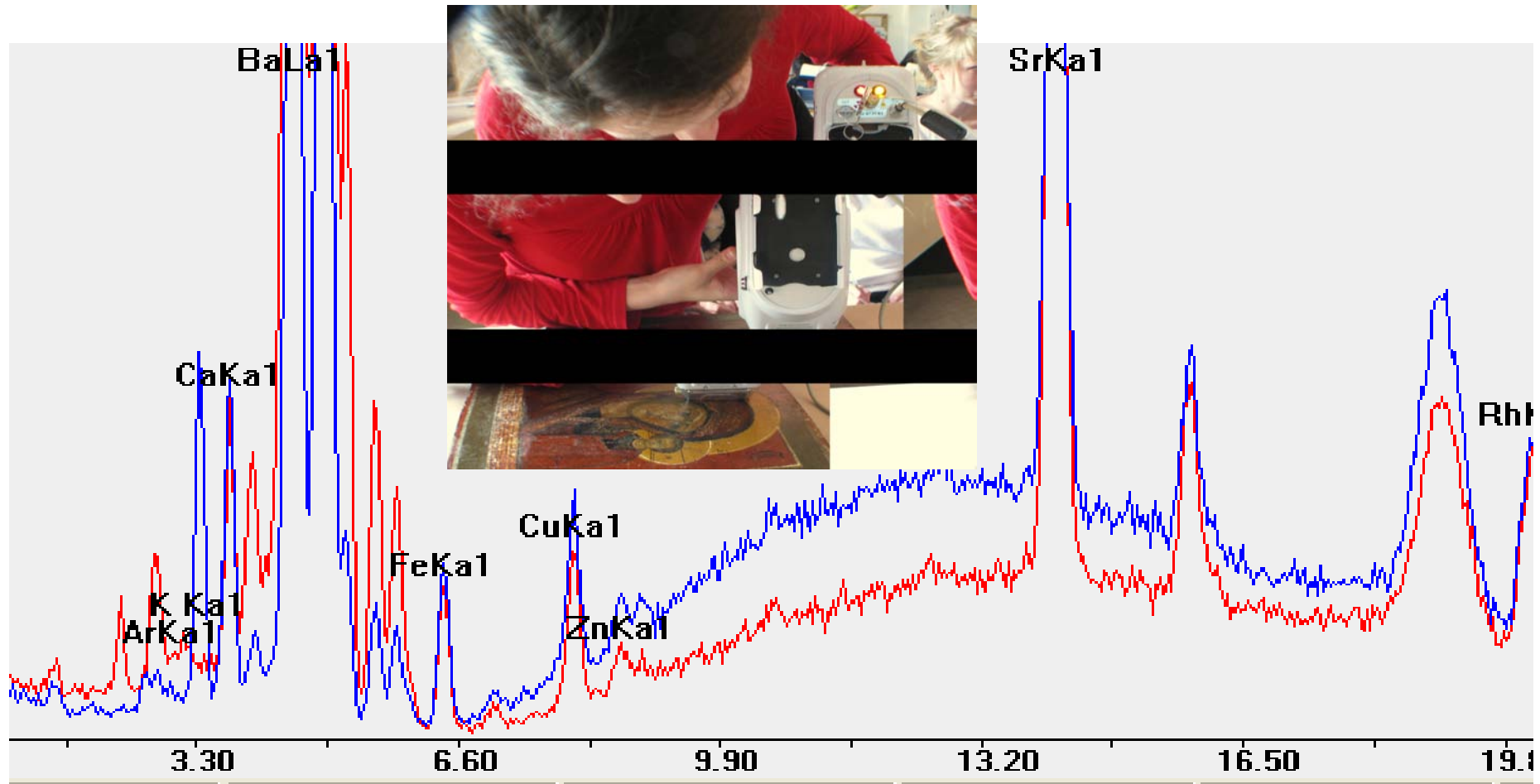
The 2 spectra, “machined side” and “Fe pure std” show no Cl. There is a trace of Cl in the “machined chips”, there is more Ar in the chip spectrum because there is more air around them. The chips were created by removing .001” from the center section of the side of the rivet”, see photo below.. The machine chips were captured and measured. Only trace Cl was detected on the chips because the Cl is only present on the Fe interface, in a very, very thin layer. The machining exposes much, much more surface on the chips so the Cl is just detectable. This also proves that the Cl has not penetrated into the bulk Fe, measuring the machined side of the rivet shows that the Cl, that was present before machining is gone when less than 0.001” was removed.

It is apparent as well that the rivet is composed of an Fe alloy that contains Ca. This is not present in modern Fe alloys. The Ti is from the secondary target used in the instrument and the Al comes from the instrument collimator.



Sweat analysis: Each individual wiped a tissue across their forehead just below the hair line. The tissue was then put on the analyzer and backed with pure Fe. A 0.001 Ti filter was used and the HV and Current were set at 12 kV and 35 micro amps. Note the variation in Cl, K and Ca between the individuals. Bruce and Jenna apparently sweat more. Blf and gls had a shower but even their Cl is above the blank. K and Ca appear to go hand and hand with Cl.

Layered Paint Element Location



The paint on the front contains Ba and Ti. From this view of the spectra we can also see that it contains S and Ca. K and Ca are visible in the back, they are in the linen. Ti and Ba are also visible from the back but are attenuated some by the linen. Note that the paint as viewed from the front attenuates all the K x rays that come from the linen. The reason you still see Ca is because it is in the paint, the Ca presence would be expected because as you can see on the details highlighted on the following slides this paint contains large amounts of Sr. Sr and Ca go hand and hand in nature. When looking from the back no S is present thus indicating the S is only in the paint and the linen stops the S x rays from reaching the detector.

ppm Analysis of Elements *in Si Matrixes*

To cover the full range of elements it is recommend that the analysis be done with 2 different setups

For high mass elements

- 40 kV
- 3 micro amps
- .006" Cu, .001" Ti, .012 Al filter
- no vacuum
- Analyze for about 120 seconds

For low mass elements

- 15 kV
- 25 micro amps
- Ti filter/secondary target
- vacuum
- analyze for about 120 sec

•The settings for high mass elements allow all the x rays from 17 keV to 40 keV to reach the sample thus efficiently exciting the elements from Fe to U. These are some of those key to sorting and identifying the origin of the Si matrixes. There is little or no sensitivity to elements below Fe with these settings.

•The settings for low mass elements allow all the x rays from 2 keV to 15 keV to reach the sample thus efficiently exciting the elements from Mg to Fe. These are those key to sorting and identifying the Si matrixes. Note these settings also efficiently excite the L and M lines of the higher mass elements.

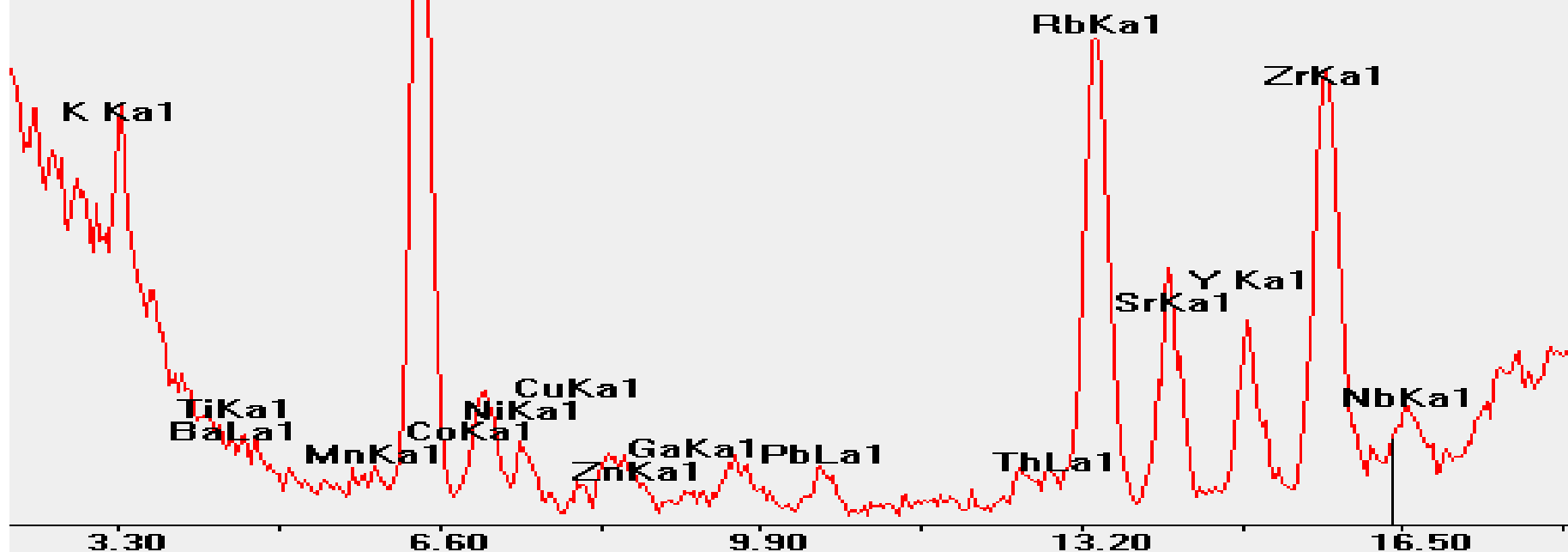
Ensemble, Europe, c 18th century
Venice, 18th century
79.2.3953
Request of Jerome Strauss

Covered Chalice
Venice, late 18th century
62.2.118
Gift of George D. Macbeth

Faenza Goblet-Vase
Italy, about 19th century
60.3.72
Gift of George D. Macbeth

OBSID PPM

K Ka1	40,486.8
BaLa1	364.4
TiKa1	1,007.8
MnKa1	383.5
FeKa1	6,807.4
NiKa1	5.5
CuKa1	3.1
ZnKa1	53.0
GaKa1	16.2
PbLa1	33.4
ThLa1	17.2
RbKa1	161.2
SrKa1	68.0
Y Ka1	19.0
ZrKa1	100.2
NbKa1	15.2



Al and Si analysis in Cu alloys

- Use .001 Ti filter/secondary target
- Analyze alloy at
 - 10kV
 - 20 micro amps
 - 3 minutes
 - Use vacuum
 - Utilized cal for Cu/Al/Si
- The Ti filter used removes most of the backscattered x rays, adds 4 keV x rays to excite Al and Si effectively in Cu.
- 10 keV tube settings excites at a lower rate Cu.
- Still measures Sb, Sn and Pb content with L and M lines



How deep am I measuring?

A narrow beam of mono energetic photons with an incident intensity I_0 , penetrating a layer of material with mass thickness x and density ρ emerges with intensity I given by the exponential attenuation law

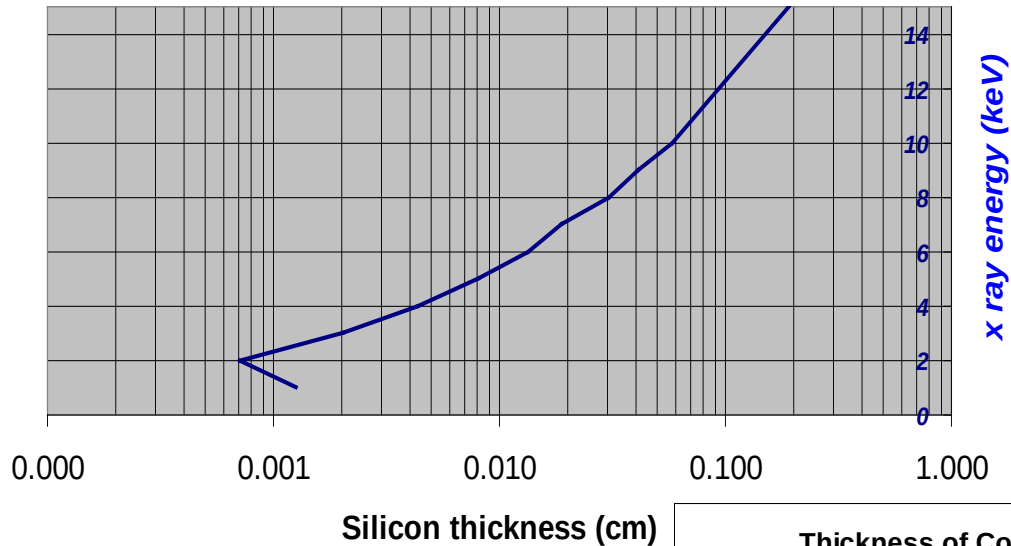
$$I/I_0 = \exp[-(\mu/\rho)x] .$$

Note that the mass thickness is defined as the mass per unit area, and is obtained by multiplying the thickness t by the density ρ i.e., $x = \rho t$



OK, so it is time to whistle Dixie!!

Thickness of Silicon required to reduce x ray beam to 1% of initial intensity



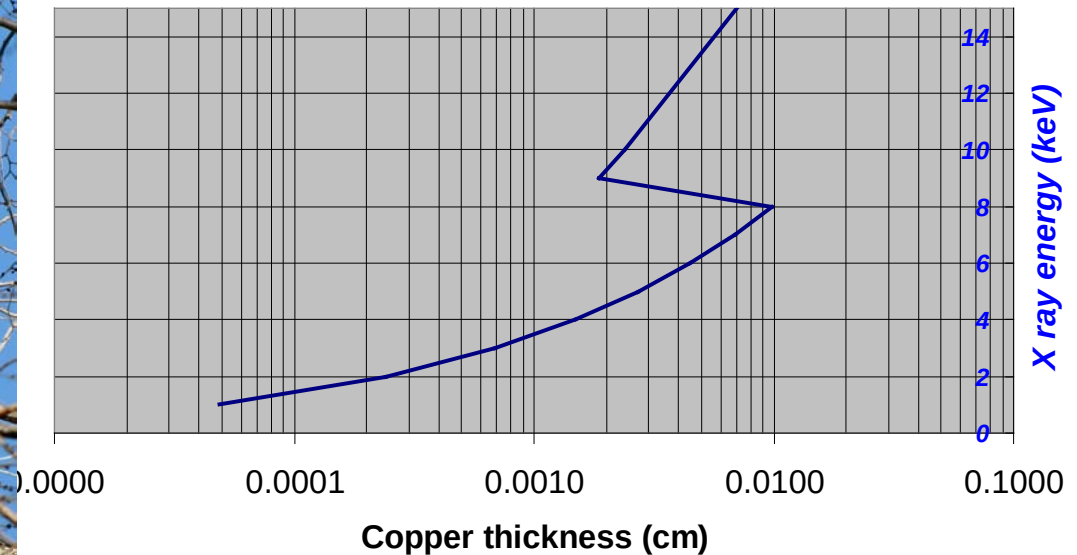
web site

<http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html>

*Are you
paying
attention?*



Thickness of Copper required to reduce the x ray beam intensity to 1% of its initial intensity



Heavy metal poisons analysis on ethnographic collections

- 0.001" Cu, .001" Ti,
and .012 Al Filter
- 40 kV
- 4 to 8 micro amps
- No vacuum
- These settings allow
 - All the x rays from 14 keV to 40 keV to reach the sample thus efficiently exciting the elements Hg, Pb, Br, As.
 - There is little or no sensitivity to elements below Ca with these settings reducing unneeded detector activity
 - Eliminates any background x rays under the peaks of interest



Measurement of Toning Agents on Photographs

- Use .006" Cu, .001 Ti, .012" Al filter
 - Analyze at photograph
 - 40kV
 - 6 micro amps(what is available)
 - No vacuum
 - 5 to 10 min in
 - White area where there is no toner
 - Areas tone varies grey to black
 - Take the difference (toned – white)
-
- The difference will give you a very good clean spectrum of the toning agent. And the grey to black variation will give you an estimate of the amount of agent. The reason this works so well are
 - The toning materials are very thin and have very little effect on the spectrum from the paper
 - The white area is just the paper and mounting materials
 - The filter used removes most of the backscattered x rays

