Fundamental XRF Technology Overview

By
Dr. Bruce Kaiser

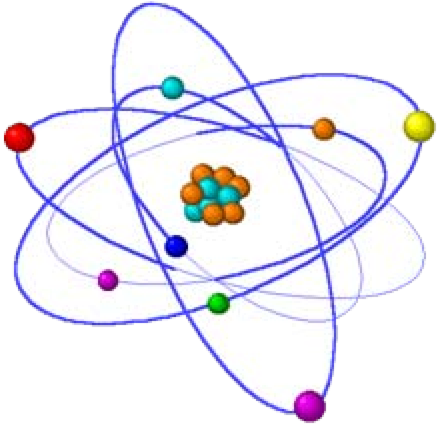
Reliable analysis, anywhere, any time of any substance composed of elements above Na on the Periodic Table; liquid, gas, solid, powder down to ppm.

Archeological Digs
Museum Artifact Analysis
Conservation and Restoration
University technical experiment & training
Electric utility industry
Engine Assembly
Airframe assembly
Scrap industry
Metal producers
Foundries

- Incoming artifact elemental inspection
- Rapid nondestructive elemental analysis in the lab and field
- Archeological dig-site verification
- Collection verification and control
- Technical studies
- Melt analysis
- Weld analysis
- Maintenance assessment

Energy Dispersive X-Ray Fluorescence (XRF)

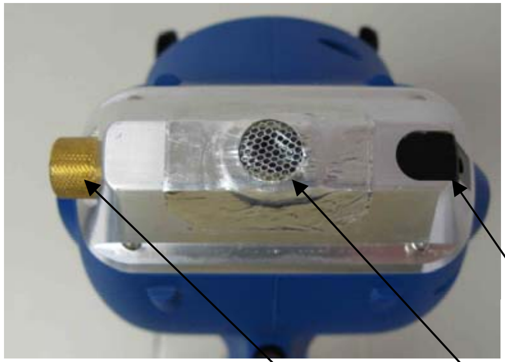
Properties of x-rays



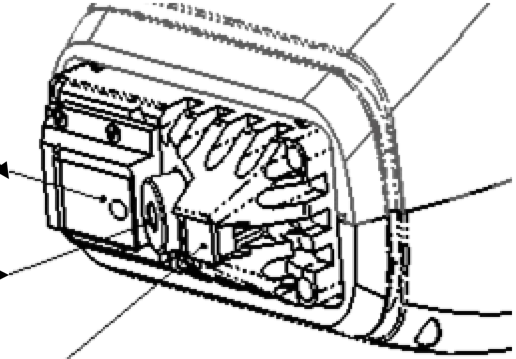
Each element has its own characteristic electron binding/x ray emission energies.

By counting the number of emitted x rays, it is possible to determine the concentration of the various elements in a sample.

The XRF Analyzer

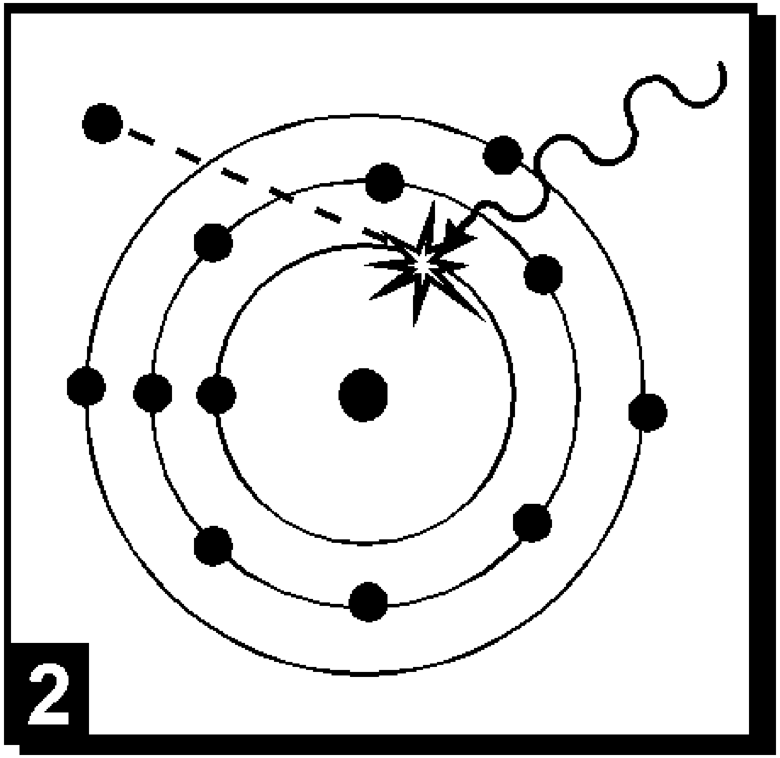


- **X-ray Tube Ag, Rh or Re Target**
- **Up to 45kV X rays**
- **170eV Resolution Si PIN Detector**
- **13μ Be Detector Window**
- **IR Safety Sensor**
- **Vacuum window**
- **User selectable filter/target**



The

Physics

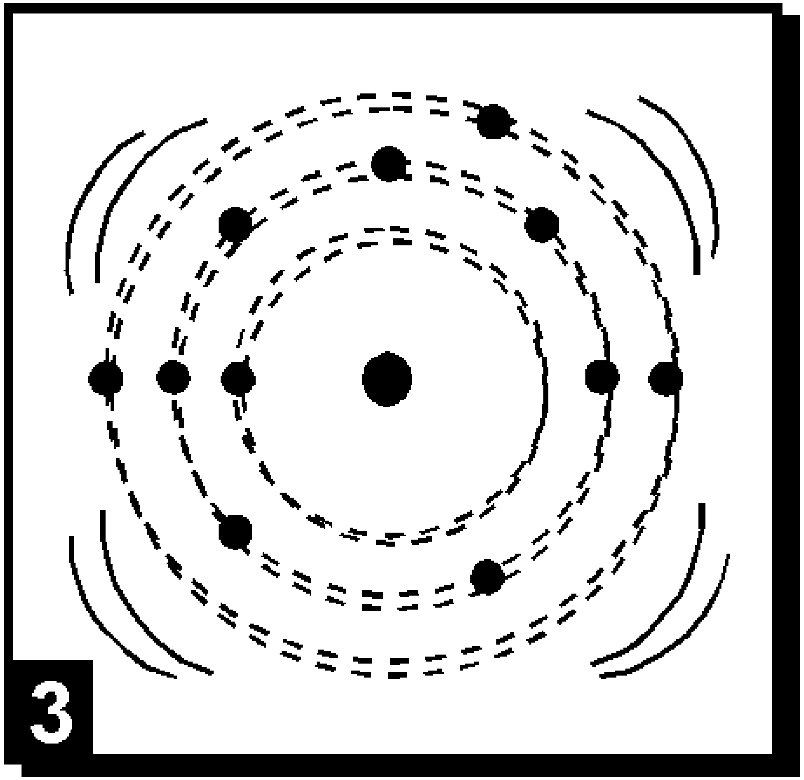


When the switch is pulled, activating the Analyzer's x-ray tube, the x-rays strike the inner shell electron of the atoms in the sample and it is ejected from the atom.*

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

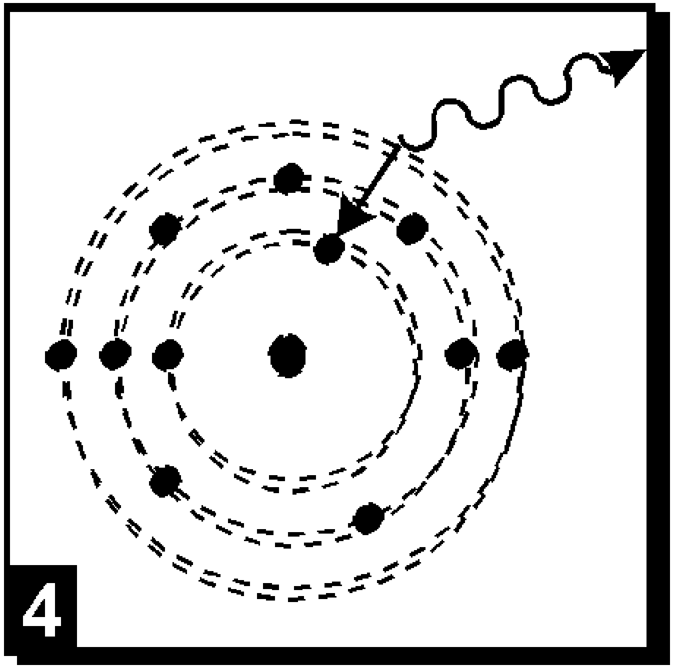
Issac Newton: Chickens at rest tend to stay at rest, chickens in motion tend to cross roads.

The Physics



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

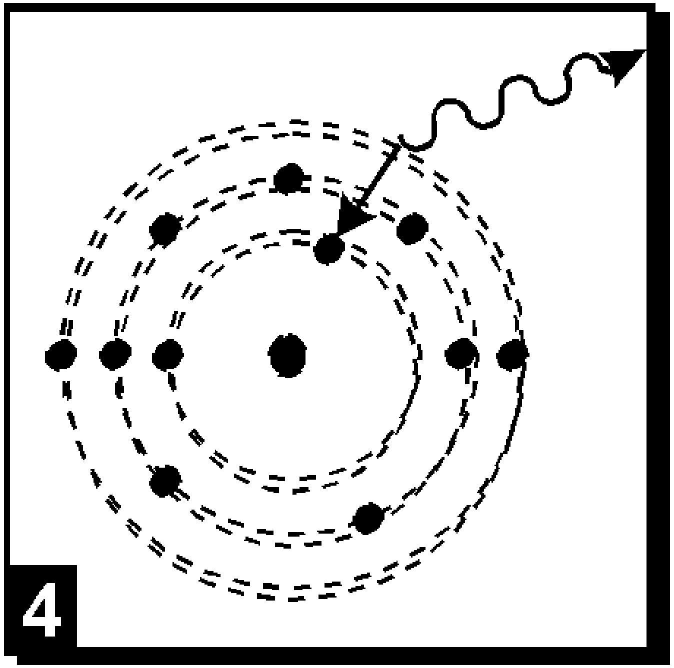
The Physics



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)

*The process in which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "**photoelectric effect.**"*

The Physics



Electron Volt

The change of potential energy experienced by an electron moving from a potential value of “V” to a place with a value of “V+1” volt).

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

Alkali Metals

Alkaline Earth Metals

Key To Energy Values

Kα		Kβ
	Cd 48 Cadmium	
Lα		Lβ

	IIA	IIIB	IVB	VB	VIIB	VIIB		---VII---			IIB	IIIA	IVA	VA
H 1 Hydrogen														
Li 3 Lithium	0.108 . **Be** 4 Beryllium											0.185 . **B** 5 Boron	0.282 . **C** 6 Carbon	0.392 **N** 7
1.04 . **Na** 11 Sodium	1.25 . **Mg** 12 Magnesium											1.49 .56 **Al** 13	1.74 1.83 **Si** 14 Silicon	2.02 **P** 15 Phosphoru
3.31 3.61 **K** 19 Potassium	3.69 4.04 **Ca** 20 Calcium	4.09 4.46 **Sc** 21 Scandium	4.51 4.93 **Ti** 22 Titanium	4.95 5.43 **V** 23 Vanadium	5.41 5.95 **Cr** 24 Chromium	5.90 6.49 **Mn** 25 Manganese	6.40 7.06 **Fe** 26 Iron	6.93 7.65 **Co** 27 Cobalt	7.48 8.26 **Ni** 28 Nickel	8.05 8.90 **Cu** 29 Copper	8.64 9.57 **Zn** 30 Zinc 1.01 1.03	9.25 10.26 **Ga** 31 Gallium 1.10 1.12	9.89 10.98 **Ge** 32 Germanium 1.19 1.22	10.54 11 **As** 33 Arsenic 1.28 1.32
13.39 14.96 **Rb** 37 Rubidium 1.69 1.75	14.16 15.83 **Sr** 38 Strontium 1.81 1.87	14.96 16.74 **Y** 39 Yttrium 1.92 2.00	15.77 17.67 **Zr** 40 Zirconium 2.04 2.12	16.61 18.62 **Nb** 41 Niobium 2.17 2.26	17.48 19.61 **Mo** 42 Molybdenum 2.29 2.40	18.41 20.59 **Tc** 43 Technetium 2.42 2.54	19.28 21.66 **Ru** 44 Ruthenium 2.56 2.68	20.21 22.72 **Rh** 45 Rhodium 2.70 2.83	21.18 23.82 **Pd** 46 Palladium 2.84 2.99	22.16 24.94 **Ag** 47 Silver 2.98 3.15	23.17 26.09 **Cd** 48 Cadmium 3.13 3.32	24.21 27.27 **In** 49 Indium 3.29 3.49	25.27 28.48 **Sn** 50 Tin 3.44 3.66	26.36 29.72 **Sb** 51 Antimony 3.61 3.84
30.97 34.98 **Cs** 55 Cesium 4.29 4.62	32.19 36.38 **Ba** 56 Barium 4.47 4.83	33.44 37.80 **La** 57 Lanthanum 4.65 5.04	55.76 63.21 **Hf** 72 Hafnium 7.90 9.02	57.52 65.21 **Ta** 73 Tantalum 8.15 9.34	59.31 67.23 **W** 74 Tungsten 8.40 9.67	61.13 69.30 **Re** 75 Rhenium 8.65 10.01	62.99 71.40 **Os** 76 Osmium 8.91 10.35	64.89 73.54 **Ir** 77 Iridium 9.17 10.71	66.82 75.74 **Pt** 78 Platinum 9.44 11.07	68.79 77.97 **Au** 79 Gold 9.71 11.44	70.82 80.26 **Hg** 80 Mercury 9.99 11.82	72.86 82.56 **Tl** 81 Thallium 10.27 12.21	74.96 84.92 **Pb** 82 Lead 10.55 12.61	77.10 87.34 **Bi** 83 Bismuth 10.84 13.02
86.12 97.48 **Fr** 87 Francium 12.03 14.77	88.49 101.14 **Ra** 88 Radium 12.34 15.23	90.89 102.85 **Ac** 89 Actinium 12.65 15.71	**Rf** 104 Rutherfordiu	**Ha** 105 Hahnium	**Sg** 106 Seaborgium	**Ns** 107 Neilsborium	**Hs** 108 Hassium	**Mt** 109 Meiterium	**Uun** 110 Ununnilium	**Uuu** 111 Unununium	112 Element	113		

K-shell
Aluminum
1.48 keV

K-shell
Iron (Fe)
6.40 keV

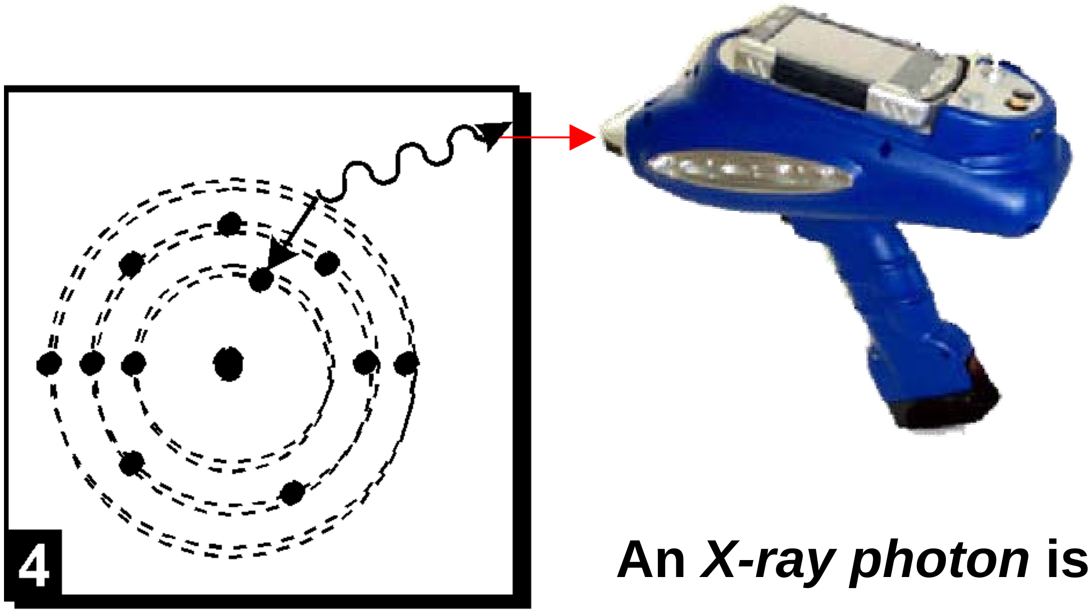
7

Lanthanide Series

Actinide Series

34.72 39.26 **Ce** 58 Cerium 4.84 5.26	36.02 40.75 **Pr** 59 Praseodymiu 5.03 5.49	37.36 42.27 **Nd** 60 Neodymium 5.23 5.72	38.65 43.95 **Pm** 61 Promethium 5.43 5.96	40.12 45.40 **Sm** 62 Samarium 5.64 6.21	41.53 47.03 **Eu** 63 Europium 5.85 6.46	42.98 48.72 **Gd** 64 Gadolinium 6.06 6.71	44.47 50.39 **Tb** 65 Terbium 6.28 6.98	45.99 52.18 **Dy** 66 Dysprosium 6.50 7.25	47.53 53.93 **Ho** 67 Holmium 6.72 7.53	49.10 55.69 **Er** 68 Erbium 6.95 7.81
93.33 105.59 **Th** 90 Thorium 12.97 16.20	95.85 108.41 **Pa** 91 Protactinium 13.29 16.70	98.43 111.29 **U** 92 Uranium 13.61 17.22	101.01 114.18 **Np** 93 Neptunium 13.95 17.74	103.65 117.15 **Pu** 94 Plutonium 14.28 18.28	106.35 120.16 **Am** 95 Americium 14.62 18.83	109.10 123.24 **Cm** 96 Curium 14.96 19.39	111.90 126.36 **Bk** 97 Berkelium 15.31 19.97	114.75 129.54 **Cf** 98 Californium 15.66 20.56	117.65 132.78 **Es** 99 Einsteinium 16.02 21.17	120.60 136.08 **Fm** 100 Fermium 16.38 21.79

The Physics



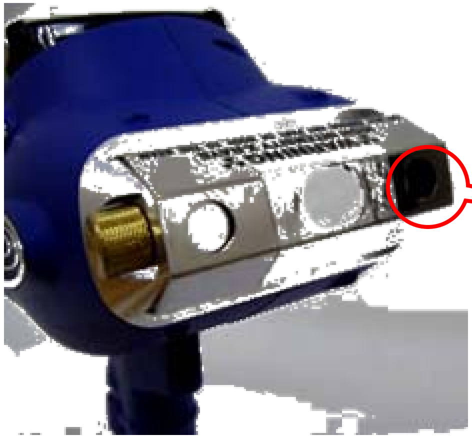
An *X-ray photon* is released and hits the analyzer’s SiPIN detector.

*The process in which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "**photoelectric effect.**"*

Safety Features

Key Switch Power Activation
(Turns on Tube High Voltage
and Peltier Cooler)

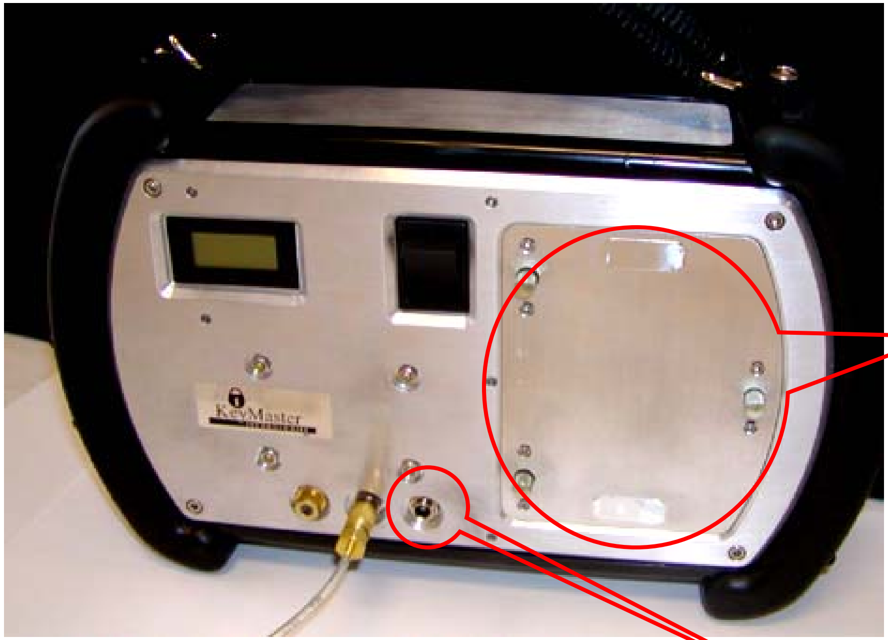
Power & X-ray
Indicator Lights



Infrared Sensor
X-ray Cutoff

TRACeR III-V

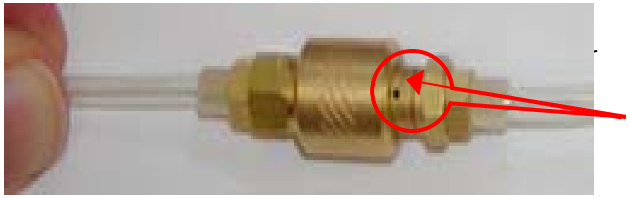
Parts



Battery Door

(NiMH Battery packs--4hrs ea.)

A/C Power input



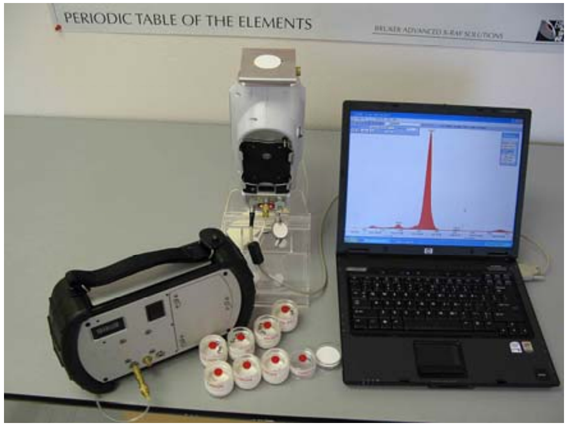
Valve Open

Open ← → Close

Vacuum Release Valve

The
Physics

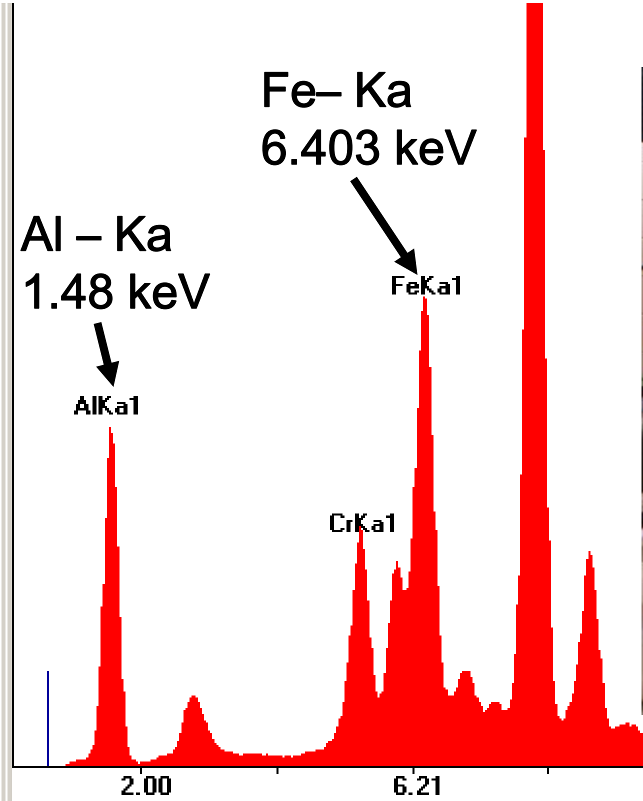
In the Field



Very sensitive elemental analysis by
anyone in seconds anywhere

The signal passes from the instrument's SiPIN Detector to the digital pulse processor, then to the CPU where the data is transformed from counts per channel, to spectra and quantitative chemistries in seconds with *__no__* sampling .

Each Element has its Own Signature Energy for K and L Electron Shells.



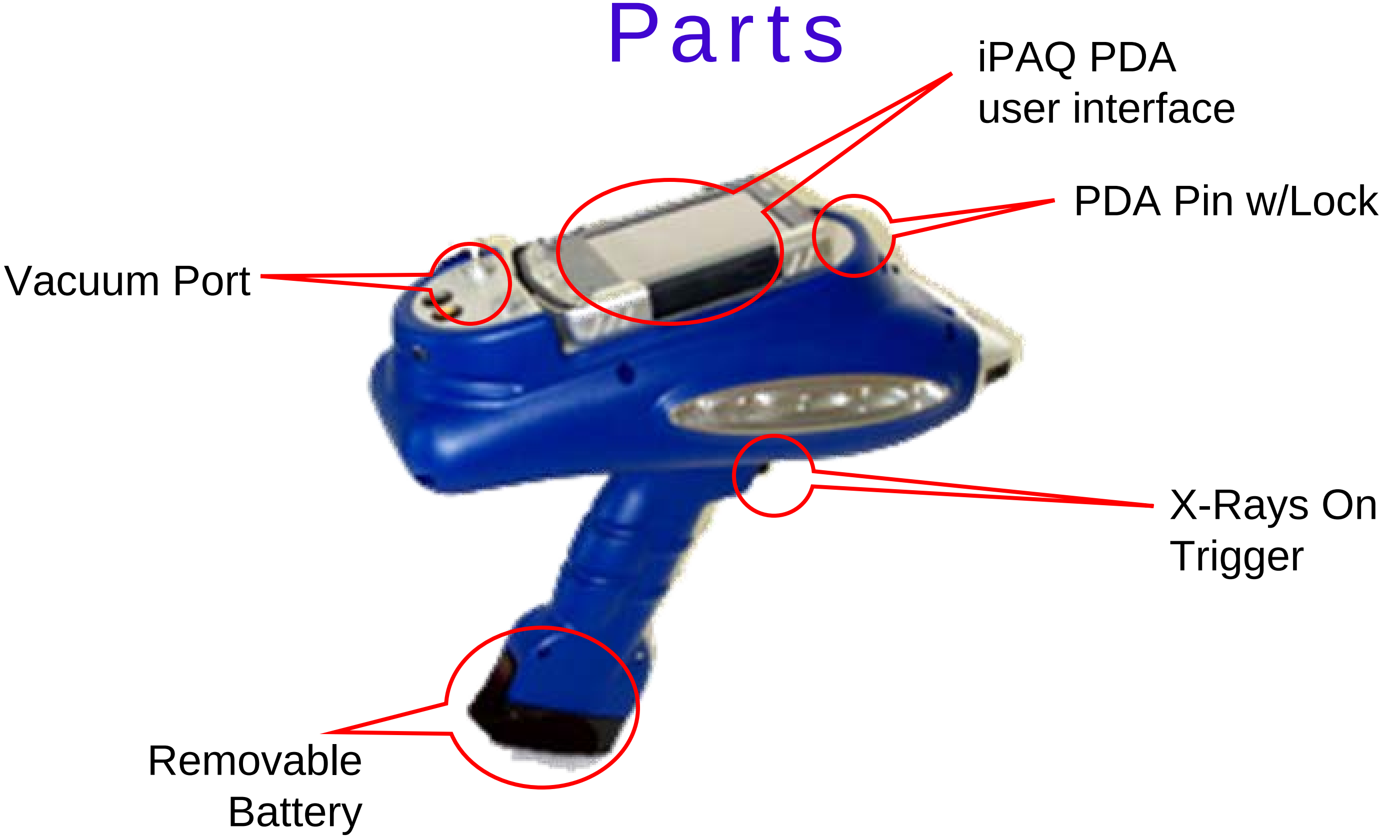
Al – Ka
1.48 keV

Fe– Ka
6.403 keV

CFW team focused on "where did that element come from?"

Albert Einstein: Whether the chicken crossed the road or the road moved beneath the chicken depends upon your frame of reference.

TRACeR III-V
Parts



Low Z / Vacuum Mode
Getting Started

1. **Remove Filter cover**

2. **Remove Ti/Al Filter for vacuum operation (remember to re-insert for non-vacuum mode.)**

Now for some applications of interest:

But first some physicists interpretation of the chicken crossing the road question?

Why did the chicken cross the road?

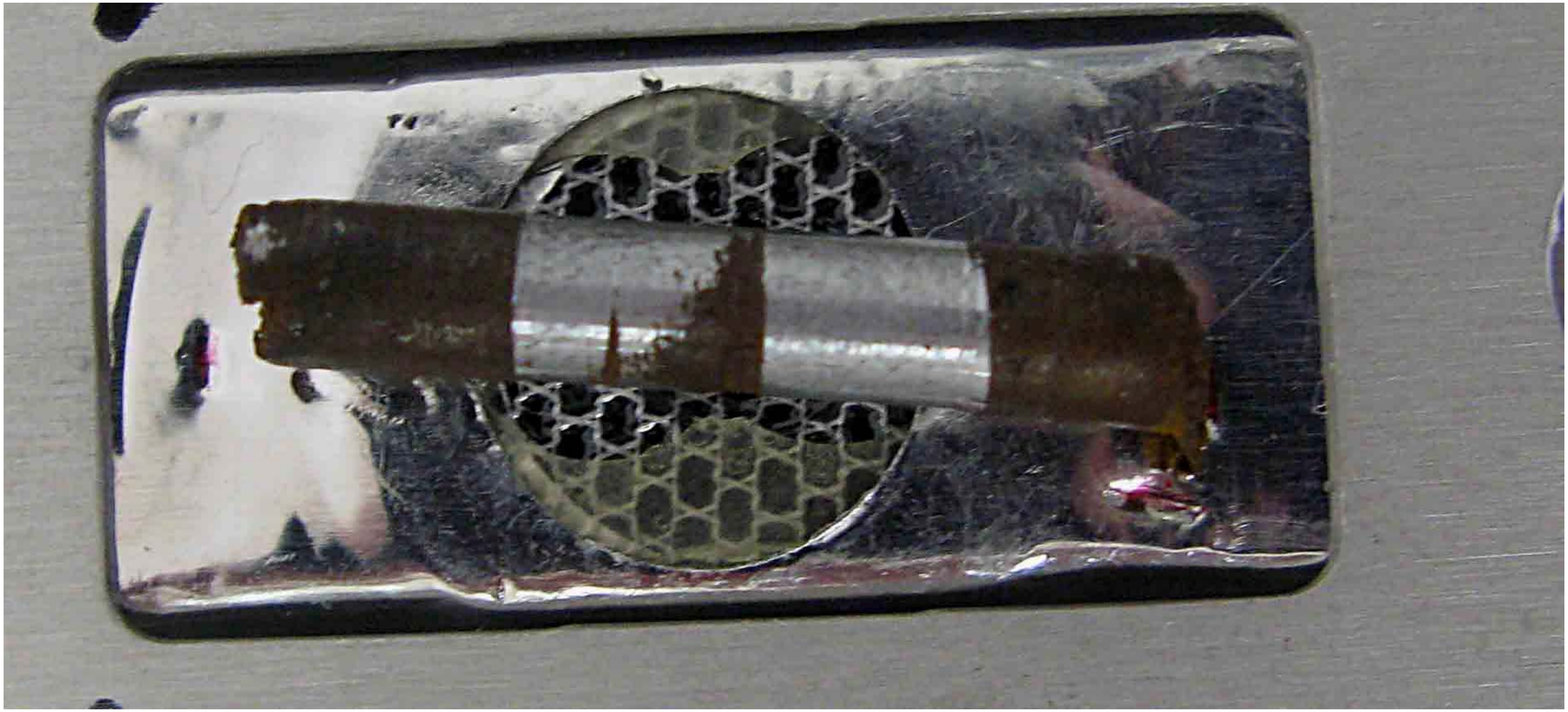
Issac Newton: Chickens at rest tend to stay at rest, chickens in motion tend to cross roads.

Albert Einstein: Whether the chicken crossed the road or the road moved beneath the chicken depends upon your frame of reference.

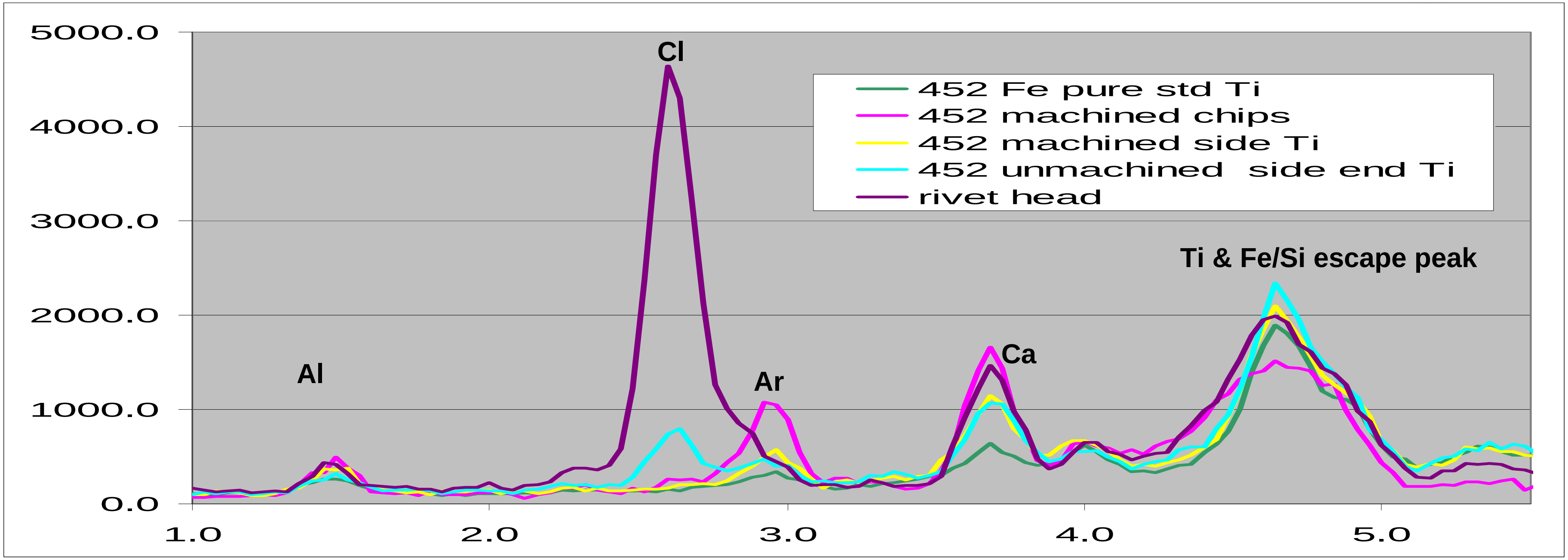
Werner Heisenberg: We are not sure which side of the road the chicken was on, but he was moving very fast.

Wolfgang Pauli: There already was a chicken on this side of the road.

The measurement of Cl on a rivet taken from the USA Civil War submarine, Hunley. The rivet was cut from the Hunley to remove some of the panels to gain access to the interior. Cl was present on both ends and a smaller amount could be seen on the side. It was felt that the Cl on the side was the result of cross contamination. This study was done to verify that theory.

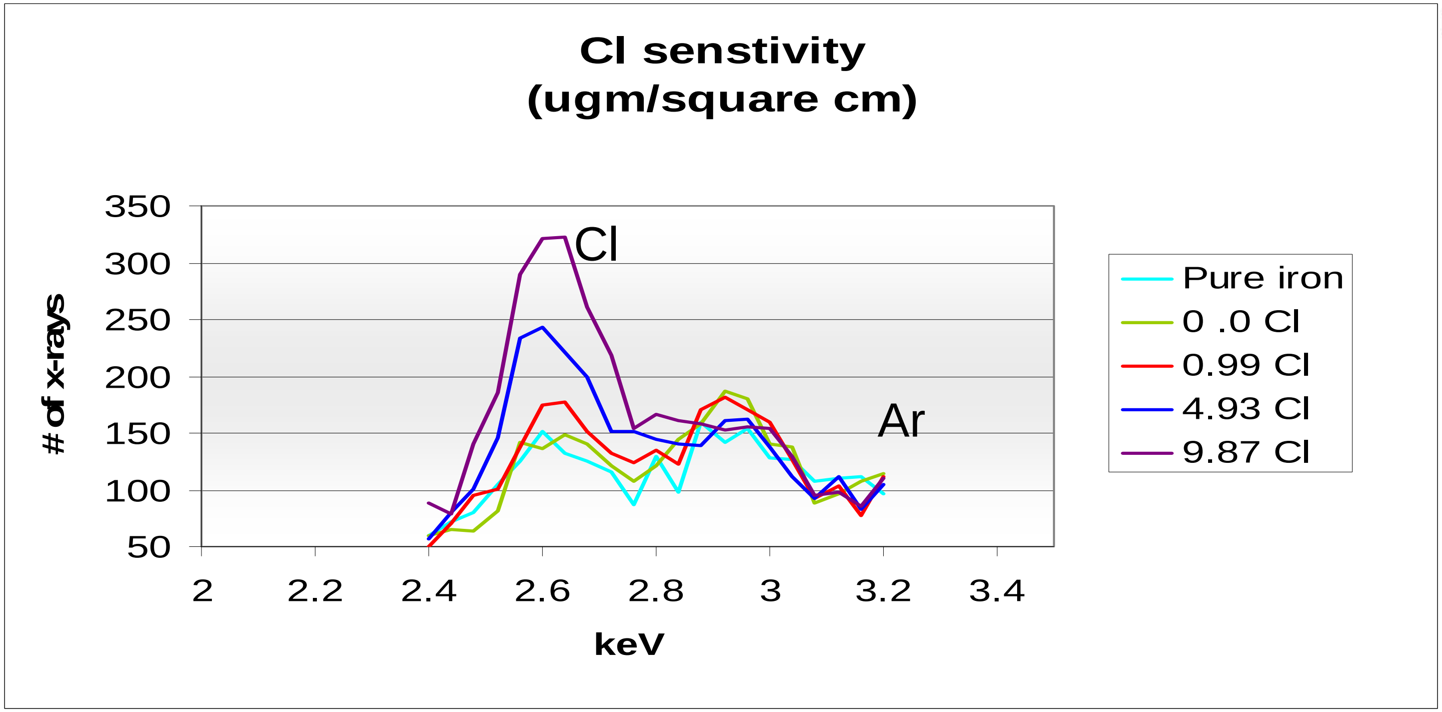


Above is the photograph of the rivet sitting on the instrument after the center section was machine .001" The side facing the XRF instrument has no dark corrosion present. The dark area in the center of the machined portion is because the rivet had a gouge on visible side so the machining process did not remove the corrosion in this location.

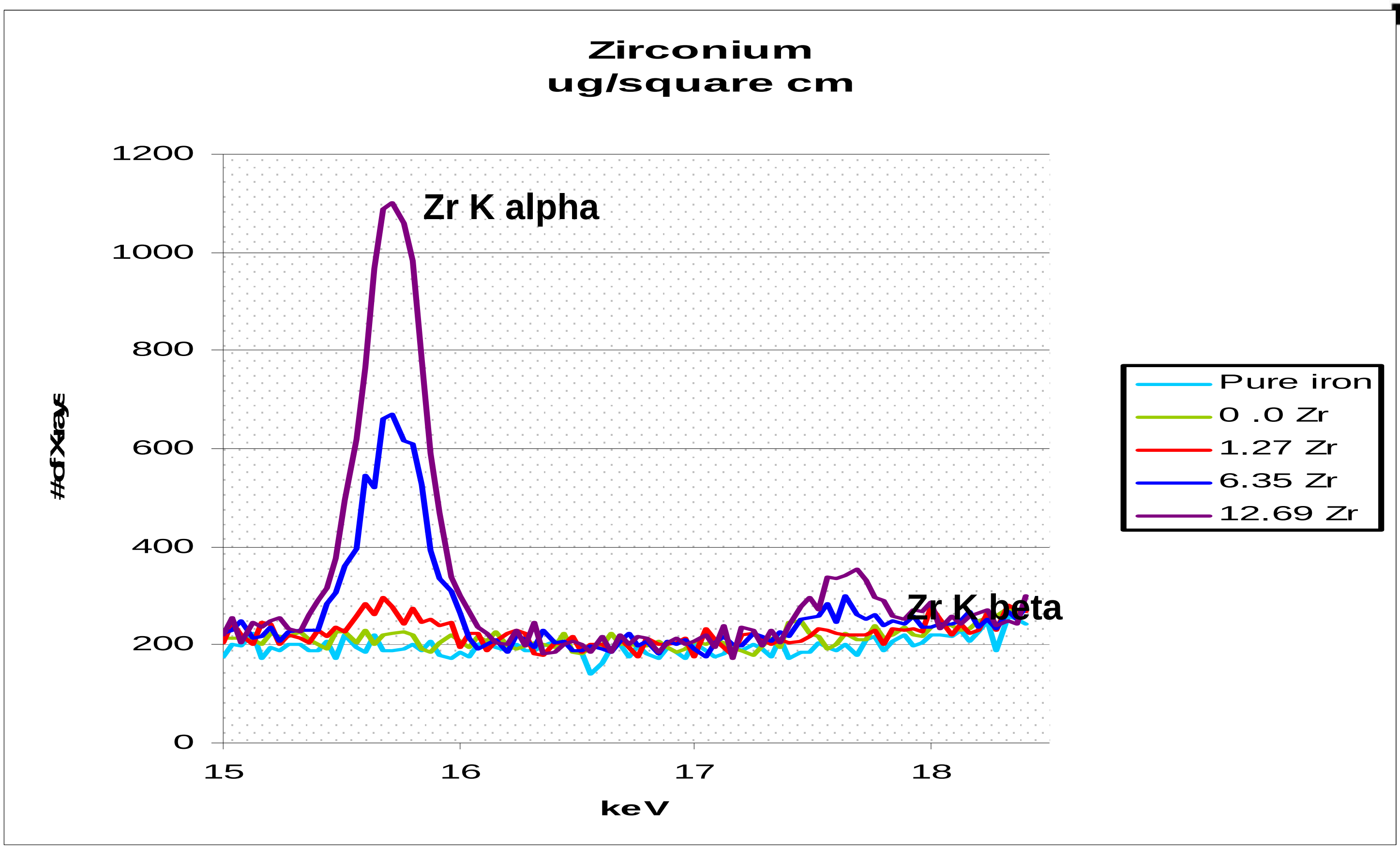


Rivet Analysis: The "**rivet head**" and "**unmachined side end**" both show Cl present on the side of the rivet. The "**unmachined side end**" was taken near the end of the rivet.

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 form the instrument collimator.



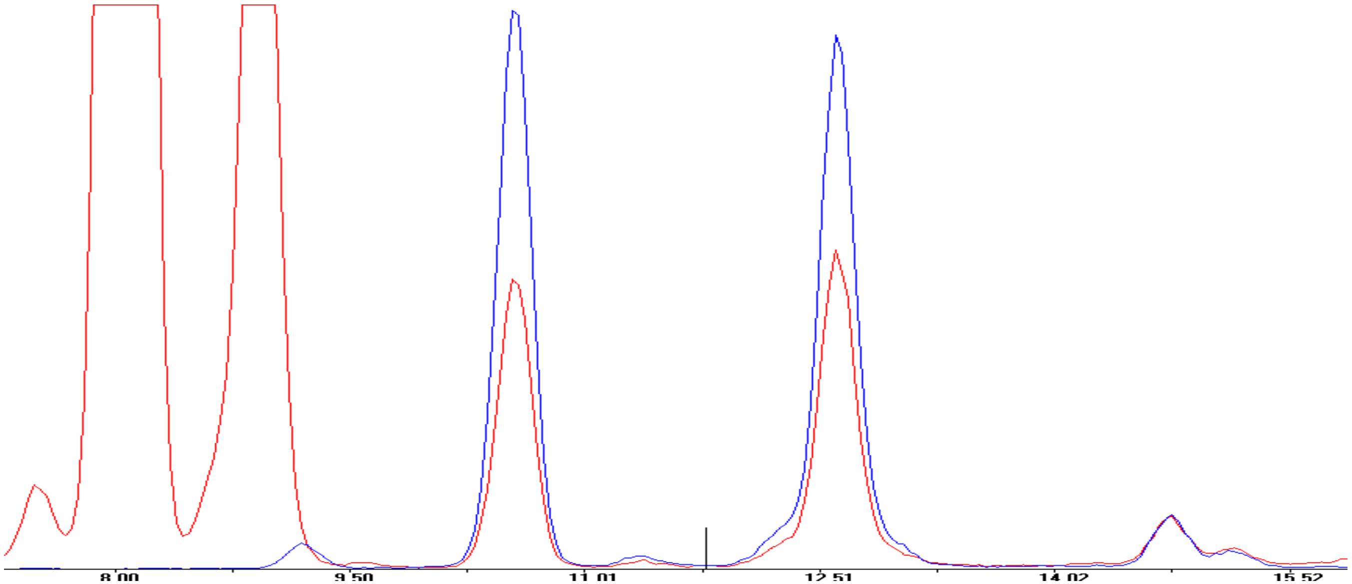
Each standard was analyzed for 3 minutes at 2 different voltage and current settings. A 0.001” Titanium foil was used in both cases to eliminate the Rh L lines and generate Ti x-rays to excite Cl efficiently. The thin paper standards were backed by pure Fe to mimic Cl corrosion on Fe. The above is a plot of the measurements that were taken at 8 kV and 35 micro amps. The peak at 2.6 keV is the Cl K x-ray. The peak at 2.95 keV is a constant amplitude and is a result of Ar K x-ray which is in the air in the paper. It is clear the system is sensitive to Cl down to levels as low as 1 microgram/square cm.



The above chart is a plot of the measurements that were taken at 40 kV and 1.5 micro amps. The peak at 15.6 keV is the Zr K alpha x-ray. The peak at 17.8 keV is a result of Zr K beta x-ray. It is clear the system is sensitive to Zr down to levels as low as 1 microgram/square cm. Comparing the ratio of the Cl and Zr peaks for each concentration it is apparent as well that the Cl is stable and did not evaporate during the drying process.

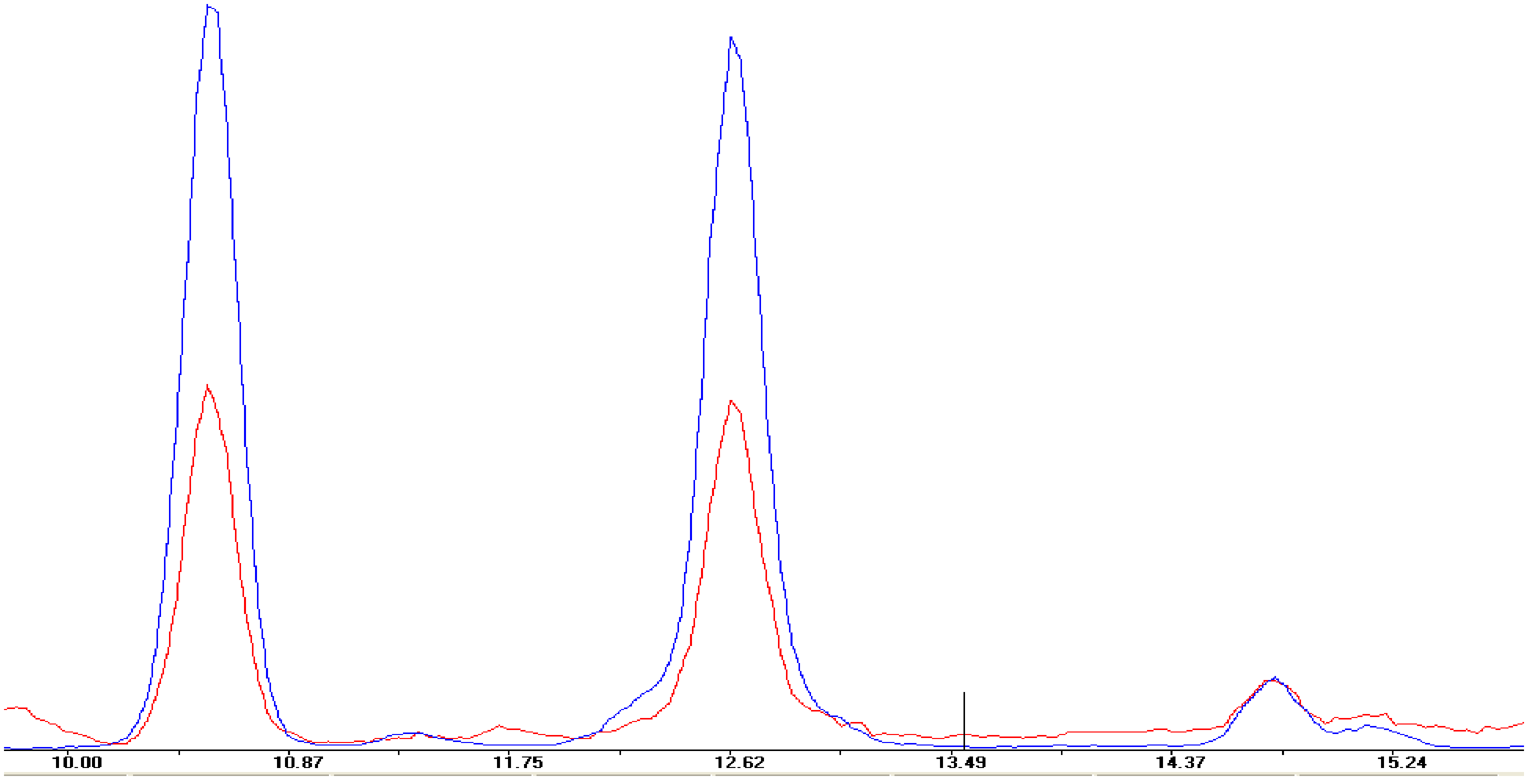
Copper, Lead, and Arsenic Inter- element XRF Monkey Business

The physics of copper, lead, arsenic and x-ray fluorescence is very complex. To begin with they strongly interact with each other! Copper's absorption edge is at 9keV. Lead has major L lines at 10.6, 12.6 and 14.8 keV . In just that short range the mass attenuation coefficient of copper goes form 278 gm/cc to 74 gm/cc. So while we are effectively creating lead x-rays the copper is absorbing them almost as quickly. And it absorbs the 10.6 a factor of 2 better than the 14.68keV ones. So, when you have pure Lead spectrum (**BLUE)** the peak ratios are very different than when you have a copper alloy with lead in it, as you can see in the **PINK** UPB 82 copper alloy spectrum below.



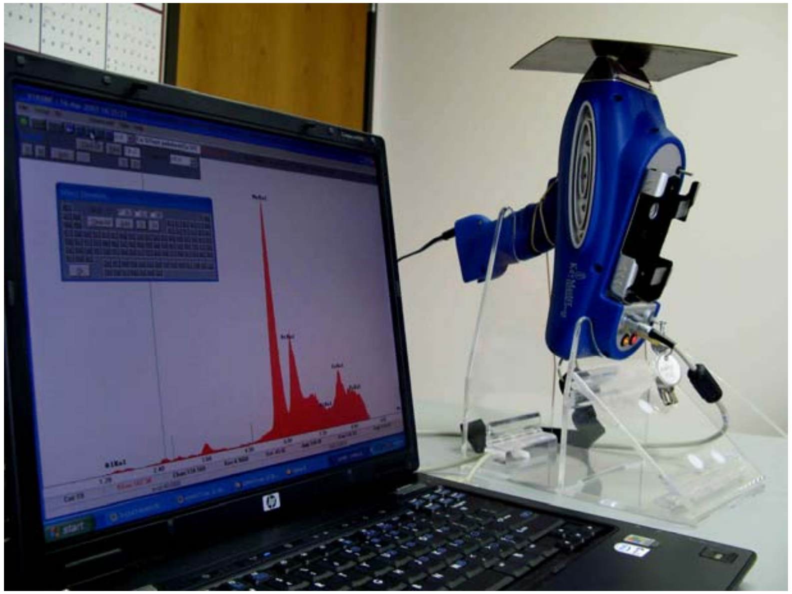
So in the case when just lead and copper are present you can use this information to determine whether the lead is on the surface, in which case the spectrum should look more like the blue spectrum above. This might indicate that the copper has corroded away leaving lead on the surface.
Or if the 3 lead peak ratios look more those in the pink spectra above you can assume that the lead is dispersed in the copper. Note that the 10. 6 keV peak is more effected than the 12.6 keV peak. These spectra were normalized to the 14.68 peak.

So, when you have pure Lead spectrum (**BLUE)** the peak ratios are very different than when you have a copper alloy with lead and arsenic in it, as you can see in the **PINK** 7134 copper alloy spectrum below. Note however that the 10.6 keV line is now above the 12.6 keV line in the pink spectra, almost matching the pure lead ratio of these 2 peaks. This is caused by the presence of a small amount of arsenic which has a K alpha line at 10.7 keV. You can see the very small K beta of arsenic at 11.7keV. So you can still see the copper effect of both lines relative to the 14.7 keV lead line but the ratio of the 2 lower energy lines is not the same as when there is no arsenic. These spectra were normalized to the 14.7 keV.



Setup the KeyMaster Handheld XRF System for Cu Patina Analysis

- Put in a Cu secondary target 0.001” into filter slot
- Use 10kV and 30 micro amp setting for the x ray tube
- Hook up the vacuum pump and turn it on
- The instrument is now optimized for patina analysis



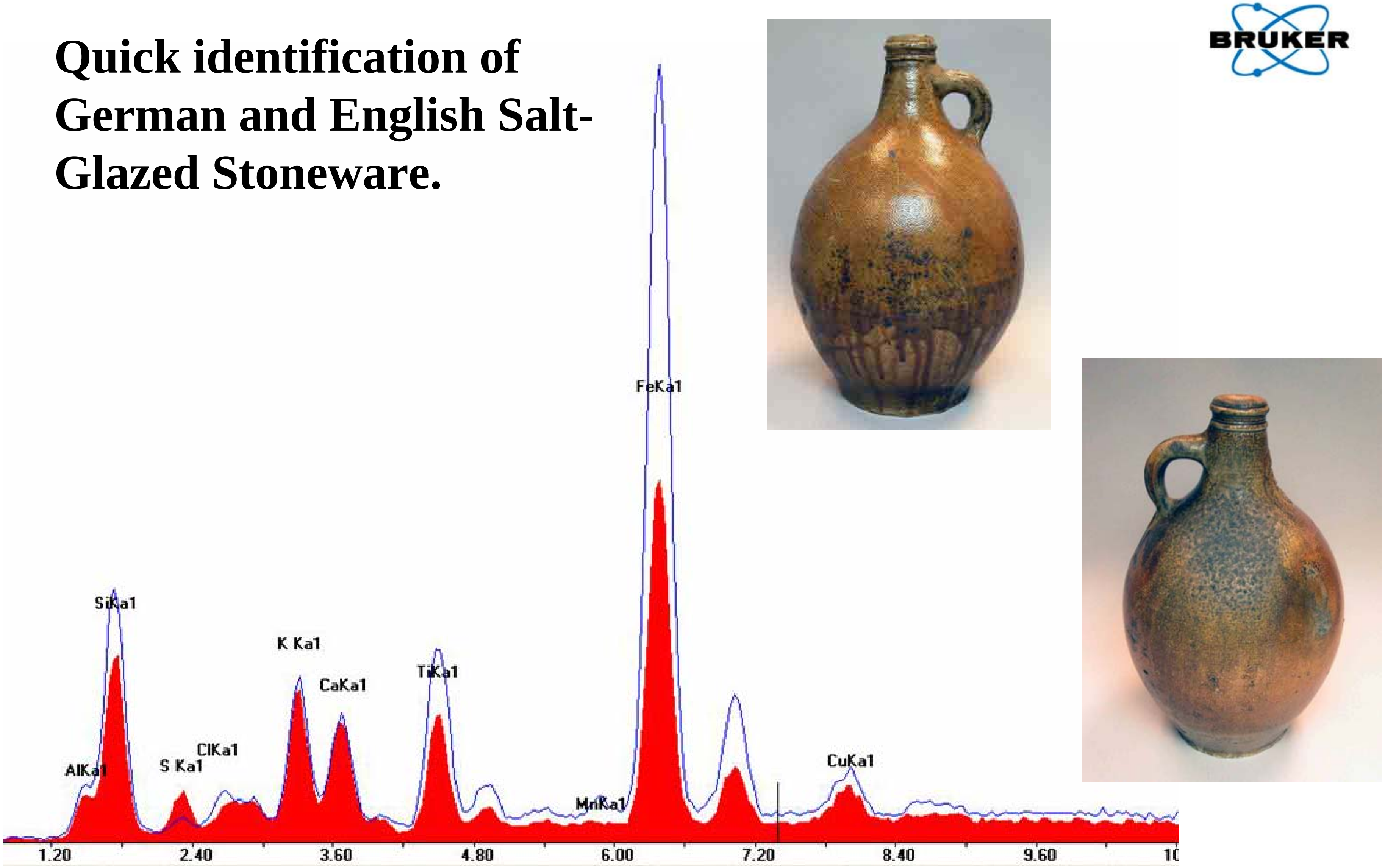
This setup does 4 things:

- it eliminates the Rh L lines
- it efficiently excites all elements below Cu K lines and the L lines of elements above Tc
- it does not effectively excite the Cu K lines, so even though you are on a Cu substrate it does not interfere with the patina analysis
- it effectively only analyzes the very surface of the copper (the patina)

Note this work was all done at the Colonial Willaimsburg Foundation

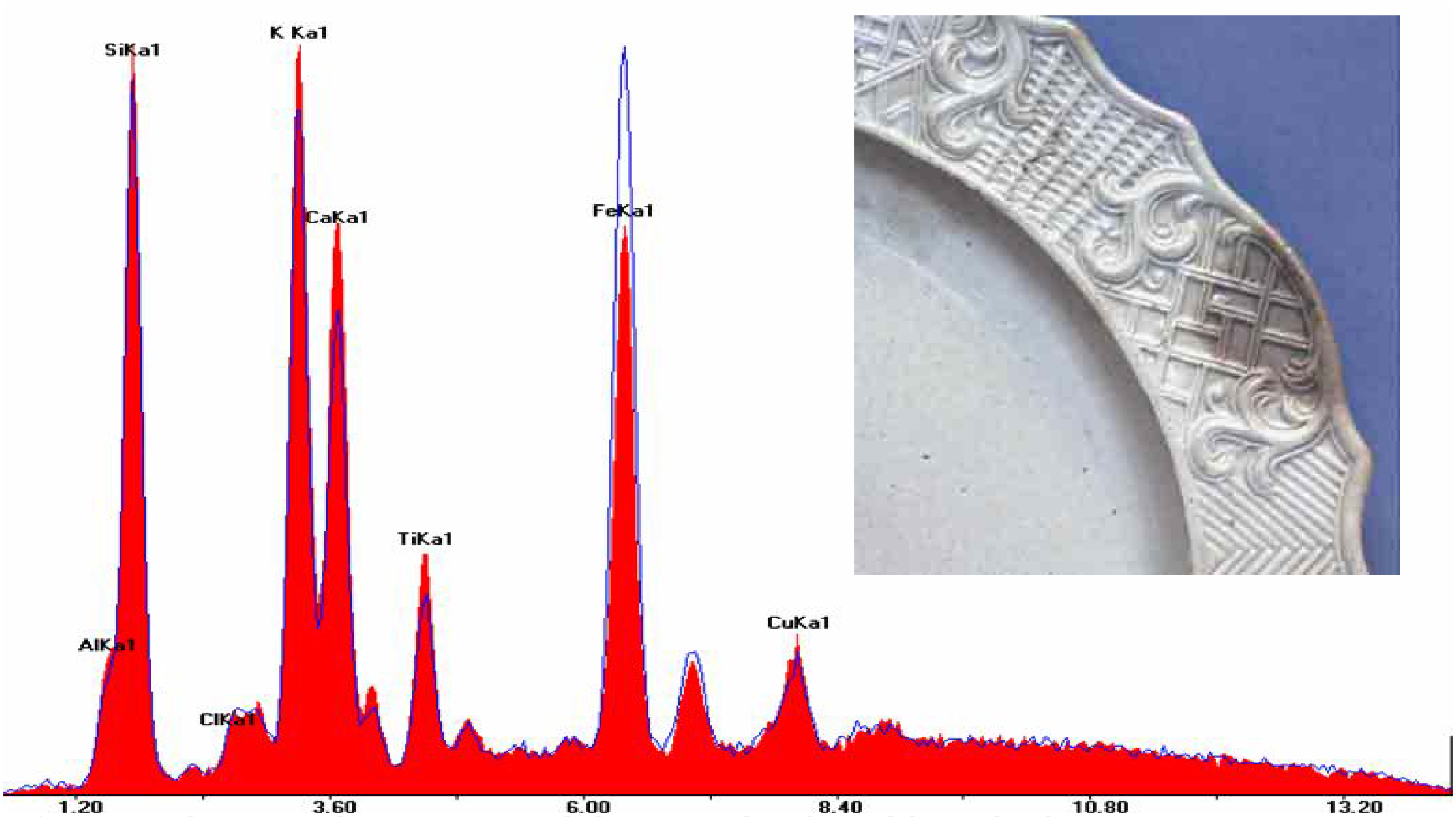
- **Quick identification of German and English Salt-glazed Stoneware. Origin discovered**
- **Identification of iron staining in a Staffordshire Salt-Glazed Stoneware Plate. Cleaning time saved.**
- **An elemental comparison of a pair of English 17thC. Glass Decanters. A fake and a lie discovered.**
- **Determining salts in an American Archaeological 18thC. Red Earthenware Bank. A problem solved.**
- **Identifying ‘invisible’ restoration on a Chelsea Bullfinch that is unaffected by UV light for purposes of cleaning and documentation. A lie discovered.**

Quick identification of German and English Salt-Glazed Stoneware.



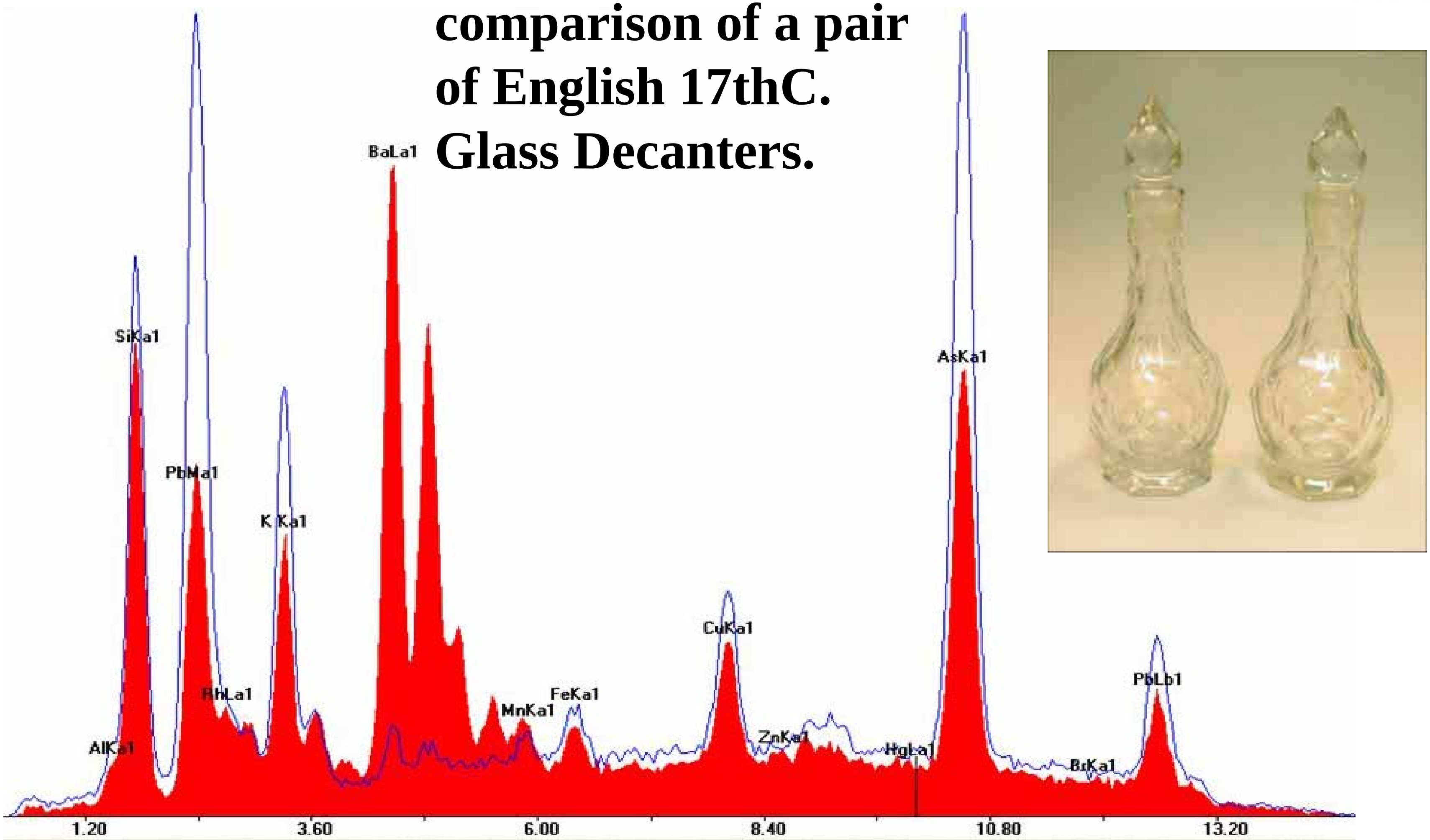
The English Stoneware (blue) contains significantly more iron than the German Stoneware (red). (English– top image). Origin discovered.

Identification of iron staining in a Staffordshire Salt-Glaze Stoneware Plate.



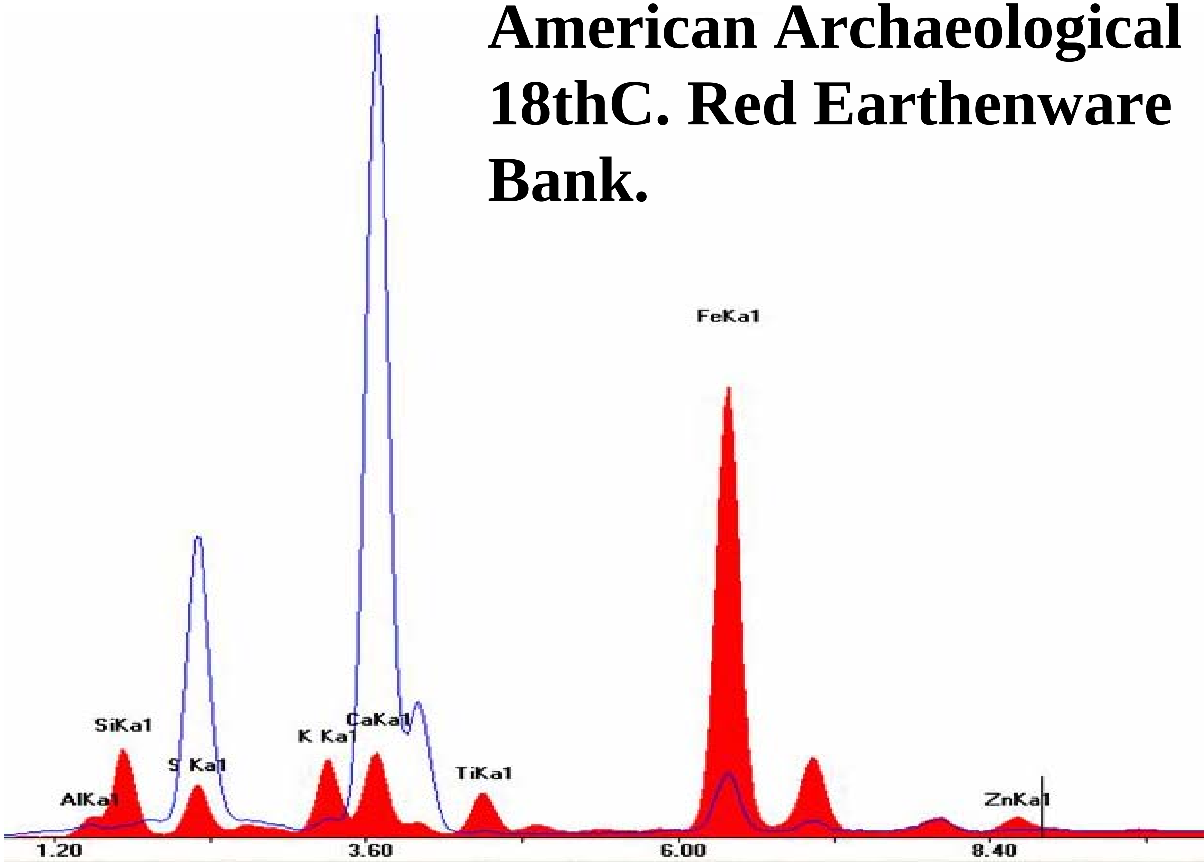
After poultice cleaning, some staining remained at chipped edges on the plate. The red spectra shows the main elements in the plate in an unstained area, whilst the blue spectra shows the elements of a stained area indicting a higher iron presence. Time saved.

An elemental comparison of a pair of English 17thC. Glass Decanters.



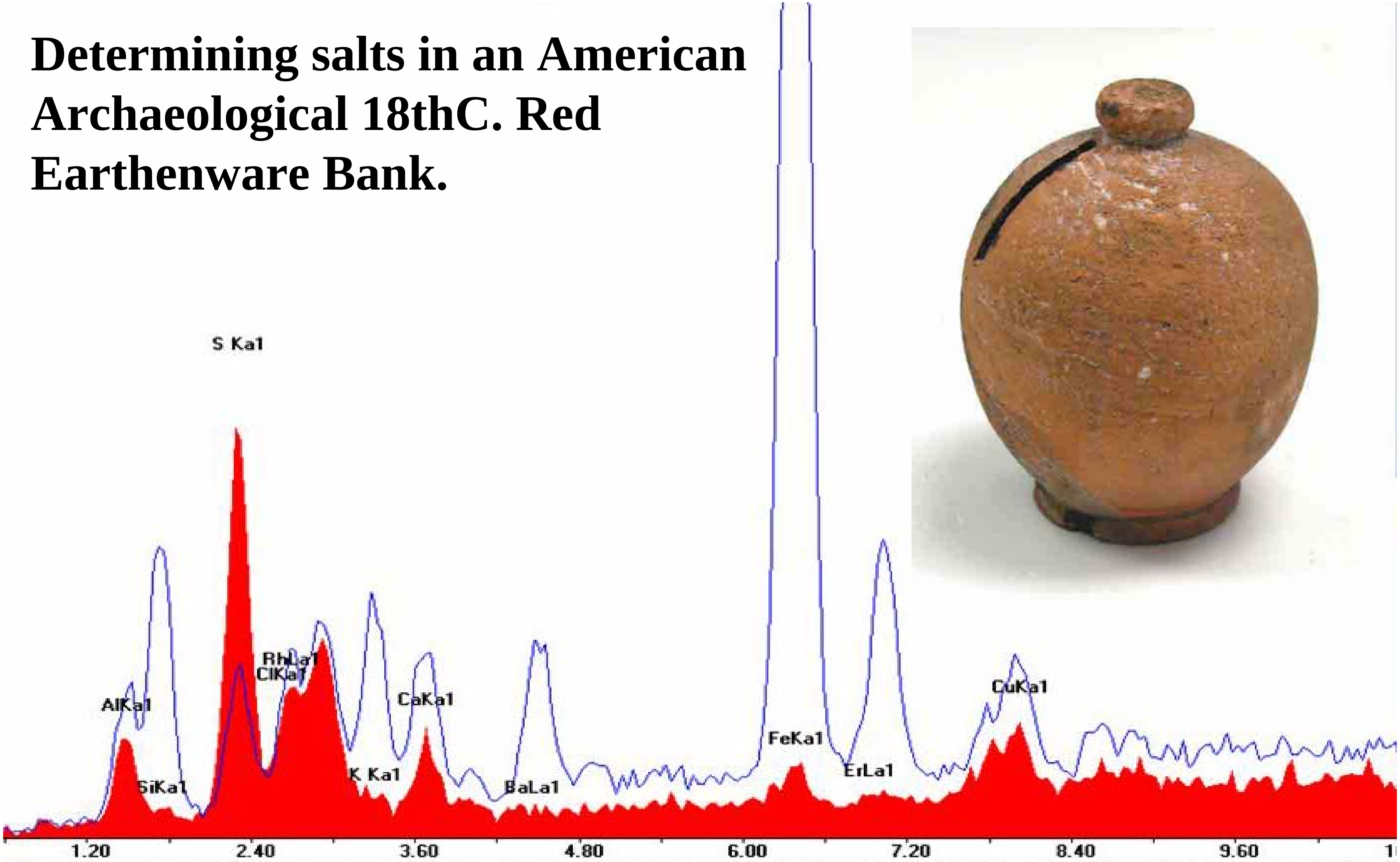
The decanter on the right has a significant amount of barium in it, whilst the other does not. Barium was not documented to be used in glass manufacture until the early 1800’s. A substitution and a lie.

Determining salts in an American Archaeological 18thC. Red Earthenware Bank.



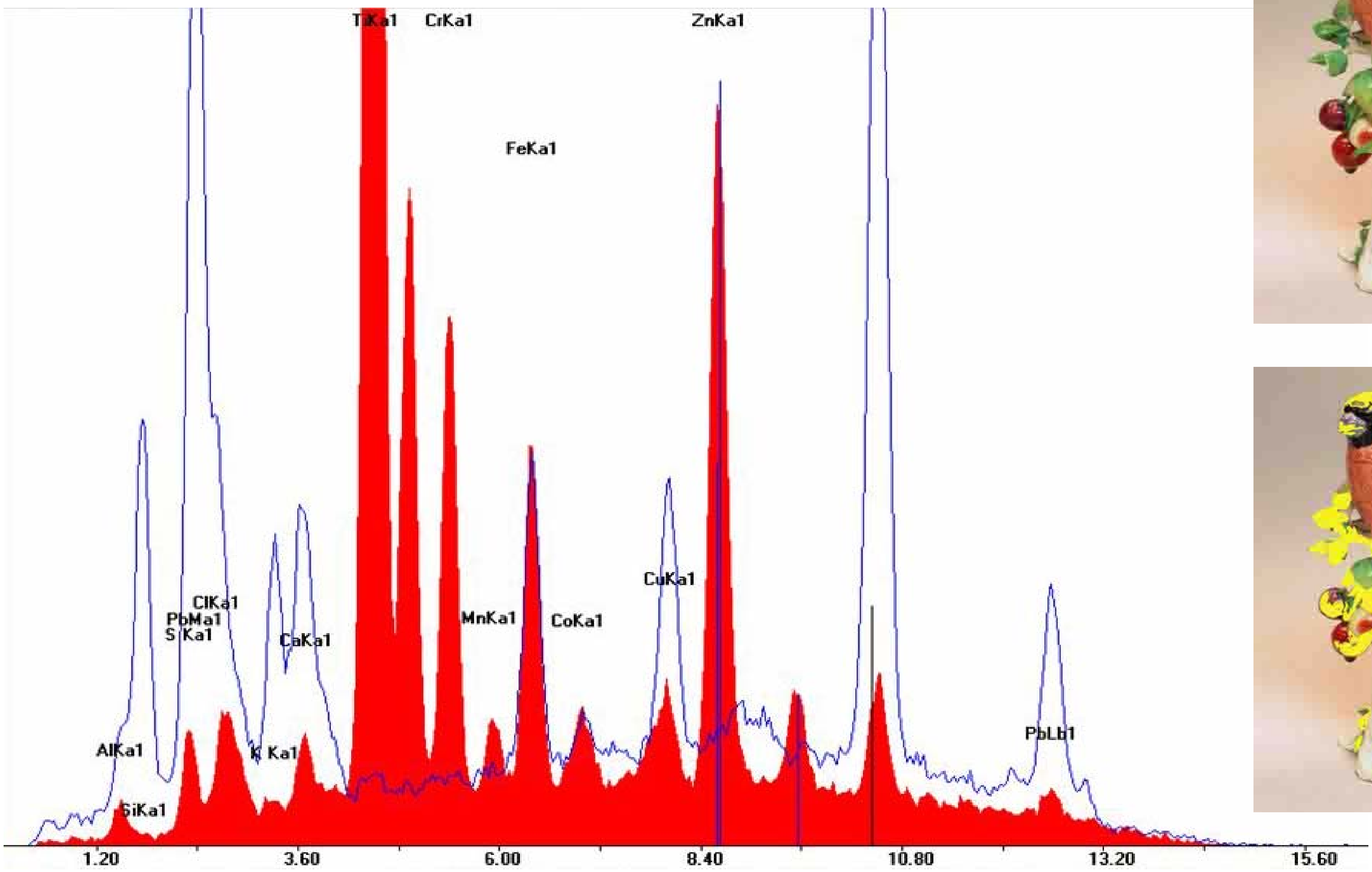
This bank was found in a burial excavation at a marine site near Williamsburg. The blue spectra indicates that the blue-grey accretions on the ceramic consists mainly of Ca and Fe sulfate. The red spectra shows the lighter (red) areas of the earthenware primarily consists of Fe with Al, Si, S, K, Ca, Ti and Zn. White calcium carbonate crystals are also found scattered about the surface.

Determining salts in an American Archaeological 18thC. Red Earthenware Bank.



The blue spectra shows that this earthenware primarily consists of Si, Fe, K and Ca; the labels stating the general elements found in the ceramic. The red spectra shows the salt content consists mainly of S and lower mass elements such as Na.

Identifying restoration on a Chelsea Bullfinch.



The two images are of the same bird. The yellow areas on the lower bird indicate the areas of 'invisible' restoration. The blue spectra is of an original glazed ceramic leaf, whilst the red spectra represents an over-painted / restored leaf. A lie discovered.