

Chlorine Analysis



By
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Measuring Chlorine

Measurement of Cl is very important as it is often involved in corrosion and degradation of artifacts in marine environments. Or in some cases is a key constituent of pigments or other coatings, or an issue in paper conservation.

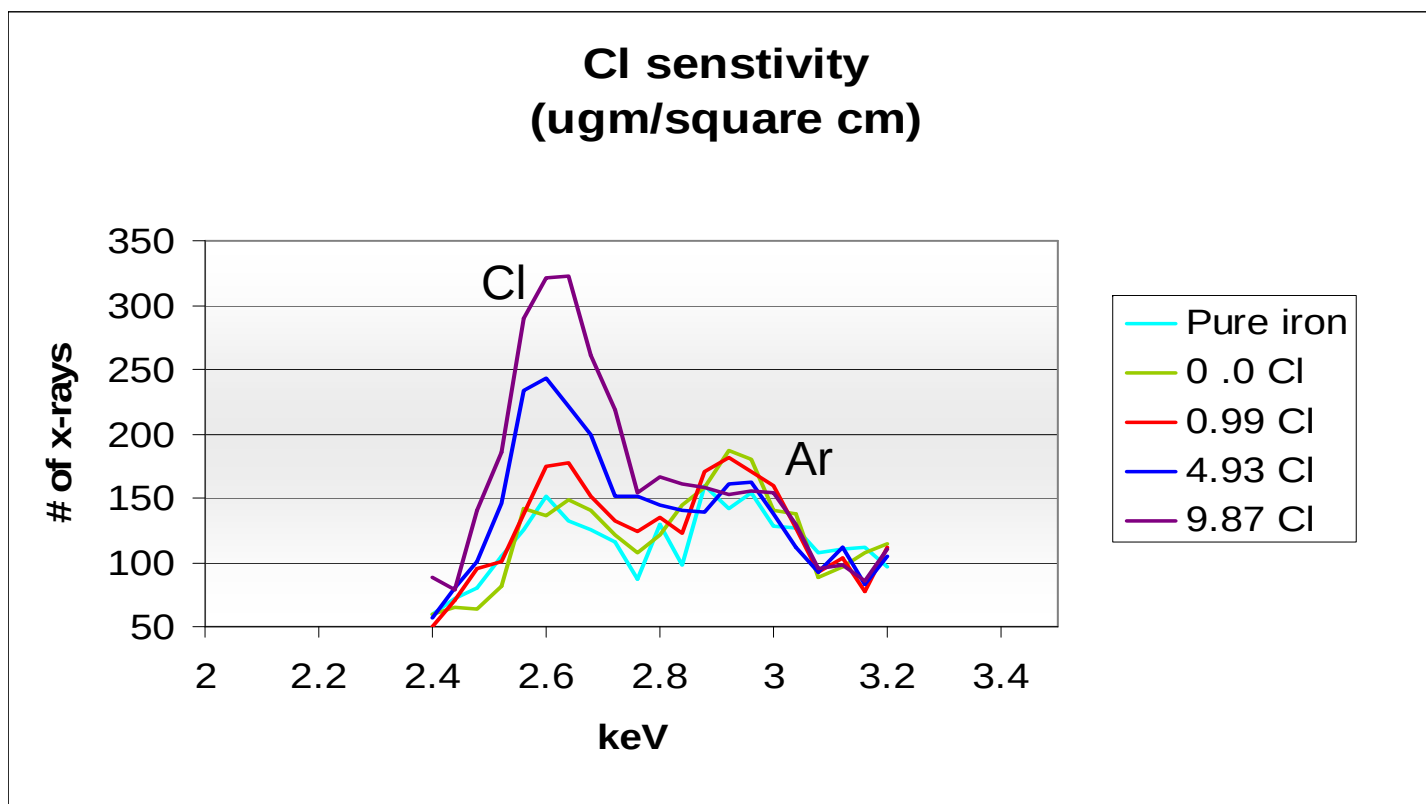
The following slides first depict how to make up thin film standards to determine the Cl surface content in micro grams per square centimeter. And then how to set the Bruker handheld xrf instrument up to measure levels as low as 10 micro grams per square and shows 2 applications.

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.

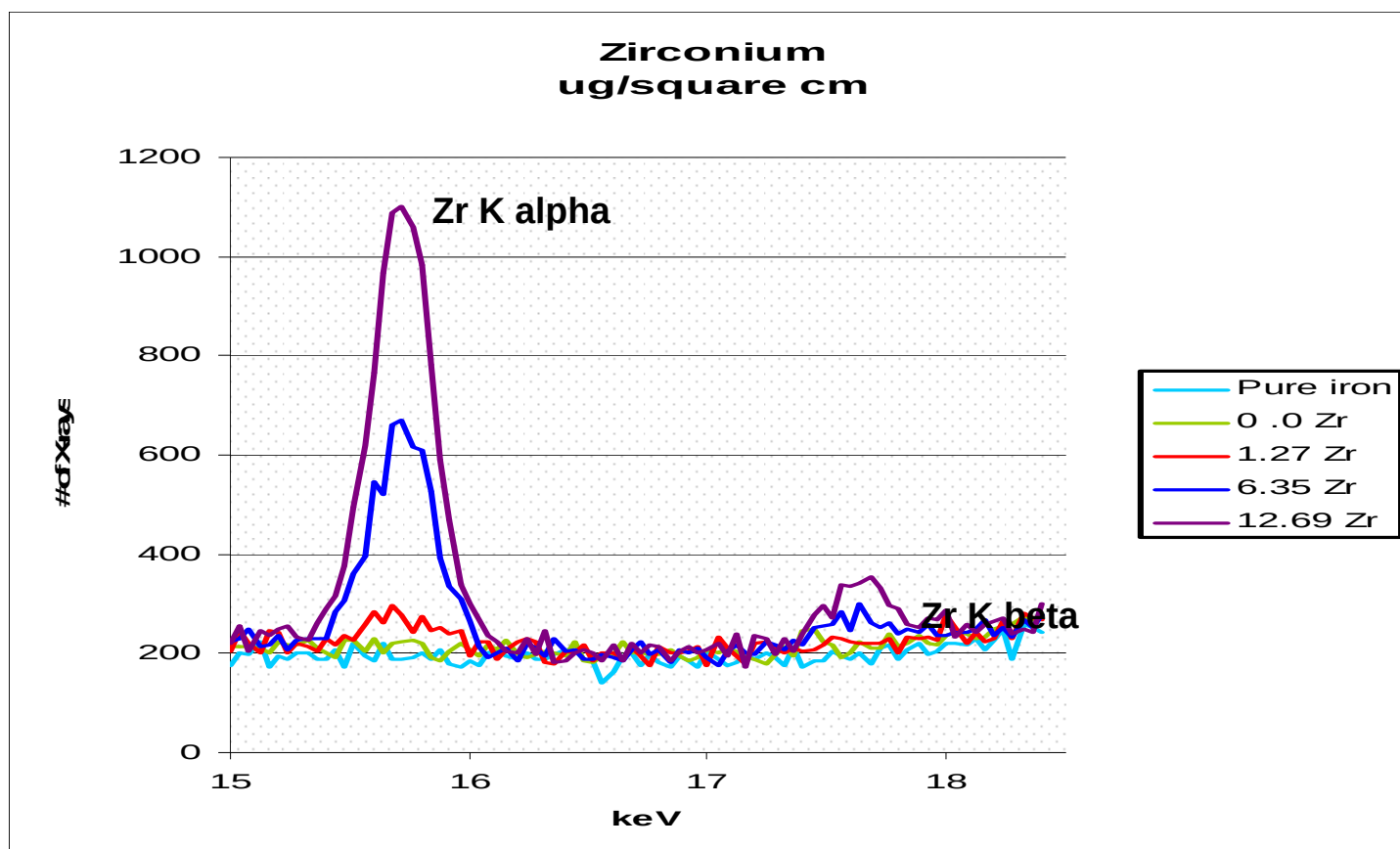
Creation of very very thin film Chlorine Standards

- 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

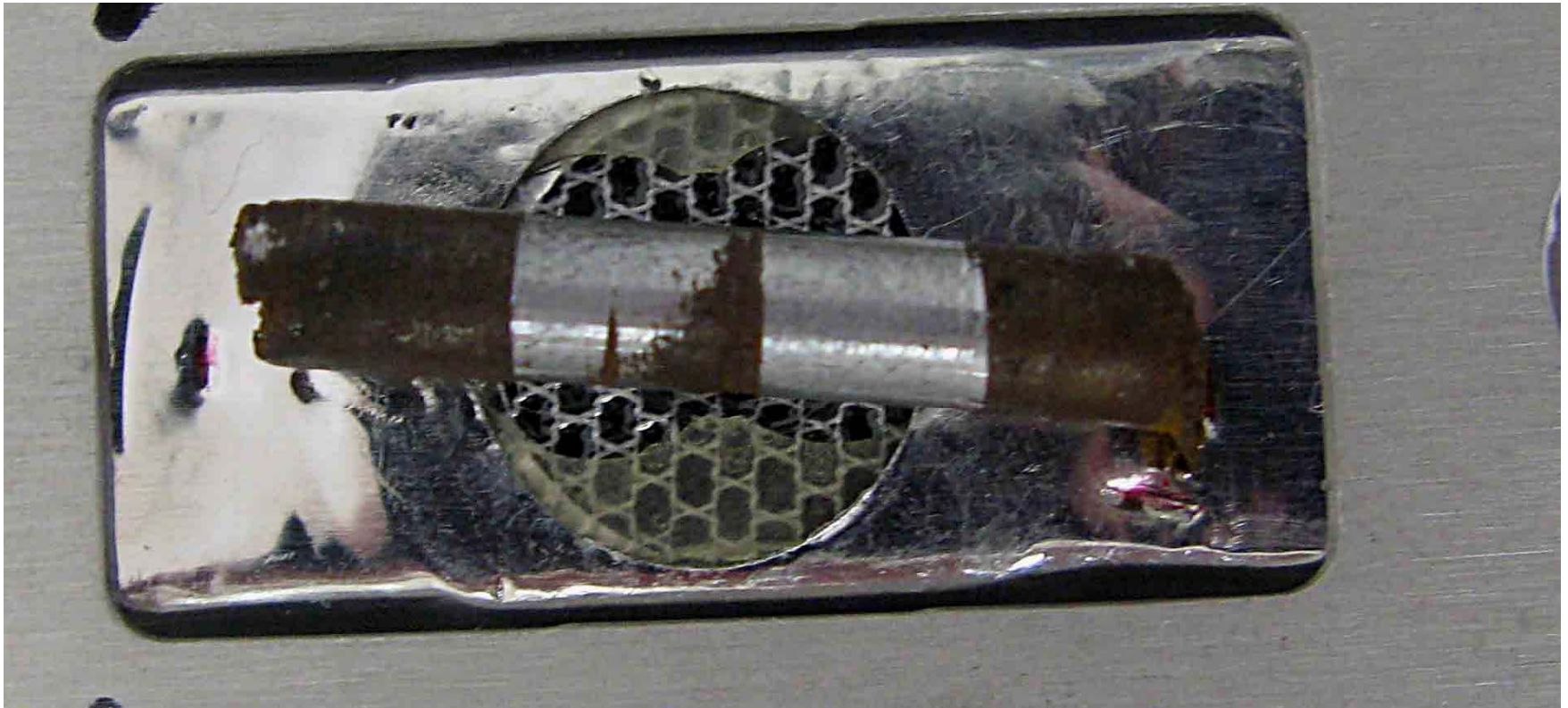


Each standard was analyzed for 3 minutes at 2 different voltage and current settings. A 0.001" Titanium foil was used in both cases to eliminate the Rh L lines and generate Ti x-rays to excite Cl efficiently. The thin paper standards were backed by pure Fe to mimic Cl corrosion on Fe. The above is a 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

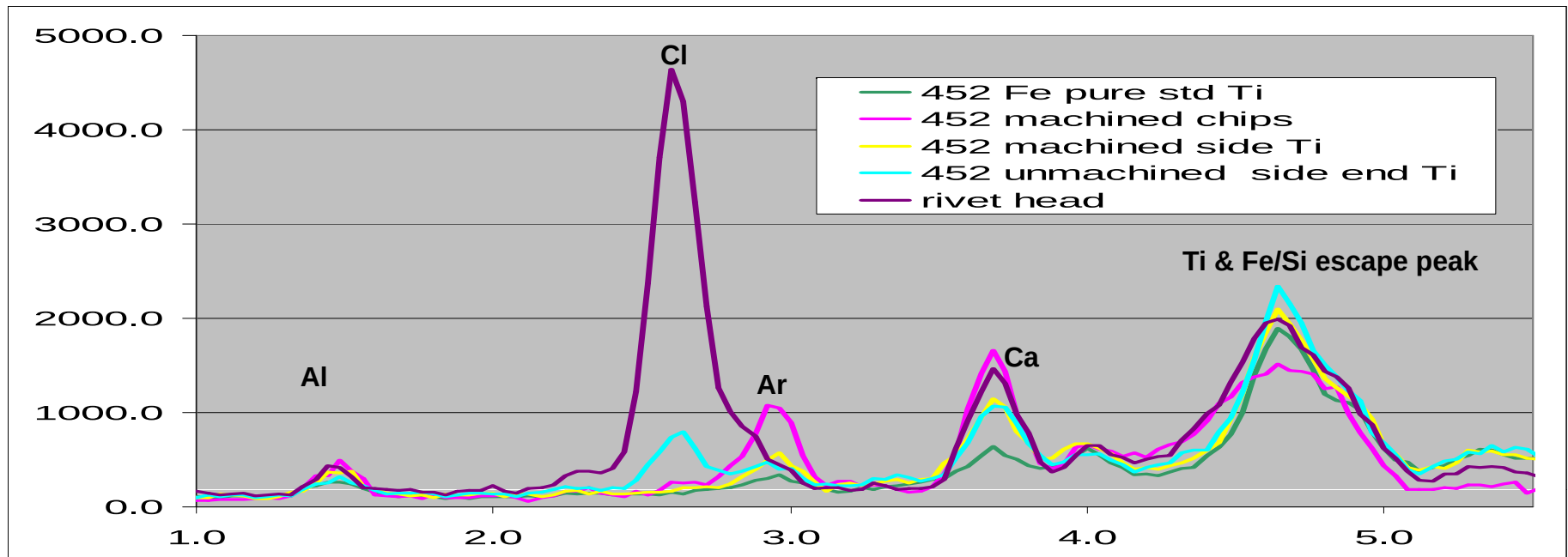


The above chart is a plot of the measurements that were taken at 40 kV and 1.5 micro amps. The peak at 15.6 keV is the Zr K alpha x-ray. The peak at 17.8 keV is a result of Zr K beta x-ray. It is clear the system is sensitive to Zr down to levels as low as 1 microgram/square cm. Comparing the ratio of 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.

The First Application was 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.



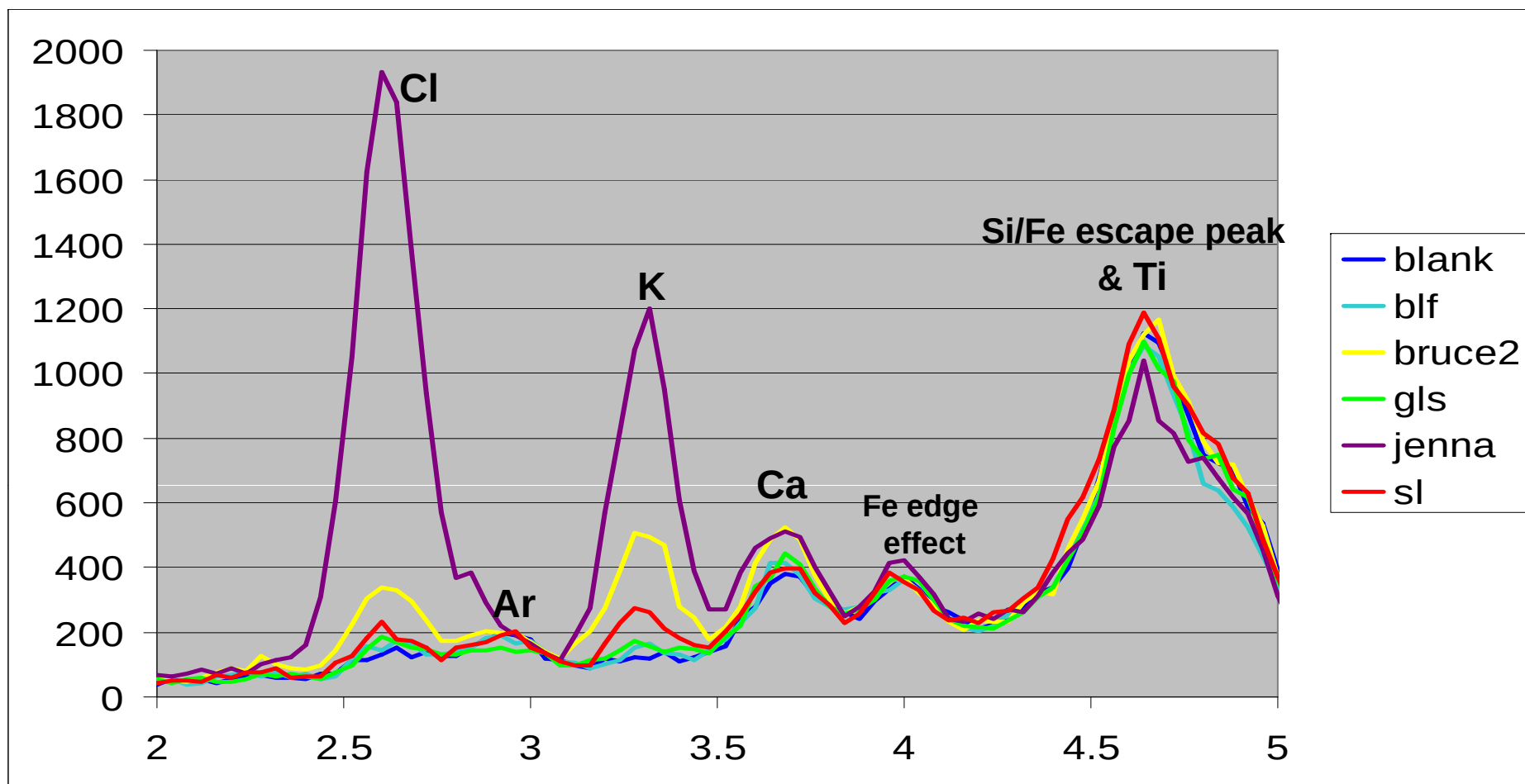
Above is the photograph of the rivet sitting on the instrument after the center section was machine .001" The side facing the XRF instrument has no dark corrosion present. The dark area in the center of the machined portion is because the rivet had a gouge on visible side so the machining process did 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 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.