Jennifer L. Mass, Ph.D.
Scientific Analysis of Fine Art
843 Old State Rd.
Berwyn, PA 19312
Jennifer.Mass@gmail.com
302-382-2733

ANALYSIS REPORT

REPORT NO.: SAFA075 **DATE:** 8/25/2007

REQUESTOR: Mr. Ric Gillespie
2812 Fawkes Drive
Wilmington, DE 19808
tigharic@mac.com
Phone: (302) 994-4410

OBJECT DESCRIPTION (form, material, color, etc): Archaeological material excavated from the Republic of Kiribati in the summer of 2007: one copper alloy zipper pull, two copper alloy snap components, one copper alloy tool handle/blade, one button, two beveled glass fragments.

REASON FOR ANALYSIS: Could these objects have an early twentieth-century American provenance? Could they have been manufactured prior to 7/2/37? Specific questions include: The zipper pull was made by an American manufacturer. What is the alloy? Is the red material on its surface a paint containing a cadmium, mercury, or iron pigments or is it cuprite, a red copper oxide corrosion product? What is the composition of the two round artifacts? Is it consistent with their shapes which suggest two components of a snap? What is the composition of the button? Was it made using first quarter of the twentieth century technology? What is the composition of the tool handle and blade? Is there any paint on either? Were the beveled glass fragments silvered suggesting that they were part of a mirror such as a compact mirror?

SAMPLING: Microgram sized samples were removed from the button and the zipper surfaces for FTIR analysis and for Raman analysis respectively using a size 11 steel scalpel blade. All samples for chemical analysis were transferred to glass containers to prevent contamination prior to analysis. A diamond scribe was used to remove milligram-sized fragments of the glass samples for SEM-EDS analysis (to be performed as part of SAFA project 076). All other analyses were performed nondestructively.

ANALYSIS PROTOCOL: Fourier transform infrared spectroscopy (FTIR) was used to identify the polymer and pigments/fillers comprising the button. X-ray fluorescence (XRF) was used for elemental analysis of the zipper, snap components, tool, and glass fragments; it detects all elements heavier than potassium. Samples were removed from the glass fragments for scanning electron microscopy/energy-dispersive x-ray microanalysis (SEM-EDS) analysis to allow for elemental analysis of elements heavier than sodium. Raman spectroscopy was used to augment x-ray fluorescence and scanning electron microscopy (SEM-EDS) data by providing molecular/phase identification (such as identifying copper carbonate rather than just the presence of copper) in addition to the elemental analysis data for the red material on the zipper surface. See Appendix I for experimental details of analyses.

RESULTS and DISCUSSION:

Button Analysis: The FTIR spectra for the button samples revealed two components, kaolinite clay and a cellulosic polymer (see Figure 1). The polymer is partially decomposed, and its spectra match most closely with cellulose nitrate that has partially degraded into amorphous cellulose (through loss of nitric acid). The first industrial production of cellulose nitrate plastics in the United States was in 1870, and it was a common raw material for buttons, photographic film, and paints. The majority of cellulose nitrate objects were made between 1846 and 1950.[1] A number of different inorganic pigments/fillers were added to the translucent polymer to prepare an opaque plastic such as zinc oxide, titanium dioxide, zinc carbonate, and kaolinite clay.

Zipper Analysis: XRF analysis of the zipper revealed that it is a copper-zinc alloy – a brass (see Figure 2). While brass alloys have been produced since 1000 BC, the absence of any minor element impurities in the alloy (elements such as lead and tin) indicate that this artifact dates to after the invention of the electrolytic refining of copper (after 1869).[2] XRF analysis of the red spots on the zipper did not reveal any additional elements, but rather a higher ratio of copper to zinc, suggesting the potential presence of cuprite (Cu_2O), a red copper corrosion product (see Figure 3). Trace amounts of chlorine, calcium, and iron were also observed. Calcium and iron are ubiquitous components of surface dirt, and the presence of chlorine suggests that the zipper may have been exposed to seawater. Raman analysis of the red material on the zipper surface revealed the presence of a band at 625 cm^{-1} which corresponds to a prominent band in the cuprite reference spectrum. This reveals that the red material present on the zipper surface is cuprite corrosion rather than a red paint, which would contain iron oxide, cadmium sulfoselenide, or mercuric sulfide pigments.

Snap Components Analysis: The larger snap component, analyzed by XRF, contains iron, copper, and zinc major elements and calcium, manganese, strontium, and chlorine minor elements. Despite the high iron content, this again appears to be a brass alloy (see Figure 4) with the iron coming from surface soil entrapped in the corrosion layers. Calcium is a common component of surface accretions, particularly in a coastal environment, and strontium is geochemically associated with calcium. The lack of impurities in the alloy suggests again that this was produced after electrolytic refining (after 1869). The zinc content of the corrosion crust is quite high, suggesting that this object is in the process of dezincification – copper/zinc alloys that have been exposed to water, in particular saltwater, will preferentially leach zinc from their surfaces. This is most commonly observed with brasses that contain less than 85% copper.[3] The red material in the center of this object showed a higher copper/zinc ratio than the rest of the object, suggesting that it is the copper oxide corrosion product cuprite (see Figure 5). The red material on the edges of the object had a high iron content, suggesting an iron oxide accretion.

The smaller snap component also appears to be a copper/zinc alloy or brass. Minor elements identified were calcium, chlorine, manganese, strontium, and iron, likely components of surface soil/surface accretions.

Glass Analysis: The first beveled edge glass fragment analyzed was found to contain silicon, strontium, chlorine, potassium, calcium, titanium, iron, manganese, zirconium and zinc (see Figure 6). This composition suggests a potash-lime-silica base glass, however SEM-EDS analysis is required (and will be performed as project SAFA076) to determine its sodium and aluminum contents, as these elements are too light to be measured by air path x-ray fluorescence. Iron is a ubiquitous impurity in glasses, and this impurity plus titanium typically result from the presence of ilmenite ($FeTiO_3$) particles in the glassmaking sand. Strontium enters the glass as an impurity in the lime source, and zinc was often intentionally added as a flux in nineteenth- and twentieth-century glasses to control

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1 J.Reilly, "Celluloid Objects: Their Chemistry and Preservation" JAIC, 145-162, 1991.

2 See, for example, R. F. Tylecote, *A History of Metallurgy* (2nd edition, Institute of Materials, London 1992).

3 See, for example, David C. Scott, *Metallography and Microstructure of Ancient and Historic Metals*, The Getty Conservation Institute, Los Angeles, 1991

the melting point and degree of polymerization of the silicate network. The zirconium typically enters glasses as an impurity in the glassmaking sand. Manganese was often intentionally added to glasses as a 'decolorant' to cancel out the green color imparted to the glass by the presence of the iron impurities, but it could also be a component of any surface soil entrained in the glass surface. Chlorine impurities are often observed in ancient and historic glasses, and can result from the alkali source used, as well as from environmental causes such as exposure to seawater. Argon can also be observed in some of the XRF spectra – this is an inert gas present in the air path spectrometer. The glass fragment was analyzed for silver on both sides for as much as 600 seconds in each sample location, but silver was not identified.

The iridescent nature of the surface of the glass is a result of a reaction between the glass surface and atmospheric water. Water extracts alkali ions such as sodium and potassium from the glass surface, and replaces them with hydronium ions (H_3O^+). The hydronium ions have a smaller ionic radius than the alkali ions, and this causes the aluminosilicate network of the glass to collapse around them. The thin layers of the collapsed aluminosilicate network create an iridescent appearance similar to the thin film interference effect observed on the surface of a soap bubble. These colorful effects are caused by certain wavelengths of visible light being removed (by destructive interference) as they pass through the film, leaving the remaining wavelengths to add together thus creating colored light from incident white light.

Metal Tool Analysis: The blade of the knife was found to be a copper/zinc alloy – a brass (see Figure 7). The minor elements observed, calcium and iron, result from surface soiling and accretions. The knife bolster was analyzed in two different areas and found to contain nickel, copper, and zinc as major elements and iron, cobalt, calcium, and chlorine as minor elements. This suggests a nickel-plated brass bolster or a handle made from nickel silver/German silver, a white alloy composed of copper, nickel, and zinc (approximately 50-80% Cu, 10-35% Zn, and 5-35% Ni). The technology of electroplating nickel onto a base alloy substrate was developed in the 1850s, and was commonly employed in the early decades of the 20th century.[4] The cobalt present is likely an impurity from the nickel ore used, and the iron, calcium, and chlorine are components of surface soil/accretions embedded in the copper corrosion products on the handle's surface. No elemental evidence for a painted surface could be identified.

X-ray fluorescence analysis of the knife bolster at two different energies (50 kV and 30 kV) revealed the same apparent ratio of nickel to copper, suggesting that the nickel is alloyed with the copper rather than plated on its surface. In other words, the bolster is made from nickel silver rather than a nickel-plated brass. The pin going through the knife bolster had a similar response to x-ray fluorescence at two different x-ray energies, suggesting that it is also made from nickel silver.

CONCLUSIONS: The zipper, two snap components, and tool blade are all made from brass. The red cuprite corrosion product was confirmed on the zipper, and is likely the red material present on the snap components and tool handle as well. The tool handle is a nickel-plated brass, and the beveled edge glass fragment appears to be a potash-lime-silica glass with no silvering present on either side. SEM-EDS will be conducted on the both glass fragments to identify any potential aluminum coating on either side. The button was found to be made from cellulose nitrate with a kaolinite clay filler. Both the nickel-plated brass tool handle and the cellulose nitrate button are consistent with an early 20th century provenance for these artifacts.

APPENDIX I. EXPERIMENTAL:

FTIR analysis:

For FTIR (Fourier transform infrared) analysis, samples were transferred directly to a diamond compression cell half. The samples were rolled flat to transparency with a steel roller and then analyzed using the Thermo-Nicolet Magna 560 infrared bench with the Nic-Plan infrared microscope with MCT-A detector (range 4000-650 cm^{-1}, 120 scans, 4 cm^{-1} resolution). Resulting spectra were interpreted with the aid of commercial and art conservation infrared

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4 G.S.Brady, *Materials Handbook*, McGraw-Hill Book Co., New York, 1971 p. 545

reference spectral libraries.

ED-XRF (Energy-dispersive x-ray fluorescence) analysis:

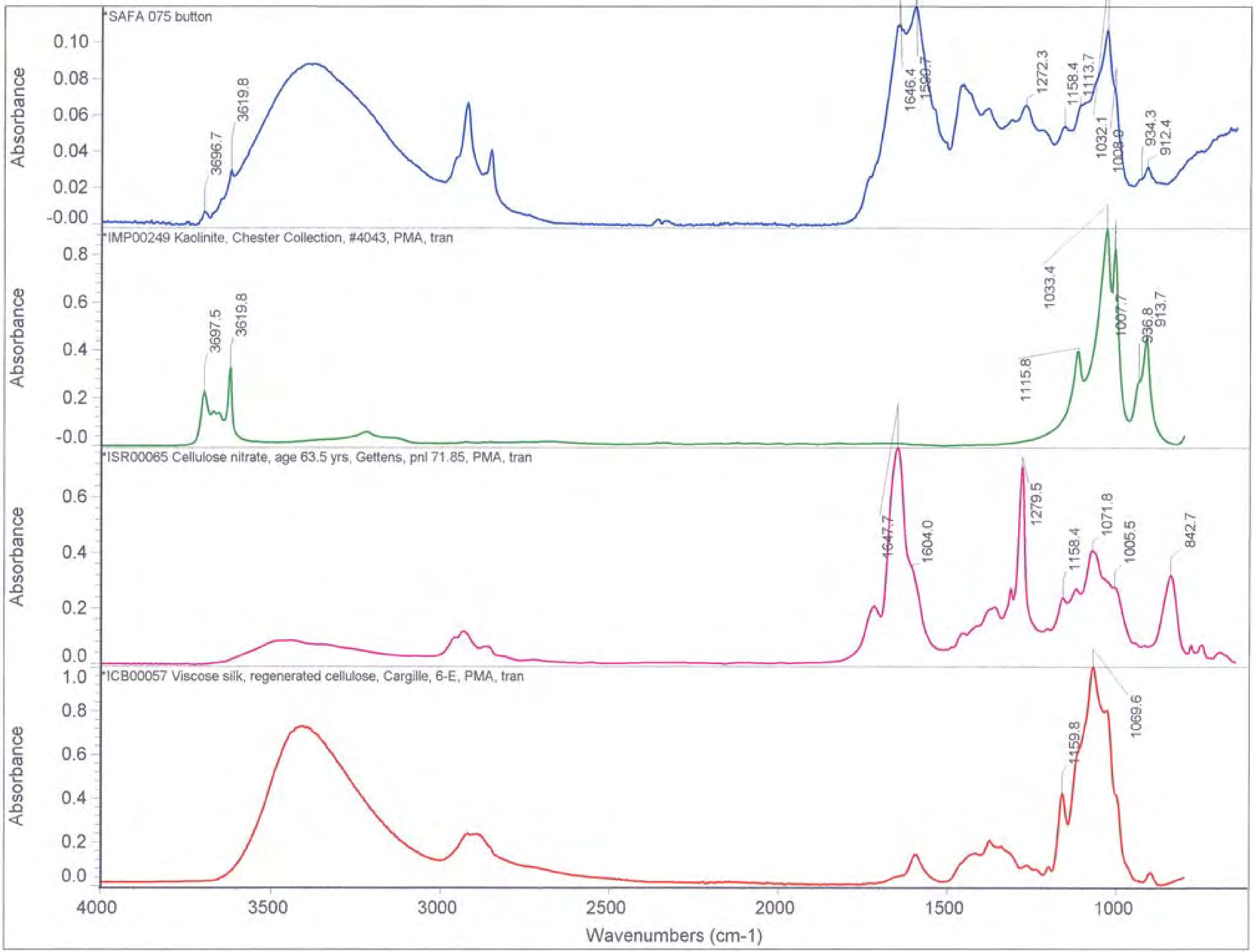
Non-destructive qualitative energy-dispersive x-ray fluorescence analysis (ArtTAX μ-XRF spectrometer, molybdenum or tungsten tube, 50 kV, 600 μamps, 100 sec, 20) was performed on each metal and glass artifact to determine its elemental composition.

Raman microspectroscopy analysis:

Raman analysis:

A Renishaw InVia Raman spectrometer was used to conduct dispersive Raman spectroscopy using a 50 mW 785 nm (red) laser , 1200 line/mm diffraction grating, and a spectral resolution of 3 cm^{-1}. Spectra were collected over a 100 cm^{-1} to 3200 cm^{-1} range for 20s collection times with a laser power of 1%.

Figure 1a



*SAFA 075 button
*IMP00249 Kaolinite, Chester Collection, #4043, PMA, tran
*ISR00065 Cellulose nitrate, age 63.5 yrs, Gettens, pnl 71.85, PMA, tran
*ICB00057 Viscose silk, regenerated cellulose, Cargille, 6-E, PMA, tran
Absorbance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
3696.7
3619.8
1646.4
1590.7
1272.3
1158.4
1113.7
1032.1
1008.0
934.3
912.4
3697.5
3619.8
1115.8
1033.4
1007.7
936.8
913.7
1647.7
1604.0
1279.5
1158.4
1071.8
1005.5
842.7
1159.8
1069.6

Figure 1b

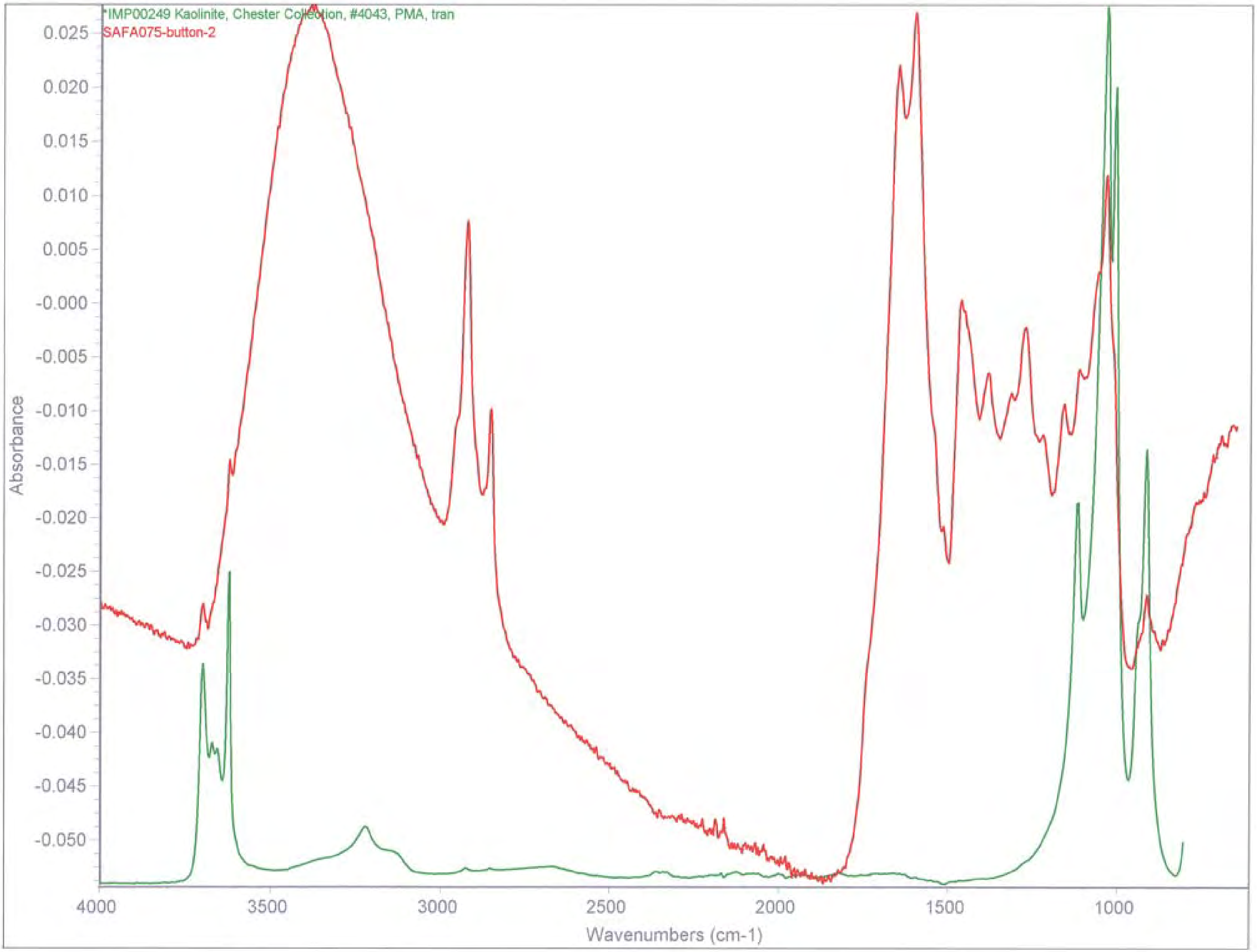

*IMP00249 Kaolinite, Chester Collection, #4043, PMA, tran
SAFA075-button-2
Absorbance
0.025
0.020
0.015
0.010
0.005
-0.000
-0.005
-0.010
-0.015
-0.020
-0.025
-0.030
-0.035
-0.040
-0.045
-0.050
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

Figure 1C

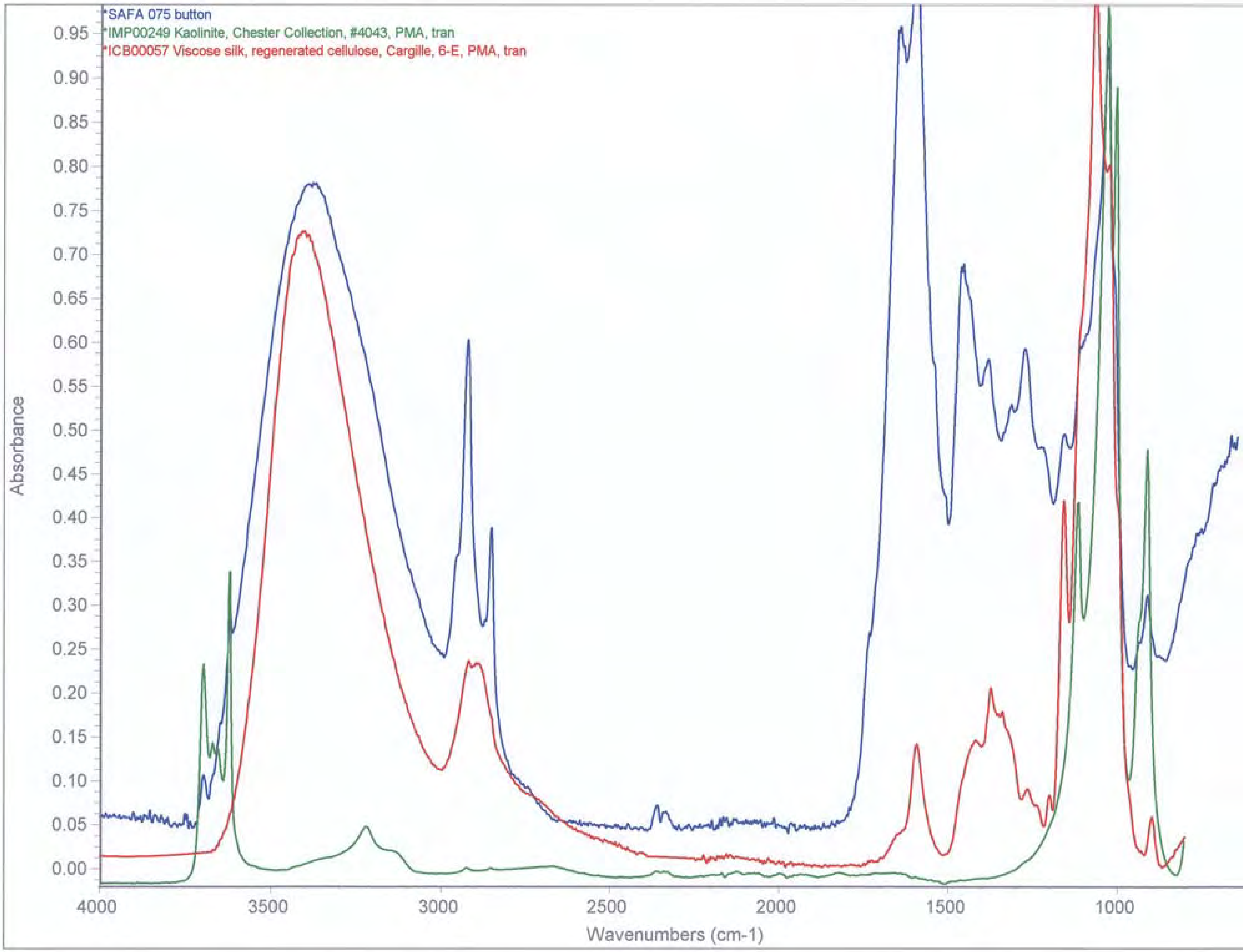

*SAFA 075 button
*IMP00249 Kaolinite, Chester Collection, #4043, PMA, tran
*ICB00057 Viscose silk, regenerated cellulose, Cargille, 6-E, PMA, tran
Absorbance
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

Figure 2

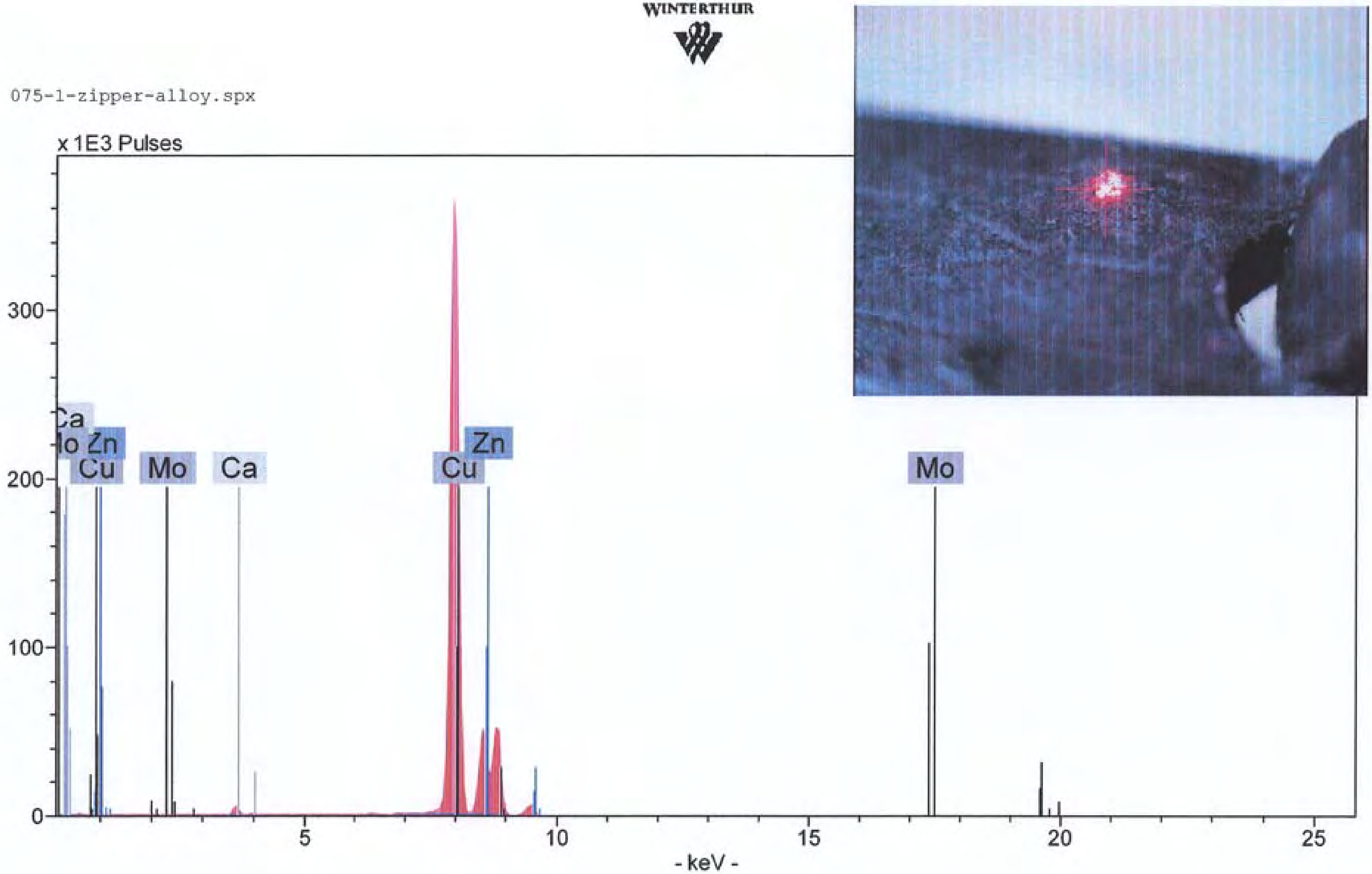

075-1-zipper-alloy.spx
x 1E3 Pulses
300
200
100
0
Ca
Mo Zn
Cu
Mo
Ca
Cu
Zn
Mo
5
10
15
20
25
- keV -

Figure 3

WINTERTHUR

075-2-zipper-red-spot-1.spx

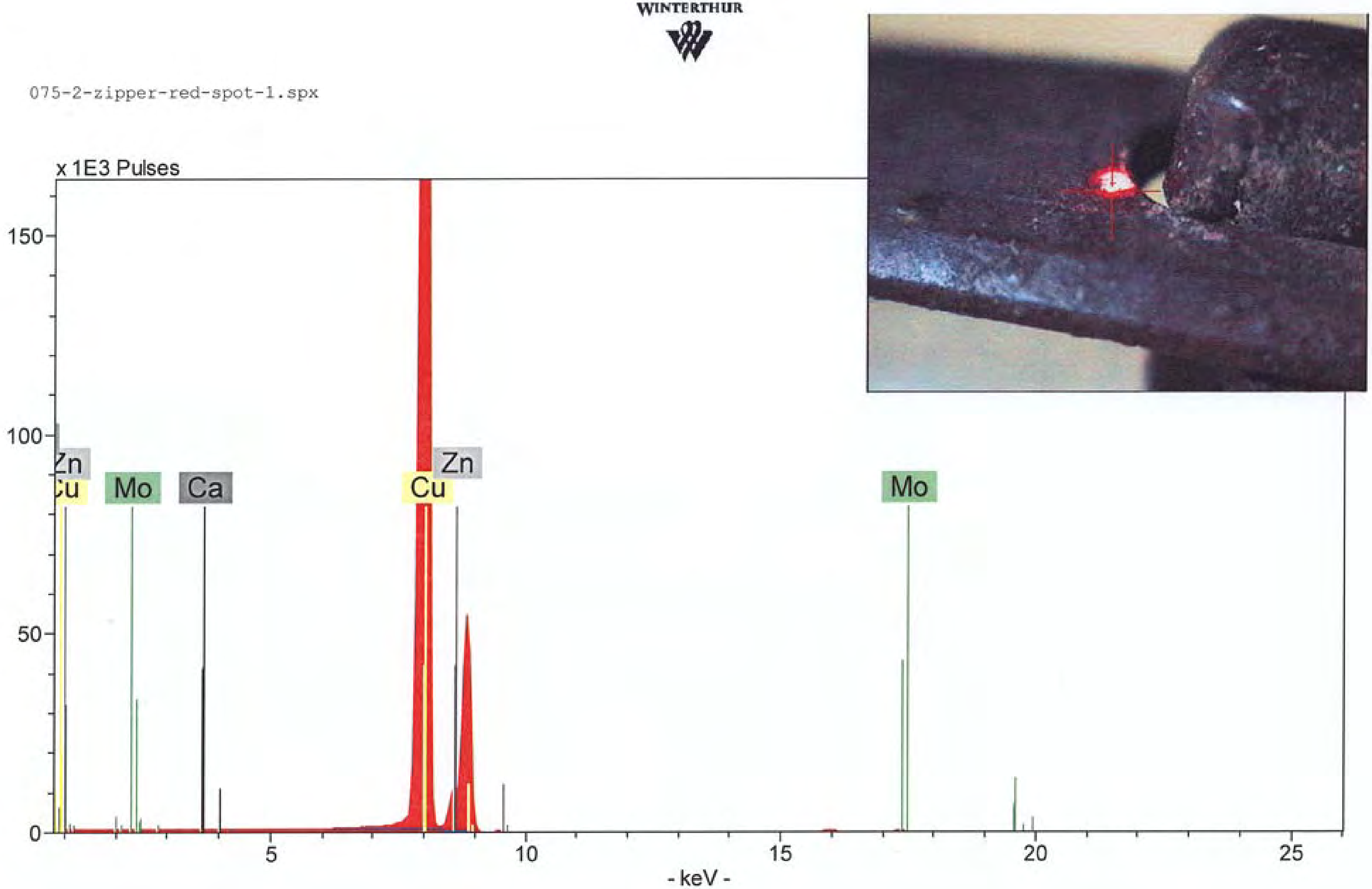


Figure 4

WINTERTHUR

075-4-larger-snap-alloy.spx

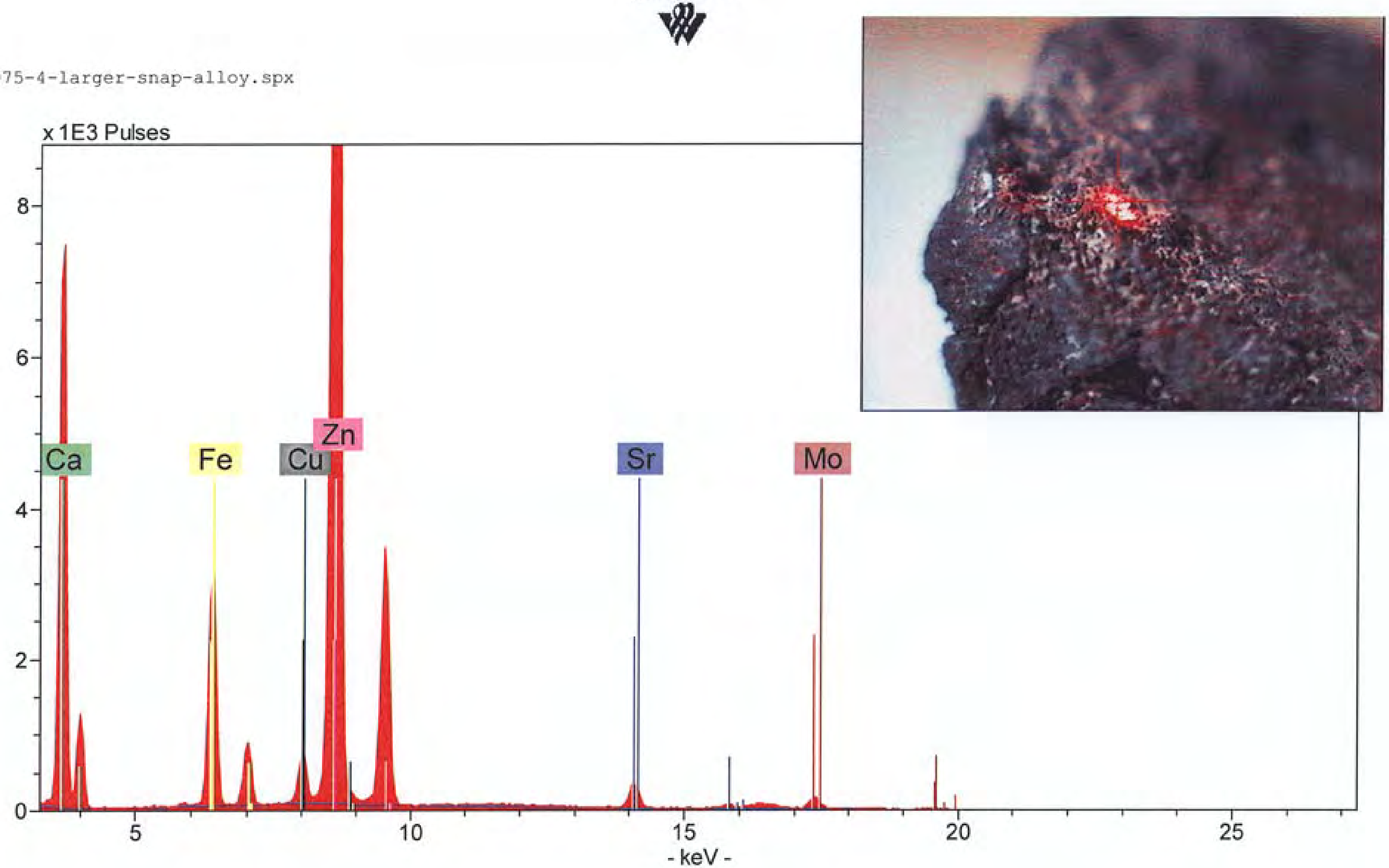


Figure 5

WINTERTHUR

075-7-larger-snap-red-interior.spx

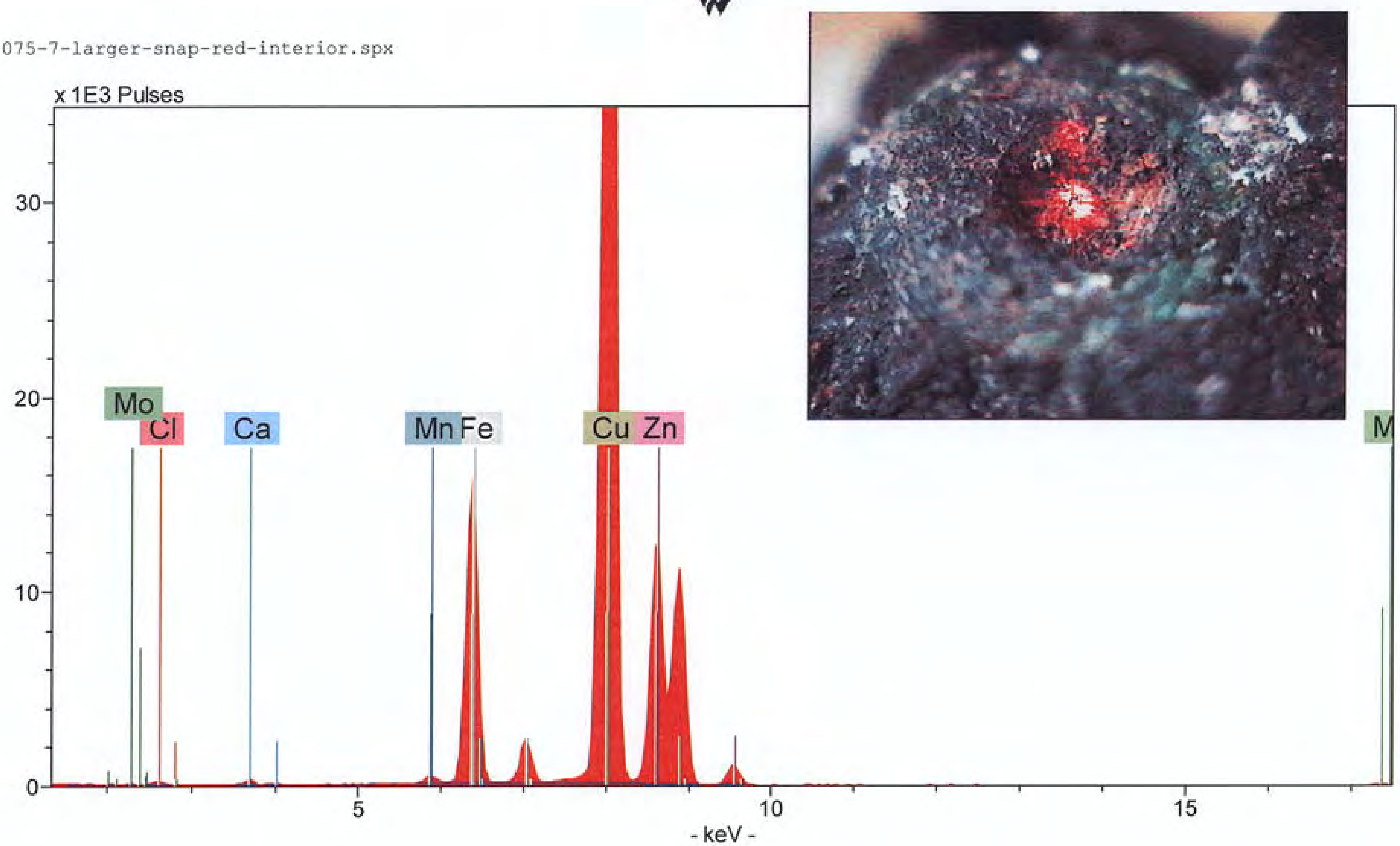


Figure 6a

WINTERTHUR

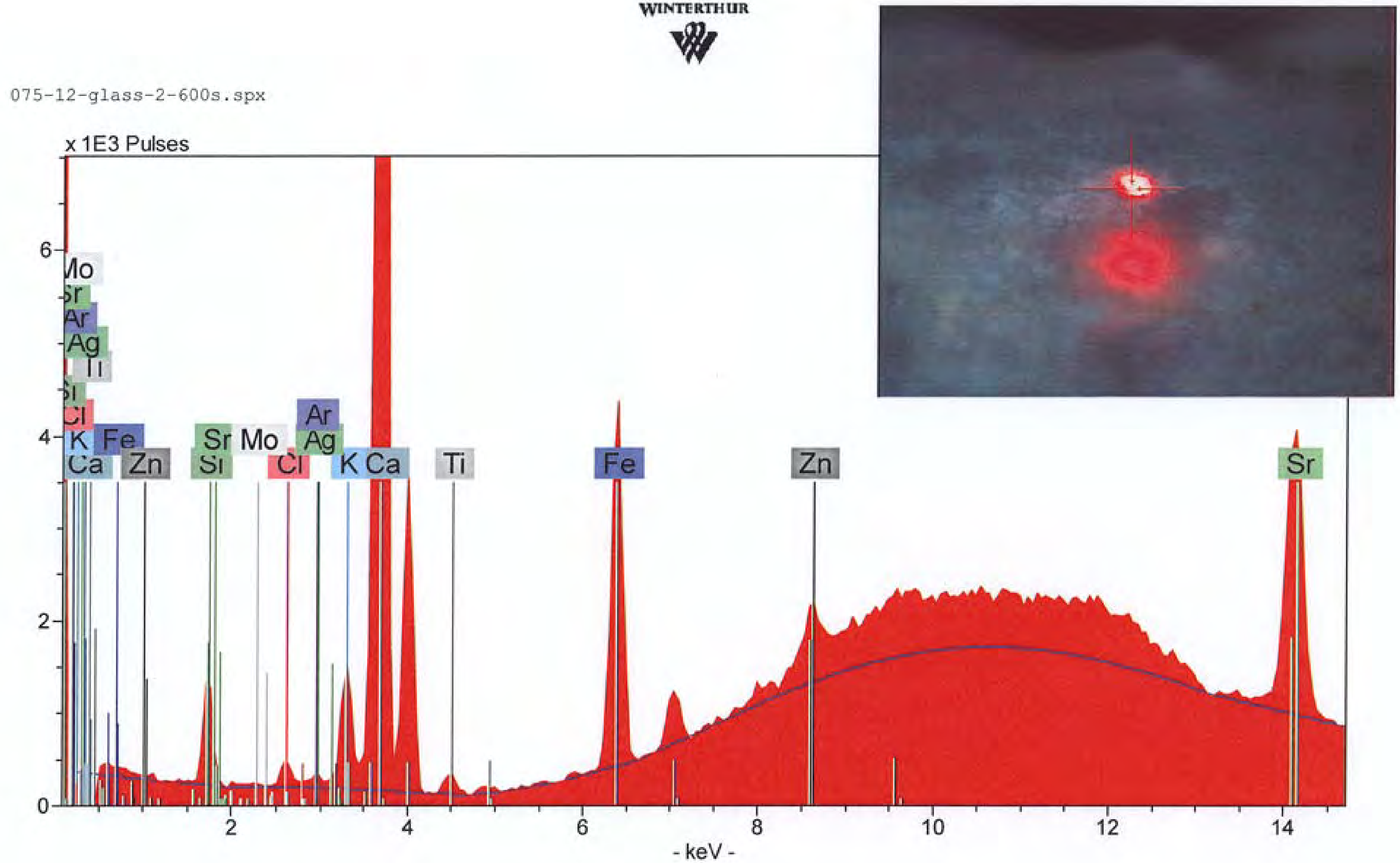


Figure 6B

WINTERTHUR

075-13-glass-3-Wtube-600s-irid-side.spx

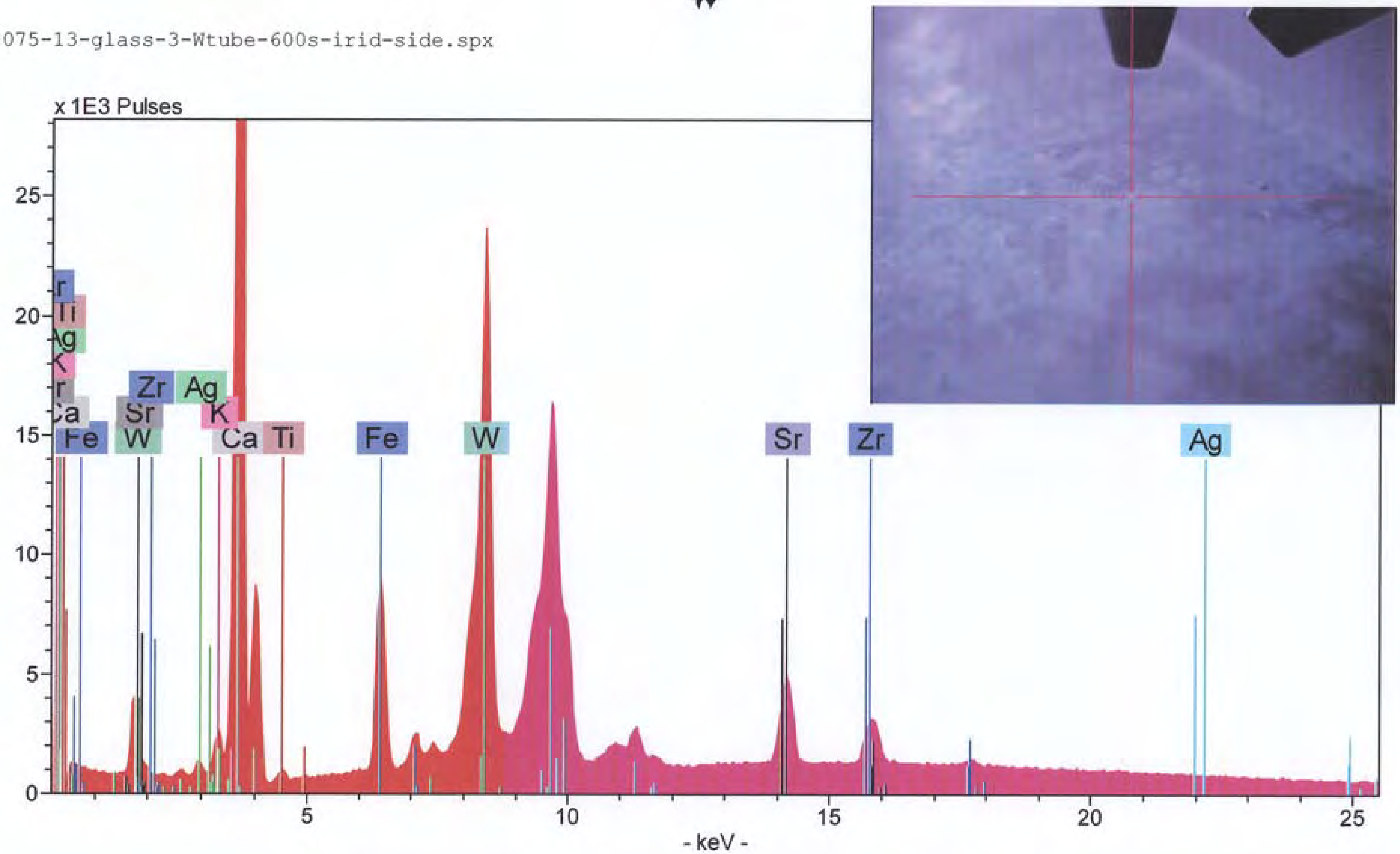


Figure 7

WINTERTHUR

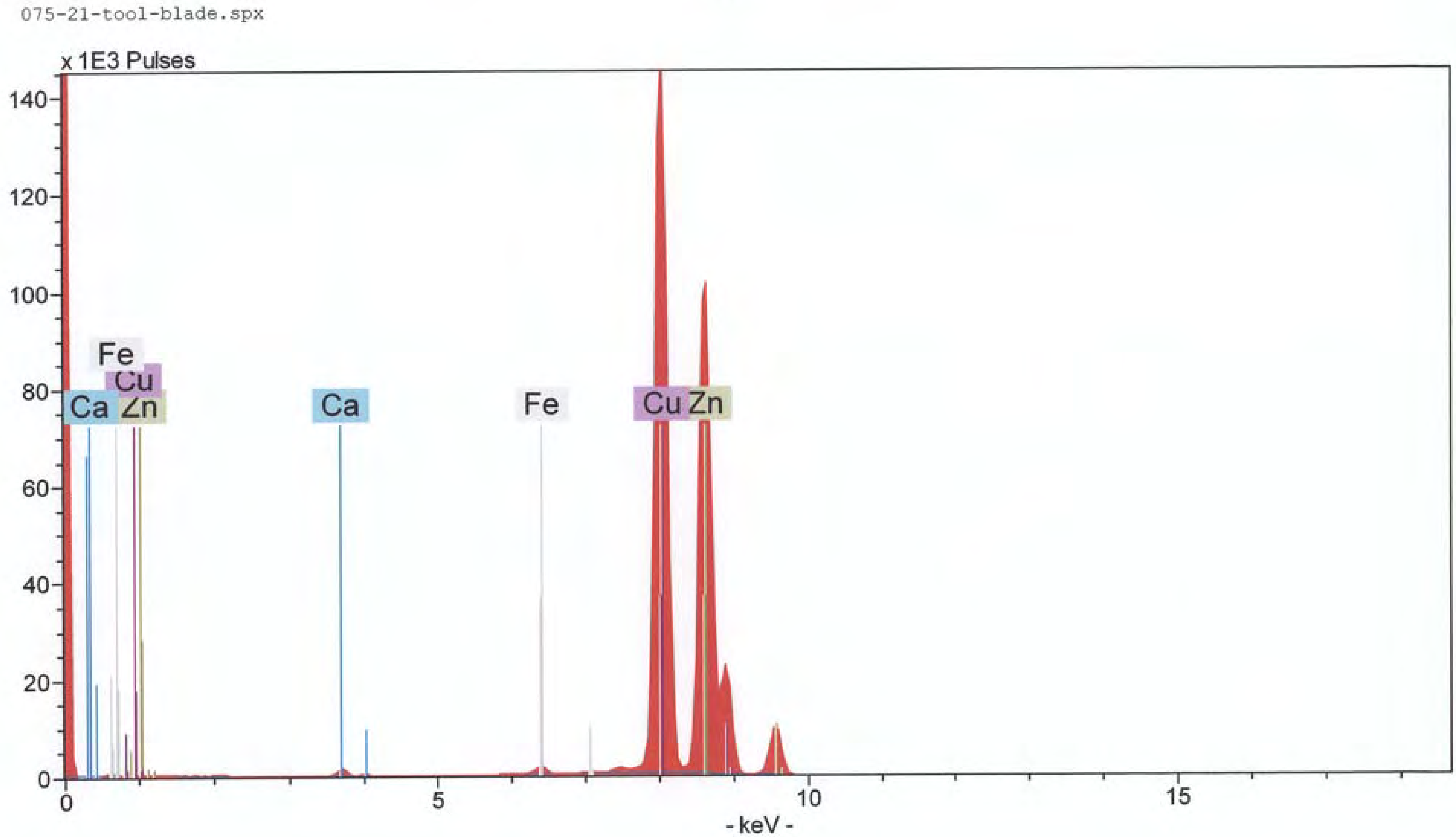
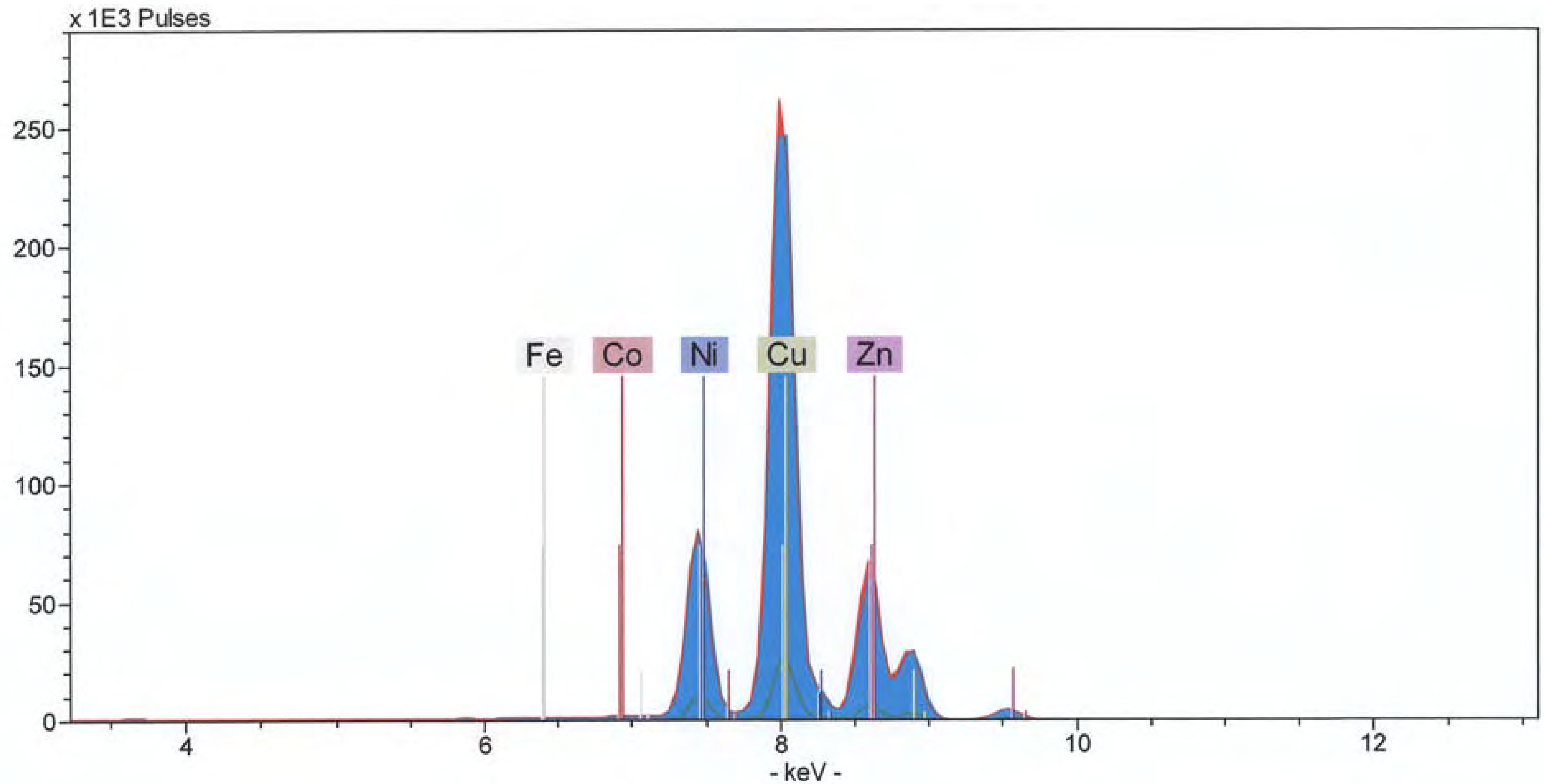
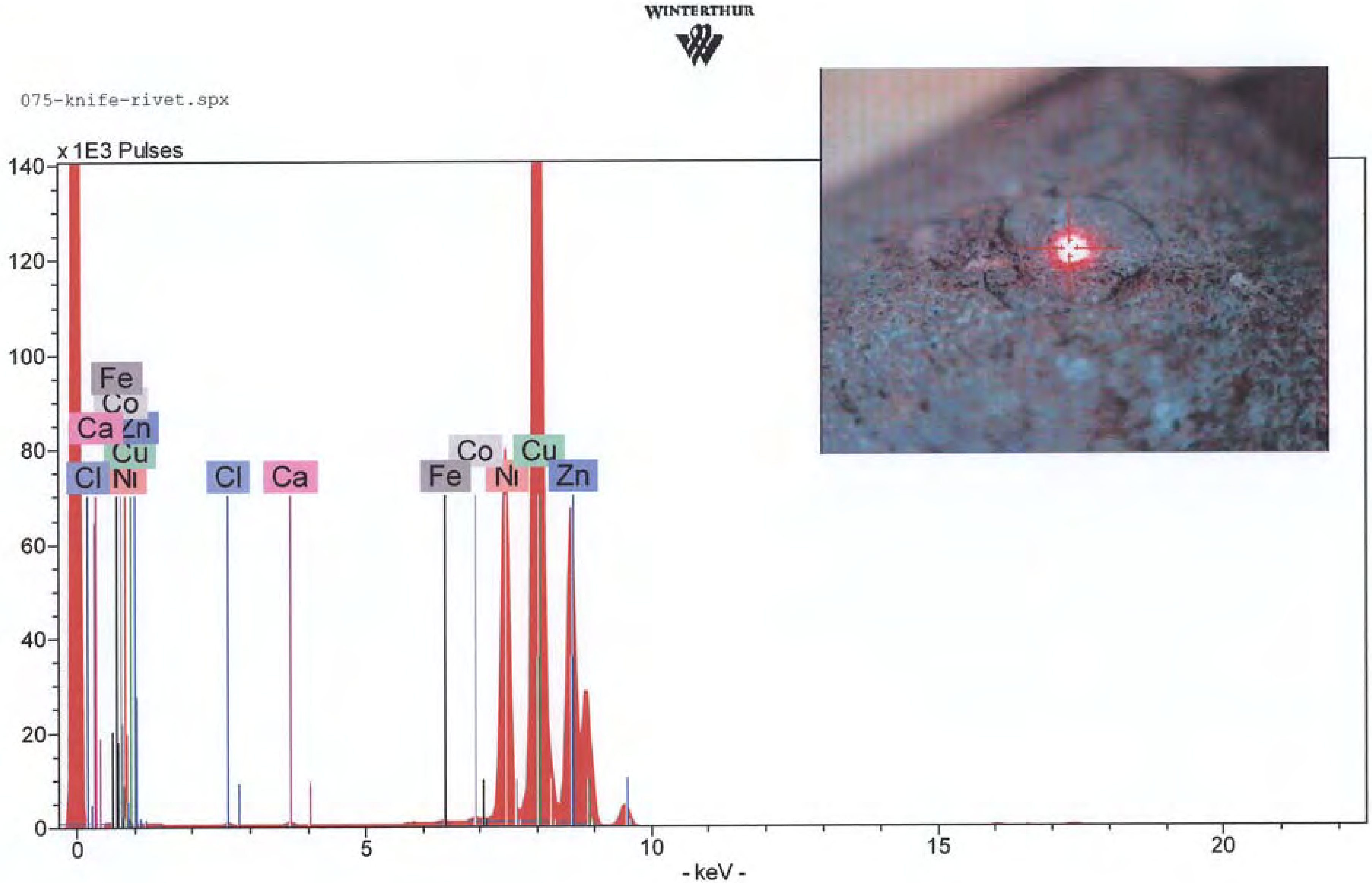


Figure 8a



No.	Element Line	Energy/keV	Cycl.	Netto	Backgr.	Sigma	Chi	Conc./%
17	Cl K12	2.622	0	1126	1850	69	0.00	0.00
26	Fe K12	6.405	0	1484	3851	96	0.00	0.00
27	Co K12	6.931	0	2461	5151	113	0.00	0.00
28	Ni K12	7.480	0	157043	5447	410	0.00	0.00
29	Cu K12	8.046	0	527677	4823	733	0.00	0.00
30	Zn K12	8.637	0	127138	2938	365	0.00	0.00

Figure 8b



50 kV 600uA