Bruker AXS

TRACER III-V Handheld XRF

Portable XRF in Archeology and Conservation Science

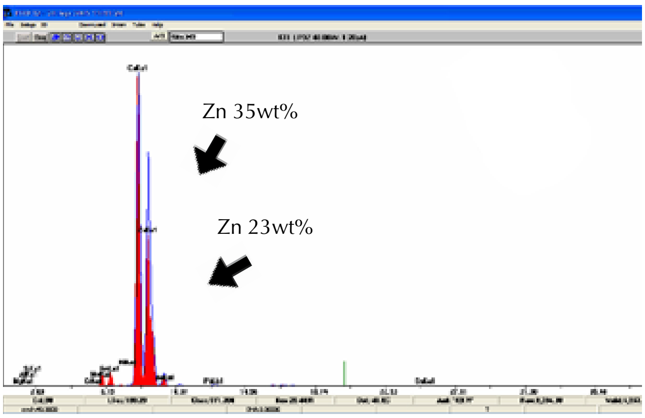
A variety of laboratory- bound X-ray fluorescence (XRF) spectrometers have been used successfully for the investigation of archaeological, historical and art materials for more than fifty years. It is only recently through the advent of powerful portable systems that this non-destructive technology can be fully exploited. Working in situ, portable spectrometers have extended the range of XRF technology to virtually any type of object.

Use of Elemental Composition in Art and Archaeology

Elemental composition is frequently used in the study of archaeological and historical materials to ascertain provenance and fabrication technology. It can help to distinguish non-original materials and, in some cases, to spot fakes. Increasingly it is used in conservation, where knowledge of elemental information and the aggregation of the elements can prove very useful. The following discussion outlines some materials of archaeological and historical interest and the information which can be obtained through portable XRF elemental analysis.[1,2]

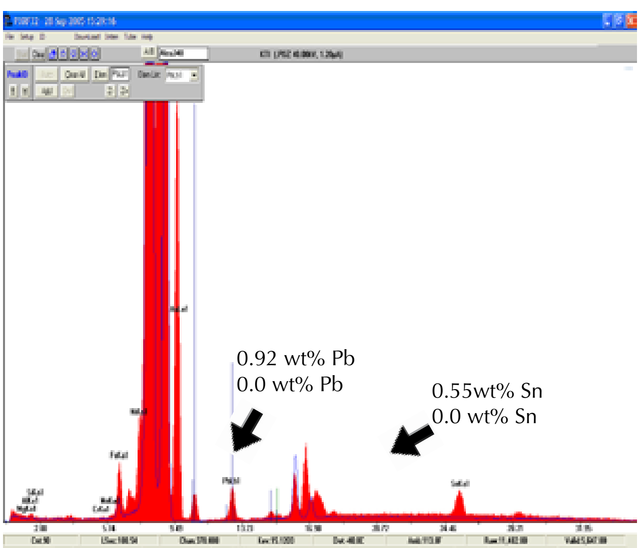
TRACER III-V Handheld XRF Spectrometer.

Graph 1



TRACER III-V: ARMI Cu Standards with Zn -- any work of art containing zinc outside of the historical boundaries of 28-32% zinc and no impurities would be suspect.[3]

Graph 2



TRACER iII-V: ARMI Cu Standards with Pb and Sn. The blue spectra contains no Pb or Sn compared with the red spectra containing 0.92% Pb and 0.55% Sn.

Bronzes and Copper Alloys

Because metal can be re-melted, there are limits to what the compositional data alone can tell us about the origin of any artifact. Nevertheless, differences in elemental composition can be correlated with the materials used at a specific time and by a specific artist. With this information, conservators can authenticate original works and identify non-original variations in statues and other art objects. Used in combination with microanalysis, elemental analysis can provide insights on the fabrication technology, such as casting, soldering and repairing.

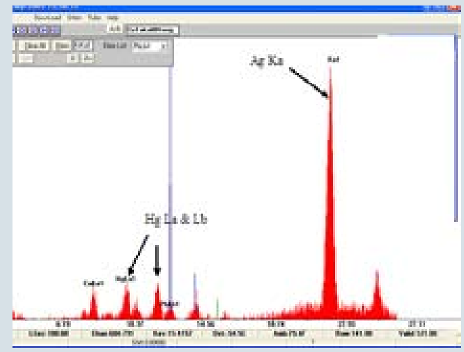
12th/13th Century Islamic Bronze and Copper Mirrors

For example, "in the Renaissance, copper was alloyed with tin or lead to make bronze simply by melting and mixing the metals together. Brass, an alloy of copper and zinc, could not be prepared in this simple way, since zinc boils well below the melting point of copper and oxidizes and evaporates before alloying can occur. Even though the alloying of copper with zinc was a more complicated process than manufacturing bronze, brass could be made more cheaply than bronze because zinc was more abundant and readily available than tin. The standard method for European brass production from the first century B.C. to the nineteenth century A.D. was the cementation process." In this process, zinc ore is calcined at elevated temperatures forming zinc oxide. Copper fragments are added to the resulting zinc oxide in a sealed furnace. When the copper and zinc are held at temperature for many hours, an equilibrium condition produces brass with 28-32% zinc. Introducing 2% tin into the mixture during heating would reduce the absorption of zinc in copper by 2%, whereas 2% lead would reduce the absorption of zinc by 4%. Since the foundry's goal would be to produce a brass with 28-32% zinc and electrolytic refining of copper was not available until after 1869, any brass work of art before 1869 containing zinc outside of the historical boundaries of 28-32% zinc and no impurities at all would be suspect.[3]

Table 1

Color	Key Element	Class of Pigments	Compound	Notes
Yellow Brown Red Green	Fe	Earths, ochres	Minerals composed of iron oxides and silicates	
White	Pb	Lead white	Basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$	
Blue	Co	Smalt	Glass SiO_2 (65-70%), K_20 (10-20%), Al_20_3 (0-8%), CoO (1-18%) (trace-Hg,Ni,As,Ca,K)	
Yellow	Cd	Cadmium yellow	Cadmium sulfide CdS	modern
Yellow	Pb	Lead-Tin Yellow	Type I-Pb_2SnO_4; Type II-$PbSnO_3$	
Yellow	Pb	Naples Yellow	$Pb_3(SbO_4)_2$ or Pb_2SnSbO_6	
Red	Hg	Vermilion	Hg_2S	
White	Ti	Titanium dioxide	Titanium dioxide TiO_2	modern

Graph 3



TRACER III-V: Antique Photo Spectra with Evident Mercury and Silver Content.

Paintings

Many paints are carbon based organic materials, which cannot be detected via XRF analysis, except possibly for trace elements. However, many pigments, (especially modern pigments), contain inorganic compounds composed of elements such as titanium, lead, mercury, copper and zinc. Qualitative analyses can often identify pigments by the presence of one or two characteristic elements. Some examples are shown in Table 1.

Photographic Prints

It is often difficult to identify the specific print process used to produce a photograph without additional data. XRF can be used to provide supporting evidence about the photographer's print process. Where multiple print processes are used, XRF alone may not be conclusive, but the elemental information may be helpful in analyzing the print. The selected photographic print processes in Table 2 is provided by Lisha Glinsman and shows the elements associated with each process.[4]

Ceramics

The elemental composition of a ceramic clay can often be tied to a specific geographic region. This makes portable XRF analysis a key tool for field archeology as well as providing information that can be used in conservation and authentication.

Obsidians

Archeological provenance studies are based on the ability to trace culturally modified objects back to their geologic source. Obsidian is a rare product of volcanic activity and has been used extensively by ancient man. It is generally brilliant black, but can sometimes be red or green. XRF and neutron activation analysis have been used to identify 300-400 separate compositions/sources in the Western Hemisphere.[5] XRF elemental analysis alone is a good indicator of obsidian sources. This is an excellent application for portable elemental analysis. Typically, zinc, rubidium, strontium, yttrium, zirconium, niobium, titanium, manganese, iron and barium are the key elements that distinguish obsidium sources.[6]

Glass

Like metals, glass can also be re-melted, thus the composition of glass cannot be absolutely tied to its origins. Elemental analysis can provide important indicators as to when, where and how the glass was made; especially in the use of various fluxes - which can be related to different geographical areas and historical periods. Identification of colorants, decolorants, opacifiers and fining agents further helps to define the object's provenance and authenticity. Knowledge of the elemental composition can also be applied to conservation of glasses and provide information on how objects should be stored and protected from deterioration.

Table 2

Photographic Process	Date Invented	Final Image Material	Binder	Support/Sub-bing	Image	Toner	Support
Salted Pepper Print	1834	Silver	None	Paper, Cotton Fiber	Ag	Au, Pt (rare)	Ca, Fe
Calotype	1840	Silver	None	Paper	Ag		Ca, Fe
Cyanotype	1842	Prussian Blue	None	Paper	Fe	None	Ca, Fe
Albumen	1850	Silver	Albumen	Paper, Cotton Fiber	Ag	Au	Ca, Fe
Collodion	1865	Silver	Collodion	Paper	Ag	Pt, Au	Ba, S
Platinotype	1873	Platinum	None	Paper	Pt	Hg	Ca, Fe
Gelatin Printed-Out Print	1874	Silver	Gelatin	Baryta Coated, Paper	Ag	S, Se, U, Au, Ni, Pb, Co, V, Fe	Ba, S, Ca, Fe
Satista	1913	Silver & Platinum	None	Paper	Ag, Pt	None	Ca, Fe
Palladiotype	1916	Pd	None	Paper	Pd	Hg	Ca, Fe
Resin Coated Silver Print	Mid 1900s	Ag	Gelatin	Paper, Polyeth-ylene	Ag	Se, S	Ti

Summary

The Bruker TRACER III-V incorporates X-ray tube and patented vacuum technologies to provide multi-elemental analysis Mg to U. The tube based technology eliminates the cumbersome regulations typically associated with isotopes. The vacuum technology was developed for NASA's Space Shuttle Program, and is jointly patented with NASA. This innovative solution enables low detection limits of light elemental analysis, for the first time in a Handheld, and does not require expensive gas consumables. Our PC-based analytical software allows current and voltage adjustments to optimize analytical results giving the user much more flexibility and better precision.

The TRACER III-V is ideal for analyzing ceramics, paintings, photos, glass, obsidians, bronzes & coppers alloys and much more. This versatile point-and-shoot XRF System provides quick and accurate results in-situ, as well as in a laboratory setting. From archeological digs to conservation laboratories, the TRACER III-V provides accurate analytical information to assist the conservator in their efforts. The TRACER III-V enables you to bring your laboratory to the gallery or the field.

References

[1] E.T. Hall, M.S. Banks and J.M. Stern Uses of X-ray Fluorescence Analysis in Archaeology Archaeometry 7 (1964) 84-89.

[2] Claudio Caneva, Marco Ferretti, XRF Spectrometers for Non-Destructive Investigations in Art and Archaeology: the Cost of Portability

[3] Lisha Deming Glinsman, The Application of X-Ray Fluorescence Spectroscopy To the Study of Museum Objects, Dissertation, November 16, 2004, pp. 80-91.

[4] Lisha Deming Glinsman, The Application of X-Ray Fluorescence Spectroscopy To the Study of Museum Objects, Dissertation, November 16, 2004, pp. 32.

[5] Robert J. Speakman et al. "Chemical Differentiation of Obsidian within the Newberry Volcanic Complex by Laser Ablation ICP-MS, INAA and XRF", Geological Society of America, Annual Meeting, October, 2002.

[6] G.Poupeau, "Obsidian Characterization and Obsidian Trade in Prehistorical Times: An Overview of Physico-chemical Methods," Natural Glasses Conference, France, August, 2002.

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