New Portable X-Ray Diffraction/X-Ray Fluorescence Instrument (XRD/XRF)

Introduction

The primary goal of most analyses of art objects is to identify the material composition of the object. This may lead to more information regarding the technical art history of the object and help guide the object's conservation.

As the result of a cooperative venture between the Science department of the Getty Conservation Institute (GCI) and InXitu, Inc., a portable, non-invasive XRD/XRF was designed and built to fill a gap in the quality of information obtainable from an art object without invasive sampling of the object.

Discussion

In the laboratories of the GCI (as in many museum laboratories today), handheld X-ray fluorescence (XRF) devices are used extensively. These devices can easily identify pigments and other materials by quickly showing their elemental composition.

There are limitations, however. Only elements heavier than potassium can be detected. This means, for example, that the most common salts that damage cultural heritage (e.g., carbonates, sulfates, and nitrates) cannot be identified using XRF. Often, the knowledge of which elements are present is not enough to identify the substance. Therefore, at the GCI we also use portable infrared and Raman spectroscopies, which successfully provide information on molecular composition. The drawback in their use is that the information obtained is only relative to the surface of the object. X-rays, on the other hand, are able to penetrate an object, according to the average absorption of its atoms.

X-ray diffraction (XRD) is a technique used to characterize the crystal composition, grain size, and preferred orientation in polycrystalline or powdered solid samples. XRD detects the molecular or mineralogical composition and can distinguish among various phases of a compound of a given chemical formula—for example, calcite, aragonite, and vaterite, which all have the same formula ($CaCO_3$). XRF analysis of the same sample would only show the presence of calcium. It is obvious that being able to combine the two techniques into one portable, non-invasive instrument is of great value in characterizing materials.

The non-invasive XRD/XRF developed by the Science department of the GCI and InXitu is able to collect both XRD and XRF data on the same spot of an object in a relatively short amount of time—as little as a few minutes for non-complex mixtures. It is portable and requires only three sturdy cases, each weighing less than thirty pounds.

Figure 1. The head of the instrument is positioned in front of a painting and is supported by a sturdy tripod. On the front, there is a control unit. The whole system can be shipped in the three pelican cases seen in the back.
Photo: G.Chiari.

We can see the image of what a CCD camera records in a two-dimensional plane. This image gives useful information on the size of the crystallites. For a very fine powder, the crystals are randomly distributed and the arcs of diffraction are continuous lines. If some large crystal is present, an intense spot is generated; this can be a nuisance to be removed by software in order to obtain intensities that better match the standards. On the other hand, the detection of large crystals is, in itself, valuable information.

From the CCD image, using the energy discriminating facility, the photons corresponding to copper radiation wavelength (the X-ray tube has a copper anti-catode) are integrated for XRD, while the others are used for XRF.

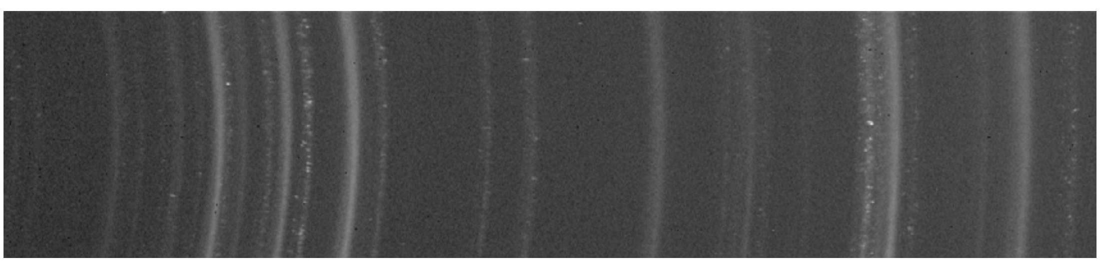

Figure 2. Image of the CCD detector. One can see the continuous diffraction lines, indicating that the crystals are very fine as randomly oriented. There are a few dotted lines, due to the presence of large crystals in a poorly crushed powder. The sample analyzed was a cadmium orange commercially manufactured color.

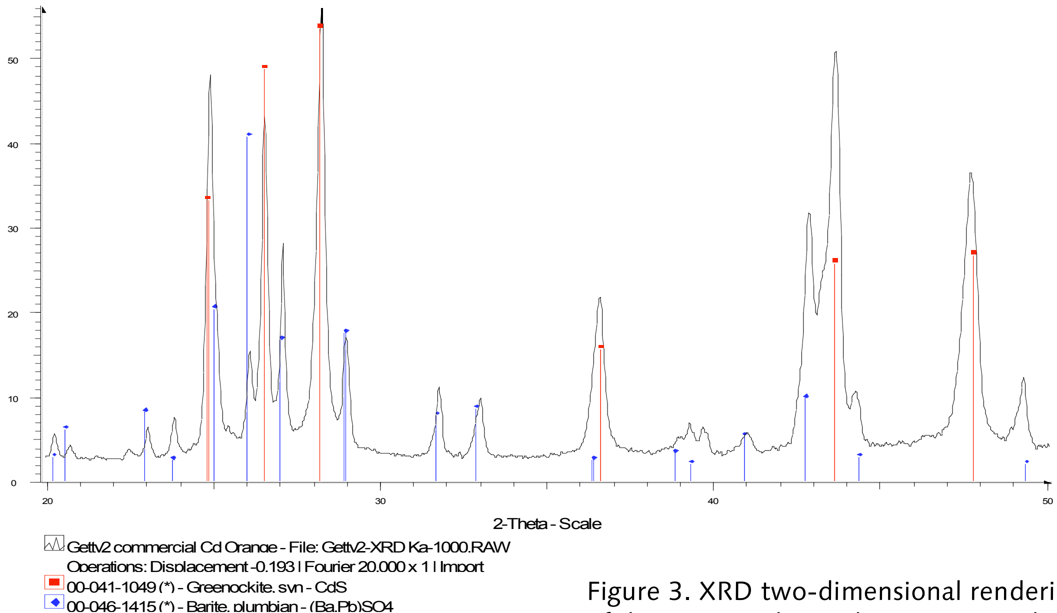

Figure 3. XRD two-dimensional rendering of the same analysis. The continuous lines are identified as cadmium sulfite and selenite (CdS /CdSe – in red), while the dotted lines are due to barite (barium sulfate – in blue), added as a filler.

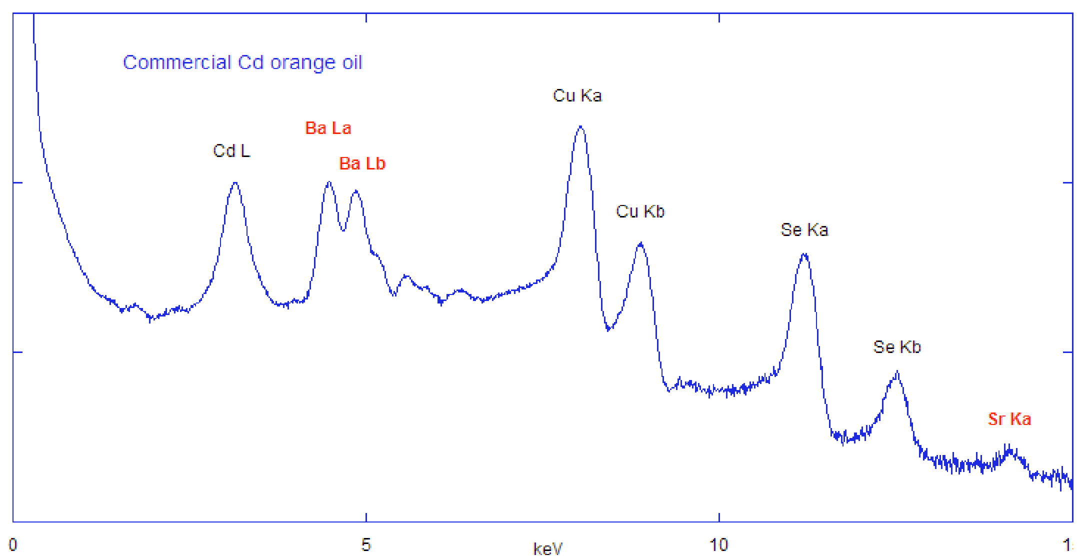

Figure 4. XRF pattern which shows cadmium, selenium and, unexpectedly, barium. The two lines of CuKα and CuKβ are due to the X-ray tube emission and are always present.

Conclusion

A portable XRD/XRF prototype was used in analyzing the Red Shroud Mummy that is part of the J. Paul Getty Museum collection. A final version of the instrument was used to analyze the painting *An Old Man in Military Costume* by Rembrandt van Rijn, also part of the Getty Museum collection. These preliminary applications, together with the results of other tests designed to validate the accuracy of the equipment, have demonstrated the accuracy of the results obtainable using this instrument.

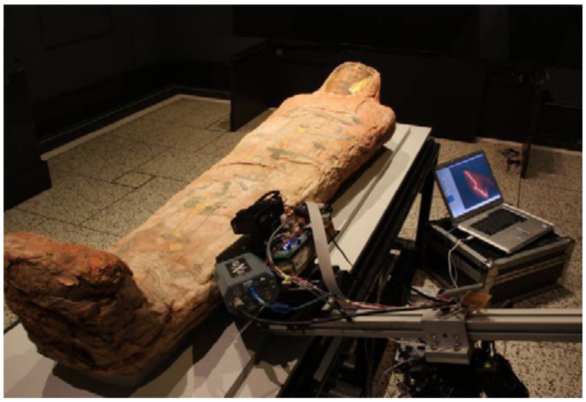

Figure 5. The XRD/XRF prototype, still to be fine-tuned, was used to analyze the pigments of the Red Shroud Mummy of the J. Paul Getty Museum's Antiquities 91.AP.6. Photo: G. Chiari.

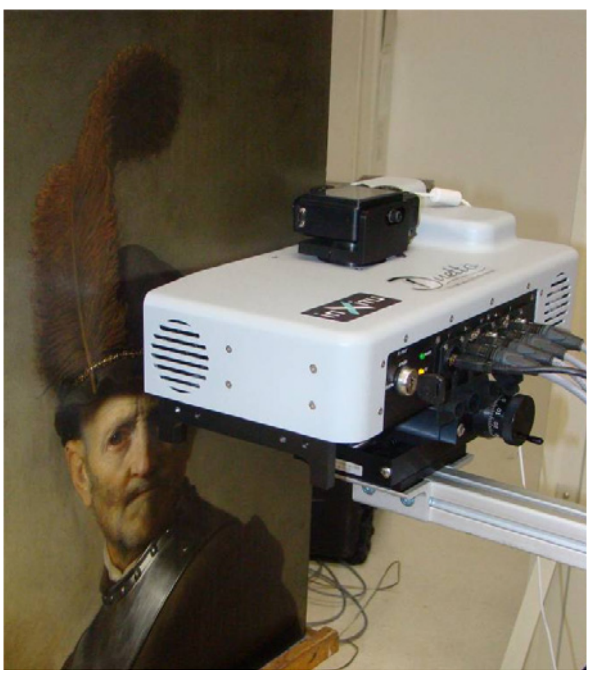

Figure 6. The instrument is ready to analyze the pigments of underpainting in the *An Old Man in Military Costume* by Rembrandt van Rijin, J. Paul Getty Museum 78.PB.246. Photo: G. Chiari.

This instrument is likely to radically change how analytical imaging is carried out, reducing the number of samples that are taken. Objects can be fully analyzed while preserving their complete integrity, provided that they are made of crystalline materials. The conservation science community will eventually have access to this much needed instrument when it becomes commercially available.

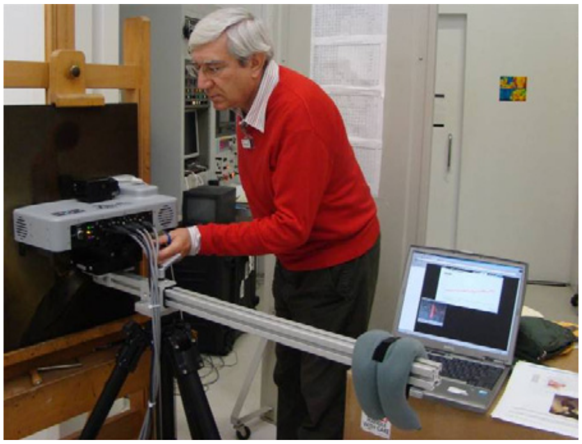

Figure 7. The distance between the instrument and the object must be exactly 2 mm. This is achieved using a fine tuned stage. The red laser line seen in the small window of the PC allows for positioning as precise as 20 μm in the focal plane. Photo: C. Namowicz.

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