

## A PORTABLE NON-INVASIVE XRD-XRF INSTRUMENT FOR THE STUDY OF ART OBJECTS.

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### ABSTRACT

A non-invasive XRD/XRF instrument for study of works of art has been developed jointly by the Getty Conservation Institute and inXitu Inc. (California). Many aspects of the instrument are based on technologies initially developed for NASA's planetary XRD/XRF instrument CheMin and used in inXitu's portable transmission XRD/XRF instrument (Terra). A new geometry was designed based on a reflection configuration to allow analyzing large flat objects such as mural paintings in a non-destructive way. The instrument uses a miniature X-ray tube and a CCD detector to collect both XRD and XRF signatures. All components are in fixed position relative to each other to guarantee a rugged stable geometry. The instrument also includes an imaging camera to collect high magnification images of the area analyzed and allow precise control of its positioning in the focusing plane. The instrument prototype was tested on a number of mockup samples and on art objects of the Getty collection.

### INTRODUCTION

For an analytical procedure to be considered non-invasive, it requires not only that no samples are taken from the object analyzed, but also that the object does not move from its normal location. This is particularly important in Conservation Science as transport of art objects to an analytical facility -even within the same premises- presents a risk of accidental damage. Therefore, portable instruments taken to the object are a highly favored choice. Portable instruments typically used include various models of handheld X-ray fluorescence (XRF) spectrometers that have become one of the major tools in diagnostics. However, these XRF spectrometers have limitations in that only elemental data are provided, with no information on the way elements are combined with one another. X-ray diffraction (XRD) is the most definitive technique for studying the phase composition of matter. Field deployable XRD instruments for such analyses have been reported<sup>1,2,3,4</sup> though these instruments offer limited portability. A rugged very compact instrument was jointly developed by the Getty Conservation Institute and inXitu, Inc. (California) to provide parallel XRD and XRF capabilities to assess the phase composition and the chemical composition of surface materials of works of art<sup>5,6,7,8</sup>. Many aspects of the instrument are based on technologies initially developed for NASA's planetary XRD/XRF instrument<sup>9</sup> on-board the Mars Science Laboratory rover and applied to inXitu's commercial portable XRD/XRF instrument Terra shown in Figure 1. The transmission geometry of this instrument being incompatible with the non-invasive nature required for the analysis of works of art, a new geometry was designed based on a reflection configuration.



*Figure 1: Portable XRD-XRF instrument Terra developed and marketed by inXitu Inc. Based on a transmission geometry, it requires insertion of crushed materials ( $<150\ \mu\text{m}$  grain size) in a vibrating sample cell<sup>10</sup>*

## INSTRUMENT LAYOUT

One of the primary specifications for the instrument was the possibility to analyze large flat surfaces such as mural paintings. Due to the surface irregularities of such objects and the desire to perform the analysis in a non contact way, the decision was taken to keep the diffraction plane 2mm away from the instrument front face. Achieving this requirement while maintaining the compact size of the instrument was a major effort in the conversion of the system from the existing transmission geometry. The general layout of the instrument is shown in Figure 2 and the X-ray geometry illustrated in Figure 3.

A small custom micro-focused X-ray source (Cu) is combined with miniature slits to produce a low divergence beam illuminating the sample at a  $10^\circ$  incidence angle. The slit sizes can be modified to optimize resolution / throughput compromise. A Nickel foil mounted on a solenoid motor can be placed at will in the direct beam to remove most of the  $K_\beta$  radiation of the X-ray spectrum and facilitate the interpretation of XRD data.

A custom CCD camera developed with Andor™ Technology collects the XRD signal over a range of  $20\text{-}50^\circ\ 2\theta$ . The low angle cut-off is substantially higher than that of the transmission instrument the system derives from ( $5\text{-}55^\circ\ 2\theta$  coverage).  $20^\circ\ 2\theta$  cut-off was chosen as a compromise between mechanical constraints and usable detection range. In spite of the fact that some substances like clay minerals have their most characteristic diffraction peaks at much lower angles,  $20\text{-}50^\circ\ 2\theta$  may be sufficient to identify them on the basis of their secondary peaks. For example palygorskite (principal line at  $2\theta=8.54^\circ\ 2\theta$ ) was the first candidate in an automatic search on a diffraction pattern limited to  $20\text{-}50^\circ\ 2\theta$ . Sections of diffraction rings are collected in 2D images. XRF data are obtained with the same Peltier cooled CCD exposed directly to the X-ray signal (no scintillator) and operated in single photon counting mode. All components are in fixed position relative to each other to guarantee a stable geometry and a rugged design for field applications.

The geometry was first tested using ray tracing simulations to compute XRD patterns and evaluate the performance of each particular design. The ray tracing code used for this work was

modified from a code developed for the refinement of the NASA Mars XRD/XRF instrument<sup>11</sup> and inXitu Terra instrument. This approach is particularly useful to accelerate the development of a prototype since specific configurations can be tested before any hardware has been built. The accuracy of the method was previously validated, and was once again verified in this development as shown in Figure 4 comparing the diffractogram computed with the ray tracing code with that of the equivalent experimental configuration.

The general performance specifications are listed in Table 1.

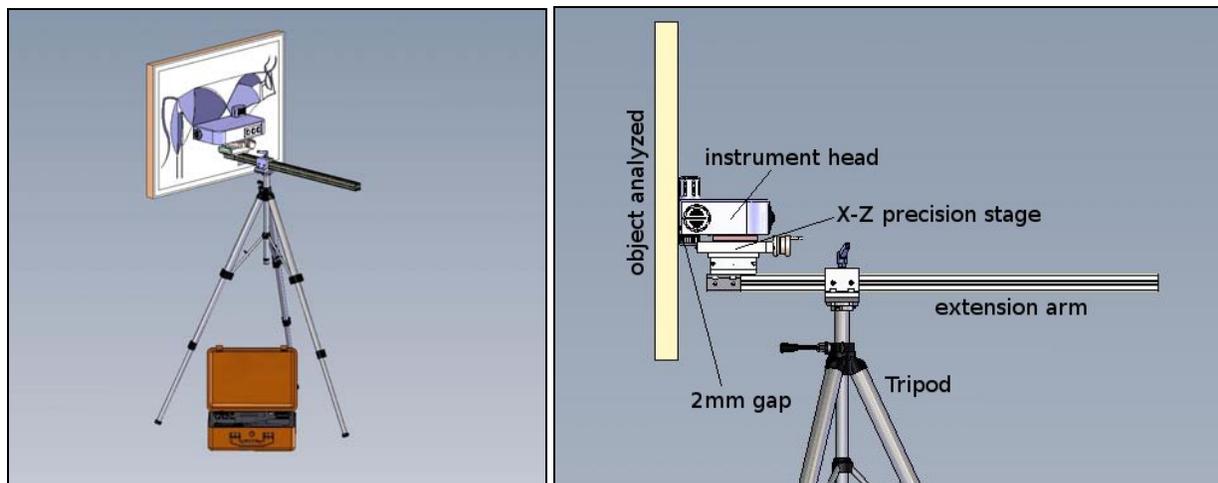


Figure 2. Schematic layout of the instrument. Main components are the instrument head (8kg), alignment stages, tripod with extension arm, and power/control unit (12kg).

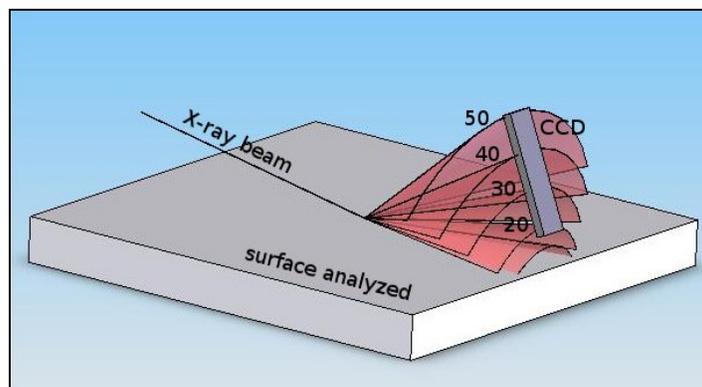


Figure 3. Schematic diagram of the instrument geometry: an X-ray beam illuminates a small spot (1x0.4 mm) on the sample surface at 10° incidence; a CCD collects the diffraction signal from 20 to 50° 2θ; symbolic diffraction cones are shown at various 2θ angles.

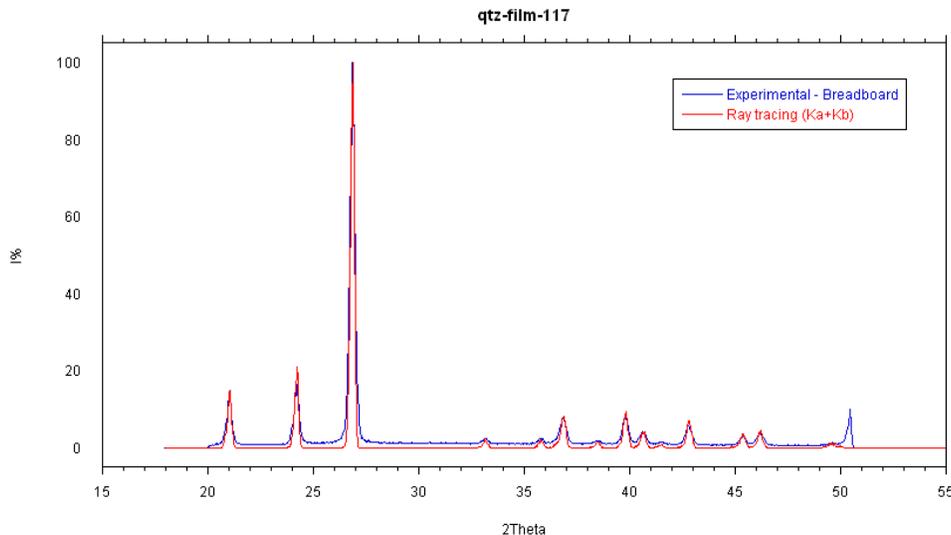


Figure 4. Comparison of ray tracing simulations and experimental data using a breadboard instrument, quartz,  $K_{\alpha}+K_{\beta}$  radiation.

Table 1. Specifications of the instrument

| Parameter         | values       | comments                      |
|-------------------|--------------|-------------------------------|
| XRD angular range | 20° - 50°    | Fixed CCD position            |
| XRD resolution    | 0.3°         | Controllable by slit settings |
| XRF resolution    | 250 - 300 eV |                               |
| XRF energy range  | 3 - 15 keV   |                               |
| X-ray source      | Cu           | 10 W in normal operation      |
| Kb filter         | Ni           | Removable foil filter         |
| translations      | X-Y-Z        | Manually controlled           |
| Position Control  | n/a          | digital camera + laser beam   |

In addition to XRD and XRF analyzes, the instrument can produce high-magnification color images of the area under investigation using an embedded high-resolution digital camera with macro adapter lens. A custom LED lighting system was implemented to allow controlling the sample illumination (normal or grazing) and reveal the topography of the sample.

The instrument is held in position in front of the sample using a sturdy photographic tripod fitted with an extension arm and precision translation stages. Due to the low incidence of the X-ray beam on the sample, accurate  $2\theta$  calibration of the XRD data requires a precise control of the distance from the surface analyzed. This positioning is made possible using a micro-focused laser embedded in the instrument head that produces a thin vertical line in images collected by the photographic camera. The low incidence of this laser beam results in a lateral shift in the laser trace on the sample depending on the sample-instrument distance. Proper positioning is obtained when the laser trace is in a predefined position in the digital camera images. This method allows for a positioning precision of better than 50  $\mu\text{m}$ . The laser is aligned in such way that it crosses the X-ray beam in the same spot in the focusing plane, as shown in Figure 5.



Figure 5. Left: Imaging camera fitted to the instrument. High magnification images collected on the surface of a phosphor screen with the alignment laser (center) and X-ray spot (right).

For improved flexibility in instrument deployment, the system is battery powered using a Li-ion batteries providing up to 4 hours of operation between charges. The power unit, shown in Figure 6, is built in a rugged case and weighs about 12 kg. The autonomy can be further increased by hot swapping batteries during operation. The instrument is controlled by an embedded computer inside the power unit. The instrument firmware controls the X-ray source and CCD detector, processes raw data to extract 2D diffraction patterns and XRF spectra. 1D XRD patterns are calculated by circumferential integration of the diffracted intensities along diffraction rings. The data is displayed in real time through an html based Graphic User Interface (GUI) accessible from any WiFi enabled device (laptop, handheld computer, smart phones etc). The GUI also provides control of the instrument settings, and allows for download of data for detailed analysis.



Figure 6. The portable reflection XRD/XRF instrument; Left: Early implementation of the prototype (no cover) positioned for analysis of a red shroud Fayum mummy from the Getty Museum; Right: Portable power unit of the instrument that includes Li-ion batteries, AC adapter, embedded computer, lighting controls, LCD for basic control, and WiFi communication for full remote control using any handheld or laptop computer through html interface

## FIRST RESULTS

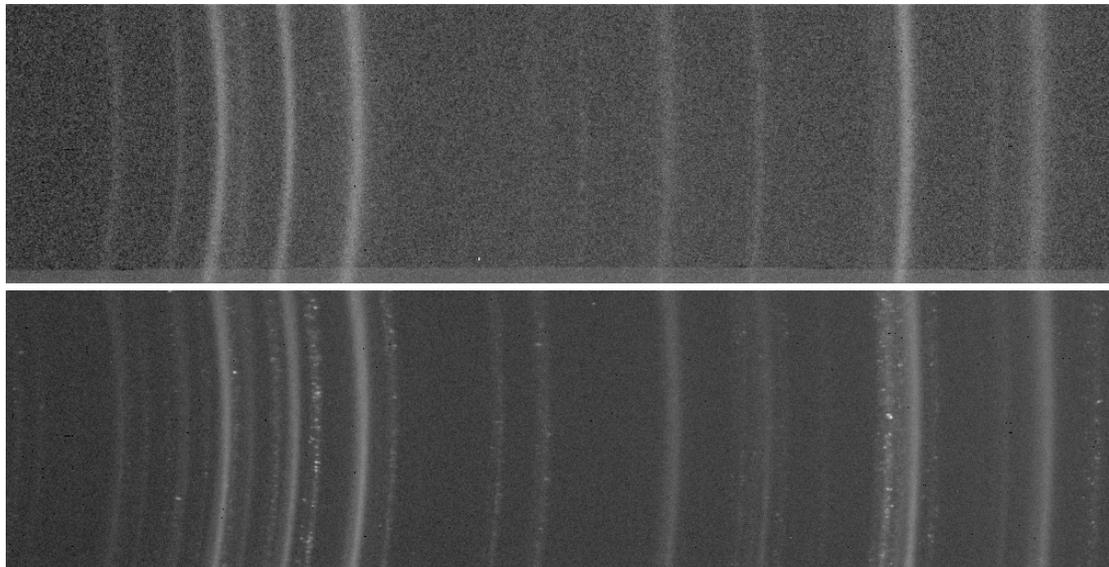
The potential of the instrument was tested using a number of prototypes at different stages of evolution. Tests were conducted in the laboratory using painted wooden samples.

One example shown in Figure 7 is the analyses of cadmium orange (chemically CdS doped with a small quantity of CdSe). The top pattern refers to the pure pigment while the lower pattern corresponds to a commercial product (Cadmium Orange in a tube for oil paint). In these data, it

can be easily seen that the lower pattern contains more diffraction rings, and that these additional rings are dotted. This indicates an additional phase in the commercial paint, characterized by coarser grains than the orange pigment. The 2-D data in Figure 7 was turned into a conventional 1-D diffractogram as shown in Figure 8, using either the instrument automatic conversion or a 3<sup>rd</sup> party application such as XRD2Dscan<sup>12</sup>. With this later application, the spatial integration can be made using the entire diffraction image or a user defined area of the image. Improved resolution can be obtained by limiting the integration area to a central sector. This corresponds to the use of a narrower slit. Additionally, bright diffraction spots produced by large grains in the sample (K $\alpha$  or other wavelength) can be masked. In Figure 8, the integration was made after different exposure time to evaluate the effect of short integration. It can be seen that even short integration times (5-10 minutes) produce interpretable XRD patterns. Statistics comparable to the output of conventional diffractometers require longer integration of a few hours.

The XRF data obtained with these cadmium orange samples are shown in Figure 10 that compares the instrument output to that of a commercial handheld XRF instrument (Bruker Tracer III). Comparable data are obtained; the major difference is the response at higher energy due to the limited excitation provided by a Cu tube compared to the Re tube used in the XRF device.

From the XRF data one can see that barium is present in the commercial oil paint but not in the pure pigment. From the XRD the barium can be better characterized as barite (BaSO<sub>4</sub>). The selenium peaks are clearly identifiable in the XRF. For comparison we reported the portion of spectrum common to X-DUETTO and the Bruker portable XRF instrument.



*Figure 7 - CdS pure pigment (top) and commercial Cadmium Orange (bottom).*

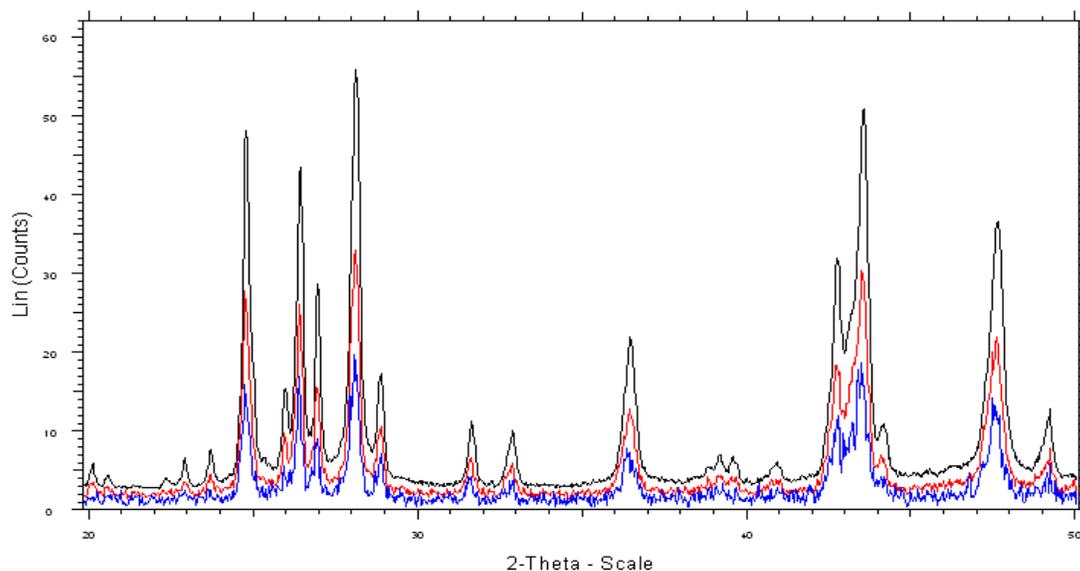


Figure 8. XRD patterns collected after 5 minutes, 50 minutes and 8.3 hours with a commercial Cadmium Orange paint. In spite of the lower peak/background ratio, the 5-minute pattern was interpretable, especially using the chemical information provided by XRF.

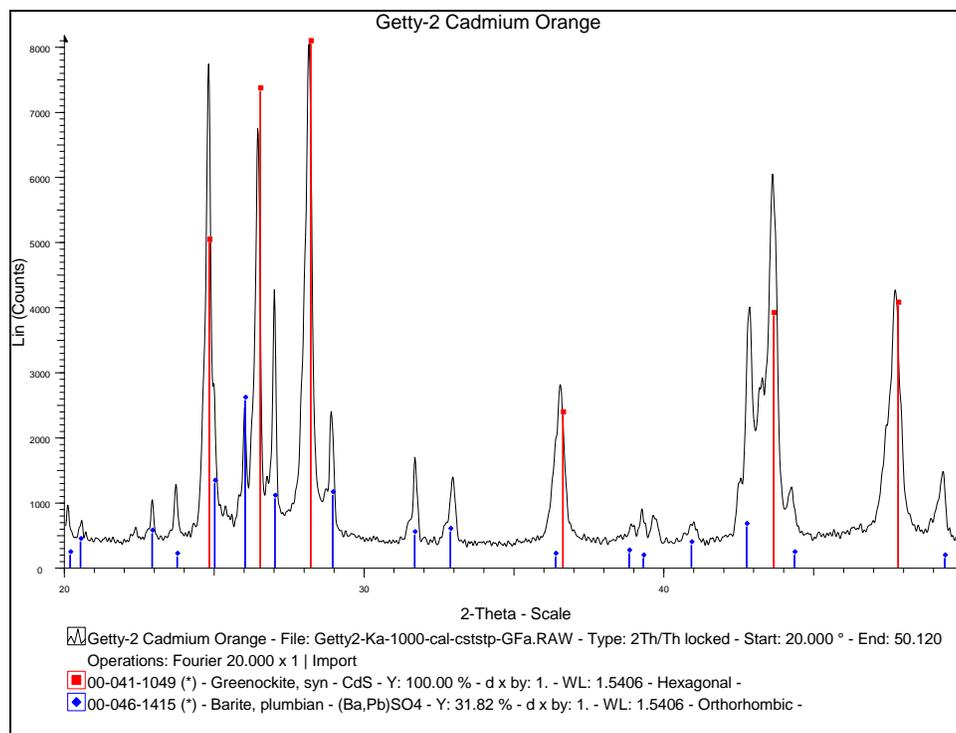


Figure 9. Interpreted XRD pattern of commercial Cadmium Orange (8.3 hours integration).

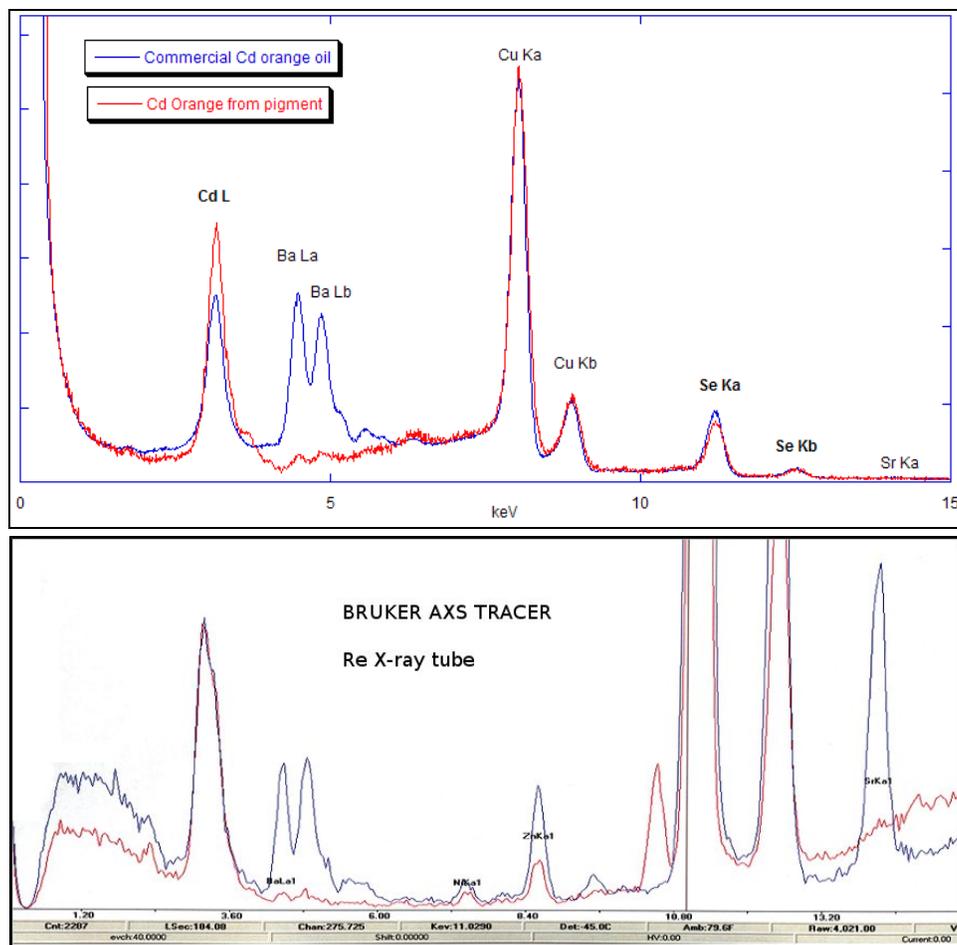


Figure 10. XRF patterns of Cadmium Orange and commercial paint as measured by X-DUETTO (top) compared to the results from a handheld XRF spectrometer (Bruker AXS).

Having XRF data on the same spot analyzed by XRD can be of great help for the interpretation of the XRD pattern. One such case was observed with the analysis of a green painted wood sample, which XRD and XRF data are shown in Figure 11 and Figure 12, respectively. The first analysis of the XRD data was done before looking at the XRF data. An automatic search showed the presence of chromite, a green chromium oxide, perfectly fitting the context of the analysis. Looking at the XRF data, though, one can see that Cr is not present, while Ti and Co are. Using the chemical information in the XRD search, the attribution of the same four peaks to the cobalt titanate green was correctly achieved. Cobalt titanate was indeed present in the sample as the main pigment of an under-layer. The green color of the top was Jenkins green, an organic derivative of Cu and Ni, which could not be identified by XRD. The presence of Ni in the XRF signature could merely suggest Jenkins green as a possible choice. This indicates that in special cases taking samples and using different techniques, although invasive, is still needed.

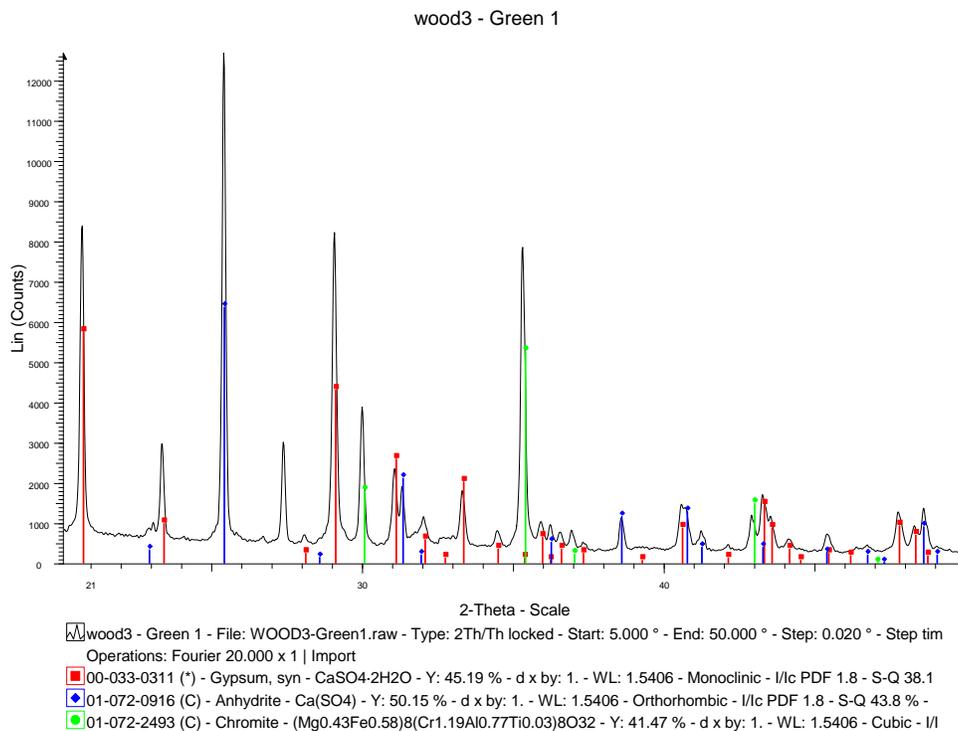


Figure 11. First interpretation of XRD data collected on a green painted wood sample.

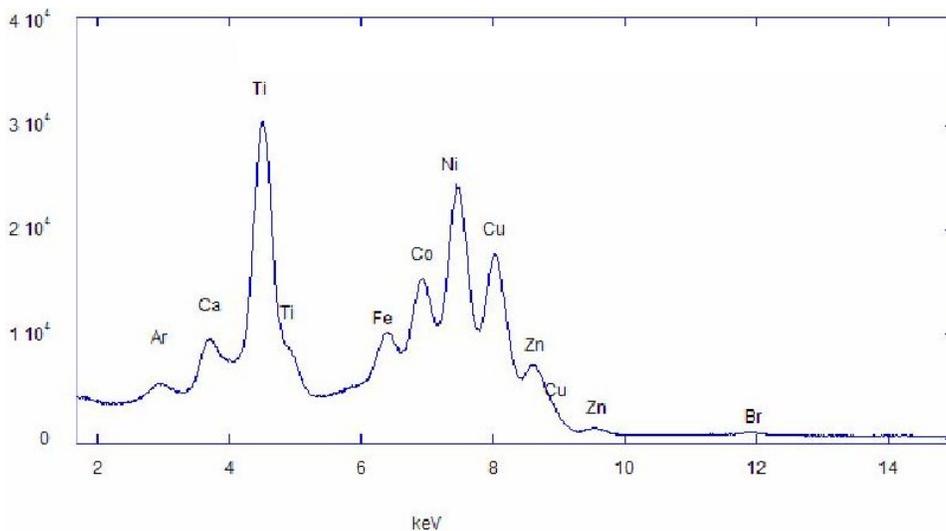


Figure 12. XRF data of a green painted wood sample

A number of art objects were also analyzed at the Getty Conservation Institute with an early prototype version of the instrument. Among these artifacts was a painting of Giovanni Boltraffio (1466-1516) from the Museum of fine Art of Budapest presently being restored at the Getty Museum (Marc Leonard), shown in Figure 13-left. The yellow used for the drapery (Figure 13-right) was analyzed using the instrument over a 50 min integration time. XRD and XRF results are presented in Figure 14 and Figure 15 respectively. Both techniques point at a Lead Tin oxide pigment. Note that the presence of lead in this and other paints analyzed resulted in lower diffraction intensities than previously experienced with the analysis of lead free pigments. While

presenting a limitation for fast analyses, this does not prevent the methods from providing useful data in reasonable integration times.



Figure 13. right: *Madonna and Child* by Giovanni Boltraffio's (Museum of Fine Arts, Budapest) – right: yellow area analyzed (photos Sarrazin).

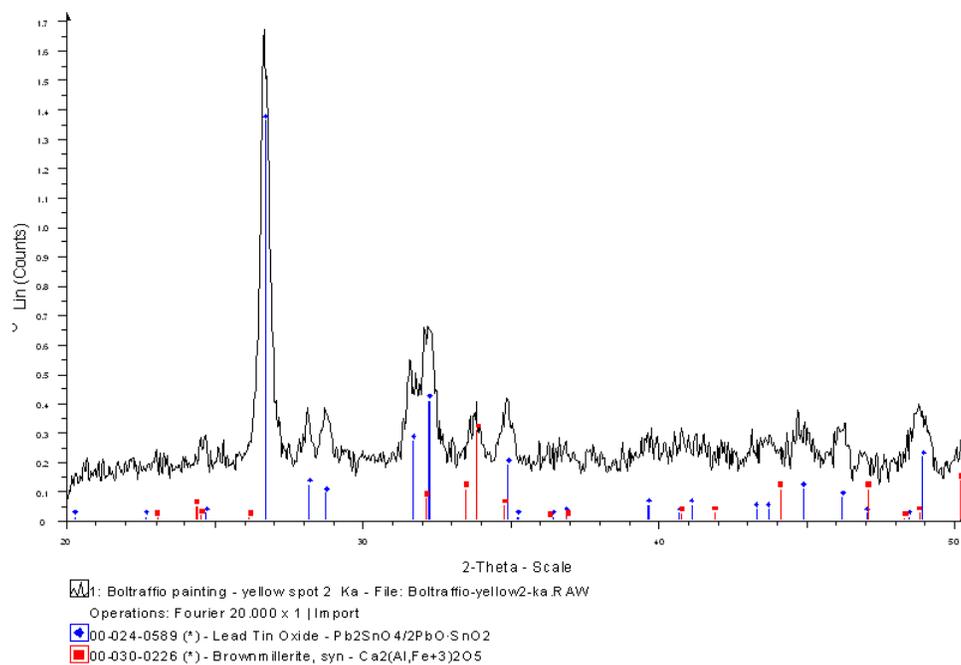


Figure 14. XRD data collected on Boltraffio's yellow – (50 min integration).

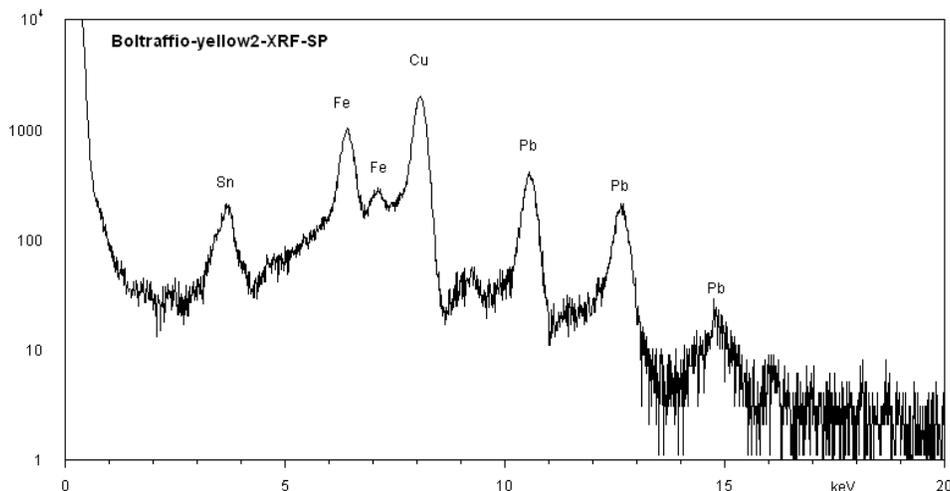


Figure 15. XRF spectrum of Boltraffio's yellow – (50 min integration).

## CONCLUSION

A new portable XRD-XRF instrument was developed for non-invasive analysis of works of art. The system will be used in museums and in the field to analyze surface materials of art objects and help to further limit the need to take samples. While the instrument  $2\theta$  resolution is lower than that of a typical laboratory instruments, it is sufficient for accurate identification of phases even in complex mineralogical assemblages. The instrument throughput allows analysis as short as a few minutes for simple well-diffracting materials, and up to several hours for complex materials. The primary limitation of the system is the limited clearance relative to the focusing plane (2mm) that restricts the application to flat and convex surfaces. Another limitation of the system, inherent to the powder diffraction method, is the limit to finely grained materials to meet particle statistics requirements. When the object can be sampled, a sample holder can be fitted to X-DUETTO to analyze ground materials in a similar way as with laboratory diffractometers, but on the site and combining XRD and XRF measurements. Analyzing prepared samples will improve quantitative XRD results and allow natively coarse grained materials to be analyzed.

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