

## PORTABLE NON-INVASIVE XRD/XRF INSTRUMENT: A NEW WAY OF LOOKING AT OBJECTS SURFACE

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### ABSTRACT

*An analytical procedure, in order to be considered non-invasive, not only requires that no sample would be taken from the object analyzed, but also that the object does not move. In fact, if one needs to transport the object to the instrument, there is always a risk of accidentally damaging it. Insurance companies understand that risk well and charge high fees. Therefore, portable instruments, which are taken to the object, are a highly favored choice. Typical instruments include various models of portable XRF that have become one of the major tools in diagnostics. However, XRF has the drawback of not giving information on the way elements are combined with one another. For this reason the advent of an instrument that simultaneously performs X-ray diffraction and fluorescence may be of great help.*

*This was obtained with a custom miniature instrument combining a microfocus X-ray tube and a CCD camera with energy dispersive capabilities to collect simultaneous XRD and XRF data. Precise alignment of the instrument on the sample is obtained with a video camera and laser beam. The active components of the instrument are confined in an instrument head approximately 400x200x80 mm. This "probe" is held in place, without touching the object, by a robust stand and connected via cables to a power-supply and control unit. Proprietary software extracts 2D XRD data using pixels having the energy of the CuK $\alpha$ , and the data is integrated into a conventional 1D diffractogram. XRF data is obtained from the energy histogram of the frames collected by the CCD. Tests have shown that usable XRD patterns can be obtained in as little as 5-10 minutes with a resolution approaching that of a laboratory diffractometer. The design of the instrument will be presented, together with results from Cultural Heritage objects of various kinds.*

“Non-invasive portable” analytical techniques (NIP) have had a large impact on the conservation science field in recent years. The importance of these techniques goes well beyond strictly technical aspects. In a profound way, these techniques have altered and continue to alter our way of thinking about how we can best analyze art objects. In fact, the ability to get valuable information without altering or having to move the object makes it possible to analyze larger sections, ultimately obtaining a more thorough description. Another very important change in operations is the fact that with NIP one can obtain results almost in real time. As a consequence, the relationship between conservation scientists and their “partners” - conservators, museum curators, art historians, site managers etc. - has also been altered.

In fact, the questions posed to the conservation scientist by his or her partners can be often answered while the whole team is present and actively discussing the object. This allows for new brainstorming to take place which include the results just obtained. It is not just a matter of reducing the time of operation: it really allows for obtaining results that were not possible before the advent of NIP.

Not so long ago, the need to maintain an art object absolutely intact was given little consideration. This attitude was basically shared by both conservation scientists and their "partners". Taking samples was not a big issue.

Fortunately in recent years attitudes towards maintaining the integrity of an art object (including archaeological and architectural sites) have changed dramatically. Preventive conservation and meticulous care of art objects are the rules of the day. Museums devote great effort in the handling and storage of the objects in their collections. But, perhaps, the pendulum has swung too far in the other direction. Nowadays taking a sample is a big issue.

Many people define as "destructive" any analysis that requires taking a sample, regardless of how small a sample is. In fact, "non-destructive" is the term used for all those analyses that do not require taking samples. We would like to question the validity of both of those terms.

In recent years the conservation field has experienced a revolution in equipment comparable only to the transition from the mainframe to the personal computer in the late '70 early '80's. Much of the "bench" lab equipment is now produced in a miniaturized portable version which is often even more powerful. The most typical and diffused example of this is X-Ray fluorescence (XRF). Let's see how having a powerful portable XRF has changed the way of working in the field and the way conservation scientists and "partners" interact.

XRF opens one more window for our observation capacities. Operated in a portable way on the whole object (without preparation), it gives us the elemental composition (at least in part) of the surface of the spot we are looking at. But, it does not give quantitative results (although often we forget this fact). It does not give an idea of the distribution on the surface of the chemical composition unless, in the rare case, a very large number of point analyses are done. XRF does not give an idea of the stratigraphy, or what it is going on underneath the surface. It does not give information on how the elements are combined to form molecules and crystals.

With such a series of drawbacks it would seem that such a technique would have little to add in helping conservation scientists in their work. On the contrary, it represents a real revolution in the field for two reasons: 1) It is "non-invasive" (no sample needed). 2) It has become portable (the machine goes to the objects and not vice versa).

The amount and quality of the data gathered is not optimal, as we have seen, but the expertise of the operator, together with observations coming from other sources can often provide valuable information. There are still dubious cases. Just consider as an example the ambiguity presented by finding lead: it may mean lead white ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), minium ( $\text{Pb}_3\text{O}_4$ ), a combination of these two, litharge ( $\text{PbO}$ ), plattnerite ( $\text{PbO}_2$ ), an alteration ...

Most of the drawbacks of XRF could be avoided by using an instrument that could perform X-ray diffraction (XRD) and XRF simultaneously.

Such NIP instrument is being designed by the authors and developed by inXitu, Inc. (California) It is called X-DUETTO for its capability to combine X-Ray diffraction with X-Ray fluorescence on the same spot (documented with high definition by a digital camera which also helps to adjust the focusing plane). In a reasonable time (5-10 minutes) a rough, but interpretable pattern, can be obtained. In order to get a better pattern, comparable to a

benchtop diffractometer, at least one hour of measurement is needed. Obviously, having the XRF data on the same spot helps tremendously in the interpretation of the XRD, especially for very quick analyses that are necessarily of limited statistics. It is always a good strategy not to rely on one type of analysis only.

Figure 1a and b show the assemblage of the instrument head on a sturdy tripod, with the possibility to fine-tune its position by acting on an X-Y-Z device after having roughly adjusted the instrument in front of the object.



*Figure 1a and 1b. Two views of the positioning of the XRD/XRF in front of a painting.*

The positioning of the instrument is critical. The internal geometry allows for a tolerance of 0.02 mm for focusing, which can be reached with an embedded laser and camera alignment system. The micro movements of the Z axis are sensitive enough to permit this adjustment with relative ease. Obviously, since the goal is to measure objects of various sorts without sampling, the coarse texture of some surfaces may degrade the XRD resolution.

The principle of the instrument relies on the use of a small X-ray sensitive CCD detector directly exposed to the X-rays (no phosphor is used). Proprietary software allows extraction of XRD and XRF signal and construction of 2D diffraction patterns.

Figure 2 shows an example of application of the instrument to the analysis of Cadmium Orange (chemically CdS doped with a small quantity of CdSe), using an early prototype of the system. The top pattern refers to the pure pigment while the lower pattern refers to a commercial product (Cadmium Orange in a tube for oil paint). It can be easily seen that more lines are present in the lower pattern, and that the substance in question has coarse grains as showed by the dotted diffraction rings.

In addition to the 2D data of Figure 2 (bottom), a real-time processing performed in the instrument allows integration into a conventional 1D diffractogram as shown in Figure 3a. Using commercial software adapted to this particular instrument (XRD2DScan), the 2D data can also be processed with manual controls to select the area of integration or remove undesired bright spots produced by very large grains in the sample. These manual controls can improve the resolution of the pattern, at the expense of intensity.

In Figure 3a the patterns collected after 5 minutes, 50 minutes and 8.3 hours are shown. In spite of a low signal/noise ratio, the 5 minutes pattern turned out to be interpretable.

In addition to the XRD analysis, an energy dispersive analysis of the signal collected by the CCD is done in parallel and results in the XRF spectra shown in Figure 3b.

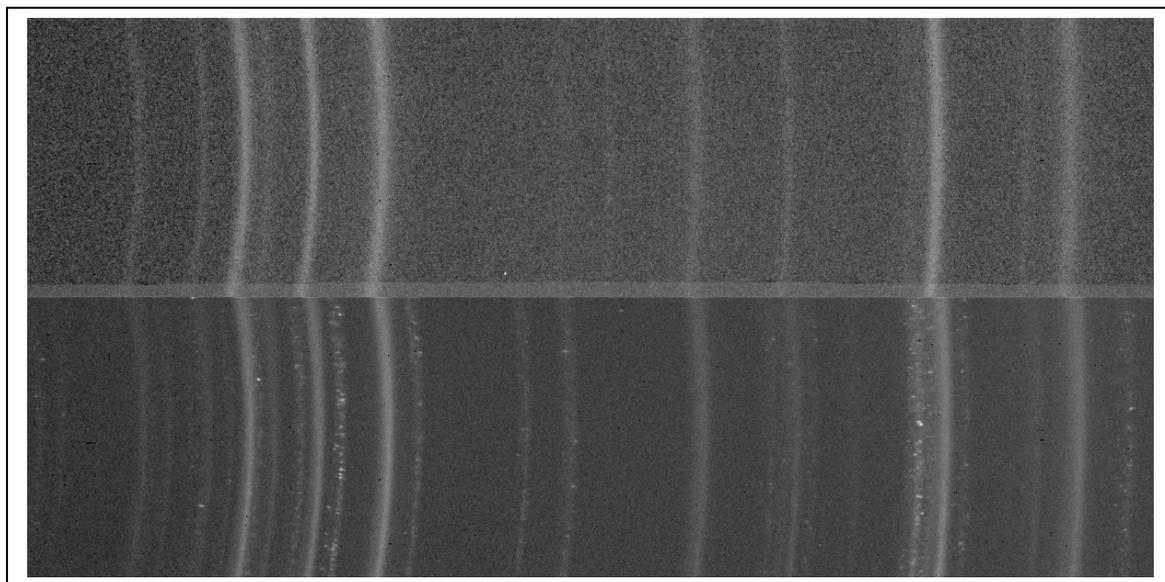


Figure 2. CdS pure pigment (top) and commercial Cadmium Orange (bottom).

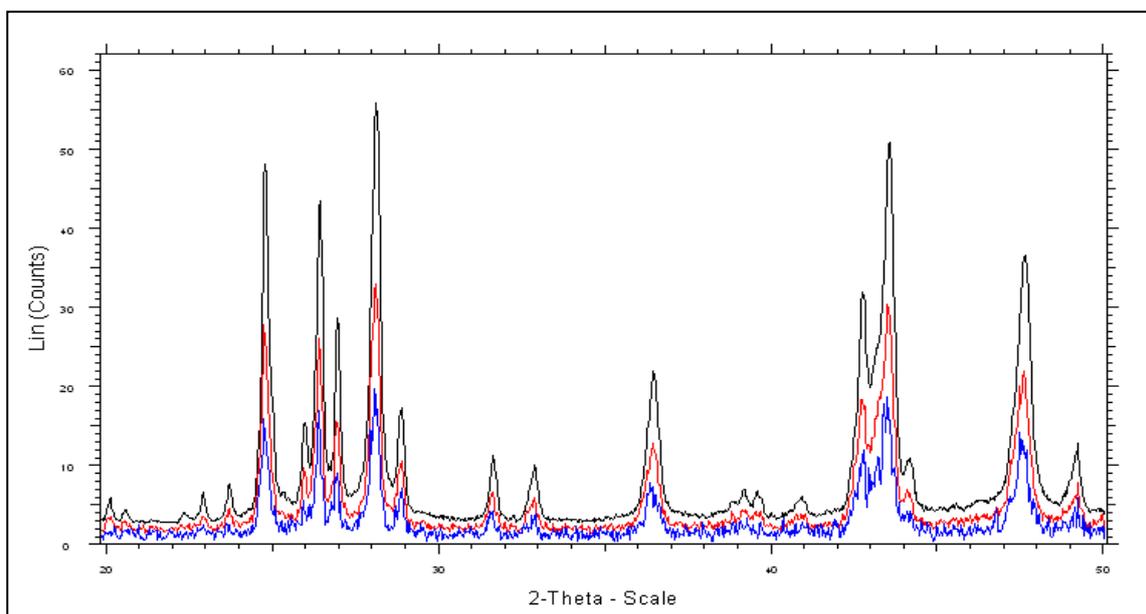


Figure 3a. XRD patterns of commercial Cadmium Orange at 5, 50 minutes and 8.3 hours exposure.

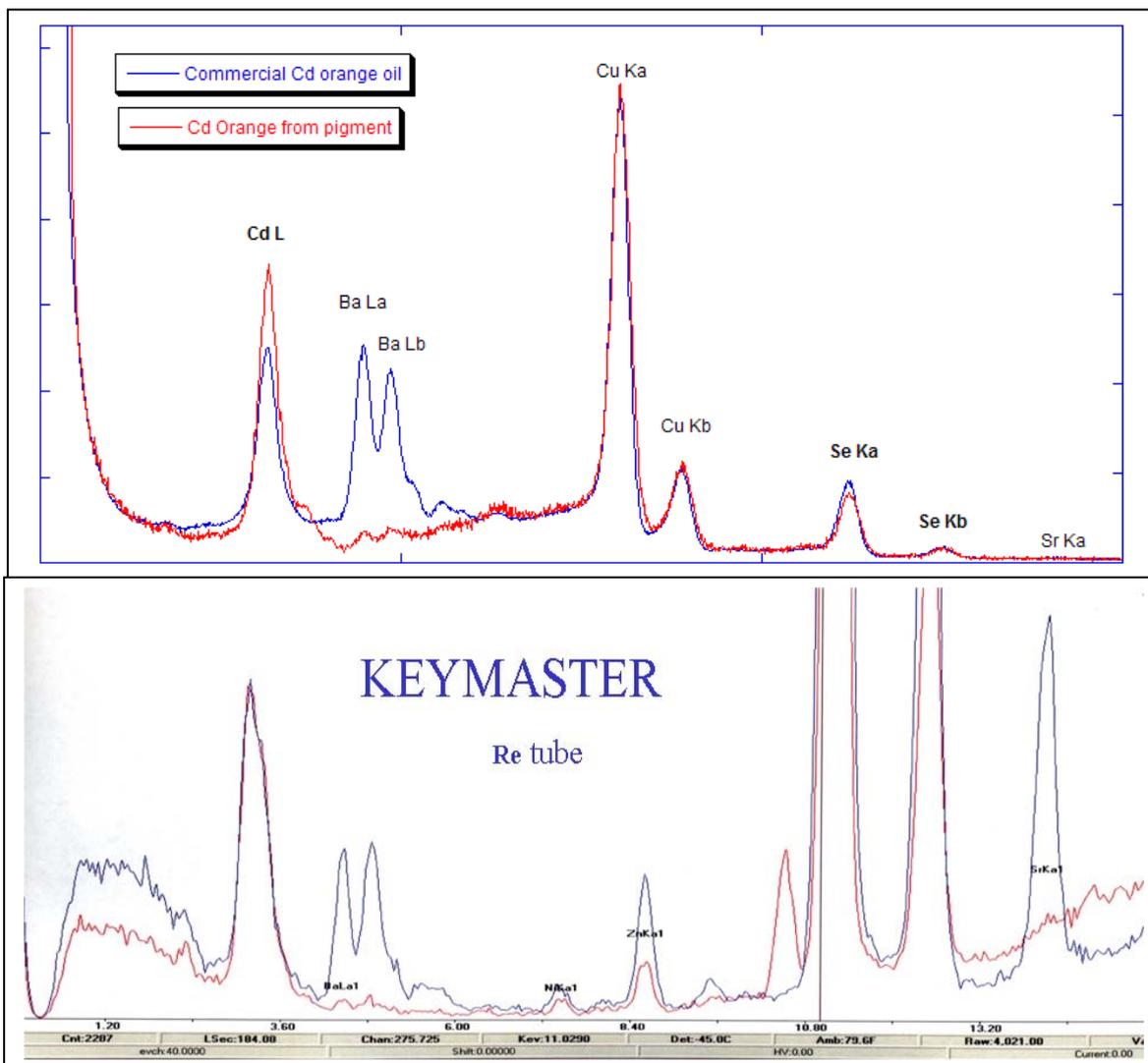


Figure 3b. XRF patterns of Cadmium Orange and commercial product as measured by X-DUETTO and a specialized portable XRF (Bruker).

From the XRF data one can see that the commercial oil paint contains Barium that is not present in the pure pigment. From the XRD the barium can be better characterized as barite ( $\text{BaSO}_4$ ). The selenium peaks are clearly identifiable in the XRF. For comparison we report the portion of spectrum common to X-DUETTO and one of a commonly utilized portable XRF. X-DUETTO is limited in energy range due to the 30kV Copper tube that cannot excite the K lines of heavy elements and the spectral sensitivity of the CCD detector limited to 3-25keV. Nevertheless the information that can be extracted from this XRF data is valuable, and corresponds exactly to the spot on which the XRD is carried out.

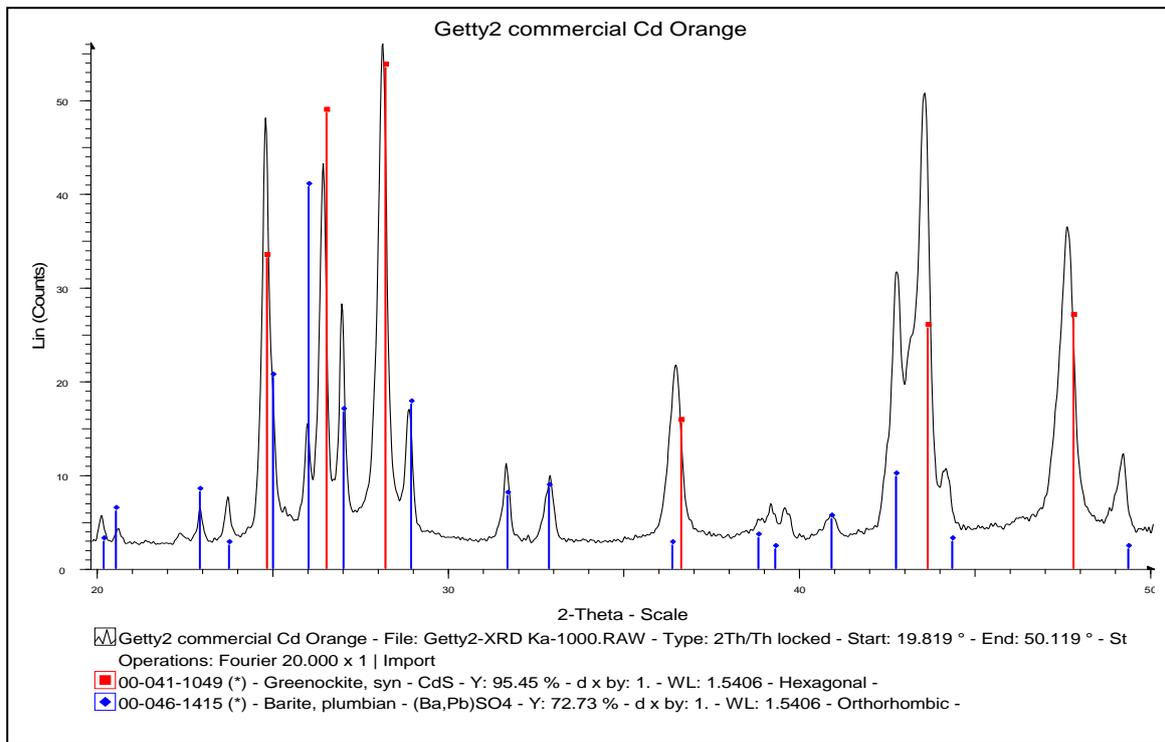


Figure 4. The interpreted XRD pattern for the commercial Cd orange.  
 In the automatic search the first two candidates were the correct ones.

The XRD performance of the system has some limitation compared to typical XRD instruments.

The  $2\theta$  range is limited to 20-50°. These limits are driven by the incidence of the beam (10°) and the size of the CCD camera. This higher than usual start angle can be a problem for substances like clay minerals that have their most characteristic lines at low angles. We analyzed palygorskite (principal line at  $2\theta=8.54$ ) and it was identified as the first candidate despite the absence of this main line.

As mentioned earlier, the positioning of the head with respect to the object is critical. Substantial positioning error result in XRD line shifts that in most cases may not allow for the identification of the material. The addition of an internal standard, such as fine silicon powder on the surface to be analyzed, would permit to correct this error by software. These grains of silicon, which do not adhere to the surface, can easily be brushed away after the data collection. Another limitation of the system is the low penetration of X-rays which may not reach deeper layers.

In conclusion, we believe that this new instrument will help to further limit the need to take samples. We will still need samples when the characteristics of the object itself require them. Stratigraphy studies presently require obtaining thin/cross sections. Immunological techniques based on antibodies reactions used to identify painting media need nanograms of material. In a few other cases, mostly concerned with quantitative data (provenance or dating), samples would always be needed.

Also we cannot expect that a small portable instrument would give the same results as the well calibrated bench instruments. Therefore these data should always be considered for what they are: a very valuable way of getting valid information in short time without having to move the object and without damaging it in any way. One should be ready to accept to take a few miniaturized and selected samples in order to answer those questions that these in-situ NIP techniques cannot resolve.