NON-DESTRUCTIVE MICRO-ANALYSIS OF ART AND ARCHAEOLOGICAL OBJECTS USING MICRO-XRF

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Abstract

The technique of micro X-ray fluorescence provides a fast, non-destructive analytical method for the analysis of elemental composition in a wide range of samples, with microscopic spatial resolution. Within archaeometry this technique is used to characterise a wide range of materials. A number of applications in this field are presented in this overview article, demonstrating the power of this technique for archaeologists and museum scientists.

Összefoglalás

A mikro-Röntgen fluoreszcens vizsgálati technika változatos anyagú műtárgyak vizsgálatát teszi lehetővé, gyorsan, roncsolás nélkül és mikroszkópi méretű felbontásban. Ezt a technikát az archeometria számos területén alkalmazzák. A tanulmány áttekintést nyújt erről a vizsgálati technikáról, gyakorlati példákkal, elsősorban régészek és múzeumi szakemberek részére.

KEYWORDS: X-RAY FLUORESCENCE, MICRO-XRF, ELEMENTAL, ANALYSIS, MICRO-ANALYSIS, NON-DESTRUCTIVE, PAINTING, PEARLS, GANGI-DAMA

KULCSSZAVAK: RÖNTGEN-FLUORESZCENCIA, MIKRO-XRF, ELEMÖSSZETÉTEL VIZSGÁLAT, MIKROANALÍZIS, RONCSOLÁSMENTES VIZSGÁLAT, FESTMÉNY, GYÖNGY, GANGI-DAMA

Introduction

X-ray fluorescence (XRF) is a widely used technique for both qualitative and quantitative elemental analysis of solids, powders and liquids (Jenkins 1932). It offers fast identification of most elements in the periodic table (typically covering the range ^{11}Na to ^{92}U), based on detection of fluorescence X-rays emitted from the sample after X-ray excitation. However, traditionally it is a macro technique and typically requires large volumes of sample and destructive sample preparation; for example, grinding and pressing into a powder pellet, or fusing with inert materials to form a glass bead. The incident X-rays can penetrate many micrometers/millimetres into the sample (depending on the precise composition). The depth from which the XRF signal is detected also depends on the sample's composition. In the case of low or medium atomic number elements the characteristic XRF X-rays emerge from a shallow surface layer of the sample – typically in the order of a few tens of micrometers or less.

The benefits of XRF include fast analysis (with measurement times of tens of seconds through to a few minutes), suitability for major and trace element analysis (% and ppm levels), and excellent quantitative capabilities. Whilst in many scientific fields the benefits which XRF provides outweighs the time consuming and destructive preparation techniques which are its major drawbacks, for museum scientists and archaeologists this is not the case. By their very nature the samples are valuable and historic, therefore non-destructive analytical methods are preferred. Additionally the area of interest is very often not of the macro scale. Scientific study of artefacts usually requires detailed analysis of individual sections/parts, and thus the capability for microscopic visualiation and analysis.

In recent years the development of high performance XRF microscopes has revolutionised the capabilities of this useful technique. Glass optics allow the creation of microscopic X-ray beams, with diameters ranging from several millimeters down to 10 micrometers (Rindby et al. 1999). Hence it is now possible to analyse individual particles or features on the microscopic scale. Furthermore, by scanning the sample underneath the X-ray beam element images can be created which show the distribution of elements across the sample (Hosokawa et al. 1997). Modern bench top systems retain the benefits of bulk XRF, but combine them with microscopy – most importantly, sample preparation is not always necessary. In such instruments, the area of interest is simply located using optical cameras integrated within the system, and the measurement is then started.

Micro-XRF can be compared with other X-ray analytical techniques, for example, SEM/EDX (X-ray analysis on a scanning electron microscope) (Goldstein et al. 2003). They both offer elemental analysis with high spatial resolution based on the detection of characteristic X-rays from the sample. The excitation method differs for each technique - X-rays for micro-XRF and an electron beam for SEM/EDX. The majority of SEM/EDX systems

require samples to be analysed in a high vacuum, a condition which is not always compatible with priceless historical objects. Furthermore, such objects are often too large for the small chambers found in typical SEM/EDX systems – in comparison, typical micro-XRF systems offer considerably larger sample chambers, allowing samples with centimeter and meter dimensions to be accommodated.

Despite being a new and emerging technique there are numerous examples of micro-XRF providing museum scientists with valuable information regarding their objects. Such composition data allows them to understand the processes and materials used during creation of the artefact, which in turn means that the most appropriate conservation methods can be selected. Other areas which benefit from the technique include corrosion identification, valuation and authenticity, and internal structure analysis (using simultaneous transmission X-ray imaging).

This article offers an overview of typical results obtained using bench top micro-XRF systems for archaeometric purposes, and should not be considered exhaustive in its content. Other reviews of the micro-XRF technique provide additional examples both for archaeometry and many other varied fields (Janssens et al. 1999).

Painting

The famous painting "Le Jardin de Daubigny" by Vincent van Gogh exists in two forms (**Figure 1**), which are normally displayed in museums in

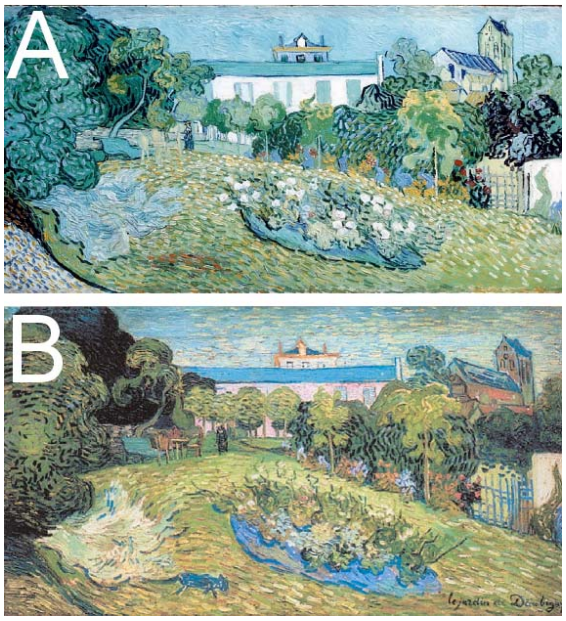

Figure 1: "Le Jardin de Daubigny" at (A) Hiroshima, and (B) Basel.

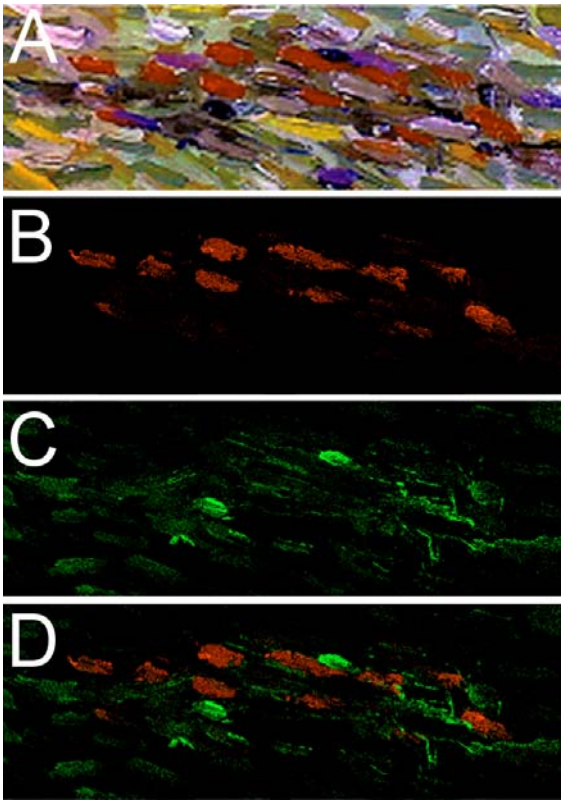

Figure 2: images of "black cat" region of "Le Jardin de Daubigny": (A) optical image, (B) iron, (C) chromium, (D) overlaid iron and chromium.

Hiroshima (Japan) and Basel (Switzerland). In the Basel painting there is a small black cat which is not visible in the Hiroshima version. Interestingly, a past photograph of the Hiroshima "Le Jardin de Daubigny" clearly shows the presence of the black cat in this version too, suggesting it has been painted over at some point after its creation. In recent work micro-XRF was used to investigate this change in picture composition (Shimoyama 2009).

The portion of the Hiroshima painting where the black cat was thought to be originally was analyzed by XRF mapping. On the canvas there are many paints which have characteristic elements, allowing them to be quickly distinguished. Using 10 μm spatial resolution the distribution of specific pigments could be followed across the painting.

The resulting image of chromium (**Figure 2**) shows the head, neck, forefoot and tail of the cat, whilst the strong brown paint which covers the original cat is linked to iron. The overlaid image of chromium and iron distribution clearly illustrates these two paints – close inspection shows that chromium and low concentrations of iron co-exist in the black cat regions, leading to the supposition that the black cat was originally painted using a mixture of chrome yellow (chromium) and Prussian blue (iron).

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Figure 3: extract from the Nepalese manuscript page – the red box highlights the analysis region.

Manuscript

An ancient Nepalese manuscript containing a coloured illustration of Amida (or Amitābha), a celestial buddha described in the Mahāyāna school of Buddhism was analysed. This sample, provided by courtesy of the Classical Manuscripts Digital Archive Study Center (Ryukoku University Library, Japan), was investigated to understand the pigments used within the illustration (**Figure 3**). Due to the penetrating nature of hard X-rays it is possible to probe not only the topmost layer of visible pigments, but also those which have been used for undercoating.

A mapping experiment over the 70 mm x 70 mm area with a 100 µm X-ray beam diameter quickly identifies the main elements used in the pigments. **Figure 4** illustrates the resulting XRF mapped images.

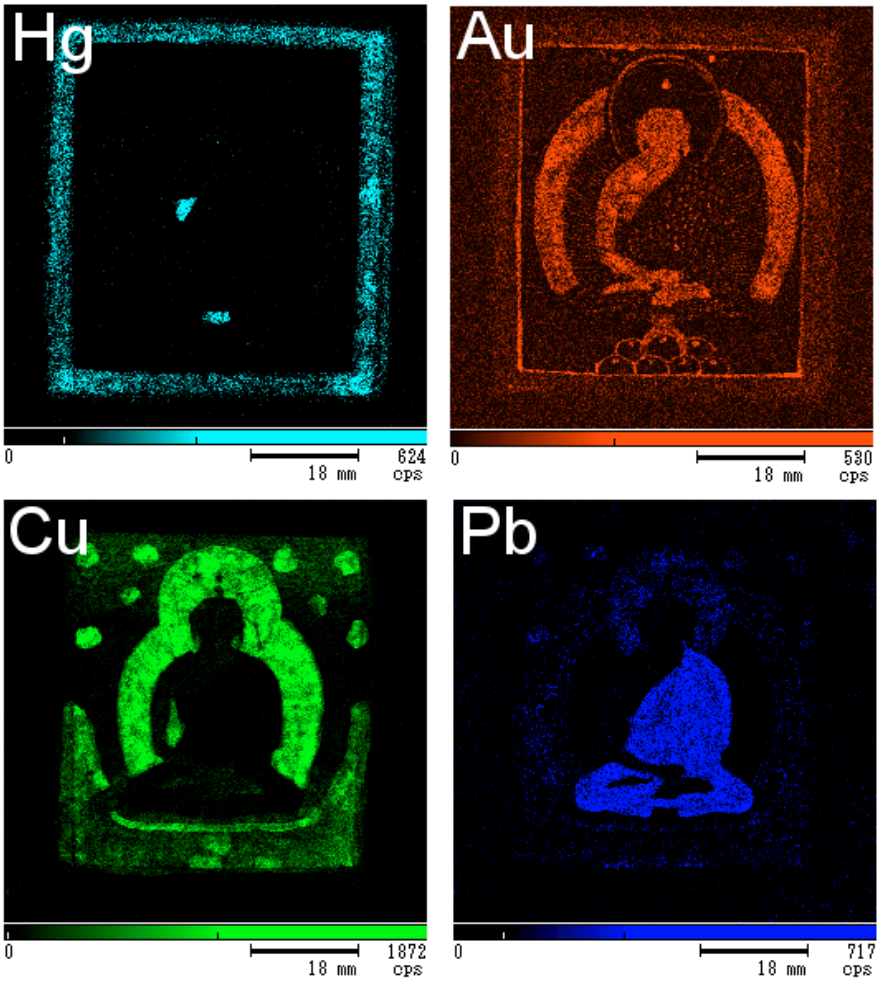

Figure 4: XRF mapped images showing the intensities of mercury (Hg), lead (Pb), gold (Au) and copper (Cu)

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Table 1: Assignment of pigments identified. Number regions are illustrated in *Figure 5*.

Analysis Points		Colour	Elements	Assignment
1	Undercoat	Yellow	Pb, Cr	Chrome Yellow ($PbCrO_4$)
2	Frame	Red	Hg	Vermilion (HgS)
3	Surplice	Orange	Pb	Diachylon (Pb_3O_4)
4	Skin	Gold	Au	Gold leaf
5	Leaf	Green	Cu	Carbonate ($CuCO_3/Cu(OH)_2$)
6	Halo	Blue	Cu	Basic copper ($2CuCO_3/Cu(OH)_2$)
7	Petal	White/Pink	Ca, Mg, Si, Pb, Cr, Cu	Mixture of CaO, $CaCO_3$ and $Mg_3(Si_4O_{10})(OH)_2$ with chrome yellow ($PbCrO_4$) painted on top of copper based containing blue pigments

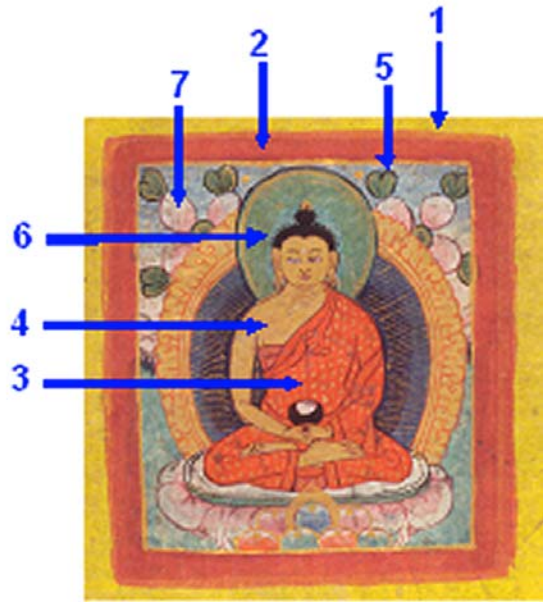

Figure 5: Detail of the painted illustration – numbered regions relate to those given in Table 1.

Analysis of seven individual points allowed tentative assignments to be made of the pigments used (**Figure 5, Table 1**). These range from pure gold leaf for the skin, to traditional lead, mercury and copper containing inorganic species for other areas. The white/pink petals contain a complicated mix of calcium and magnesium compounds, mixed with chrome yellow, all of which have been painted on to an underlying coating of blue copper pigments.

Glasses

A *gangi-dama* is a special ring/bead found or excavated within old Japanese burial mounds as a personal ornament – typical examples are made up of two or more coloured glasses. A particular *gangi-dama* from the Funaki-yama excavations, provided by Paleo Laboratory Company Ltd, was analysed by XRF to shed light on the specific elements used for the colouring of the glass. **Figure 6** shows the results of mapping experiments across the whole ring, approximately 12 mm in diameter.

The yellow-white glass of the matrix is identified as lead glass, whilst the other coloured regions are due to iron (red areas), copper (green areas), and manganese (white areas) additives.

Authenticity and provenance of pearls

Many museum objects include precious metals, gemstones and other ornaments. Micro-XRF can be used to quickly identify whether these are authentic or counterfeits. An interesting example is the identification of authenticity and characterization of pearls. The three main categories of pearls are natural, cultured and imitation (Kunz 1908). Natural pearls are formed when a small irritant is trapped inside a mollusc. The mollusc senses the irritant and deposits minerals around it, principally calcium carbonate (aragonite). In time this grows into the much sought after pearl. Cultured pearls are formed in molluscs through human intervention – for example, seeding with a specific irritant to initiate the mineralization process. Synthetic pearls can be in the form of plastic, glass and calcium carbonate imitations with a synthetic coating to give the expected colour and lustre. Imitation pearls composed of plastic or glass can quickly be categorised by their lack of calcium content – **Figure 7** illustrates optical, micro-XRF and transmitted X-ray images of two black pearls. The left hand pearl is real, as evidenced by the presence of calcium – the right hand example is a plastic counterfeit, and thus shows no XRF signal for calcium.

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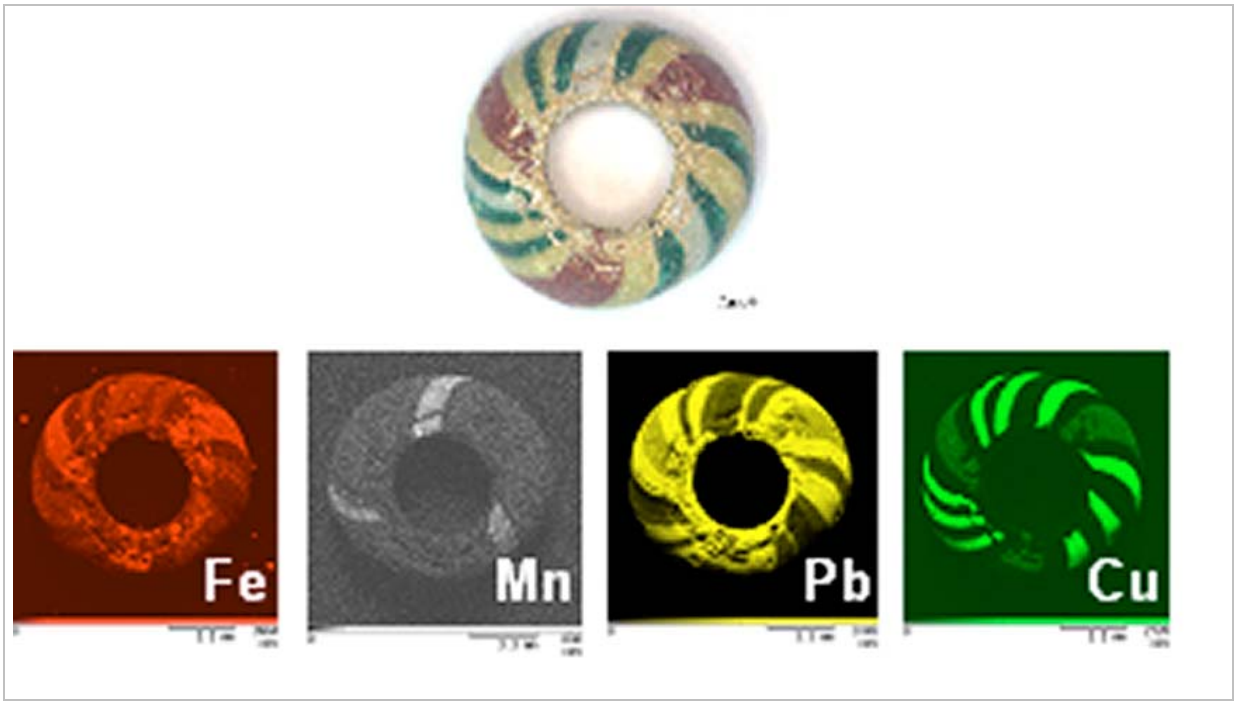

Figure 6: Optical image and XRF mapped images of gangi-dama showing intensities of iron (Fe), manganese (Mn), lead (Pb) and copper (Cu)

The internal structure of the pearls depends upon their origin. For example, natural seawater pearls are usually formed without a nucleus, whilst cultured seawater pearls typically have a nucleus and a layer of conchiolin ($C_{32}H_{48}N_2O_{11}$, a ceratin-type scleroprotein) 0.5-2mm thick. Freshwater pearls can be found both with and without nuclei, but the most common variety (Chinese) has no nucleus. They are distinguished from seawater pearls by their surface characteristics (i.e., lustre and patterning) (Kunz 1908).

X-ray transmission images (**Figure 8**) of Chinese freshwater and Tahiti seawater cultured pearls show distinct internal structures (aside from the drilled hole at the centre of the Chinese example). In particular, the clearly visible ring structure in the Tahiti seawater pearl is explained by a thick membrane of conchiolin. Chinese freshwater pearls are cultured around a minute fragment of organic tissue, and show no nuclei or conchiolin layers.

Summary

The non-destructive nature of micro-XRF analysis allows fast and easy elemental characterisation of museum objects as diverse as manuscripts, ornaments and pearls. Samples were analysed non-destructively without any time consuming or damaging preparation. Such analyses illustrate the excellent synergy between cultural and scientific disciplines, allowing curators to understand and obtain new information regarding fabrication processes, raw materials, authenticity and provenance.

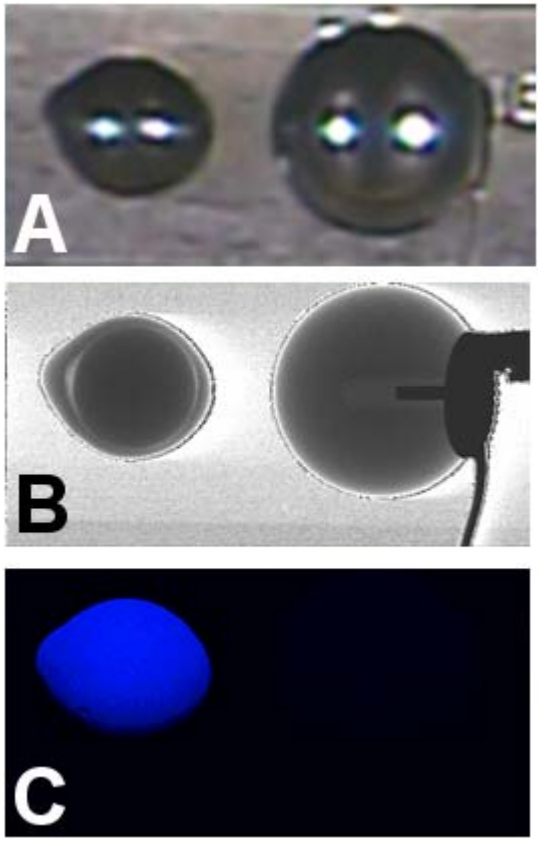

Figure 7: (A) Optical image, (B) transmission X-ray image and (C) calcium XRF image over two pearls. The dark region in the transmission X-ray image corresponds to the metal jewellery clasp set into the right hand pearl. The left hand pearl exhibits the internal conchiolin ring structure.

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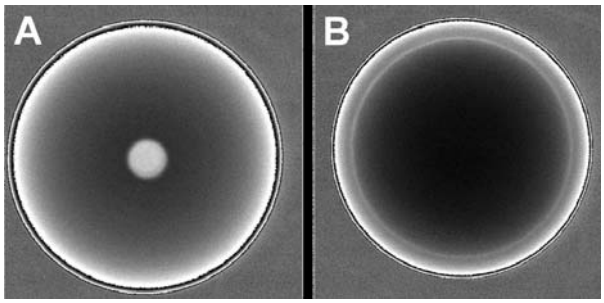

Figure 8: transmission X-ray images of two cultured pearls, (A) high quality freshwater pearl from China, and (B) seawater pearl from Tahiti. The bright centre of the Chinese pearl is due to a hole drilled through the pearl, but otherwise there are no visible features. For the Tahitian seawater the outer conchiolin ring can be observed, with the boundary observed as a bright ring in the image.

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