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NON-INVASIVE ARCHAEOMETRICAL STUDY WITH A PORTABLE MULTI-TECHNIQUE X-RAY SYSTEM

Non-invasive and *in situ* X-ray fluorescence (XRF) studies of several cultural heritage objects have been successfully performed in the last years. Determination of sensitivities of such a system is important to assess the maximum reach of a portable XRF system to solve common questions in the museum. In some cases, determining minor or trace elements is necessary for provenance study of cultural heritage as is frequently required in archaeological ceramics. In others cases, the determination of major chemical crystalline phases by X-ray diffraction (XRD) is necessary for the identification of material, such as minerals and gems in sculptures. First applications in the field of archaeometry of a specifically designed portable XRD or XRD-XRF prototypes show its potential (Nakai/Abe 2011). In spite of its crucial advantages, some limitations must be pointed out. Such are the excitation of only major chemical elements by XRF, long measurement times for XRD and/or the impossibility to take measurements in real time because of the required conversion of the XRD ring pattern (obtained on the image plate or CCD) to a conventional diffractogram and the need to add an image plate reader to the full setup.

On the other side, complementary radiography analysis is required for the authentication study of several cultural heritage objects. For instance the existence of subjacent images in paintings can be revealed and explain the extension of a specific region with different chemical composition identified by previous XRF-XRD analysis. This paper presents archaeometrical applications of a compact XRF-XRD-radiography setup for a portable X-ray system.

Results and discussion

Instrumental description and data processing

The diffractograms are obtained at a fixed angle using the energy dispersive XRD principle. Proper collimation of primary and secondary beam is used

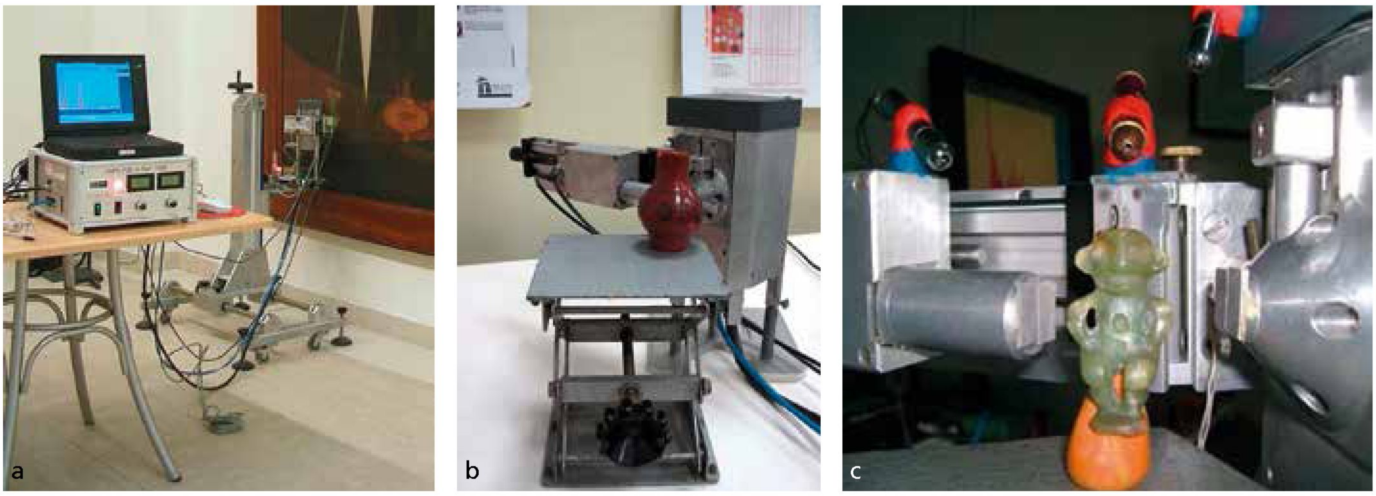

Fig. 1 Portable X-ray system: **a** full setup. – **b** measurement head during XRF analysis. – **c** XRD analysis. – (K. J. Carlson).

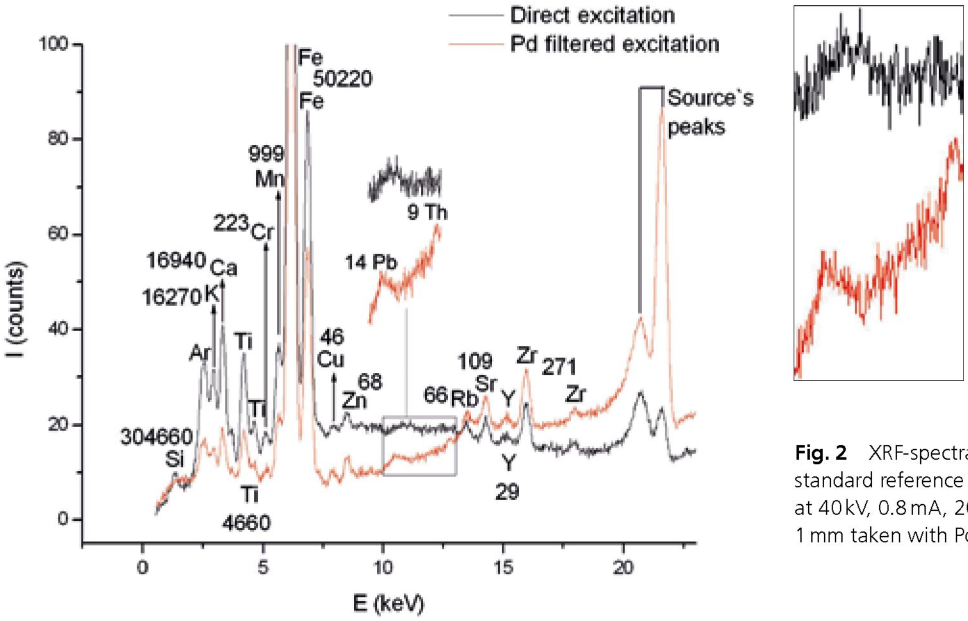

Fig. 2 XRF-spectra obtained from ceramic standard reference material (NBS, ceramic-1) at 40 kV, 0.8 mA, 2000 s, Pd anode, spot size 1 mm taken with Pd filter and without filter.

to implement the mentioned techniques. The system is based on polychromatic excitation from a single miniaturized (2 mm thickness) Pd anode X ray tube (max. voltage 50 kV, max. current 1 mA) and an energy dispersive Si-PIN detector (energy resolution 230 eV, active area 25 mm^2 and Be window thickness 0.5 mm). They are positioned in reflection geometry, which allows obtaining a compact and relatively low cost experimental setup denominated as Art × Art (**fig. 1a-c**; Mendoza Cuevas/ Pérez Gravié 2011). It includes a remote unit for power and control of X-ray tube and detector, a laptop and a support for the movement of the measurement head (X-ray tube and detector) for studies of large objects.

The geometry between the primary beam and detected beam is fixed in 45°/45° related to the perpendicular to the samples' surface for XRF analysis. A simultaneous ED (energy dispersive) XRD-XRF is obtained at lower angle. Using Ag collimators the dimension of beam is adjusted for irradiating regions on paintings of less than 1 mm to 10 mm depending on the available area of color to be analyzed. For the analysis of the ceramic, a 10 mm collimator was used to average over the inhomogeneities of clay paste. The interception of two or three diode lasers (depending on dimensions, 2D or 3D of studied region) on the surface of the object was used for the selection of the measurement region and to guarantee a reproducible positioning. XRF measurements of ceramics were taken using a Pd filtered (filter thickness of 0.13 mm) primary beam at 40 kV, 0.1 mA during 200 s. A variable slit collimator was used for EDXRD analysis and diffractograms were obtained with 25 kV, 0.8 mA and 200 s. For obtaining radiography, the instrument also allows irradiating a square-shaped region in the studied object by projecting a square X-ray beam on its surface. Radiographies of paintings were obtained at 40 kV and 0.8 mA at a distance of 100 cm during 120 and 240 s.

Data processing through the multivariate analysis using the peak area of detected chemical elements by XRF allows the study of the provenance of archaeological ceramic. Principal component (PC) analysis (PCA) implemented in the Quimiometrix software was used to reduce the number of variables from the real variable to a new variable space called PC. The real variables were independent chemical element areas selected using the modeling power criteria ($0.9 < P < 1$). The number of PC components is determined by the percentage of accumulated variance (>90 %) and the error of prediction (function's inflection point).

Provenance analysis of archaeological ceramic by PXRF

In the provenance study it is crucial to evaluate the efficiency of the developed PXRF (Portable XRF) depending on the chemical element. When the portable X-ray system »Art × Art« is used, important elements in the genesis of minerals, present also in clay as Rb, Sr, Y and Zr, are well excited even at trace levels (fig. 2). The excitation is improving with the use of the Pd filter and subsequently Pb and Th are detected. Variations of majority elements Na, Al, Mg, Si, K and Ca have been reported as indicators of recipes as they are present in the additive materials or as main components of clays. However, light elements as Na, Al, Mg and Si are not detected or weakly detected by PXRF even if vacuum or He flux is used. Other ultratrace or trace chemical elements, especially some lanthanides and actinides, have been used as marker for the provenance of different ceramic clays by Neutron Activation analysis (NAA), but they are not detected by PXRF. The application of a more sensitive technique as NAA is mandatory for several cases to solve the classification of clay when results from PXRF analysis are very similar, or to confirm these results. In this last case, PXRF analysis can be useful to statistically validate results obtained from the study of representative samples by NAA.

A comparative study between the direct analysis of ceramic fragments and the analysis of pellets, obtained by pressing powder of these ceramic fragments, was performed. Explorative multivariate analysis of the two data sets showed the same groups classification. Therefore, non-invasive analyses were carried out in all fragments and almost complete ceramic pieces found in the studied archaeological site.

»Mexican Red« is the denomination of an archaeological typology, regarded as continuator of the pre-hispanic ceramic Azteca Roja, that grouped red archaeological ceramics found in the surroundings of Mexico City, in Florida and in Old Havana City from 1570 to 1780. 104 red ceramic fragments, similar to Mexican Red ceramic (fig. 1b), from the archaeological excavation (end of 18^{th} century) at the Convent Santa Teresa de Jesus in the historical center of Havana City[1] and six Mexican Red ceramic fragments from El Templo Mayor of Mexico City (code: M1-M6) were studied by PXRF. The areas of the Kα peaks of the chemical elements K, Ca, Ti, Mn, Rb, Sr, Y, Zr and Nb, corresponding to the irradiation with the use of the Pd filter, were the real variables in the Principal Components Analysis (PCA). Each point in the graphic is the average of three measurements at the irradiated zone. Five factors were

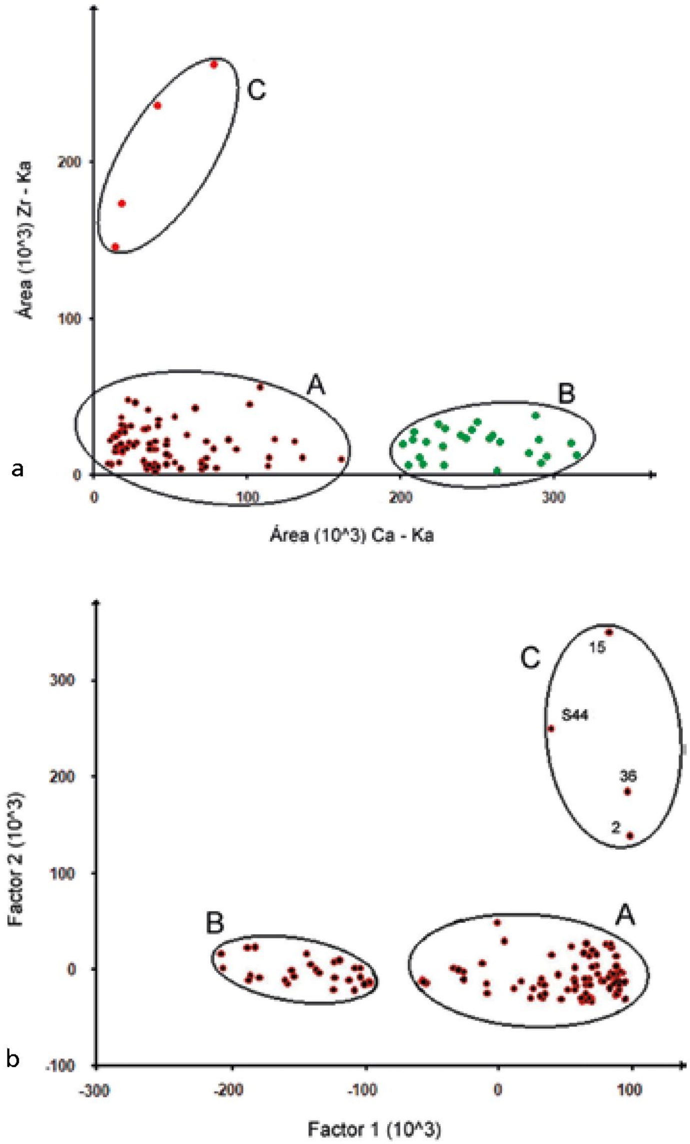

Fig. 3 **a** principal component analysis of studied ceramic fragments. – **b** real variables Zr vs Ca analysis of the same ceramic fragment.

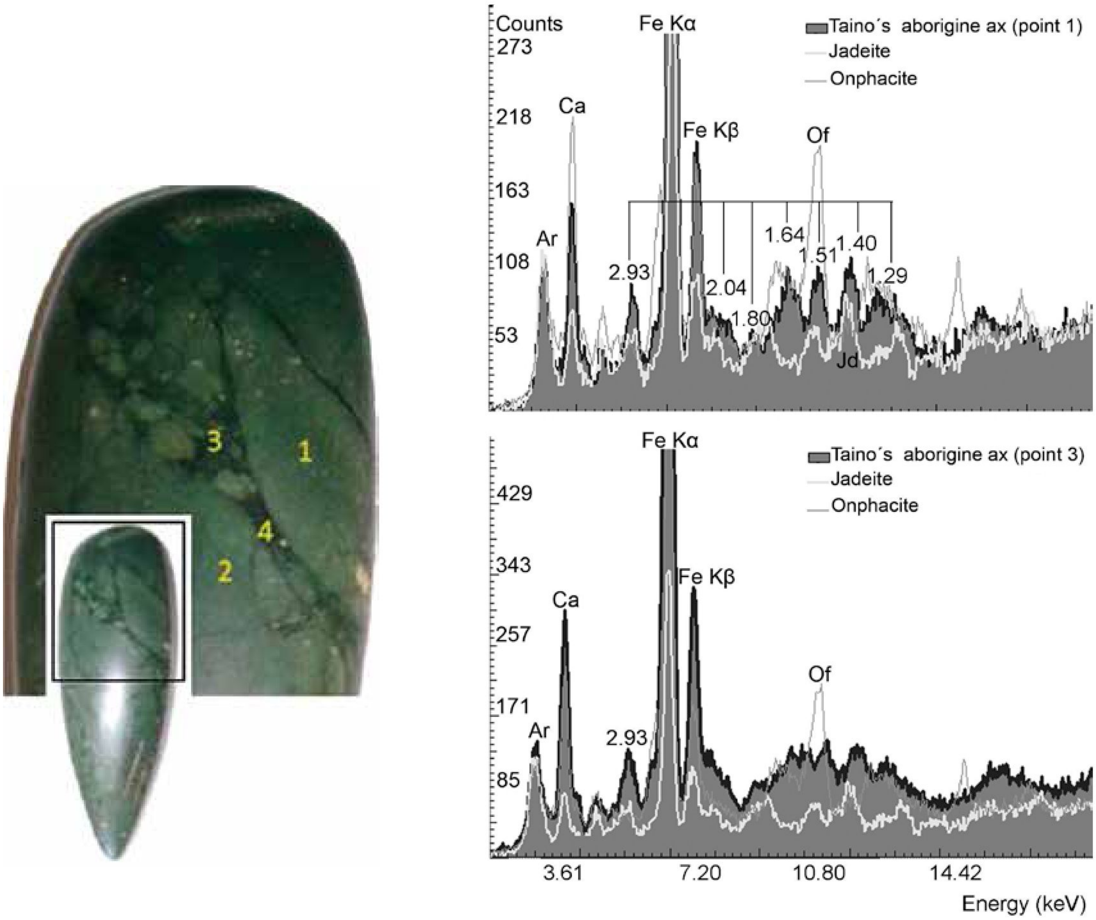

Fig. 4 Tainos's aborigine ax. Spectra XRD-XRF in clear (point 1) and dark area (point 3) of stone compared with jadeite sample from Motagua, Guatemala and onphacite from Sierra del Convento, Cuba.

obtained in this multivariate analysis, which contain the 99.87 % of the information of the real variable. The Factor 1 and Factor 2 have the 95.05 % of the initial information.

The PCA shows the formation of three groups (**fig. 3a**). The group A with 80 elements[2] and the group B with a concentration of 26 fragments[3] are the two more populated groups. The fragments with code 2, 15, 36 and S44 were grouped in the conglomerate C. The members of group C show high concentration levels for the chemical elements Ti and Zr and differ completely from the other two groups. The ceramic fragments of group B show an important presence of Ca in their matrix, indicative of difference in the recipes as it was also revealed by petrographic analysis for the presence of calcite gross grain. The conglomerates obtained by the use of the real variables Ca and Zr (**fig. 3b**) are the same as indicated by PCA analysis (**fig. 3a**). The six Mexican Red ceramic fragments from El Templo Mayor from Mexico City were grouped in the conglomerate A, which suggest a possible Mexican provenance for the other 74 pieces of this group.

Mineral identification and characterization by ED XRD-XRF analysis

Energy dispersive X-ray diffraction allows to identify crystalline phases present in gems and other minerals. Jadeite-jade is a rare mineral from the geological point of view. In the Mesoamerican and Caribbean region, jadeite-jade deposits were known only in

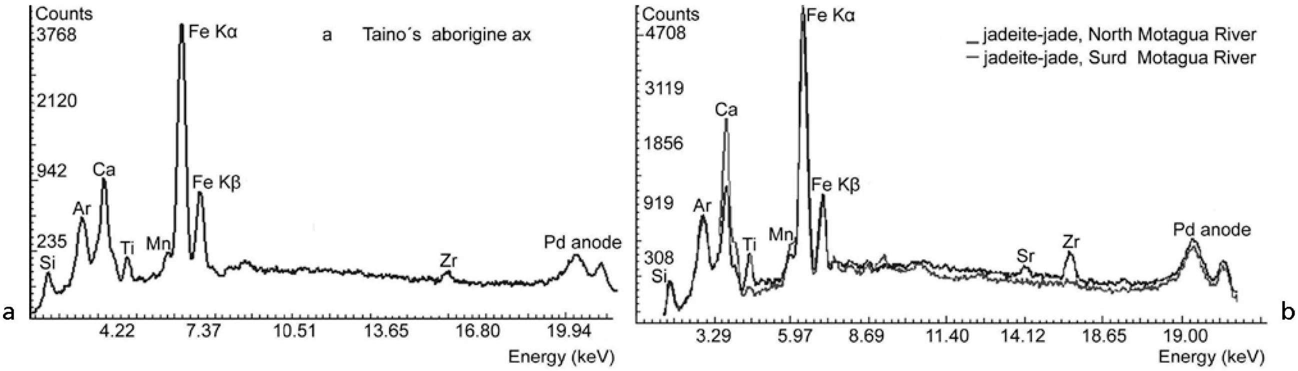

Fig. 5 XRF spectra of a Taino's aborigine ax found in Holguín/Cuba (**a**) and a Jadeite-jade sample from northern and southern part of Motagua River/Guatemala (**b**).

the Motagua River deposit/Guatemala. However, a recent discovery in the San Juan River in the Dominican Republic and in Sierra del Convento/Cuba, changes the archaeological perspective on trademarks in the region. On the other side, the perfect symmetry and beauty of style of the Taino axes might suggest the existence of a local workshop at that time on the Island. The identification of jadeite-jade in these axes and afterwards its characterization by chemical elements could assess if these pieces have a Cuban origin or not.

The analysis of the spectra XRD-XRF obtained from a Taína ceremonial ax (fig. 4), an archeological find from Holguin, in the clear and dark zones of its green stone, allows identifying, for the first time, the use of the jade for this aboriginal group. Jadeite-jade with onphacite was identified as the material of the stone by the presence of six peaks (interplane distance [Å]: 2.92, 2.04, 1.80, 1.64, 1.51 and 1.29) that identifies jadeite itself. A higher content of jadeite in the clear zones (points 1 and 2 in fig. 4) and a higher content of onphacite in the dark zones were determined (points 3 and 4 in fig. 4). In the same spectrum, XRF lines of the majority chemical elements Ca and Fe were detected, predominating the Ca presence in the dark regions with more onphacite, which correctly corresponds with higher concentrations of Ca in onphacite with respect to jadeite.

In the analysis of the XRF spectrum, besides Si and Ca that compound the crystalline majority phases, Ti and Zr were distinguished (fig. 5a), detected as much in the clear regions like in the dark ones, while southern and northern Motagua River jadeite samples spectra (fig. 5b) showed differences in the intensities of Ti, Sr and Zr lines in the first and a higher concentration of Ca and absence of Ti and Zr in the second, which coincides with the study of Guatemala jadeite-jade (Harlow et al. 2006).

A second ax, also from the Holguin province, was identified as Jaguar jade (onphacite pyroxene, jadeite pyroxene and graphite) because of the prevalence of onphacite and the absence of different elements in the XRF spectrum of the black spot on the green stone, which suggest the presence of graphite. This ax es characterized by the presence of Ti, Zn, Sr and Zr at minoritary or trace levels. However, Na, Al, Mg and Si are not detected, and they are majoritary elements of jadeite-jade ($Na[Al,Fe]Si_2O_6$), nephrite-jade ($Ca_2[Mg,Fe^{+2}]_5Si_8O_{22}[OH]_2$) and onphacite ($NaCaMgAl[Si_2O_6]_2$). Therefore, a more sensitive analysis should be performed for complete characterization. A further systematic study using Neutron Activation Analysis of the Taino axes and other green stone axes from the Mesoamerican and Caribbean region may be significant to determine the provenance of these exceptional pieces.

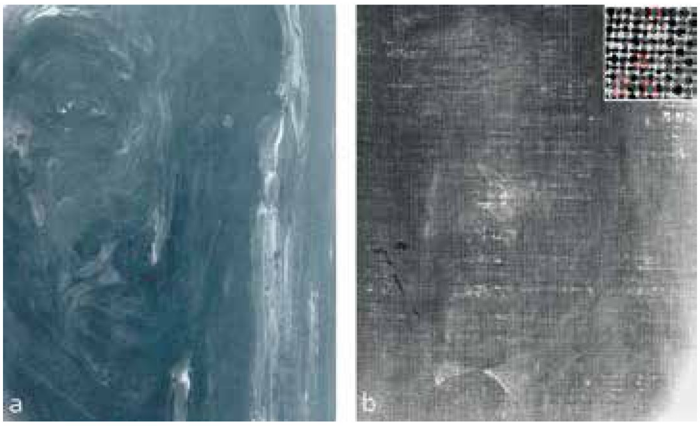

Fig. 6 **a** radiography images of painting for attribution study to the C uban painter Ponce de León. – **b** portrait of San Gerónimo with details of double canvas (right top) indicated (in blue and red).

Internal structure of paintings determined by radiography

The imaging quality of radiographies obtained with a modified PXRF spectrometer was evaluated for the study of paintings. With the spectrometer, Images are recorded in scanning mode in reflection geometry, not in transmission geometry as in conventional radiography. The spatial resolution of the obtained radiographical image makes it possible to locate and define characteristic structures to define the painter style, underlying paintings (pentimenti), to identify filling materials in a painting undergoing a restoration process, as well as radiogrametry. The radiography is also convenient as complementary study of XRF analysis in the interpretation of XRF spectra when the same chemical elements are detected and not associated to the colors. For instance, in the radiographical image taken for the study of a painting for its attribution to the Cuban painter Fidelio Ponce de León, the brushstrokes of the painter are observed that are useful in the style characterization of the painter from the determined structure of the drawing of some part of the face (fig. 6a) (see details of nose).

The painting »Portrait of Gerónimo Valdés« from the collection of University College San Gerónimo de La Habana was investigated in two regions: the face and the inferior borders. The radiographical image evidences the characteristic brushstroke of the painter, the deterioration of the original canvas (white regions in the radiography that indicate loss of canvas), and the double pattern due to a second canvas from a previous restoration and the missing of a signature (fig. 6b). After removing the last added canvas the radiography may give other evidence of pentimenti or under-sign »hidden« to X-rays because of the double canvas and also for the presence of a thick preparation layer of lead white identified by XRF that absorbed radiation (as a shielding) emitted from the pictorial layers' excitation. This effect was reduced by taking a radiography from the back part of the painting.

Conclusions

Applications of a compact portable XRF, XRD and radiography system in archaeometry are demonstrated. Provenance studies of some specific archaeological ceramics are possible because important chemical element markers such as Rb, Sr, Y and Zr at trace levels are well excited. However, chemical elements with low energy XRF lines are detected weakly and lantanide and actnide at trace levels are not detected. Identification and characterization of major mineral phases in stone sculptures can be done by ED-XRD and ED-XRF analysis. Other more sensitive multi-elemental techniques (as NAA) should be applied for provenance studies of minerals. The radiography that can be performed with such a system is sufficient for the most common questions related to internal structure of paintings for conservation and authentication purposes.

Notes

1) Code: 1-18, 20-25, 27-36, I-VI, S1-S20, S22-S37, S39-S55 and S57-S68.

2) Code: 1, 3, 5, 7-9, 11, 14, 17, 18, 21, 22, 24, 25, 27, 28, 31, 33, 34, I, II, IV, V, VI, M1-M6, S1-S7, S14-S19, S24-S27, S29-S32, S35-S37, S40-S43, S46- S55, S57-S68.

3) Code: 4, 6, 10, 12, 13, 16, 20, 23, 29, 30, 32, 35, III, S8-S13, S20, S22, S23, S33, S34, S39, S45.

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Summary / Zusammenfassung

Non-invasive Archaeometrical Study with a Portable Multi-technique X-Ray System

A non-invasive archaeometrical study with a portable X-ray system is presented. A setup for XRF-XRD (X-ray fluorescence-X-ray diffraction) based on polychromatic excitation and energy dispersive detection in the reflection mode has been utilized for *in situ* characterization of artistic and archaeological artifacts. This portable X-ray system allows analysis of chemical elements and chemical crystalline phases and internal structural analysis by radiography. As representative examples is presented: the XRD-XRF identification and characterization of minerals in green stone axes, the provenance XRF study of archaeological ceramics and the possibilities in the radiography examination of paintings.

Nicht-invasive archäometrische Untersuchung mit einem tragbaren Multi-Technik-Röntgensystem

Vorgestellt wird eine nicht-invasive archäometrische Untersuchung mit einem tragbaren Multi-Technik-Röntgensystem. Es wurde ein Aufbau für XRF-XRD (X-ray fluorescence-X-ray diffraction), basierend auf polychromatischer Anregung und energieaufgelöster Detektion im Reflektionsmodus, für die *in-situ*-Charakterisierung von künstlerischen und archäologischen Artefakten verwendet. Dieses tragbare Röntgensystem ermöglicht die Analyse von chemischen Elementen und chemischen kristallinen Phasen sowie die innere Strukturanalyse mittels Radiographie. Als typisches Beispiel werden gezeigt: die XRD-XRF-Identifizierung und Charakterisierung von Mineralien in grünen Steinäxten, die XRF-Untersuchung der Herkunft von archäologischer Keramik und die Möglichkeiten zur radiographischen Untersuchung von Gemälden.

Keywords

non-invasive analysis / portable X-ray system / XRF / XRD / radiography / archaeometry / cultural heritage