Activities in the IAEA XRF Laboratory

A few selected examples of the recent activities and results in the field of XRF are presented.

Handheld XRF analysis of a 16th century Mexican Feather Headdress

Introduction

The 16th century feather headdress in the Weltmuseum Wien (WMW), an affiliated institution of the Kunsthistorisches Museum (KHM) in Vienna, is the most renowned of the few remaining pre-Columbian “Arte Plumaria” artefacts, which were made by feather artisans (Amantecas) using traditional techniques in the territory of present day Mexico [1]. The recorded history of the headdress begins in 1596, when it is first mentioned in the estate inventory of the art collection of Archduke Ferdinand II of Tyrol at Ambras Castle [2]. Due to its age, the variety of materials used, its history and former restoration treatments, the artefact is today one of the most sensitive and demanding care objects of the museum.

Fig. 1. Feather headdress from ancient Mexico (Photo: Christian Mendez, February 2010, Kunsthistorisches Museum, Wien)
Despite the object’s long history, very little documentation on past interventions exists. From 2010-2012, a bi-national research project between Mexico (Instituto Nacional de Antropología e Historia) and Austria (Weltmuseum Wien) performed a systematic investigation focused on the identification of manufacturing techniques and the various materials, the old restoration measures and its conservation [1, 3].

Handheld x-ray fluorescence (XRF) spectrometers are extremely useful for the study of art works in museum collections [4]. The possibility of bringing the instrument to inspect the objects on-site facilitates the study of artefacts that cannot be moved either due to their extreme fragility or due to their large size and/or weight. In addition, non-destructive analysis constitutes a preferred alternative to invasive sampling techniques, which are usually not allowed in the study of unique or extremely valuable objects. The aim of the XRF analysis was twofold: to investigate the possible presence of inorganic toxic elements that could be associated to the use of pesticides in past conservation interventions and; to characterize the chemical composition of the authentic gold and the gilded brass ornaments, which were added in the 19th century. The results of the XRF analytical study on the Mexican Feather Headdress were published recently in the X-Ray Spectrometry journal (2014) [5].

Experimental

The handheld XRF analyzer utilized during the in-situ measurements uses a miniaturized air-cooled transmission X-ray tube with a thin Ag layer as anode material. The tube can be operated up to 50 kV and 200 μA, providing that a maximum power of 2.5 Watts is not exceeded. The tube current is automatically adjusted for each measurement so that the detector counting rate does not lead to a maximum dead-time fraction. The analyzer is equipped with a Silicon Drift Detector (30 mm²) with energy resolution better than 178 eV (Mn-Kα). Different excitation conditions can be selected to optimize the elemental sensitivity for low, medium or high atomic number elements by using different settings of the high voltage and by introducing different filters in the excitation beam path. The analyzed area can be considered to have a circular shape with a diameter of about 8 mm.

During the measurement, the feather headdress was lying horizontally on a supporting acrylic glass table, allowing its investigation under minimal risks of damage (see Figure 2, XRF measurements performed by Dr. Padilla-Alvarez Roman).

Results

a) Analysis of the feathers for pesticides

In the Museum of Ethnology Vienna the use of pesticides is documented since the 1950s, but its introduction could date much earlier. The feather headdress consists of a combination of different organic and inorganic materials and exhibits substantial damages caused by a former insect infestation (in all probability cloth moths). These facts make a contamination with pesticides most probable. Three characteristic spectra collected in the main condition of the handheld XRF operational mode are shown in Figure 3.

![Figure 3. Spectra collected in the main operational condition of the handheld XRF analyzer (enhanced sensitivity for medium atomic number elements)]](image-url)

The spectrum 171 (blue line) corresponds to the measurement in a spot of green feathers that are supposed to be the originally used in the making of the headdress. The measurement 177 (brown line) corresponds to the measurement of green-feathered bird skin fragments, whereas the measurement in the spot 185 (olive line) corresponds to blue-feathered skin fragments. Both of these skin fragments were presumably added to the headdress in 1878 as part of the first documented restoration. New
feathers have been integrated to the headdress especially in those areas, which were damaged by a previous insect infestation. About one third of the whole front side of the headdress shows feathers added during the restoration process (1878). The spot 177 contains high intensity arsenic peaks, whereas bromine and lead peaks are also noticed in the measurement at spot 185. Such elements could be indicative of the use of arsenic, bromine and lead containing pesticides such as arsenic soaps, bromadiolone and lead arsenate (as both elements Pb and As were detected in other spots).

b) Analysis of the metal ornaments

The use of the x-ray radiography performed by Dr. Manfred Schreiner, Institute for Natural Sciences and Technology in the Arts, Academy of Fine Arts Vienna revealed two different chemical compositions for the metal ornaments; one corresponding to a highly absorbing material (gold alloy) and another one of much lower atomic number. The XRF measurements were performed to assure the classification based on microscopic investigation and the limited quantitative results obtained using wet chemical analysis [6]. For each gold ornament one single measurement (see Figure 4) was performed by carefully targeting the inspected area. In some cases replicate measurements were done to ensure that there were not elements detected from adjacent ornaments.

The composition of the original ornaments was calculated using one of the factory calibrations provided with the instrument, which accuracy has been verified through the measurement of two sets of reference 14kt to 23kt gold alloys. The quantification results of the gold ornaments using the instrument pre-existed calibration (“Precious Metals” mode) are presented in Figure 5.
The measurements taken from the later added ornaments revealed high intensity peaks for Cu, Zn and to a less extent of Pb, as well as smaller Au peaks as compared to the spectra from the gold ornaments (Figure 6). The presence of these peaks in the spectra suggests that such ornaments are replacements made from gilded brass pieces. The two layered system, namely the presence of a gold gilding layer on the top of a brass alloy cannot be handled by the equipment quantitative analysis software in a straight forward manner. Thus, an analytical methodology was followed with the aim to determine the thickness of the gilding layer and to correct the brass elemental concentrations as obtained by the instrument software for the effect of attenuation of the radiation through the gilding layer [5]. The chemical composition of the gilded brass is presented in Fig. 7 and the thickness was found to be in general less than 1-2µm.

Conclusions

The in-situ examination allowed the determination of the chemical composition of the original gold ornaments and that of the gilded brass replacements including an estimation of the thickness of the surface gold layer. Furthermore, it was noted that the added feathered-bird skin fragments were treated with various pesticides prior to their integration during the first documented restoration in 1878. The results of the pesticide analysis indicate a potential risk for museum staff and appropriate precautions should be followed when getting in contact with contaminated material or dust. The results of this study demonstrate the usefulness of handheld XRF measurements, when interpreted following a well-sustained analytical methodology. Fast screening results can be produced on the spot to answer different questions arising from a prior detailed documentation of the artefact to be analyzed or even during the in-situ investigation, whereas a more detailed interpretation of the measurements carried out can be performed “off-line” to enhance significantly the information gathered from of the analysis.

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References


