Implementation of a portable EDXRF measurement chain for characterization of metallic objects of cultural interest in Colombia

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Abstract. The study of cultural heritage requires sophisticated equipment that does not alter or destroys the materials composing the objects under study. The main requirement about an artifact or an ancient work of art, for its restoration or conservation processes, is information about its constituting elements. Energy-dispersive X-ray fluorescence (EDXRF) is a very versatile and relatively inexpensive technique for conducting a non-destructive elemental analysis. In this paper, we present the design and implementation of a hand-held X-ray fluorescence spectrometer. Although the EDXRF measurement chain appears to be a simple technique to assemble and use, it requires extensive knowledge about the proper handling of the X-ray beam, the analysis of the spectrum and whether the obtained spectrum is appropriate for a qualitative and quantitative analysis. Even geometry is one of the most important factors since the source-sample-detector distances must be handled with meticulousness to obtain optimal spectra. Acquisition time and the amount of accumulated counts to obtain high resolution spectral peaks are very important as well.

This work shows the results obtained from metallic samples of Colombian cultural interest belonging to the collection of Museo Universitario Universidad de Antioquia.

1. Introduction

The study of cultural heritage requires the use of sophisticated and portable equipment. This is because analysis must be carried out at the museums and most objects of study cannot be transported to a laboratory. Furthermore, analytical techniques must be completely non-destructive or invasive. Thus, much of the instruments’ equipment has been manufactured in such a way that they can be portable and manipulated easily by experts from different disciplines of natural sciences, industry applications, archaeology and arts. One of the most popular techniques implemented and applied to the study of cultural heritage is the energy-dispersive X-ray fluorescence (EDXRF). In the last decades, different types of portable equipment have been designed to make measurements in situ [1-3]. This hand-held spectrometer is applied in elemental and chemical analysis of materials such as ceramics, metals, glass, and soils. For instance, it can be employed to determine the thickness of gold or silver layers applied to objects of archaeological interest from different cultures of the ancient world.
This paper shows the results of the implementation of a hand-hold portable EDXRF measurement chain to study pre-Hispanic gold artefacts. The efficiency and versatility of the portable equipment has been demonstrated in the analysis of two metallic objects of Museo Universitario Universidad de Antioquia (MUUA) and were compared with standard samples of Au, Ag and Cu.

2. Materials and Methods

The measurement setup is composed by an Oxford Instruments X-ray tube with I2C communication, and a SDD X-ray spectrometer. Both instruments are attached in such a way that the incident X-rays are dispersed from the sample and detected by the spectrometer. The X-ray tube maximum operating voltage and current are 40 kV and 100 μA respectively. A custom-made USB-I2C controller was built to adjust and monitor the tube parameters. The X-ray spectrometer is a compact, handheld instrument with USB communication, a (1 keV – 40 keV) range with a resolution of (139 eV - 260 eV) FWHM at 5.9 eV [4]. The spectrometer’s data acquisition display and control are provided by the DPPMCA software. Both the X-ray tube and the spectrometer were coupled with custom made collimators and filters, in order to achieve the conditions required to record X-ray fluorescence measurements and avoid detector saturation, beside filter any other type of spurious radiations that yields a high background in the spectrum. The complete measurement chain is shown in Figure 1.

Figure 1. (a) on the left, the detector. On the right, the X-ray tube showing the collimator. (b) on the right, the EDXRF chain diagram in full measurement of a sample, it also shows the spectrum that is being obtained.

Working conditions for the measurement setup
Prior to the experiment, users must establish the X-ray tube’s high voltage and current. To facilitate this process, a custom graphical interface was designed to control and monitor tube parameters such as power supply current and voltage, tube high voltage, current, and filament temperature [5,6]. Once users validate the proper functioning of the tube, X-rays can be activated using the interface controls. The graphical user interface built using LabView software is shown in figure 2.

Calibration process
Prior to spectrum measurement, the equipment must be calibrated to change the data recorded mode from channels number to energy (eV). The calibration of the measurement chain is made with a standard sheet (Au-76 – Ag-24 alloy). For example, if a gold-silver foil is used, one can determine the positions in channels of the two main gold peaks (L-α and L-β) and the main peak of silver (K-α). See figure 3.
Figure 2. Graphical user interface designed to control and monitor the X-ray tube.

Figure 3. Typical spectrum of a standard sample of Au (76 %) - Ag (24 %). The spectrum acquisition screen displays the following parameters: total accounts, dead time and spectrum acquisition time.

Spectrum measurement can begin once calibration is ready and the following factors are considered: (a) the experimental arrangement must be the same throughout all the measurements that will be carried out, (b) the X-ray source-sample-detector source distances must not change. Often you can see some peaks that do not correspond to the sample studied. In Figure 3, a small peak corresponding to the titanium (Ti) filter being used can be observed (4.53 keV). The peaks belonging to the filter and collimator used in the output of the incident beam can provide erroneous information. It is necessary to use a filter to eliminate the background radiation and especially for the quantitative analysis, where the spectrum obtained should be as clean and defined as possible. There are peaks of the spectrum that correspond to the same X-ray tube and that can generate overlap of other peaks, it also produces peaks of the medium where the measurement is carried out. One of the peaks that one can see is the peak of argon, very common in the air [7]. In our case, for the quantitative analysis, two methods can be used: (a) Standard patterns (use of several samples whose elementary content is known) and (b) Quantification software.
3. Applications and results

The importance of portable EDXRF equipment has been demonstrated in the study of ancient metalwork and especially in gold pieces of archaeological origin [8-10]. The results obtained in real time and the accuracy of the found values, compared to other techniques (more expensive) make EDXRF one of the tools with more applications in this area of the cultural patrimony. In this paper, the EDXRF measurement chain implemented was used to analyze two metal pieces belonging to the collection of MUUA. The first one is a golden object that has zoomorphic shape of a mantis, and the second is an animal with amorphous features (see Figure 4). On both objects an X-ray beam was applied on 6 points on their surface. The X-ray tube was operated with 40 kV and 19 μA.

![Figure 4](image_url)

Figure 4. (a) mantis and (b) zoomorphic objects and their corresponding measured points.

From the archaeological context, the Mantis (Figure 4(a)) object was found in the Municipality of Medellín - Colombia. Which is attributed to Quimbaya culture. This object was found inside an urn of the Brown Incised ceramic style; attributed form of "Praying Mantis". It is 1.3 cm height, 1.1 cm width, and 3.4 cm depth. It weighs 2.7 grams. The other one, zoomorphic piece (Figure 4(b)), was found in the Municipality of Carmen de Viboral, 60Km far way northeast to Medellin. It is 1.9 cm height, 1.4 cm width, and 2.7 cm depth. It weighs 8.7 grams. The spectra was carefully measured and the X-ray beam was incised on various surfaces and flat sections of the objects (see points in Figure 4). Twelve spectrum were recorded. The beam diameter hitting the surface must be adequate, otherwise a surface phenomenon that produces spectra with heights and incorrect areas that do not correspond to the real values may be produced. As some objects have several curved surfaces, this is an important aspect to consider for measurement taking. A Pymca software was used to quantify the amounts of gold, silver and copper present in each object (Figure 5). The Pymca quantization software is based on the fundamental parameter method. To calculate the percentages of Au, Ag and Cu, the type of radiation of the x-ray tube used must be taken into account, in our case the target (anode) is rhodium [13]. The measurement time was 120 seconds in each spectrum record.

![Figure 5](image_url)

Figure 5. Spectra of the mantis (a) and the zoomorphic object(b) and the values obtained from Au, Ag and Cu.
Table 1. The elementary values obtained are average values of the six measurements taken in each object analyzed. The results show that each object has a ternary metal composition.

4. Conclusions
This paper presents the implementation of a portable X-ray fluorescence measurement chain and the factors that should be considered for its correct operation, when analyzing artefacts related to the study of cultural heritage materials [11,12]. A quantitative analysis can be done with portable equipment in samples of cultural heritage at a low cost. The EDXRF measurements can be taken “in situ”. In order to conduct a quantitative and qualitative study, various aspects about the equipment operation must be considered. The best results are obtained using the Pymca software.

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5. Bibliography
[1] Marco Ferretti (2014). The investigation of ancient metal artefacts by portable X-ray fluorescence devices. Journal of Analytical Atomic Spectrometry, 29: 1753-1766.
[2] S. Ridolfi (2013). Portable X-ray Fluorescence Spectrometry for the Analyses of Cultural Heritage. Joint ICTP-TWAS Workshop on Portable X-ray Analytical Instruments for Cultural Heritage.
[3] Roberto Cesareo et al. (2017). Radiography and transmission measurements on gold and silver from the Moche tomb “Señora de Cao”. Radiology and Diagnostic Imaging. Volume 1(1): 1-6. DOI: 10.15761/RDI.1000106.
[4] http://www.amptek.com/pdf/x123.pdf
[5] Antonio Brunetti et al. (2015). A high-quality multilayer structure characterization method based on X-ray fluorescence and Monte Carlo simulation. Appl. Phys. A., 118:497–504.
[6] Claudia Pelosi et al. (2018) In situ investigation by X-ray fluorescence spectroscopy on Pian di Civita Etruscan lituus from the “monumental complex” of Tarquinia, Italy. Eur. Phys. J. Plus 133: 357.
[7] Roberto Cesareo et al (2016). Analysis of the spectacular gold and silver from the Moche tomb ‘Señora de Cao’. X-ray Spectrometry vol. 45, issue 3, pp. 138-154.
[8] Roberto Cesareo et al. (2011). Evolution of pre-columbian metallurgy from the north of Peru studied with a portable non-invasive equipment using energy dispersive X-ray fluorescence. Journal of material science and engineering B, 48-81.
[9] J.L. Ruvalcaba et al. (2010). SANDRA: a portable XRF system for the study of Mexican cultural heritage. Volume39, Issue 5, Pages 338-345.
[10] A. Perea et al. (2013). Pre-hispanic goldwork technology. The Quimbaya Treasure, Colombia. Journal of Archaeological Science 40, 2326-2334.
[11] G. Capobiano et al. (2018). X-ray fluorescence investigation on yellow pigments based on lead, tin and antimony through the comparison between laboratory and portable instruments. Journal of Cultural Heritage, Volume 29, Pages 19-29.
[12] Roberto Cesareo et al. (2010). Energy dispersive X-ray fluorescence analysis of a pre-columbian funerary gold mask from the Museun of Sican, Perú. X-ray spectrometry. Vol 39, pag. 122-126.
[13] https://sourceforge.net/projects/pymca/files/pymca/PyMca5.1.1/