Recent developments in atomic/nuclear methodologies used for the study of cultural heritage objects
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Recent Developments In Atomic/Nuclear Methodologies Used For The Study Of Cultural Heritage Objects

Carlos Roberto Appoloni

Abstract. Archaeometry is an area established in the international community since the 60s, with extensive use of atomic-nuclear methods in the characterization of art, archaeological and cultural heritage objects in general. In Brazil, however, until the early '90s, employing methods of physics, only the area of archaeological dating was implemented. It was only after this period that Brazilian groups became involved in the characterization of archaeological and art objects with these methodologies. The Laboratory of Applied Nuclear Physics, State University of Londrina (LFNA/UEL) introduced, pioneered in 1994, Archaeometry and related issues among its priority lines of research, after a member of LFNA has been involved in 1992 with the possibilities of tomography in archaeometry, as well as the analysis of ancient bronzes by EDXRF. Since then, LFNA has been working with PXRF and Portable Raman in several museums in Brazil, in field studies of cave paintings and in the laboratory with material sent by archaeologists, as well as carrying out collaborative work with new groups that followed in this area. From 2003/2004 LAMFI/DFN/IFUSP and LIN/COPPE/UFRJ began to engage in the area, respectively with methodologies using ion beams and PXRF, then over time incorporating other techniques, followed later by other groups. Due to the growing number of laboratories and institutions / archaeologists / conservators interested in these applications, in may 2012 was created a network of available laboratories, based at http://www.dfn.if.usp.br/lapac. It will be presented a panel of recent developments and applications of these methodologies by national groups, as well as a sampling of what has been done by leading groups abroad.

Keywords: Archaeometry; Atomic/Nuclear Methodologies; Brazilian Groups; Cultural Heritage

PACS: 29.90.+t; 34.90.+q; 89.90.+n; 89.20.Mn

INTRODUCTION

Archaeometry is an established area since the 60's, with extensive use of atomic-nuclear methods in the characterization of art objects, archaeological and cultural heritage in general. In Brazil, until the early '90s, employing methods of physics, it was implemented only the area of archaeological dating, especially those involving the technique of thermoluminescence.

Only in some punctual cases, very few brazilian works employed “non conventional” methodologies for the characterization of archaeological objects (in almost of them the measurements were done abroad). No brazilian group worked systematically employing atomic-nuclear methodologies before '90s, besides dating methodologies.
In 1992 a member of the Laboratory of Applied Nuclear Physics, State University of Londrina (LFNA / UEL) studied the possibilities of CT in archaeometry [1], as well as the technique of EDXRF analysis of ancient bronzes (Figure 1), working with Prof. Roberto Cesareo, Italy. LFNA measurements in Brazil initiated in 1993 at LIN/CENA/USP and IFUSP/Pelletron. It led in 1994 to formalize Archaeometry (and related issues) among the research lines of LFNA.

The first LFNA research on cultural heritage was the study of a selection of fragments of the archaeological pottery collection of the Historical Museum of Londrina / UEL by Energy Dispersive X-Ray Fluorescence (EDXRF), Rutherford backscattering (RBS) and Gamma-ray transmission (GRT) [2,3].

Since then, other brazilian research groups began to get involved with archaeometry.

Due to the growing number of laboratories and institutions / archaeologists / conservators interested in these applications, in may 2010 a network of 11 available laboratories was created, based at http://www.dfn.if.usp.br/lapac.

**FIGURE 1.** Scanning of a page of the 1992 notebook, which shows the EDXRF data analysis of a bronze Etruscan bracelet (VIII BC, tomb in the region of Genova).
BRAZILIAN GROUPS INVOLVED WITH THE CHARACTERIZATION OF CULTURAL HERITAGE OBJECTS

This list will never be completed, as new groups are being formed in Brazil and it is possible that some information could be missing. Only groups which are continuously working on characterization of Cultural Heritage with atomic/nuclear techniques will be nominated. Groups or individuals with works scattered over time, without continuity, will not be mentioned, which doesn’t mean that they are not important. Data were taken from CV Lattes / CNPq database (http://lattes.cnpq.br) at august, 2012.

Table 1 shows data about the groups which began to work on this issue in the 1990s. In the table are cited the first publication and the first article about Cultural Heritage, respectively. Similarly, Tables 2 and 3 present data about the groups which began to work on this issue in the 2000s and 2010s, respectively.

**TABLE 1.** List of the groups which began to work on characterization of Cultural Heritage in the 1990s. For each group are cited the first publication and the first article about Cultural Heritage, respectively.

<table>
<thead>
<tr>
<th>GROUP</th>
<th>University</th>
<th>City/State</th>
<th>First Published work performed in Brazil on Cultural Heritage objects employing atomic/nuclear methodologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Nuclear Physics LFNA Physics Department</td>
<td>UEL</td>
<td>Londrina PR</td>
<td>1994 (EDXRF, RBS, GRT) [2 - 4]</td>
</tr>
<tr>
<td>Physical and Nuclear Chemistry Group Chemistry Institute</td>
<td>UFF</td>
<td>Niterói ES</td>
<td>1995 (NAA) [5,6]</td>
</tr>
<tr>
<td>Group of Meteoritic, Mineralogy and Archaeometry</td>
<td>CBPF</td>
<td>Rio de Janeiro RJ</td>
<td>1996 (Mossbauer) [7,8]</td>
</tr>
<tr>
<td>Nuclear Analytical Techniques Applied to Environmental and Archeological Studies</td>
<td>IPEN CNEN</td>
<td>São Paulo SP</td>
<td>1997 (NAA) [9,10]</td>
</tr>
</tbody>
</table>

The articles cited in these tables give a good picture of how each brazilian group begin in the field of characterization of Cultural Heritage objects and the range of methodologies employed at that time.
TABLE 2. List of the groups which began to work on characterization of Cultural Heritage in the 2000s. For each group are cited the first publication and the first article about Cultural Heritage, respectively.

<table>
<thead>
<tr>
<th>Group</th>
<th>University</th>
<th>City/State</th>
<th>First Published work performed in Brazil on Cultural Heritage objects employing atomic/nuclear methodologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory of Cultural Heritage Characterization</td>
<td>USP</td>
<td>São Paulo SP</td>
<td>2003 (XRD, MEV, EIE) [11,12]</td>
</tr>
<tr>
<td>Labens / Chemistry Engineering Department POLI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied Physics with Accelerators</td>
<td>USP</td>
<td>São Paulo SP</td>
<td>2004 (PIXE) [13, 12]</td>
</tr>
<tr>
<td>GFAA/DFN/IF/USP +P.R. Pascholati/DFE/IF/USP</td>
<td>UFRJ</td>
<td>Rio de Janeiro RJ</td>
<td>2004 (EDXRF) [14,15]</td>
</tr>
<tr>
<td>Physics Institute</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nuclear Instrumentation Laboratory</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3. List of the groups which began to work on characterization of Cultural Heritage in the 2010s. For each group are cited the first publication and the first article about Cultural Heritage, respectively.

<table>
<thead>
<tr>
<th>Group</th>
<th>University</th>
<th>City/State</th>
<th>First Published work performed in Brazil on Cultural Heritage objects employing atomic/nuclear methodologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Archaeological and Heritage Metrology Group</td>
<td>UFPE</td>
<td>Recife PE</td>
<td>2010 (EDXRF) [16,17]</td>
</tr>
<tr>
<td>LACICOR/EBA Laboratory of Conservations Sciences</td>
<td>UFMG</td>
<td>Belo Horizonte MG</td>
<td>2011 (PXRF; other techniques) [18]</td>
</tr>
</tbody>
</table>

LFNA RECENT WORKS ON CULTURAL HERITAGE

LFNA / UEL has been involved since 1994 with a large variety of Cultural Heritage objects and questions to be answered, with different geometries and matrix, implying in a large range of experimental difficulties to face and solve [19]. Archaeological ceramics has been one of the more frequent object of study since the beginning [2 – 4]
and until the present [20], but other materials from polychromatic wood statues to mural paintings, from metal objects to art rock, among many other different kind of objects, have been studied.

Recent study cases performed by LFNA are briefly presented as follows.

Analysis of 179 coins from Portugal, Colonial Brazil and Imperial Brazil, belonging to the Historical National Museum (RJ) were performed in situ by PXRF at the museum, coins of Ag, Au and Cu were measured. One of the interesting results was the verification of currency devaluation in Portugal during the reigns of kings Fernando I (1367-1383) and João I (1385-1433) of Portugal, as depicted in Figure 2 [21].

![Ag and Cu content in percent for coins minted during the reigns of kings Fernando I (1367-1383) and João I (1385-1433) of Portugal [20].](image)

**FIGURE 2.** Ag and Cu content in percent for coins minted during the reigns of kings Fernando I (1367-1383) and João I (1385-1433) of Portugal [20].

Another example is the non-destructive study of obsidians sourcing by PXRF. This study was performed employing obsidians from Ecuador, in collaboration with R. B. Scorzelli (CBPF / RJ) and G. Poupeau (Université Bordeaux 3, Pessac, France). Measurements were performed with two X-rays tubes, one with Ag anode and another with W anode. Twenty samples from three regions were studied: “Mullumica-Callejones” type (obsidians from the Mullumica and Callejones lava flows, Oyacachi samples, and from their related Rio Guambi secondary sources), “Quiscatola-Yanaurcu” type (obsidians from various sub-primary sources of the Quiscatola area) and samples collected among various volcanoclastic deposits of the Cotopaxi volcano (south of Quito). Grouping results obtained by PXRF are as good as PIXE and ICP, as presented at Figures 3A, B and C, respectively [22, 23].
FIGURE 3A. Two-dimensional plot of the ratios between the concentrations Rb / Rb and Fe / Sr for the Ecuadorian samples measured by PXRF.

FIGURE 3B. Two-dimensional plot of the ratios between the concentrations Rb / Rb and Fe / Sr for the Ecuadorian samples measured by ICP.
Rock art is another interesting and important object of study, due to the large amount of archeological sites in Brazil which presents these kind of paintings. Portable systems allow analysis in the field. The first study was carried out at Jaguariaíva Shelter 1 (Paraná State), by PXRF [24]. More recently, both portable Raman spectroscopy and PXRF have been used to study paintings at Morro Azul Caves 1, 2 and 3, also in Paraná State, employing PCA analysis of the data [25]. As an example of the results, Figure 4 presents the PCA analysis of Raman spectra of different figures and pigment colours.

**MORE DATA ABOUT OTHER TWO BRAZILIAN GROUPS ON CULTURAL HERITAGE**

Two Brazilian groups which entered in the Cultural Heritage area during the 2000’s (Table 2) also evolved to use many complementary methodologies in order to enhance the quality and confidence of the results, as well as to solve more complex problems presented by conservators and archaeologists.

GFAA/DFN/IF/USP group nowadays employs, besides PIXE, also UV and IR examination, Digital Radiography and Portable XRF. Among the last published papers on Cultural Heritage of this group, it is interesting to cite a work about Pre-Hispanic ceramics analyzed using PIXE and radiographic techniques [26].

LIN/COPPE group, besides EDXRF, employs PXRF, Tomography, Digital Radiography, XRD and Raman spectroscopy. Among the last published papers on Cultural Heritage of this group, it is important to cite a systematic work about the characterization of Brazilian artists palette from the XIX century using PXRF [27].
FIGURE 4. PCA analysis of Raman spectra of different figures and pigment colours at Morro Azul Caves [25].

SOME LEADING RESEARCHERS ABROAD

It is very difficult to choose among so many important researches which have been devoted to the study of Cultural Heritage objects, some of them to talk about. There is also my personal bias. So, taken this into account, I’ll present some information about the work of three leading researches abroad.

René Van Grieken, from the Environmental Analysis Group, Micro and Trace Analysis Centre, University of Antwerp, Antwerp, Belgium has published his first paper on Cultural Heritage in 1997. It was about the evaluation of environmental effects on stone decay phenomena at the cathedral of Bari, Italy [28]. More recently he has performed many works about the characterization of indoor atmospheric particles in museums and their sources, employing many complementary techniques. Two recent papers are representative of these researches [29,30].

Roberto Cesareo, now retired from the Dipartimento di Matematica e Fisica, Università di Sassari, Sassari, Italy, has published his first paper on Cultural Heritage in 1973. It was about nondestructive analysis of early Etruscan gold objects by XRF [31]. Since then he has published hundreds of papers about his researches on Cultural Heritage and also develop scientific collaborations with many Brazilian groups. A representative work is a research which has been taken more than a decade and involved collaborations with many researches in Peru, Italia and Brazil is about the evolution of Pre-Columbian metallurgy from the North of Peru, studied mainly with PXRF and some complementary techniques. The last publication about it was published in 2011 in a 34 pages article [32]. Among the co-authors of this paper are...
members of three Brazilians groups, LFNA – UEL (Table 1), GFAA – USP and LIN – COPPE (Table 2).

Maria Luisa Carvalho, from Atomic Physics Centre, Lisbon University Lisbon, Portugal, has published his first paper on Cultural Heritage in 2002. It was about Arsenic detection in nineteenth century Portuguese King post mortem tissues by energy-dispersive X-ray fluorescence spectrometry [33]. A representative work among her recent research employing many complementary techniques is the study of mural paintings using In Situ XRF, Confocal Synchrotron μXRF, μXRD, Optical Microscopy and SEM-EDS of the Frescoes from Misericordia Church of Odemira, Portugal [34].

As final remarks, for who wants to work in the field of archaeometry, or wants to follow what is going on in this area, among dozens of international congresses about Cultural Heritage (or with sessions on Cultural Heritage), pay attention specially to:

(a) International Symposium on Archaeometry (ISA), the 39th International Symposium on Archaeometry - “50 years of ISA” took place in Leuven, Belgium, 28 May – 1 June 2012, web site is http://ees.kuleuven.be/isa2012, where the abstracts can be downloaded - the next meeting will be in 2014; (b) Non-destructive and Microanalytical Techniques in Art and Cultural Heritage (TECHNART) Congress, the TECHNART 2011 took place in Berlin, April 26 - 29, 2011, web site is http://www.technart2011.bam.de, where the abstracts can be downloaded - next meeting will be in 2013.

REFERENCES


34. S. Valadas et al., *Microscopy and Microanalysis*, v. 17 (05), 2011, p. 702 709.