Evaluation submitted by Croatia

00CRO409: Development of nuclear microprobe x-ray spectroscopy for applications in conservation of national cultural heritage

Contribution received from UNESCO: 15000 USD

Evaluation of the project or activity implemented:

a) Purpose and objectives

Several nuclear techniques are today widely accepted as an analytical tool that is used in the process of cultural heritage conservation. Carbon dating is for example among the most recognized nuclear techniques in this field. Among the other similar techniques, particular attention deserves x-ray spectroscopy. The most sophisticated among the x-ray spectroscopy variations is certainly PIXE (particle induced x-ray emission) spectroscopy that uses the focused scanning ion microbeam for x-ray excitation. This technique (later referred as microPIXE) is unfortunately rather expensive since it requires large accelerator and not simple to use ion beam focusing device (microprobe). Therefore there is today only one dedicated accelerator facility for the microprobe applications in art and archaeology (AGLAE in Louvre).

However, in the collaboration of museums or conservation workshops with research Institutes or Universities having already microPIXE system set-up, many advantages of such analytical technique can be utilized efficiently as well. Since in Croatia, nuclear microprobe laboratory already exists at the Ruđer Bošković Institute in Zagreb, adopting the existing equipment for its analytical applications related to conservation of national cultural heritage was the main project task.

In order to achieve that goal, purchase of a new x-ray detector was proposed as the core investment of this project. That was planned to follow with other activities such as study visits, purchase of various materials, publications, organization of workshops, etc., resulting finally in established and routine link between the Ruđer Bošković laboratory for ion beam interactions and the analytical laboratory of the Croatian Conservation Institute (HRZ in later text).

Since the approved UNESCO contribution was lower then requested (15000 instead of 25000 USD), it could cover only the purchase of x-ray detector (silicon drift detector – SDD with associated electronics and vacuum equipment) that was installed at the IRB nuclear microprobe (Figure 1). All other planned activities were or would be performed using the alternative funding sources.

However it can be stated that the main objective of the proposed project has been reached. This will be more clearly elaborated in the following sections.
b) Results, benefits and impact

A new scattering chamber presented at Figure 1 was installed at the nuclear microprobe facility in summer 2001. After the order of SDD x-ray detector made by Ketek Gmbh, and other necessary vacuum and electronics parts from Ortec and K. Lesker companies, final installation of x-ray detector was performed during January and February 2002, with first x-ray spectra obtained on 18\textsuperscript{th} February. The analysis set-up is presented in the close view at Figure 2.
As it is seen, several samples can be mounted on the holder. Using the sample micromanipulator, user can direct particular sample region to be exposed to the focused beam at the center of the chamber, while viewing optical microscope image at the monitor (Figure 3). Then, the focused ion beam is scanned over the surface of sample. During the irradiation time, ion beam (typically these are protons of 3 MeV energy and 100 pA current) ionizes atoms in the sample. Among other processes, ionized atoms emit x-rays that have characteristic energy, which depends on the atomic number. Using SDD x-ray detector, data acquisition system and information from the beam-scanning device, computer program selects different energy x-rays into images of particular element distribution in the sample. Schematic presentation of microPIXE analysis is given in Figure 4.
Figure 3. Cabinets of electronic modules that control operation of the nuclear microprobe, including the sample-viewing monitor (up).

Figure 4. Schematic presentation of microPIXE experiment and formation of elemental images that are result of the analysis.
As it is explained, the main result of this project is finalized microPIXE facility at the R. Bošković Institute. From our past experience in working with samples of materials that have been subject of conservation process, several ways of microPIXE application can be and will be performed:

- Analysis of homogeneous microscopic samples
In the case of objects such as statues made of alloys or other objects of homogeneous materials, it is possible to cut very small amount of material from the object. In the case of microPIXE analysis, object size that can still be successfully analyzed may be of dimensions as small as 10 µm (one hundredth of mm). In such cases, beam is directed towards this microscopic sample and positioned at its center. By acquiring PIXE spectrum of that point, quantitative PIXE analysis will give concentration of all elements in the sample.

- Analysis of sample cross sections
Standard technique used in conservation of wall paintings, large statues, and similar object where larger samples (few mm) can be taken, is preparation of cross sections for optical microscopy. These samples are embedded in resin with one side polished. Such samples are ideal for microPIXE without the need of additional sample preparation. Using the ion beam that scans over the sample, elemental images can lead towards understanding of composition of different layers in the original painting and therefore to the knowledge of pigments used.

In order to illustrate these options an example of our recent analysis of Apoxiomenos statue found two years ago at seabed in the vicinity of Lošinj island in the Adriatic see. Figure 5 presents PIXE spectrum of one part of alloy. In the table 1 below it is also given typical result of PIXE analysis of two different sample regions.

![Figure 5. Typical PIXE spectrum of alloy (Apoxiomenos)](image-url)
<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.22</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
<td>66.54</td>
<td>7.80</td>
<td>25.24</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0.07</td>
<td>0.00</td>
<td>0.02</td>
<td>91.57</td>
<td>5.99</td>
<td>2.21</td>
</tr>
</tbody>
</table>

Table 1. Typical PIXE analysis results of two different alloy sample regions

Figure 6. Photograph of typical sample cross section, indicated the region scanned by microbeam. Elemental maps obtained by microPIXE are given as well.
There are many benefits of our approach to use microPIXE in problems of interest to conservation. From the financial point of view, it is impossible at the moment to purchase different analytical techniques for the use at HRZ laboratory. From the expertise point of view it is very difficult also to achieve that HRZ personnel can use successfully these analytical techniques. And finally sophisticated techniques such as PIXE can now be used for HRZ need as well.

c) Difficulties

Limited funds available were our major difficulty. However, the main task has been successfully accomplished. Other planned activities will be delayed until the funding source will be found.

d,e) UNESCO

Since the first results were obtained just recently in February, no announcements to the media have been made. It is planned however that after the first successful joint work involving PIXE analysis at some conservation project will be publicized. Project summary and some results are also available now on web address: [http://www.micro.irb/projects/unesco.html](http://www.micro.irb/projects/unesco.html)

In the all activities regarding the project realization, UNESCO field office help was of great significance.

IV. Follow-up, long term plans.

No follow-up is planned. It has to be stressed that the long-term plans exists since the main purpose of the project is actually to establish routine and long term link between IRB laboratory and HRZ. It is therefore expected conservation activities will further increase in future, partly because of involvement of new analytical techniques such as microPIXE.

V. Other funding sources

Due to the interdisciplinary nature of nuclear microprobe techniques, other sources of funding were used in the establishment of facility. In particular these were several projects financed by Ministry of science and technology of Croatia that also include IRB staff salaries and IAEA (International Atomic Energy Agency) CRP project on light element analysis using ion microbeam. Using the funds from these projects the main scattering chamber at the microprobe facility has been rebuilt.
VI. Other observations

Authors and project collaborators from Ruđer Bošković Institute and Croatian Conservation Institute greatly acknowledge UNESCO funding of this interdisciplinary project.

VII. Stamp, signature and date

Dr Milko Jakšić                  Dr Stjepan Marčelja
Project coordinator               Director

Date: 26th February 2002.