**Methodological approach in the study of multi-material artefacts by the use of portable X-ray Fluorescence Spectrometry**

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# METHODOLOGICAL APPROACH IN THE STUDY OF MULTI-MATERIAL ARTEFACTS BY THE USE OF PORTABLE X-RAY FLUORESCENCE SPECTROMETRY

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## 1 - INTRODUCTION

Obtaining reliable data through portable and non-invasive techniques is often a necessary condition in the study of Cultural Heritage. In fact, this study deals with the methodological approach adopted in the analysis of three reliquaries kept at Musée de Cluny (Paris, France) with which there is a consolidated collaboration. The main particularity of these important medieval works lies in the diversity of the materials that constitute them: they are usually made of gilded metal decorated with glass, enamels, and gemstones as real pieces of jewellery [1].

Moreover, reliquaries are objects of cult that are sometimes carried in procession and exposed to the touch of the devout and they are often re-arranged over time or have been reproduced in copies. Elemental analysis allows the recognition of authentic parts and remakes and provides very useful information on production techniques and the provenance of raw materials.

Among other things, it allows comparisons to be made with other products of the same period but of different manufacture. The adoption of X-ray Fluorescence Spectrometry has enabled an accurate characterisation of artefact materials by exclusively non-invasive approach:

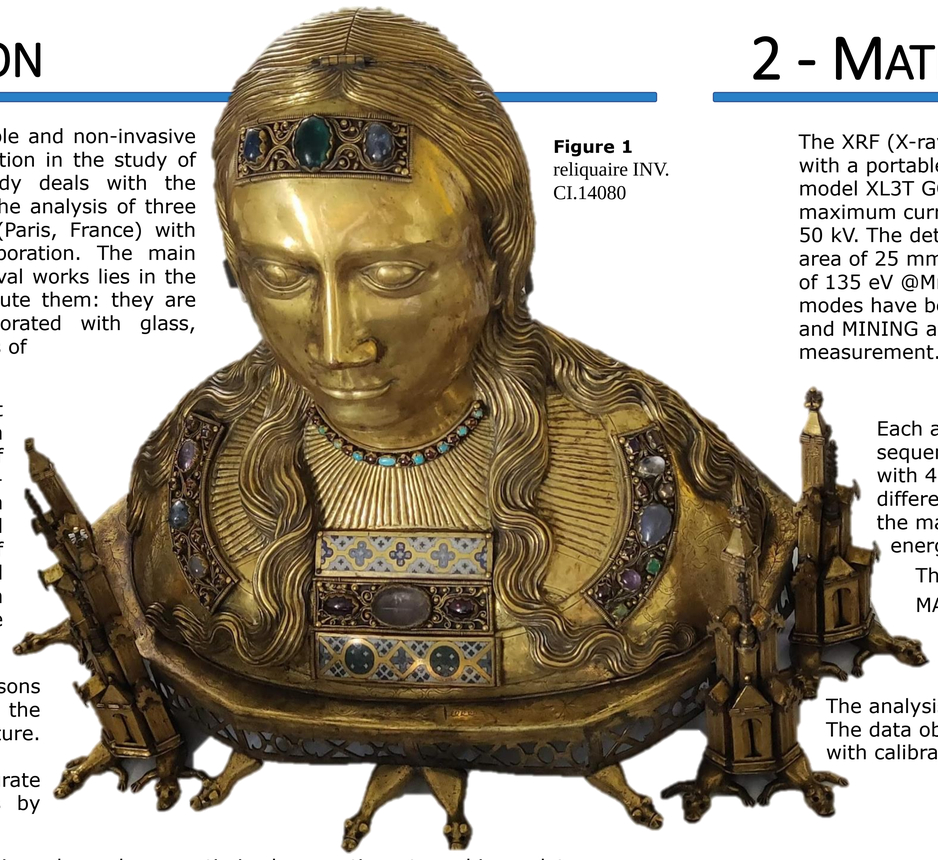

**Figure 1**
reliquaire INV. CI.14080

different measurement conditions have been optimised over time to achieve data comparable with those presented in the literature concerning medieval jewellery [2].

The outcomes are of certain relevance given the lack of systematic diagnostic studies in the scientific literature specifically concerning materials of European late medieval anthropomorphic reliquaries [3]. The combination with optical microscopy allowed a characterisation of the appearance and the colours of the various surfaces investigated. (*Fig.1*).

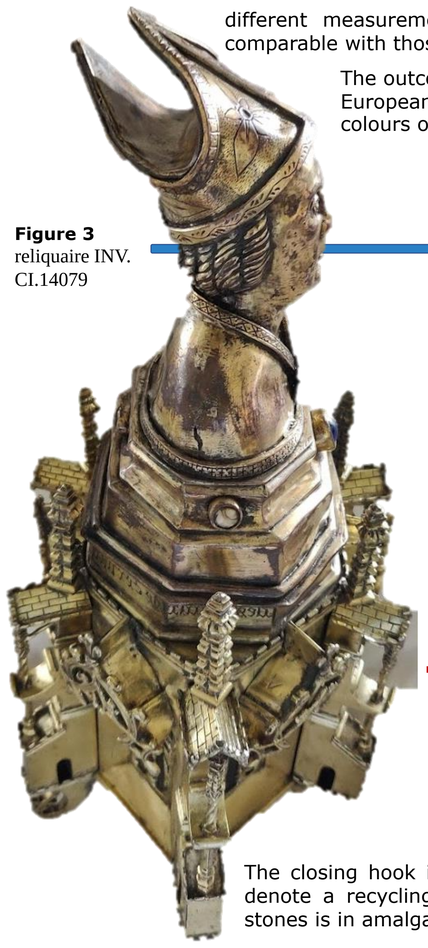

**Figure 3**
reliquaire INV. CI.14079

## 2 - MATERIALS AND METHODS

The XRF (X-ray fluorescence) analyses were performed with a portable instrument (East Greenbush, NY, USA) model XL3T GOLDD equipped with an Ag target with a maximum current of 100 μa and voltages between 8 and 50 kV. The detector is a large drift (LDD) with a surface area of 25 $mm^2$ and an energy resolution of 135 eV @MnKα. Two acquisition modes have been adopted: METALS and MINING and 120 second measurement.

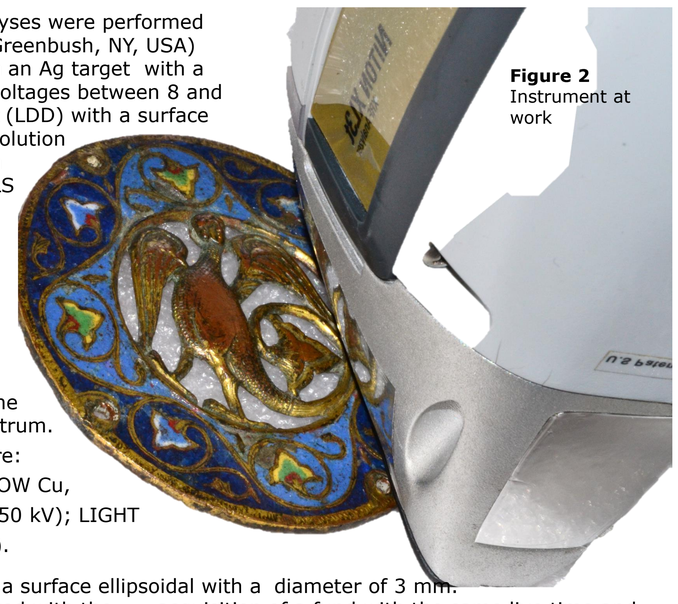

**Figure 2**
Instrument at work

Each analysis provided 4 sequential measurements with 4 voltages and 3 different filters to improve the material response in the energy range of the spectrum.

The conditions used are:
MAIN Al/Fe (40 kV); LOW Cu, 20 kV; HIGH MO (50 kV); LIGHT no filter (8 kV).

The analysis was performed on a surface ellipsoidal with a diameter of 3 mm. The data obtained were compared with the acquisition of a fund with the same live time and with calibration standards (NIST, SGT, CORNING, MBH). (*Fig. 2*).

**Figure 4**
reliquaire INV. CI.14079

## 3 - RESULTS

The blue gem (CI.14079_1) is a lead glass that uses potassic-based flux (probably from continental plant ash).

Chromophore is cobalt ($Co^{2+}$) with associated zinc impurities. The origin of glass is certainly modern.

The green gem (CI.14079_3) and brown gem (CI.14079_4) are also glasses. The first one presents analogies with which it differs only by chromophore, in this case, copper ($Cu^{2+}$). The second, closer to an opaque enamel with lead arsenate, also has a high content of calcium antimoniate. The presence of antimoniate, used especially at the end of the Roman period, leads to a fascinating hypothesis of modern recasting of an ancient glass. The color is given by the presence of high concentrations of manganese ($Mn^{2+}$).

The white stone (CI.14079_2) is actually a marble composed of a double calcium and magnesium carbonate.

| | BaO | $Sb_2O_5$ | SrO | $As_2O_3$ | PbO | ZnO | CuO | CoO | $Fe_2O_3$ | MnO | CaO | $K_2O$ | $SiO_2$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14079 1 | 0 | 0 | 0 | 0 | 40.3 | 0.06 | 0.11 | 0.02 | 0 | 0 | 0 | 4.6 | 35.8 | 0.9 |
| 14079 2 | 0.04 | 0 | 0.15 | 0 | 0 | 0 | 0.20 | 0 | 0 | 0 | 59.4 | 0 | 0 | 0 |
| 14079 3 | 0 | 0 | 0 | 0.0 | 51.0 | 0 | 0.44 | 0 | 0 | 0 | 0 | 0.7 | 24.4 | 1.6 |
| 14079 4 | 0 | 0.8 | 0 | 2.3 | 28.3 | 0.04 | 0.37 | 0 | 0.3 | 2.1 | 2.3 | 5.1 | 36.4 | 0.5 |

The reliquary INV. CI.14080 is much more complex in terms of composition, it is copper gilded with amalgam of mercury, in which the characteristics of antimony impurities are again noted.

The composition of the posterior cap is still gold copper, but the antimony impurities observed on the face are not observed, so it is assumed that it was performed at a different period than that of the head.

The closing hook is made of copper with lead, tin and antimony impurities, which denote a recycling source. The filigree which decorates the plates containing the stones is in amalgam gilded copper.

| | $Sb_2O_5$ | $SnO_2$ | SrO | PbO | CuO | CoO | $Fe_2O_3$ | MnO | CaO | $K_2O$ | $Al_2O_3$ | $SiO_2$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14080 1 | 3.35 | 0.02 | 0.04 | 0.2 | 0.3 | 0 | 0.8 | 0.2 | 8.6 | 0.7 | 2.4 | 76.7 | 0.6 |
| 14080 2 | 3.08 | 0.03 | 0.04 | 1.0 | 0.3 | 0.05 | 0.9 | 0.4 | 6.9 | 0.7 | 2.3 | 59.1 | 0.5 |
| 14080 3 | 3.11 | 0.02 | 0.04 | 0.9 | 0.4 | 0.12 | 0.9 | 0.3 | 6.8 | 0.5 | 2.5 | 54.8 | 0.5 |
| 14080 5 | 3.21 | 0.02 | 0.04 | 0.5 | 0.5 | 0.06 | 1.1 | 0.6 | 8.6 | 0.8 | 2.8 | 77.9 | 0.6 |
| 14080 6 | 1.49 | 0.06 | 0.04 | 1.8 | 2.9 | 0 | 1.4 | 0.3 | 6.6 | 1.0 | 2.6 | 58.8 | 1.0 |
| 14080 7 | 3.73 | 0.04 | 0.04 | 0.3 | 0.9 | 0 | 0.6 | 0.2 | 7.2 | 0.6 | 1.7 | 56.0 | 0.6 |

**Figure 5**
Enamels on reliquaire INV. CI.14080

Analysis of the metals of the reliquary INV. CI.14079 shows some differences in composition on the alloys used for making the bust and base.

The bust was made of pure copper, with an amalgam gilding of mercury (now completely disappeared at analysis point 5).

| | Sn | Ag | Au | Hg | Pb | Zn | Cu | Fe |
|---|---|---|---|---|---|---|---|---|
| **14079 5** | 0 | 0 | 0 | | 0 | 0 | 99.1 | 0 |
| **14079 6** | 0 | 0 | 18.0 | X | 0 | 0 | 81.6 | 0 |
| **14079 7** | 0 | 0 | 53.9 | X | 0.44 | 0 | 45.2 | 0 |
| **14079.base 8** | 0 | 46.0 | 51.2 | X | 0.39 | 0 | 0.6 | 0 |
| **14079.base 9** | 0 | 42.9 | 54.4 | X | 0.36 | 0 | 0.7 | 0 |
| **14079.base 10** | 2.9 | 58.2 | 30.0 | X | 0.79 | 6.2 | 0.6 | 0.6 |
| **14079.base 11** | 0 | 35.8 | 54.8 | X | 0.43 | 0 | 0.7 | 0.1 |

Points 1, 2, 3, 5, 6 and 7 refer to the composition of the enamels present on the two plates located on the chest of the reliquary bust. They are enamels of different colors, white (1 and 7), light blue (2 and 5), blue (3) and green (6). These are opaque enamels with calcium antimoniate, melting ashes of littoral plants essentially based on sodium. The stabilizers are of calcium and magnesian origin

Chromophores are copper ($Cu^{2+}$) for green and cobalt ($Co^{2+}$) for dark blue and light blue.

## 4 - CONCLUSIONS

In conclusion, it was possible to determine how there is an affinity of composition between the busts Cl.14080 and Cl.14083, which are made of gilded copper that has common antimony impurities, which are reminiscent of a medieval manufacture.

The shell of the bust Cl.14080 seems to be a replacement.

The composition of the bust Cl.14079, in copper with gilding with amalgam of mercury, is also compatible with a medieval production, although it shows no affinity of composition with the two previous busts.

The bases, which are certainly newer, more precious structures in gilded silver is those of the objects Cl.14079, compared to the structure of the Cl.14080 in gilded brass.

The enamels of the bust Cl.14080 are extremely interesting because probably of Rhine origin.

The precious stones of all works are also precious, except when they are replaced by glass.

MUSÉE DE CLUNY
le monde médiéval

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