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METHODOLOGICAL APPROACH IN THE STUDY OF MULTI-MATERIAL ARTEFACTS BY THE USE OF PORTABLE X-RAY FLUORESCENCE SPECTROMETRY Agostino A.*⁽¹⁾, Maria L.⁽¹⁾, Operti L.⁽¹⁾, Cimino D.⁽²⁾, Tixier F. ⁽³⁾ and Descatoire C.⁽⁴⁾

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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].



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 mm² and an energy resolution of 135 eV @MnKa. Two acquisition modes have been adopted: METALS and MINING and 120 second measurement.



Moreover, reliquaries are objects of cult that are sometimes carried in procession and exposed to the touch of the devout and they are often rearranged 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 3

CI.14079

reliquaire INV.

of ee h n ee s,

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*).

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 2 Instrument at work

U.S Patel

CI.14079

reliquaire INV.

The blue gem (CI.14079_1) is a lead glass that uses potassic-based flux (probably from continental plant ash). Chromophore is cobalt (Co²⁺) 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 ₂ O ₅	SrO	As ₂ O ₃	PbO	ZnO	CuO	CoO	Fe ₂ O ₃	MnO	CaO	K ₂ O	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.

14080 1 0.6 14080 2 0.5 140803 0.6 14080 5 77.9 0.02 140806 2.6 58.8 1.0 0.04 0.6 1.7 56.0 0.6 140807 0.04 0.9 0.6 0.2 7.2 0.3



MUSÉE DE CLUNY

le monde médiéval

14079.base 8 14079.base 9 14079.base 10 14079.base 11 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 🗧
0	0	0		0	0	99.1	0
0	0	18.0	Х	0	0	81.6	0
0	0	53.9	Х	0.44	0	45.2	0
0	46.0	51.2	Х	0.39	0	0.6	0
0	42.9	54.4	Х	0.36	0	0.7	0
2.9	58.2	30.0	Х	0.79	6.2	0.6	0.6
0	35.8	54.8	Х	0.43	0	0.7	0.1



Chromophores are copper (Cu²⁺) for green and cobalt (Co²⁺) 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.

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