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Unusual Composition of the Sarezzano Reliquary Busts

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Abstract: The interdisciplinary study of two reliquary busts from Sarezzano (Piedmont, Italy) is a perfect example of the necessity to provide for material characterisation as a recurring common practice in historical studies and a mandatory step in conservation assessment. Furthermore, the diagnostics of cultural heritage play a crucial role in art historical research, providing relevant information on artefacts' genesis, production technology, and conservation history. The study of the materials of the reliquary busts was performed by non-invasive (portable X-ray fluorescence spectrometry) and micro-invasive (stereomicroscope, attenuated total reflection Fourier transform infrared spectroscopy and powder X-ray diffraction analysis) methods. According to the results, the busts were found to be made of a tin–lead alloy, a rather unusual material for mediaeval reliquary busts. Moreover, the outcome suggests that the busts were originally silvered, except for the hair and beard which are still gilded. The analysis reveals the use of colophony as an adhesive buffer layer on the busts' alloy, as well as inside them, to favour the metal working process, since it is found as degraded residue. Finally, even the typology of alloy decay is defined. All this information has enabled us to determine the artistic technique and estimate the value and quality of the material employed. In addition, it has led to the correct choice of materials and methods to be adopted during the restoration, and therefore the usage of more suitable solvents and tools.

Keywords: reliquary busts; tin–lead alloy; gilding; colophony; conservation; non-invasive analysis

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1. Introduction

The study concerns two 15th-century reliquary busts analysed before the necessary restoration work. Saint Ruffino and Saint Venanzio (Figure 1) were first analysed and subjected to an interdisciplinary study for the exhibition '*Ritratti d'oro e di argento. Reliquiari medievali in Piemonte, Valle d'Aosta, Svizzera e Savoia*', held in 2021 in Palazzo Madama (Museo Civico d'Arte Antica in Turin) [1]. The busts were found in the early 2000s, in the parish church of Saint Ruffino and Saint Venanzio in Sarezzano (Italy, province of Alessandria) and are now kept in *Oratorio della Madonna Addolorata* in Sarezzano. The research aimed at an in-depth study from both an art-historical and a conservation perspective, as well as investigating the materials of the artefacts.

The Sarezzano busts portray two hermit saints, specifically, Saint Ruffino and Saint Venanzio, who lived in the 6th century. Coming from the monastery of Bobbio (Italy, province of Piacenza), they eventually established their ascetic home in the peace of the hills near Tortona (Italy, province of Alessandria), starting their work of evangelisation in the rural areas around the hamlet of Sarezzano. Their names are deeply connected with the events of the *Evangeliario di Sarezzano* or *Codex Purpureus Sarzanensis*, a purple codex produced between the second half of the 5th century and the beginning of the 6th century, containing the text of the four Gospels written with gold ink on parchment coloured in purple. The two saints are not considered the scribes of the codex, but rather a sort of guardians of it. When the codex was accidentally discovered in 1585 during the inspection of the local bishop to the parish church of Sarezzano, it was found next to the sarcophagus of the two hermits, becoming known in popular piety as "the book of the Saints".

(**a**) (**b**)

Figure 1. The reliquary busts of (**a**) Saint Ruffino; (**b**) Saint Venanzio. Studio Gonella, courtesy of Fondazione Torino Musei. Published in Castronovo, S.; Vallet, V.M. *Ritratti d'oro e d'argento. Reliquiari Medievali in Piemonte, Valle d'Aosta, Svizzera e Savoia*; L'Artistica Editrice: Savigliano (Italy), 2021, [1].

Even at first glance, the two busts look different from the other reliquaries from the same period on show in the previously mentioned exhibition. They come from different places in Piemonte and Valle d'Aosta (north-western Italy) with manufacturing dated from the 12th to the 16th century. At this event, many works were collected for a total of 24 reliquaries from both Italian regions, but those present in the area turn out to be more than double. Several other examples were produced in other places in Italy and Europe since the Middle Ages [2,3]. Reliquary busts and heads are also called speaking reliquaries or anthropomorphic reliquaries, sometimes including arm or foot shapes. Many of them represent a sophisticated expression of mediaeval goldsmithing. These works depict saints, and contain, whether currently or originally, different kinds of relics, in some cases exhibited in a theca and others contained within the reliquary. In many cases, they are formed by assembling worked metal plates. These were embossed and engraved to create works in the round. Several reliquaries consist of partially amalgam-gilded silver and copper sheets. The gilded portions are usually the hair, eyebrows, moustaches, and beards, and sometimes even the robes. The most commonly used gilding technique was fire gilding by applying an amalgam of gold and mercury, with subsequent volatilisation of this obtained by the appropriate heating. Most of the reliquaries are made of very precious materials. In many cases, they were decorated with pearls, gemstones or glass bezels, and enamels. According to sources, the speaking reliquary, documented as the oldest in Western Europe and which was destroyed by the Huguenots in the second half of the 16th century, is the one that held a fragment of Saint Maurice's skull, found in the cathedral of Vienne (France). It was made entirely of gold and covered with gems, silver bells, and eyes made of agate and chalcedony. It also had a gold crown with pearls, rubies, sapphires, and emeralds. It is considered to be a progenitor of this kind of jewellery manufacturing. Some reliquaries are instead carved in wood with painted and gilded details. The value of the materials used in the manufacturing depended on the availability of the commissioners. Often, some of the reliquaries were damaged as they were displayed to the devotees or carried in processions. Some have been rearranged over the centuries with details added, remodelled, or replaced. Moreover, some relics are kept inside churches, cathedrals, or abbeys, where optimal conservation conditions have not always been ensured.

The characterisation of the materials of the Sarezzano busts has become urgent due to their state of conservation. Diagnostics can provide relevant information on artefacts' genesis, production technology, conservation history, and essential indications for conservation purposes [4,5]. Despite this, analysing materials is currently just an optional choice, closely linked to the sensitivity of professionals involved in the conservation assessment. It can also be very dangerous for the work's integrity and this could have been the case for the reliquaries of Saint Ruffino and Saint Venanzio. Investigation played a crucial role in art historical research and is a fundamental phase for restoration planning.

2. Materials and Methods

Reliquary busts of the saints are shown in Figure 1. Although very similar to each other, careful observation of them makes it possible to distinguish Saint Ruffino (the oldest) and Saint Venanzio (the youngest). Also, having different dimensions, there are indeed many differences, including the height (Saint Ruffino is 43 × 52 × 19 cm and Saint Venanzio is 41 × 52 × 19 cm). They consist of sheets of casted metal which are then chiselled, embossed, and engraved. There are many gilded details, including the long beards, the hair, and the eyebrows. In addition, they both have a gilded cross on their shoulder. The back of the heads has a rectangular window, currently open for Saint Venanzio and closed by welding in the case of Saint Ruffino's scruff. Particularly, from the inside of the busts, it is possible to observe that each bust is made up of four sheets, soldered along the shoulders and the neck. The ends resting on the bases have a metallic reinforcing bar internally fixed by nails. The internal perimeters of the heads' windows are surrounded by a metal frame that probably originally supported another kind of window, perhaps transparent or sliding, arguably to make the relics visible.

The state of conservation was not optimal; the busts' surface is characterised by some globular alteration products, quite evident on the faces, and in the case of Saint Venanzio holes also formed. Additionally, the gilding was cracked with some detachment in different parts, and the remaining unknown parts were very fragile and prone to dusting. Moreover, inside Saint Venanzio's head was the remnant of a potter wasp's nest.

To identify the composition of alloy and metal coatings, X-ray fluorescence spectrometry by portable instrumentation was adopted [6]. The gilding and surfaces were examined under the microscope. Some samples of brown-reddish organic materials were taken from the shoulder (Figure 2a) and the inside (Figure 2b) of the Saint Ruffino bust to be analysed by infrared spectroscopy. The sampling on the shoulder was performed near the edge of a detachment. Sampling from the inside of the bust was performed at the abundant substance that had to be identified.

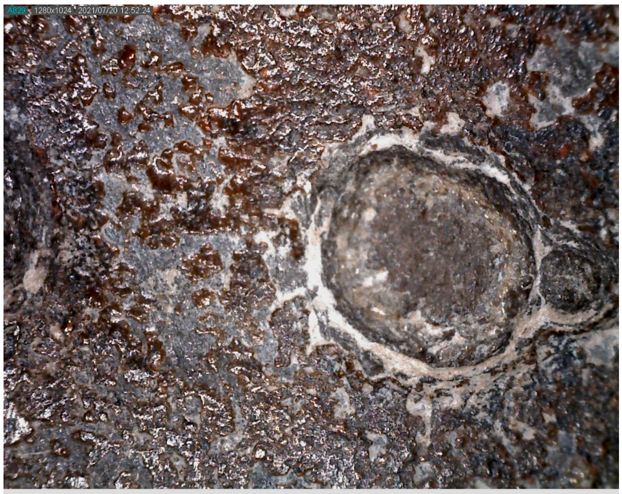
(**a**)

(**b**)

Figure 2. Area of sampling of brown-reddish organic materials: (**a**) Saint Ruffino shoulder; (**b**) inside Saint Ruffino.

Additionally, in the interest of defining some globular alteration products located on the busts' faces (Figure 3a,b), a very small sampling was examined by powder X-ray diffraction spectroscopy. The sampling was expertly carried out by the appointed restorer and concerned a small globular protruding fragment located on the cheekbone of Saint Ruffino.

(**a**)



(**b**)

Figure 3. Globular alteration products: (**a**) photography of the face of Saint Venanzio; (**b**) details acquired by optical microscopy on the face of Saint Ruffino.

2.1. Optical Microscopy

Different optical microscopy instruments were used to analyse the surfaces of the reliquaries and for the sampling. A Dino-Lite (New Taipei City, Taiwan) handheld digital USB microscope, AM4113T-FV2W model, used in situ, acquired digital images at different magnifications. For the sampling, the optical microscopy instrumentation used was a Leica MZ16 stereo microscope (Wetzlar, Germany) with 45° illumination and a light source Leica Schott KL 1500 LCD.

2.2. Portable X-Ray Fluorescence Spectrometry (pXRF)

The elemental analyses were carried out by XRF spectrometry. The portable instrumentation was a Thermo NITON spectrometer, XL3T-900 GOLDD model (East Greenbush, NY, USA), equipped with a Ag anode, max. voltage 50 kV, max. current 100 µA, and power 2 W. The spot size on the sample was 8 and 3 mm in diameter. Each measurement lasted 120 s and consisted of acquisitions under different conditions in voltage, intensity, and kind of filters. The measurements were carried out by holding the analytical head on a stand.

Quantitative analysis based on a mixed method (fundamental parameters and standards) was performed by XRF spectra processing with software bAxil (Version 1.1, Bright-Spec NV/SA, Belgium), derived from the academic software QXAS (Version 3.6) from IAEA. Certified Reference Materials (91XS63PR1G56 and 91XS10PR2C16) consisting of alloys with a similar composition to those investigated were used (MBH Analytical Ltd., Teddington, England). The study of coatings was made by superimposing micro-foils of gold or silver (Goodfellow Cambridge Limited, Huntingdon, England) with different thicknesses (0.1, 0.25 and 0.5 μm). The micro-foils were measured under the same conditions as those adopted in the artefacts' analyses. The composition and thickness of the micro-foils were known; they were analysed and placed on top of the metal samples with a known composition, compatible with the busts' composition, allowing a calibration to be defined. The thickness of the coatings of the busts was ensured by employing a linear regression.

2.3. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (FTIR-ATR)

The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) has been performed on a sample of about 1 cm^2 taken from the inside of the bust of Saint Ruffino. The measurements were carried out with Bruker Vertex 70 instrumentation using the Platinum set-up with diamond ATR crystal. Each spectrum is the result of 32 scans. The spectral resolution is 2 cm^{-1}. This technique allows qualitative information to be obtained to characterise molecules and materials. The spectra were examined using OPUS version 6.0 (Bruker Optics GmbH & Co., Ettlingen, Germany).

2.4. Powder X-Ray Diffraction Analysis (XRPD)

Powder X-ray diffraction analysis (XRPD) was performed on a corrosion product sampling belonging to Saint Ruffino's reliquaries to integrate information concerning the degradation mineral phase present in the specific investigated areas with non-invasive results. The instrumentation is X'Pert Panalytical diffractometer (Almelo, The Netherlands), equipped with a copper anode and an Ultrafast PixCell1D detector, and operating at 40 kV, 30 mA, 0.002° step, 100″ per step Bragg–Brentano geometry. The sample was ground to minimise the effect of any preferential orientations. Diffractograms were interpreted with the software DIFFRAC.EVA (Version 7, Bruker, Billerica, MA, USA) and International Centre for Diffraction Data (ICDD) database.

3. Results and Discussion

3.1. The Alloys

The alloys were analysed in different measurement points, outside and inside the busts, to understand their composition and production techniques. The primary elements detected were tin and lead, namely pewter, which were found in highly variable concentrations across different areas of the busts as shown in Table 1.

Table 1. XRF analysis results presented in percentage by weight (w/w%). They were obtained from measurement areas from the inside and outside of Saint Ruffino (SR_inside and SR_outside). These measurements refer to selected areas without coatings.

Title 1	Sn	Err±	Pb	Err±	Cu	Err±	Fe	Err±	Bi	Err±
SR_inside	77	4	20	1	1.27	0.06	1.03	0.05	1.05	0.05
	66	3	31	2	1.45	0.07	0.17	0.01	1.14	0.06
SR_outside	92	5	5	0.2	2.6	0.1	0.94	0.05	0.05	0.01
	85	4	12	0.6	2.7	0.1	0.41	0.02	0.26	0.01
SV_outside	94	5	4	0.2	1.05	0.05	0.26	0.01	0.13	0.01
	84	4	14	0.7	1.82	0.09	0.46	0.02	<LOD *	-

* Less than Limit of Detection.

Lead concentration was between 5% and 30%, while minor elements such as copper (about 1.5%), bismuth, and iron (both less than 1%) were also detected. Notably, along the edges of the rectangular hole at Saint Ruffino's head, where a window might have once been soldered, and in the areas inside the shoulder, where the front and black sheets were likely joined, lead concentrations detected were found to be greater than 30% and up to 35%, tending to the eutectic point (61.9% Sn and 38.1% Pb at 183 °C), which ensures a lower melting temperature, thus facilitating easier soldering and assembly.

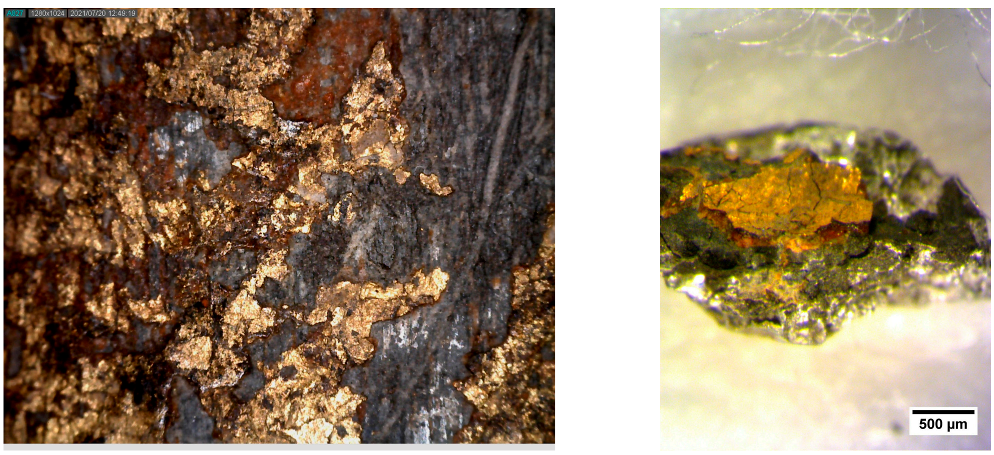
The two busts are made of the same materials and have identical production techniques, indicating a consistent manufacturing approach. The variability observed in the composition of the major elements of the alloy could be attributable primarily to the presence of alteration products and, in some areas, to the red-brown adhesive layer that occurs on the metal surfaces, which is discussed in detail in the following section. As far as we know, no other known examples of reliquary busts of this size were made of gilded or silvered tin–lead alloy, making these artefacts unique. While pewter was commonly used for everyday objects, such as tableware, liturgical objects, and other small devotional objects such as pilgrim badges and ampullae [7–9], its use in large objects like these busts is unprecedented.

The XRF analysis of the metal bar nailed internally to the base of both busts revealed that it was made of iron in both cases. The XRF results confirmed that the busts were primarily composed of pewter, which was relatively inexpensive compared to the more valuable materials typically used for mediaeval reliquary busts, such as silver and gold. While this material choice is unusual for Italian reliquary busts, it is rather more common in other parts of Europe, where tin–lead alloys have been employed in jewellery and other decorative objects. The decision to use this alloy for the bust of Saint Ruffino and Saint Venanzio could have been influenced by several factors [10], as follows: a lead-tin alloy is cheaper than precious metals, has a lower melting temperature that facilitates casting in moulds, and its hardness allows for detailed craftmanship, including the chiselling. Furthermore, the alloy tends to retain its shine for an extended period, although in the case of these busts, the surface of the alloy was not intended to be the final visible layer. This aspect is further addressed in the section discussing the coatings.

The analysis underscores the unconventional choice of materials and techniques adopted in the busts' realisation. The pewter is affordable and practical for crafting but diverges from the more treasured materials traditionally associated with such sacred objects. This choice likely reflects specific functional, economic, or aesthetic considerations that set these works apart from other mediaeval reliquaries, offering insight into the broader context of their manufacturing and the value placed on different materials in the Middle Ages.

3.2. The Coatings

Gold remains visible on various parts of the reliquary busts, including the hair, beards, crosses, and eyebrows. The absence of mercury in the measurements on gilded areas suggests that the amalgam gilding technique, a common and durable gilding process [11], was not used. Instead, the microscope observation of the gilding revealed the presence of an adhesive on gilding detachment areas and under the persisting gold leaf (Figure 4a,b), calculated to be between 0.1 and 0.25 µm. This finding indicates that the gold foil was applied using an adhesive layer.



(**a**) (**b**)

Figure 4. Picture of: (**a**) Saint Ruffino's gilded beard surface; (**b**) gilding sampling by stereomicroscope.

Further analyses of the gilded crosses and non-gilded areas detected the presence of silver, which was absent from the measurements in the inner parts of the busts. This suggests that the saints' faces, and clothing were originally silvered, although this silvering has degraded significantly over time, making it less visible today, compared to the gilding. The analysis also shows that the crosses on the bust's shoulder (Figure 2a) were made on top of the silvered layer, because measurements on the crosses detected both gold and silver in these areas, unlike all other gilded parts, where only gold was found. The thickness of the residual silver coating is similar to that of the gold, with the silver layer beneath the gilded cross estimated to be around 0.25 µm. These findings imply that the original appearance of the busts was significantly different, with extensive use of both gold and silver coatings. Over time, the silver layers degraded more rapidly than the gold, altering the busts' visual guise. The choice of these materials and techniques would have given the busts a richly decorated and sumptuous appearance, emphasising their significance as sacred objects.

3.3. The Adhesive

The silvered areas of the reliquary busts were found to be covered by a red-brown layer, originally located below the silver layer. Analysis by microscope of gilding fragment revealed an adhesive layer, approximately 100 mm thick, underneath the gold leaf (Figure 4b). To investigate this further, the red-brown layer was sampled from Saint Ruffino's shoulder (Figure 2a), together with a little piece from the busts' inside (Figure 2b), to perform infrared spectroscopy analysis, an established method for classifying organic adhesives.

The results of infrared spectroscopy are displayed in the spectra of Figure 5; the green spectrum refers to the sample from the shoulder surface, while the red spectrum corresponds to the darker sample from the interior of the bust. Based on the signals between 1690 and 1710 cm^{-1}, due to the presence of carboxylic acids, the spectra for both samples are compatible with rosin, also known as colophony or Greek pitch, according to the referenced literature [12]. The absorption between 1697 and 1710 cm^{-1} can be attributed to C = O stretching belonging to the -COOH group in abietic acid. Rosin is a resinous secretion derived from various species of *Pinus*, mainly consisting of abietic acid, dehydroabietic acid, and isopimaric acid. It was produced from fresh resin by volatilisation of terpene components. The two FT-IR spectra showed variations between 1695 and 1254 cm^{-1}, which the referenced literature attributes to the transformation of abietic acid into more oxidised species during the ageing and degradation processes [13]. The band at about 1254 cm^{-1} can be related to 15-hydroxy-7-oxo-dehydroabietic acid. The signal at 1695 cm^{-1} may show a broadening, explained by the presence of a shoulder at 1725 cm^{-1} attributable to C = O stretching of the ketone group of the 7-oxodehydroabietic and 15-hydroxy-7-oxo-dehydroabietic acids.

Rosin was widely used in mediaeval jewellery making [14], and for the case of these busts, it likely served a dual purpose as an adhesive buffer layer for coatings and as a chaser's pitch, a support material used during the cold-working process of metal sheets. The residues of this working pitch are still observable today. The slight differences in the spectra of the pitch are not due to it being older than the adhesive, but more likely because of alterations caused by repeated heating during the metalworking process. Identifying rosin as the adhesive used in the busts provided crucial information for conservation efforts. Rosin is soluble in alcohol and acetone, two solvents commonly used in restoration. This issue is a valuable instruction for the careful and controlled removal or treatment of the adhesive layer without damaging the delicate metal surfaces. Understanding the composition and features of the materials used in these artefacts not only aids in their conservation now and in the future but also provides deeper insights into the historical techniques employed by mediaeval craftsmen. The use of rosin, with its multifunctional applications, highlights the skill of the craft shop that made the reliquaries from Sarezzano, which selected materials that could fulfil multiple roles in the realisation and decoration of these complex and valuable artefacts.

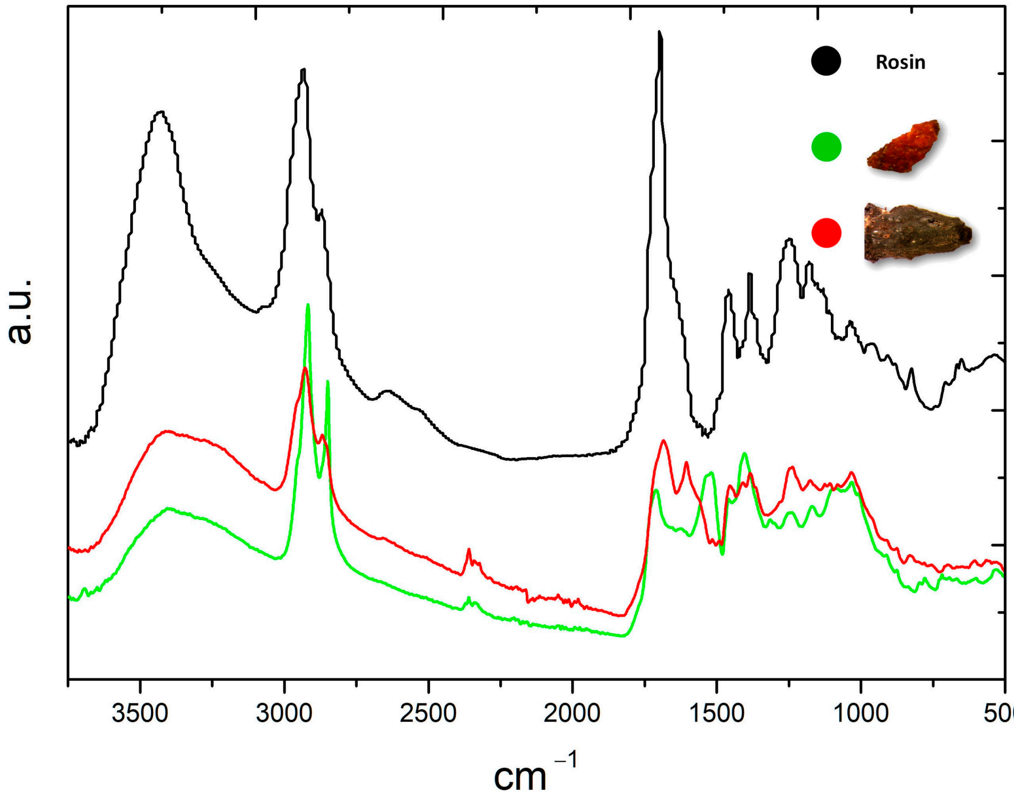


Figure 5. Comparison of ATR-FTIR spectra. The rosin spectrum is represented in black. The green spectrum refers to the sample from the shoulder surface, while the red one refers to the sample from the inside of Saint Ruffino's bust.

3.4. The Corrosion Products

The analysis of the alteration products on the Sarezzano reliquary busts was performed by XRPD on a small sample of globular degradation. The XRPD results on alteration products (Figure 6) detected mainly tin oxides and lead oxides. Additionally, the XRPD pattern includes some small peaks that could be identified as α-tin, a non-metallic allotrope of tin that is stable below 13.2 °C [15]. This transformation from metallic β-tin to α-tin is not a reaction that begins easily; it is known as tin pest or tin disease and involves a significant volume increase and lattice expansion, which compromises the structural integrity of the material [16–18]. As a result, α-becomes structurally weak and readily crumbles into powder [19], a degradation pattern that was observable on the busts before the restoration. This phenomenon is related to grain size and can be minimised by annealing. Although the alloying of tin with lead and the presence of bismuth are generally expected to inhibit this form of degradation [20], the presence of α-tin in the corrosion products of the busts suggests that other factors were at play. The cold working process used during the realisation of the busts, coupled with probable local heterogeneities in the alloy, including intergranular corrosion and tin segregation [21], likely contributed to the α-tin production. This unexpected degradation emphasised the challenges in the preserving conditions and highlighted the importance of detailed material analyses in effective restoration and conservation strategies.

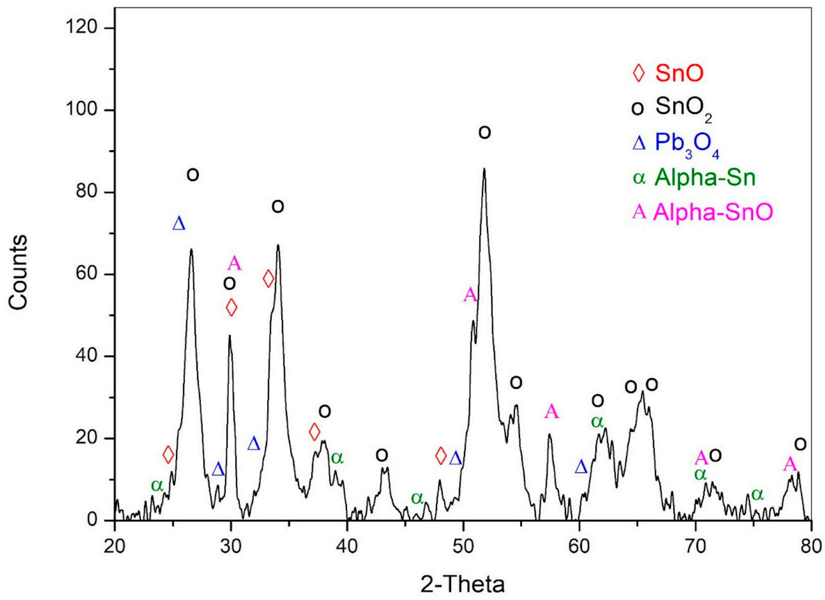


Figure 6. XRPD pattern of sampled degradation products. PDF Numbers: SnO (00-006-0395), SnO_2 (01-071-0652), Pb_3O_4 (01-073-0532), α-Sn (00-005-0390), α-SnO (00-001-0902).

4. Conclusions

This study was crucial in obtaining information useful to support the art-historical study of two undoubtedly uncommon mediaeval speaking reliquaries. Despite being two separate pieces, these works can be considered a *unicum* in the production of the period. The material's characterisation has provided valuable insights into their production techniques. In addition, it has been used to adopt the correct restoration materials, method, and tools, specifically avoiding the use of solvents that could irreparably harm the artefacts.

The diagnostic analysis yielded extensive information on the alloys, coatings, adhesive, and types of corrosion products present, allowing us to investigate the artistic technique and the relative value and quality of the materials used. The coatings had to mimic precious materials, even though the alloy adopted was inexpensive compared to traditional jewellery materials. Over time, adverse storage conditions, including exposure to moisture and neglect, led to corrosion products such as oxides forming. Additionally, there was likely the formation of the α-tin phase with an increase in volume, resulting in the lifting and detaching of the silver coating. This coating proved to be more fragile than the gilding.

The analysis of the Sarezzano busts was particularly critical for their preservation. For instance, due to the detection of rosin, which is highly soluble, a dry cleaning method was employed, and polishing was conducted using soft brushes. This approach was necessary to accommodate the delicate nature of the specific type of gilding used. Furthermore, the appropriate microclimatic conditions for the busts are suggested as a recommendation for long-term conservation. Overall, the study provided essential indications for these unique artefacts' conservation, ensuring that the chosen restoration methods not only preserve the integrity of the materials but also enhance their art-historical value.

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