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X-rays investigations for the characterization of two 17th century brass instruments from Nuremberg

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ABSTRACT
A recent finding at the Castello Sforzesco in Milan of two brass natural horns from the end of the 17th century and assigned to the Haas family from Nuremberg brought to light new information about this class of objects. The instruments were heavily damaged, but their historical value was great. In this study, a multidisciplinary approach mainly based on non-invasive analytical techniques and including X-rays investigations (X-ray radiography, X-ray fluorescence and X-ray diffraction) was used. The present study was aimed at: i) pointing out the executive techniques for archaeometric purposes; ii) characterizing the morphological and the chemical features of materials; and iii) identifying and mapping the damages of the structure and the alterations of the surface.

Section: RESEARCH PAPER

Keywords: XRF spectroscopy; x-ray radiography; brass, musical instrument; Nuremberg

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1. INTRODUCTION

In this work, two brass natural horns held in the storage of the Museum of Castello Sforzesco in Milan were investigated. One of the reasons for the extraordinary relevance of these objects is related to the makers: they are two of the most important components of the Haas family, among the most influential ones in Nuremberg (Germany), between the 17th and the 18th century. During this period, the city was the capital of brass instrument making, and the families organized into guilds were exporting the instruments throughout Europe dominating the field for several generations [1], [2]. Here the craftsmanship has been improved so much to become a reference for the future and for contemporary makers.

Brass, an alloy of copper (Cu) and zinc (Zn), has always been considered the most suitable material for the construction of brasswind musical instruments. The selection of the chemical composition of such an alloy as well as the manufacturing process used are extremely important in determining the properties of the finished instrument. In particular, the amount of Zn can affect the physical and chemical properties of the alloy such as malleability, durability, and resistance to corrosion [3], as well as the mechanical properties and the timbre of the finished instrument [4]. And if those are all crucial aspects for the makers of a new instrument, they are also essential for the modern makers who attempt to reproduce early brass wind musical instruments with the aim to find their original sound and style [5]-[8].

Due to the peculiarity of the historical and technological context, and to the poor information on the chemical composition of brass alloys before the XVII century, interest has been growing around ancient Nuremberg brass since the last century. The reference composition of the alloy was defined by study through X-ray fluorescence spectroscopy of 273 Nuremberg jetons produced during the period from 1475 to

1888: considering the Nuremberg trade laws that permitted the use of the sole local row supplies, the material used to forge the jeton must have been the same used by brasswind instrument makers [9]. Nuremberg brass features include great purity, notwithstanding such a rare and precious alloy was commonly obtained by recycling any scraps believed to contain copper or zinc. Further studies confirmed its high purity degree and the great compositional difference from other similar alloys coming from different geographical areas [4], [10].

The present study aims at contributing to the characterization of the materials used in the brass instruments' craftsmanship. Moreover, mainly non-invasive techniques have been used for documenting the executive and decorative details (e.g., diameters of tubes, depths of joints or jointing methods) and for evaluating the conservation state of instruments held in museum collections. This approach represents an essential support to define the best preservation and maintenance practices [11]-[14].

In particular, the diagnostic campaign was accomplished through photographic [15] and stereoscopic documentation of the surface details, X-Ray Radiography (RX), and X-Ray Fluorescence spectroscopy (XRF). Small amounts of powder were detached from selected areas and analyzed by X-Ray Diffraction (XRPD). Moreover, Fourier-transformed Infrared (FTIR) spectra were collected in reflection mode where the surface was suitable to permit the correct acquisition geometry [16]. Among the techniques, XRF generally affords the chemical characterization of the alloy disclosing plenty of information, even suggesting clues on the original parts, replacements, and conservation issues [17]-[19]. The realization of two 3D models acquired by a laser scanner and the prototyping of an augmented reality application for the museum exposition, detailed in previous work [20], complemented the investigation by fulfilling the collaboration with the museum. The main objectives of this investigation were: i) pointing out the executive techniques; ii) characterizing the morphological and the chemical features; and iii) identifying and mapping the structural damages and the alterations of the surface.

2. MATERIALS AND METHODS

The investigated instruments are shown in Figure 1. The oldest one (Figure 1a), cataloguing number *inv.878,* was made by Johann Wilhelm Haas (1649-1723) who represents the most important member of the family and for what concerns the model, it attests the early construction of this horn-type in Nuremberg, and it is probably dated back to the late 17th century. The second one (Figure 1b), cataloguing number *inv.877,* is datable to the 1720s and was made by Wolf Wilhelm Haas (1681-1760), son of Johann.

The photographic documentation under visible light was acquired with a Nikon D4 full-frame digital camera equipped with a 50 mm f.1.4 Nikkor objective using a softbox LED lamp.

The magnification of the surface details was performed with an Olympus stereomicroscope equipped with an Olympus HD DP73 camera. The images were recorded through Stream Essentials software.

X-Ray radiographic investigation was carried out by means of an X-Ray generating Industrial Control Machines CP 120B (settings: 110 kV, 1 μA of 100 s exposure time) and a photosensitive radiographic plate Dürr NDT GmbH & Co. scanned with CR35NDT Dürr NDT.

XRF analysis was exploited by ELIO portable X-ray fluorescence spectrometer by XGLab (Milan, Italy), with an analytical spot diameter of 1.3 mm [21]. The X-ray source worked with a Rh anode. X-ray fluorescence spectra were collected on 2048 channels with the following set parameters: 40 kV, 60 μA, and 120 s. Data were processed by ELIO 1.6.0.29 software. With the aim to minimize the errors relative to the net area, the dead time of the detector was also kept constant varying the current intensity around the declared value. A small amount of few samples of crystalline phases were analyzed by XRPD. X-ray diffraction patterns were collected on powder samples taken from areas chosen by the conservators. X-ray powder diffraction analyses were performed by a D5005 instrument by Bruker (Germany). The measuring conditions were CuKα radiation,

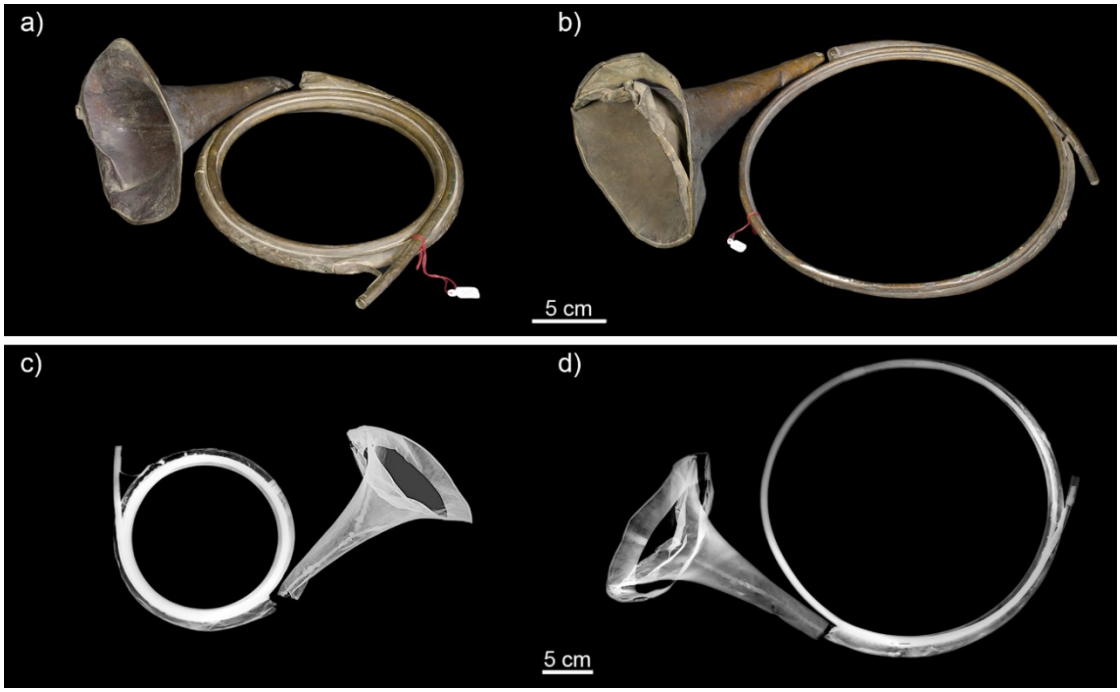

Figure 1. Visible photographic images of a) *inv.878* by Johann Wilhelm Haas (1649-1723) and b) *inv.877* by Wolf Wilhelm Haas (1681-1760); X-Rays radiographic images of *inv.878* c) and *inv.877* d) instruments.

λ = 1.54060 Å, 2θ angle ranging from 3° to 80° with a scan rate of 0.012°/min. A Bruker silicon zero background sample holder was used to allow measurements with very small amount of sample. The diffraction patterns were analyzed with EVA and Match software for the identification of the phases. FTIR spectroscopic analyses were performed using the Alpha portable spectrometer (Bruker) equipped with the R-Alpha module. The working distance of about 15 mm with a beam diameter of 5 mm, enabled non-contact examinations. Spectra were collected between 7500 and 375 cm^{-1} at the resolution of 4 cm^{-1}, with an acquisition time of 1 min. For the investigation of absorption bands, due to the occurrence of the transflection, reflection infrared spectra were observed and are shown hereby in pseudo-absorbance. Data were processed using OPUS 7.2 software.

3. RESULTS AND DISCUSSION

The horn made by Wolf bears the inscription "MACHT / JOHANN / HAAS / NURNBERG" and the initials "IWH" above a leaping hare turning backwards its head, while the other one by the father Johann, bears the hare keeping its face forwards [22]. The bells and the tubes were detached, some parts were lacking, and the surface suffered from different kinds of alteration. In both instruments, numerous deformations of the lamina, macroscopic cracks, and areas of soldering and reparations were highlighted and a magnification of some of their visible traces on the external surface has been documented by stereomicroscope.

The study of the structural features gave access to the manufacturing processes, to identifying the damages, the presence of some reparations or restorations. Even the alterations commonly found on the inner surface of tubes caused by the playing were put into evidence [23]. RX investigation suggested that the *inv.878* (Figure 1c) was characterized by a lamina with a uniform thickness joint by a nipped tooth joint between the edges (Figure 2a). Two important elements referred to the peculiar executive technique were highlighted for this instrument through RX: (i) the presence of the "gusset" (Figure 1c) which is a "V" shaped lamina inserted with nipped tooth joints on both sides added to prevent too much stretching of the edge during the hammering to obtain a larger bell; (ii) the difference in the optical density around the ring that divides the tube into two parts and that seems to join laminas of different thickness. Otherwise, the bell of the *inv.877*, which showed a unique metal joint (Figure 1d), was made of a uniform lamina, probably thinner, and characterized by numerous cracks. Moreover, the presence of the metal thread detailed in Figure 2b, confirmed a traditional making technique of the garland that was the standard bell finishing method of early brasses before the industrial revolution: sheets of brass were cut in a "Y" shape, folded, brazed, and hammered over a mandrel, the garland was then fitted over the edge without soldering [24]. On the outside of the bell, the position of the original support between the bell and the tube (the stay) is proven by a leftover. For this instrument, even the radiography (Figure 1d) suggested the use of the traditional executive technique employed up to the first part of the XIX century [24]. The tube was a single folded element probably obtained by flattering and hammering a brass lamina (cold-worked) then followed by soft annealing. With this procedure, the required shapes (bells and tubes) were produced [25].

The XRF results relating to the alloys (Table 1) revealed that both the horns were manufactured from a yellow brass which is a kind of brass that generally contains 23 - 41 % of zinc as the major alloying element and may contain up to 3 % of lead and up to 1.5 % of tin as additional alloying elements [13]. In the studied objects, a slightly variable Cu: Zn ratio was detected for the tubes and the bells, respectively. The quantity of Cu ranges between 68% and 75%, Zn between 21% and 28%, and variable additional alloying elements such as iron (Fe), nickel (Ni), and lead (Pb) in less than 1% amount, were also distinguished. Generally, Yellow Brass and in particular the α-brass (with up to about 32.5 wt. % zinc) are ductile, easily cold-worked, can be rolled or hammered into thin sheets, and have good corrosion resistance in a salt-water atmosphere [26], and for these reasons, it was extensively employed for the making of historical brasses [10], [27]. The presence of several trace elements was the proof of the traditional cementation method employed by the early craftsmen to obtain brass, which included the use of calamine (a high-grade zinc carbonate ore). This process involved many different raw materials instead of melting the two principal elements of copper and zinc directly into each other as occurred in the modern processes [10], [28], [29]. Among the trace elements commonly found in the historical brass, Pb is the most critical since it could affect the mechanical properties of the material, reducing the brass shear strength and making it prone

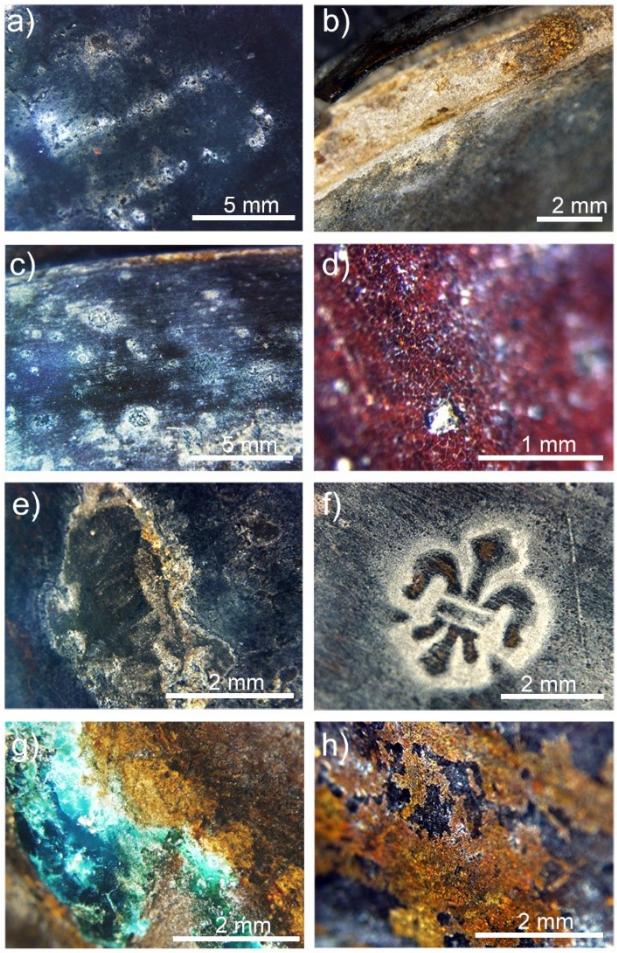

Figure 2. Details magnification by stereomicroscope: a) nipped tooth joint (*inv. 878*); b) metal thread in the garland (*inv.877*); c) corrosion morphology with pustules (*inv. 878*); d) reddish surface inside the bell (*inv.878*); e) reparation with patch and soldering (*inv.878*); f) white dusty leftovers inside punching (*inv.877*); g) translucent green matter along the tubes (*inv. 877*); h) possible residue of surface treatment (*inv.878*).

Table 1. Chemical composition of the constitutive alloy of the tube and of the outside and the inside of the bell for both the instruments, namely *inv.877* and *inv.878*. Three points for each area were acquired. The mean and the standard deviation of the wt% values are shown for the detected elements.

		Ca (wt%)	Cu (wt%)	Fe (wt%)	Ni (wt%)	Pb (wt%)	Zn (wt%)
Inv.878	Tube	2.0 ± 0.4	68.9 ± 1.1	0.6 ± 0.0	0.4 ± 0.0	0.3 ± 0.0	27.9 ± 0.6
	Bell out	1.1 ± 0.3	70.7 ± 0.6	0.6 ± 0.0	0.3 ± 0.0	0.4 ± 0.1	27.0 ± 0.8
	Bell in	2.7 ± 0.7	74.8 ± 0.6	0.6 ± 0.1	0.3 ± 0.0	0.4 ± 0.4	21.1 ± 1.7
Inv.877	Tube	2.7 ± 2.7	68.5 ± 2.5	0.6 ± 0.2	0.3 ± 0.0	0.2 ± 0.2	27.7 ± 0.6
	Bell out	2.6 ± 0.4	68.5 ± 0.8	0.4 ± 0.1	0.3 ± 0.0	0.3 ± 0.1	27.8 ± 0.6
	Bell in	3.4 ± 2.3	72.2 ± 0.5	0.4 ± 0.0	0.4 ± 0.0	0.4 ± 0.1	23.2 ± 2.0

to crack [30], [31]. In this case, the Pb amount is limited and the observed embrittlement and cracking of the laminas could be imputed to mechanical stress also probably promoted by a selective corrosion and/or dezincification process that commonly affect the ancient brass object [31]-[35] whereas the presence of calcium (Ca) detected widespread on the surface with variable and apparently random amounts must be considered independent of the brass composition and probably introduced by the environment or by cleaning procedures. In fact, a paste of precipitated chalk and water was often used with a soft cloth to remove the residue of corrosion products after the mechanical removal of dust and dirt [13], [27]. Among the trace elements, sulphur (S) was detected almost everywhere. Although it is not reported in the XRF results tables (Table 1 and Table 2) due to the low sensitivity of the technique to this element and the impossibility to provide affordable % amounts, more intense signals S were detected in correspondence of the brown and black pustules of corrosion spread on all over the surface (Figure 2c). The elemental composition of this kind of corrosion did not differ from the composition of the sound brass lamina. A low amount of powder sampled and examined through XRPD oddly revealed an unexpected amorphous nature. Nevertheless, the presence of sulphates as corrosion products was occasionally confirmed by the FTIR analysis, elsewhere, possibly in combination with acetates and carbonates. Accordingly, in Figure 3, two selected spectra acquired on the bells of the two horns (black and grey spectra) show the presence of a mixture of the inorganic compounds mentioned above. With regard to the spectral features at higher wavenumbers, the signal in the range between 3700 and 3300 cm^{-1} could be assigned to the OH stretching vibration. Instead, observing the fingerprint region, the main features of three main groups were recognized. The presence of a copper carbonate-based (i.e. malachite $CuCO_3{\cdot}Cu(OH)_2$) was identified through the absorption bands centred around 1575, 1495, 1420, 1395 cm^{-1}, all caused by the CO_3 antisymmetric stretching vibrations; and those around 1095 cm^{-1}, 820, 750 and 715 cm^{-1} generated by the CO_3 symmetric stretching [36]. Moreover, the bands peaked around 1050 cm^{-1} and 880 cm^{-1}, ascribed to the OH bending support the attribution. The presence of copper sulphate (i.e. brochantite $CuSO_4{\cdot}3Cu(OH)_2$) could be hypothesized for the bands centred around 1120 cm^{-1}, 980 cm^{-1}, 620 cm^{-1} all of them reasonably assigned to the stretching vibration of the SO_4^{2-} ion; finally, the signals around 450 cm^{-1} could be ascribed to the Cu–O vibrations [36]. Finally, also the characteristic bands of acetate (i.e. $Cu(CH_3COO)_2{\cdot}H_2O$, $Zn(CH_3COOH)_2{\cdot}H_2O$) were identified in the main bands around 1625 and 1425 cm^{-1} related to the copper carboxylates and their antisymmetric and symmetric stretching vibrations; and around 1455, 1355 and 1030 cm^{-1} possibly ascribable to CH_3 deformations [36], [37]. All those materials were supposed to be alteration products due to the interaction with the environment. In addition, the presence of the organic fraction (i.e. natural resins and oils) could be tentatively recognized through the strong sharp carbonyl band around 1740 cm^{-1} [38] and the quite strong hydrocarbon stretches for both methylene groups around 2925 (asymmetric) and 2850 (symmetric) cm^{-1}, and methyl groups around 2962 and 2872 cm^{-1}.

An outstanding result must be reported for the composition of both the instruments' bells: if the alloy of the tube and the outside of the bells are comparable (the same in *inv.877*), one of the insides of the bells was characterized by a higher amount of Cu that corresponded to a more reddish surface with respect to the others (Figure 2d). Generally, Cu enrichment of ancient brass surfaces was commonly due to the selective corrosion of the Zn or an underwent dezincification process triggered by handling or by the contact with acids [13]. In this case, the homogeneity of the surface prompted the hypothesis of a treatment done on purpose to diversely decorate the bell: finishing it with a dull coating or a fine decoration was a common practice [3].

The soldering and the patches (Figure 2e) were characterized by a coarse aspect that could be correlated to later restorations. XRF investigation shows that the nipped tooth joint was lacking the brazing as expected, and probably only the stay of the *inv. 878* results to be brazing of a comparable composition with the brass alloy. The other solder joints are soft solder assembled with Pb-Sn solder containing a variable ratio of the elements (Table 2). The use of this kind of solder is largely documented in ancient copper-based objects and the proportions of the elements can vary from 30% Pb (and 70% Sn), to as much as 98% Pb (and only 2% Sn) [26], [39]-[42]. The results about the soldering and the similarity between the alloys of the mouthpipes joint in both

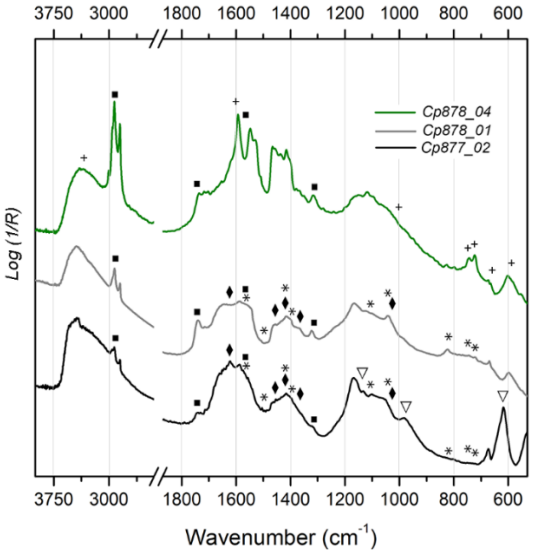

Figure 3. Reflection FTIR spectra in pseudo-absorbance collected from *inv.878* and *inv.877*. Marker bands of copper carbonate-based (*), acetates (◆), sulphates (▽), organic matter (■), and zeolites (+) are highlighted.

Table 2. Chemical composition of the selected area of interest in both the instruments, namely *inv.878* and *inv.877*. A brief description of the measuring area and the relative results expressed in wt% are reported.

				Ca (wt%)	Cu (wt%)	Fe (wt%)	Ni (wt%)	Pb (wt%)	Sn (wt%)	Ti (wt%)	Zn (wt%)
Inv.878	Soldering and reparations	Mouthpipe	Soldering	12.1	14.5	1.0	0.1	50.7	15.9	-	5.7
		Stay	Soldering	5.7	66.8	0.7	0.4	0.3	-	-	26.1
		Tube	Ring	1.5	70.6	0.5	0.4	0.5	-	-	26.5
			Patch	18.4	4.9	1.7	-	2.5	71.8	-	0.8
		Bell out	Soldering	13.6	2.0	1.0	-	21.9	61.0	-	0.5
	Others	Tube	Green	1.8	69.5	0.6	0.4	0.2	-	-	27.7
			White powdery	6.3	59.6	5.3	0.3	0.7	-	-	27.8
		Bell out	Black corrosion	2.4	69.5	0.7	0.3	0.5	-	-	26.7
		Bell in	Black corrosion	1.7	75.5	0.6	0.3	1.0	-	-	20.9
Inv.877	Soldering and reparations	Mouthpipe	Soldering	15.7	0.9	3.2	-	50.5	29.3	-	0.4
			Soldering	11.6	11.8	1.1	-	55.1	15.8	-	4.7
		Tube	Patch	-	3.3	2.9	0.1	30.9	62.4	-	0.5
			Ring	-	57.3	0.9	0.3	7.4	9.9	-	24.2
		Bell out	Patch	10.7	48.7	0.5	0.3	13.5	6.6	-	19.8
			Patch_ patina	14.0	22.8	6.1	0.1	32.1	12.5	-	12.4
			Joint	3.7	60.4	0.5	0.4	0.4	1.8	-	32.9
		Bell in	Joint	7.0	62.0	0.7	0.4	0.6	1.0	-	28.3
	Others	Tube	Green	6.4	63.2	0.5	0.3	0.2	-	-	29.4
			White ink/matter	47.2	25.8	0.7	0.2	-	-	15.0	11.1
			White powdery	26.0	52.3	0.4	0.3	0.2	-	-	20.8
			Black corrosion	8.8	65.9	1.2	-	0.3	-	-	23.8

the instruments could prove later restorations supporting the hypothesis of the conservator according to which the mouthpipes underwent replacement.

Concerning the patches, each of them showed a different chemical composition: Sn-based (tube *inv.878*), or Cu, Sn and Pb, or Pb and Sn alloy (Table 2) probably denoting different periods and restorers. About the decoration in the middle of the tubes with a ring shape, the composition of the *inv.878* one resulted to be made of an alloy of a comparable composition of the tube. Differently, in the latter (*inv.877*) the Cu/Zn alloy was enriched with Pb and Sn (more than 1%) and for this reason, it could be considered a later supplement, processed differently by the laminas the instrument was made up of. In fact, Pb is known to be added to facilitate the shape modelling or the pouring of the alloy into the mould, or the soldering of the element.

Furthermore, white dusty and adherent deposit was observed as a patina and agglomerated inside the engravings or punches (Figure 2f), and often in correspondence with the reparations. The XRF analysis detected a certain amount of Ca (ranging from 6% up to 26%), probably a cleaning residue; XRPD examination even confirmed the presence of pure quartz often found among the ingredients of the modern polish for metal surfaces. In other areas of the tubes, spots of white ink with titanium (Ti) based composition were also identified: an accidental stain of wall painting could not be excluded. With a similar distribution, a green translucent matter was found in the correspondence of small areas where the surface was more worn-out along the tubes (Figure 2g). If XRF could not highlight significant information except for a more intense peak of silicon (Si), XRPD examination clearly identified siliceous faujasite $(Na_2, Ca, Mg)_3 \cdot 5[Al_7Si_{17}O_{48}] \cdot 32(H_2O)$ and, more generally, other zeolites, probably ascribable to polish supposed to be a synthetic mixture of lubricant and small dispersed particles (zeolites). This hypothesis is also endorsed by FTIR results reported in Figure 3 (green spectrum). Here, some of the most characteristic bands of zeolites were identified [43], [44]: in particular, the bands that range from 3750 to 3450 cm^{-1} are ascribable to Si-OH, Si-OH-Al and –OH hydroxyl groups whereas the bands between 1200 and 450 cm^{-1} could be assigned to Si-O-Al, Si-O-Si, Si-O, Si-Al species. In particular, the bands ranging between 800 and 600 cm^{-1} in the green spectrum in Figure 3 is probably due to the Si-O-M where M is the ion metal species (Na, Ca, Mg). Moreover, concerning the hypothesized synthetic fraction, in the same spectrum the bands of the acetates and carbonates above-described and ascribed to the alteration products of the alloy, were accompanied to sharper bands in correspondence of the CH stretching vibration in the ranges 3200 – 2800 cm^{-1}, to the bands ascribed to the COO- vibration in the range 1590-1520 cm^{-1}, and to the bending vibration of the CH_2 around 720 cm^{-1} which could suggest the presence of a synthetic mixture or a metal soaps originated from degradation or used as lubricants, probably, for maintenance or restoration practice [45].

Finally, the documentation of a superimposed layer characterized by red particles suggested the presence of surface treatments (Figure 2h). In fact, brass tends to oxidize quickly when exposed to air and as a common practice, a varnish was applied to give shine and protection to the metal alloy [3], [39]. Unexpectedly, neither the XRF nor the FTIR analysis - even if confirming the presence of some organic matter - could clearly prove the presence of such a coating.

4. CONCLUSIONS

The non-invasive approach presented in the paper, mainly based on X-ray techniques, allowed us to obtain a map of the damages and the fragile areas of the two investigated brass horns. Besides, it provides the conservator with some tools to better define the conservation state of the objects: complete documentation was provided for both the inner structure, the morphology, and the surface aspect with high magnification of the most significant details. Moreover, information about the craftsmanship of the brass wind instrument in Nuremberg during the 17th century was disclosed with a hint to the evolution of the technique during a period of about a century in which the traditional procedures seem to be kept. The in-depth chemical characterization of the instruments highlighted the original and the superimposed parts. In many cases, the superimposed matter and the reparations seem to have the same nature, supporting the idea that the instruments were kept together in the last part of their history. Furthermore, discriminating the original parts enabled the opportunity to produce a replica of the objects to hopefully retrieve the original aspect and the timbre.
Unfortunately, further knowledge of the cold working and annealing of the laminas could only come from the microstructural investigation of the alloy. The availability of material for further investigations will be able to answer the questions left open by this study about the main corrosion products and the surface treatments that turned red on the inside of the bells, as useful and precious support for conservators and restorers in the planning of the preliminary preservation strategies.

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REFERENCES

[1] D. Smithers, The Trumpets of JW Haas: A survey of four generations of Nuremberg brass instrument makers, The Galpin Society Journal 18 (1965), pp. 23-41.
DOI: 10.2307/841975

[2] R. Meucci, Strumentaio. Il costruttore di strumenti musicali nella tradizione occidentale, Fondazione Cologni, 2008, ISBN 8831795902.

[3] V. Bucur, Handbook of materials for wind musical instruments, Springer Nature, Switzerland, 2019, ISBN 978-3-030-19175-7.

[4] A. L. Bacon, A technical study of the alloy compositions of 'brass' wind musical instruments (1651-1857) utilising non-destructive X-ray fluorescence. Diss. PhD Thesis, University of London, 2004.

[5] A. Baines, Gli ottoni, I manuali EDT/SIdM, Vol. 7, EDT srl, 1991, ISBN 8870630919.

[6] C. Pelosi, G. Agresti, P. Holmes, A. Ervas, S., De Angeli, U. Santamaria, An x-ray fluorescence investigation of ancient roman musical instruments and replica production under the aegis of the European music archaeological project, Int. J. Conserv. Sci. 7(2) (2016), pp. 847-856.

[7] G. Festa, G. Tardino, L. Pontecorvo, D.C. Mannes, R. Senesi, G. Gorini, C. Andreani, Neutrons and music: Imaging investigation of ancient wind musical instruments, Nucl. Instrum. Methods Phys. Res. B, 336 (2014), pp. 63-69.
DOI: 10.1016/j.nimb.2014.06.020

[8] B. Elsener, M. Alter, T. Lombardo, M. Ledergerber, M. Wörle, F. Cocco, M. Fantuzzi, S. Palomba, A. Rossi, A non-destructive in-situ approach to monitor corrosion inside historical brass wind instruments, Microchem. J., 124 (2016), pp. 757-764.
DOI: 10.1016/j.microc.2015.10.027

[9] M. B. Mitchiner, C. Mortimer, M. Pollard, Nuremberg and its Jetons, c. 1475 to 1888: chemical compositions of the alloys, Numismatic Chronicle 147 (1987), pp. 114–55. Online [Accessed 24 August 2022]
https://www.jstor.org/stable/42667501

[10] H. W. Vereecke, B. Frühmann, M. Schreiner, The chemical composition of brass in Nuremberg trombones of the sixteenth century, Historic Brass Society Journal 24 (2012), pp. 61-77.
DOI: 10.2153/0120120011004

[11] R. L. Barclay, Ethics in the conservation and restoration of early brass instruments, Historic brass society journal, 1989, pp. 75-81.

[12] R. L. Barclay, The Care of Historic Musical Instruments, Edinburgh, The Museums and Galleries Commission, 1997, ISBN 0-660-17116-3.

[13] S. Pollens, The manual of musical instrument conservation, Cambridge University Press, 2015, ISBN 9781107077805.

[14] G. Fichera, M. Albano, G. Fiocco, C. Invernizzi, M. Licchelli, M. Malagodi, T. Rovetta, Innovative monitoring plan for the preventive conservation of historical musical instruments, Stud. Conserv. 63.sup1 (2018) pp. 351-354.
DOI: 10.1080/00393630.2018.1499853

[15] P. Dondi, L. Lombardi, I. Rocca, M. Malagodi, M. Licchelli, Multimodal workflow for the creation of interactive presentations of 360 spin images of historical violins, Multimedia Tools and Applications, 77.21 (2018)
DOI : 10.1007/s11042-018-6046-x

[16] C. Invernizzi, G. Fiocco, M. Iwanicka, M. Kowalska, P. Targowski, B. Blümich, C. Rehorn, V. Gabrielli, D. Bersani, M. Licchelli, M. Malagodi, Non-invasive mobile technology to study the stratigraphy of ancient Cremonese violins: OCT, NMR-MOUSE, XRF and reflection FT-IR spectroscopy, Microchem. J. 155 (2020)
DOI: 10.1016/j.microc.2020.104754

[17] T. Rovetta, C. Invernizzi, G. Fiocco, M. Albano, M. Licchelli, M. Gulmini, G. Alff, D. Fabbri, A.G. Rombolà, M. Malagodi, The case of Antonio Stradivari 1718 ex-San Lorenzo violin: History, restorations and conservation perspectives, J. Archaeol. Sci. 23 (2019), pp. 443-450.
DOI: 10.1016/j.jasrep.2018.11.010

[18] C. Invernizzi, G. Fiocco, M. Iwanicka, P. Targowski, A. Piccirillo, M. Vagnini, M. Licchelli, M. Malagodi, D. Bersani, Surface and interface treatments on wooden artefacts: Potentialities and limits of a non-invasive multi-technique study, Coatings 11(1) (2021) art. no. 29, pp. 1-24.
DOI: 10.3390/coatings11010029

[19] M. Albano, S. Grassi, G. Fiocco, C. Invernizzi, T. Rovetta, M. Licchelli, R. Marotti, C. Merlo, D. Comelli, M. Malagodi, A preliminary spectroscopic approach to evaluate the effectiveness of water-and silicone-based cleaning methods on historical varnished brass, Appl. Sci. 10 (2020) art. No. 3982, pp. 1-14.
DOI: 10.3390/app10113982

[20] M. Albano, G. Fiocco, P. Dondi, F. Tasso, V. Ricetti, D Comelli, D., M. Licchelli, C. Canevari, M. Malagodi, Preliminary study for the preservation of two natural horns from the end of the 17th century, Proc. of the 2020 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage Trento, Italy, October 22-24, 2020. Online [Accessed 24 August 2022]
https://www.imeko.org/publications/tc4-Archaeo-2020/IMEKO-TC4-MetroArchaeo2020-087.pdf

[21] M. Albano, G. V. Fichera, T. Rovetta, G. Guida, M. Licchelli, C. Merlo, P. Cofrancesco, C. Milanese, M. Malagodi, Microstructural investigations on historical organ pipes. J. Mater. Sci. 52(16) (2017), pp. 9859-9871.
DOI: 10.1007/s10853-017-1134-2

[22] W. Waterhouse, L. G. Langwill, The new Langwill index: a dictionary of musical wind instrument makers and inventors, Tony Bingham, London, 1993, ISBN 0-9461130-4-1.

[23] M. Fantauzzi, B. Elsener, F. Cocco, C. Passiu, A. Rossi, Model Protective Films on Cu-Zn Alloys Simulating the Inner Surfaces of Historical Brass Wind Instruments by EIS and XPS, Front. Chem. 8 (2020), pp. 272.
DOI: 10.3389/fchem.2020.00272

[24] R. L. Barclay, The art of the trumpet-maker: the materials, tools, and techniques of the seventeenth and eighteenth centuries in Nuremberg, Clarendon Press; Oxford University Press, 1992, ISBN 0198166052.

[25] G. J. Van Der Heide, Brass instrument metalworking techniques: The Bronze Age to the Industrial Revolution, Historic Brass Society Journal 3 (1991), pp. 122-50. Online [Accessed 24 August 2022]
https://www.historicbrass.org/edocman/hbj-1991/HBSJ_1991_JL01_012_VanDerHeide.pdf

[26] D. Ashkenazi, D. Cvikel, A. Stern, A. Pasternak, O. Barkai, A. Aronson, Y. Kahanov, Archaeometallurgical investigation of joining processes of metal objects from shipwrecks: three test cases, Metallogr. Microstruct. Anal. 3 (2014), pp. 349–362.
DOI: 10.1007/s13632-014-0153-5

[27] M. Megahed, M. M. Abdelbar, Characterization and treatment study of a handcraft brass trumpet from dhamar museum, Yemen. Archeomatica, 9(3) (2018), pp. 36-41.
DOI: 10.48258/arc.v9i3.1481

[28] D. Bourgarit, F. Bauchau, The ancient brass cementation processes revisited by extensive experimental simulation, JOM 62(3) (2010), pp. 27-33.
DOI: 10.1007/s11837-010-0045-3

[29] D. A. Scott, R. Schwab, The metallurgy of pre-industrial metals and alloys. In: Metallography in Archaeology and Art. Cultural Heritage Science. Springer, Cham. (2019), pp. 133-206.
DOI: 10.1007/978-3-030-11265-3_5

[30] C. Vilarinho, J. P. Davim, D. Soares, F. Castro, J. Barbosa, Influence of the chemical composition on the machinability of brasses, J. Mater. Process. Tech. 170.1-2 (2005), pp. 441-447.
DOI: 10.1016/j.jmatprotec.2005.05.035

[31] F. Cocco, Sustainability in cultural heritage: from diagnosis to the development of innovative systems for monitoring and understanding corrosion inside ancient brass wind instruments, Diss. PhD Thesis, University of Cagliari, 2017.

[32] C. Breckon, P. T. Gilbert, Dezincification of alpha brasses, Chemistry and industry (1964), pp.35-36.

[33] H. Sugawara, H. Ebiko, Dezincification of brass, Corros. Sci. 7(8) (1967), pp. 513-518.
DOI : 10.1016/S0010-938X(67)80090-8

[34] S. Selvaraj, S. Ponmariappan, M. Natesan, N. Palaniswamy, Dezincification of brass and its control-an overview, Corros. Rev. 21(1) (2003), pp. 41-74.
DOI: 10.1515/CORRREV.2003.21.1.41

[35] L. Campanella, O. C. Alessandri, M. Ferretti, S. H. Plattner, The effect of tin on dezincification of archaeological copper alloys, Corros. Sci. 51(9) (2009), pp. 2183-2191.
DOI: 10.1016/j.corsci.2009.05.047

[36] C. Zaffino, V. Guglielmi, S. Faraone, A. Vinaccia, S. Bruni, Exploiting external reflection FTIR spectroscopy for the in-situ identification of pigments and binders in illuminated manuscripts. Brochantite and posnjakite as a case study, Spectrochim. Acta A Mol. Biomol. Spectrosc. 136 (2015), pp. 1076-1085.
DOI: 10.1016/j.saa.2014.09.132

[37] T. Ishioka, Y. Shibata, M. Takahashi, I. Kanesaka, Y., Kitagawa, K. T. Nakamura, Vibrational spectra and structures of zinc carboxylates I. Zinc acetate dihydrate. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 54(12) (1998), pp. 1827-1835.
DOI: 10.1016/S1386-1425(98)00063-8

[38] M. R. Derrick, D. Stulik, J. M. Landry, Infrared spectroscopy in conservation science, Getty Publications, 2000, ISBN 0-89236-469-6.

[39] H. Maryon, Metal work and Enamelling, 5th ed., USA, 1971, pp. 35. ISBN 0-486-22702-2

[40] H. Maryon, Archaeology and metallurgy I. Welding and Soldering, Man. 41 (1941), pp.118-124.
DOI: 10.2307/2791583

[41] Z. Goffer (2007), Archaeological Chemistry, John Wiley & Sons, Inc., Hoboken, 2nd, USA, p. 205, ISBN 978-0-471-25288-7.

[42] C. Deck (2016), The Care and Preservation of Historical Brass and Bronze, Benson Ford Research Center Online [Accessed 24 August 2022]
https://www.thehenryford.org/docs/default-source/default-document-library/the-henry-ford-brass-amp-bronze-conservation.pdf/?sfvrsn=2

[43] D. W. Breck, Zeolite Molecular sieves-Structure chemistry and use, Ed. Wiley Interscience, New York, (1973). ISBN 0471099856

[44] D. Nibou, S. Amokrane, H. Mekatel, H., N. J. P. P. Lebaili, Elaboration and characterization of solid materials of types zeolite NaA and faujasite NaY exchanged by zinc metallic ions Zn2+. Phys. Procedia, 2(3) (2009), pp. 1433-1440.
DOI: 10.1016/j.phpro.2009.11.113

[45] F. Rosi, L. Cartechini, L. Monico, F. Gabrieli, M. Vagnini, D Buti, B. Doherty, A. Anselmi, B. G. Brunetti, C. Miliani, Tracking metal oxalates and carboxylates on painting surfaces by non-invasive reflection mid-FTIR spectroscopy, in: Metal Soaps in Art. F. Casadio, K. Keune, P. Noble, A. van Loon, A., E. Hendriks (editors). Springer: Cham, Switzerland, 2019, pp. 173–193.
DOI: 10.1007/978-3-319-90617-1_10