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Characterization of the Santa Maria del Fiore cupola construction tools using X-ray fluorescence

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ABSTRACT
This paper presents the characterization of different tools employed in the construction of the Santa Maria del Fiore cathedral in Florence; they are part of the Opera di Santa Maria del Fiore collection and are currently exhibited in the Museo dell'Opera del Duomo. The analysed objects are turnbuckles, pulleys, three-legged lewises, and pincers; indeed, despite their uniqueness and their importance from the historical point of view, this study is the first one that investigates their alloys composition. Actually, this information can be of great interest for curators to find the best conservation strategies and to have new insights on the production techniques typical of the Renaissance. The study was performed using X-Ray Fluorescence (XRF) in order to identify the materials constituting the objects. Then, XRF spectra were analysed using chemometric techniques, namely Principal Components Analysis (PCA), in order to investigate possible similarities among different alloys and thus provide new indications to help collocating these tools in a specific historical period.

Section: RESEARCH PAPER

Keywords: X-ray fluorescence; PCA; non-invasive measurements; cultural heritage; metals; archaeometry

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1. INTRODUCTION

The Santa Maria del Fiore Cupola (Dome), located in Florence, is a unique Renaissance creation. Indeed, the Brunelleschi's Cupola is an extraordinary masterpiece, still being the biggest masonry dome in the world. Its dimension, together with the innovative construction project that led to its realization, made the Cupola one of the most famous buildings in history.

The history of the Santa Maria del Fiore Cathedral spans through a wide time frame and is a really complex one. In the 14th century Florence was a flourishing city, with the reputation of being one of the most important in Europe. The city wanted to increase its relevance, visibility and pride, in order to wipe out all the nearby competing cities. To this aim, the Florentine citizens decided to build a very large cathedral, similar to the ones in the other most important European cities [1]-[3].

The history of the Santa Maria del Fiore Cathedral started with the Italian architect Arnolfo di Cambio, who developed the initial project and supervised the beginning of the construction in 1296. About 100 years later, just the main body was completed, without the facade and the dome. In 1418 an open competition started, to find a project for the construction of the biggest Cupola in the world. The competition ended only in 1420, when Filippo Brunelleschi was entrusted with the work. However, his project was always surrounded by skepticism [2]-[4].

Among the many challenges that Brunelleschi had to face, the main one was the size of the dome. Indeed, the regular techniques employed in the 14th century involved the use of internal support structures, which would not be possible for the construction of the Santa Maria del Fiore Dome. Due to their

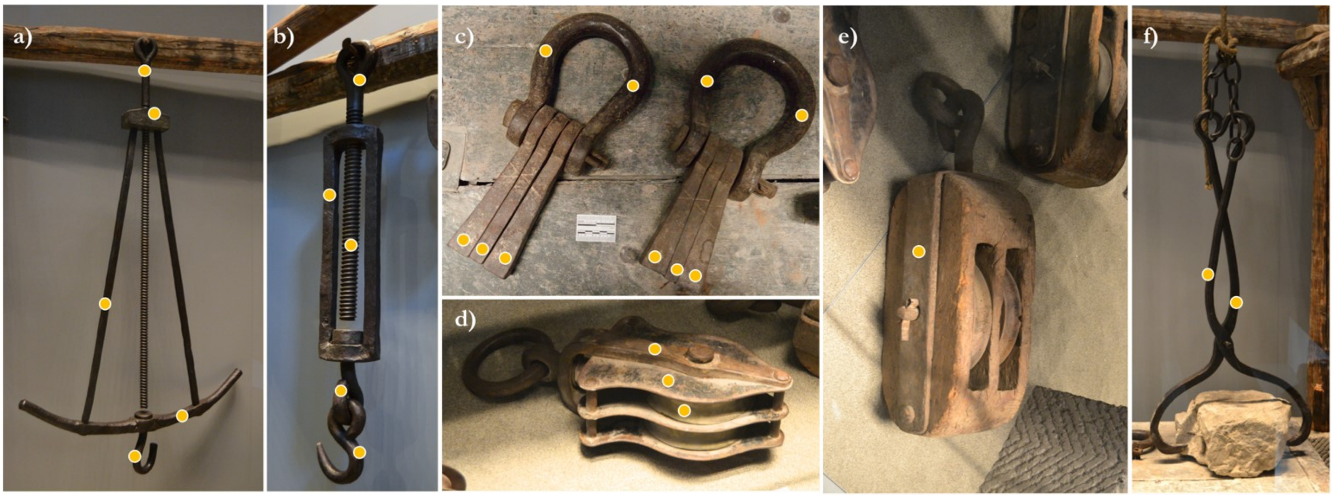

Figure 1. Historical tools employed for the construction of the Santa Maria del Fiore cathedral in Florence. The instruments are displayed in the Museo dell'Opera del Duomo, Florence: a), b) turnbuckles, c) three-legged lewises, d), e) pulleys, f) pincers. Yellow circles indicate the analyzed areas.

size, these frameworks would have not been capable of supporting even their own weight.

Brunelleschi, who had spent many years studying the ancient roman architectural techniques in Rome, in order to solve this major issue, together with many other challenges related to the project, found a way to build a self-supporting double-walled dome, thanks to the insertion of particular pattern of bricks, called "a spina di pesce". The construction was carried on employing suspended platforms which were progressively moved up along with the construction [1]-[8].

Another remarkable novelty employed by Maestro Brunelleschi was the design and development of specific machines and tools, that were used on the construction site. The employment of these new tools, used to lift the building materials, allowed to save both time and money.

Today, some of these unique tools, such as pulleys, turnbuckles, pincers, winches, and ropes, are part of the Opera di Santa Maria del Fiore collection, exhibited in the Museo dell'Opera del Duomo, in Florence.

Even if these tools were a great innovation for the Duomo project, they did not attract the attention of researchers so far. Nevertheless, these unique objects and their history could provide important information regarding the production techniques and the materials employed during the Brunelleschi era.

For instance, a lot of information can be deducted from a visual inspection of the tools, by comparison with the historical sources. Indeed, it is possible to find drawings of similar tools made by Taccola, Francesco di Giorgio, Bonaccorso Ghiberti, Giuliano da Sangallo and even in the Codex Atlanticus by Leonardo da Vinci [1], [9]. On the other hand, the provenance, the materials and the production techniques of some of these tools are more complex to reconstruct. In such cases, conservation science and engineering can provide useful tools to reconstruct these tools' history. Indeed, tailored analytical strategies can be applied to investigate the constituent material and to develop specific conservative approaches [10]-[12].

In this paper, the first characterization of these construction tools with a non-invasive and in-situ approach is presented. A previous study has examined the preliminary results from the X-rays fluorescence analyses performed on these objects [13]. In the present manuscript a complete survey of the constituent materials is provided, discussing the possible role of different elements in the alloys. Then, obtained data were processed using multivariate analysis to find possible similarities in the spectra acquired on different tools and thus formulate hypotheses on the historical collocation of these objects.

2. MATERIALS AND METHODS

This Section presents the characterized historical tools and the analytical techniques employed in the study; moreover, the performed data analysis is described in detail.

2.1. Historical tools under study

This study is focused on thirteen objects which are part of the Opera di Santa Maria del Fiore collection and are currently exhibited in the Museo dell'Opera del Duomo, in Florence. They are tools and equipment that were used in the construction of the Santa Maria del Fiore cathedral. As previously discussed, the construction of this building took several centuries, so it is difficult to collocate each of the tools in a specific historical period. The investigated objects are two turnbuckles, eight pulleys, two three-legged lewises and a pincer. The photographs of some of the characterized tools are shown in Figure 1, where some of the points of analysis are marked.

2.2. X-ray fluorescence

All objects were characterized using X-ray fluorescence in order to investigate the composition of the constituent materials. Measurements were performed using a Brucker Tracer 5i analyser, which allowed to perform non-invasive measurements without moving the tools from their collocation in the Museum. The instrument is equipped with a 20 mm² silicon drift detector and a Rhodium (Rh) anode. The Ti-Al filter was used in order to reduce the intensity of peaks related to Rhodium and Palladium (Pd) [14]. Analyses were carried out using a voltage of 40 kV and a current of 40 μA, with the 3 mm collimator. Spectra processing and elements identification were performed using Artax Spectra (8.0.0.476) software.

2.3. Multivariate analysis

In order to investigate similarities among different alloys, acquired spectra were processed by means of Principal Component Analysis (PCA). Using this chemometric technique it is possible to identify patterns in acquired measurements and classify spectra in different groups. PCA was performed on XRF spectra using a Python script, as described in [15], by means of the Scikit-learn library [16]. Before computing the Principal Components (PCs), spectra were pre-processed as follows:

1) the interval of interest was limited to the range from 1 keV to 12.2 keV for iron alloys and from 1 keV to 15.5 keV and from 24.5 keV to 30 keV for bronzes. Actually, in these energy ranges all significant peaks for the two materials are present and thus only relevant parts of the spectra are included in the PCA.
2) Spectra baseline was subtracted using the embedded function in the Artax Spectra software.
3) Signal-to-noise ratio was improved applying the Savitzky-Golay filter [17]. A second order polynomial and a window length of 90 eV were used in order to avoid any over-smoothing.
4) Spectra were normalized using the Standard Normal Variate Transformation (SNVT) [18].

After performing the pre-processing, principal components were computed and results were graphed as biplots, in which eigenvalues for different spectra are plotted. Similarities among different spectra were evaluated using a Gaussian mixture model probability distribution and confidence ellipses were accordingly drawn using the *sklearn.mixture.GaussianMixture* class from the Scikit-learn library.

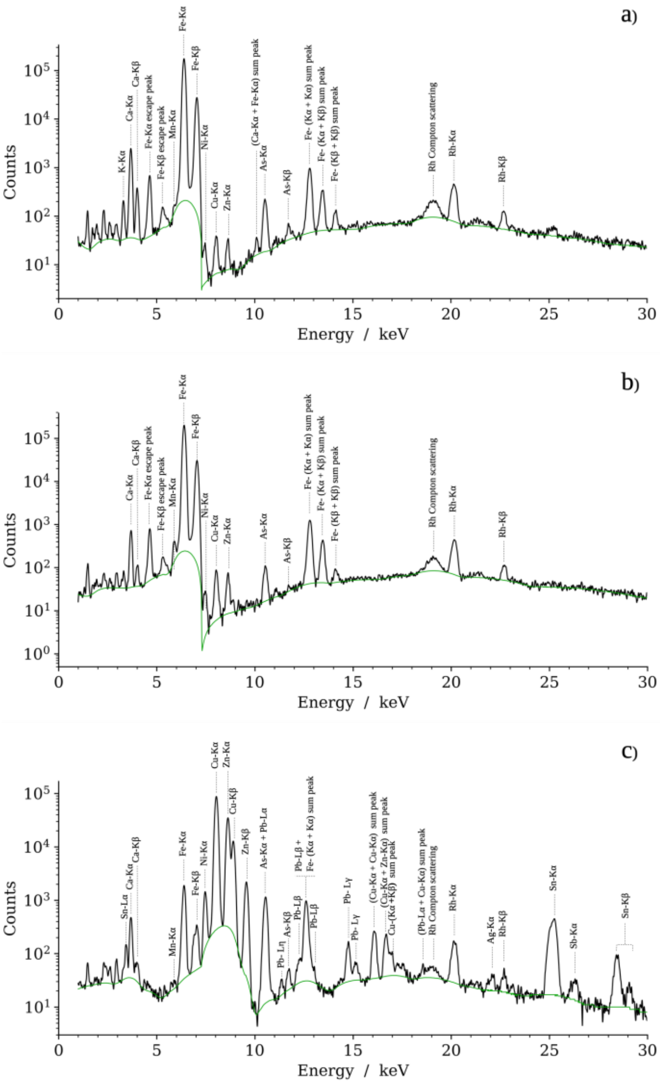

Figure 2. XRF spectra collected on pulleys: frame of one of the ‘wooden’ pulleys (a), main body of one of the ‘metallic pulleys’ (b), wheel of one of the ‘metallic pulleys’ (c). The black line is the acquired spectrum, while the computed baseline is in green.

3. RESULTS AND DISCUSSION

3.1. Alloys identification

XRF analyses were performed on all investigated tools choosing different points of interest on each object. The primary goal was to identify the alloys constituting the different parts of the tools.

Most of the analysed objects are pulleys, as these tools were commonly used in the cathedral construction site during the centuries and many of them are still preserved in the museum. It is interesting to notice that two kinds of pulleys can be identified among those present in the Museum collection: one is characterized by both the main body and the wheel made in wood (shown in Figure 1e), and the other is made completely in metal (shown in Figure 1d). Even if at a first glance it could appear easy to collocate the two typologies of pulleys in different historical periods, the only available information in literature dates also the metallic pulleys to the Renaissance era [3]. So, this simple example further highlights the need for an archaeometric approach to study these important tools.

Figure 2 shows some representative spectra acquired on different pulleys. In Figure 2a, the spectrum acquired on the metallic frame of a wooden pulley is reported; as can be seen in Figure 1e, this typology of pulleys had a metallic frame needed to hold and anchor the tool. The material can be identified as an iron alloy, considering the two main peaks at 6.40 keV and 7.06 keV, which correspond to characteristic Kα and Kβ lines of iron respectively. The material is then characterized by the presence of manganese, copper, zinc, and nickel demonstrated by the presence of peaks at 5.90 keV (Mn-Kα), 8.05 keV (Cu-Kα), 8.64 keV (Zn-Kα), and 7.48 keV (Ni-Kα) respectively. Finally, it is possible to identify calcium by the 3.69 keV and 4.01 keV peaks, corresponding to the Kα and Kβ emission lines, and potassium (Kα 3.31 keV); these are present in all acquired spectra and can be related to environmental contamination.

Additional peaks are present at higher energies. In particular a triplet of peaks can be attributed to iron sum peaks, i.e., 12.81 keV (Kα + Kα), 13.46 keV (Kα + Kβ), and 14.12 keV (Kβ + Kβ). Moreover, the couple of peaks at 4.67 keV and 5.32 keV can be assigned to the Fe-K lines escape peaks.

Furthermore, the peaks related to the rhodium anode can be identified by the Kα and the Kβ lines at 20.22 keV and 22.72 keV respectively. The broad peak at 19.06 keV can be attributed to the Compton scattering of the Rh characteristic photons.

Arsenic is present too, as can be seen from the presence of the peaks at 10.54 keV (Kα) and 11.72 keV (Kβ). For these peaks, the K shell intensity ratios (Kβ/Kα) is respected, as it has an average value close to 0.14 [19]. Arsenic was a common contaminant in iron ores and thus was often present in iron alloys [20], [21].

The spectrum acquired on the main body of a metallic pulley is then presented in Figure 2b. In this case, too, it can be identified as an iron alloy, in which most of the peaks mentioned for the spectrum in Figure 2a can be found. At the same time, the relative intensity of peaks changes with respect to the ones in the spectrum shown in Figure 2a.

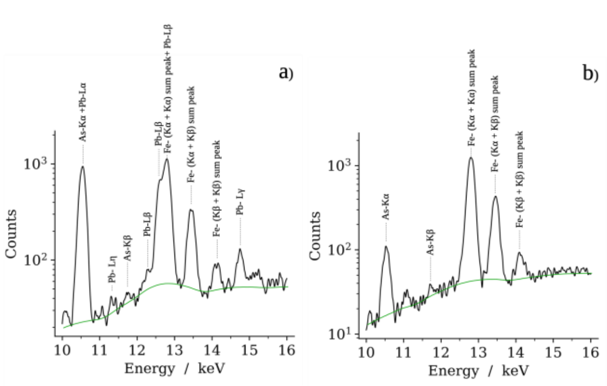

Figure 3. Comparison of two spectra acquired on different pulleys: on the left, the spectrum corresponding to 'Pulley 6', where lead and arsenic are present; on the right, spectrum acquired on one of the remaining pulleys, characterized by the presence of arsenic but not lead. Only the energy interval from 10 keV to 16 keV is reported. The black line is the acquired spectrum, while the computed baseline is in green.

It is worth noticing that for the three points of analysis acquired on one of the metallic pulleys (referred in the next section as 'Pulley 6'), a different spectrum was obtained. The material can be identified as an iron alloy, characterized by the additional presence of lead. In Figure 3a a detail of a spectrum obtained from this pulley is reported. Lead can be identified considering different features. First, it is possible to notice that the arsenic Kβ over Kα ratio is not respected, thus deducing that the peak at 10.55 keV is due to the overlapping of both the Pb-Lα and As-Kα lines. Furthermore, it is possible to notice the presence of a left shoulder on the sum peak of iron (Kα + Kα) at 12.61 keV, corresponding to the Pb-Lβ line. Other characteristic Pb lines are identified at 11.35 keV and 14.76 keV, being the Pb- Lη and Pb- Lγ1 respectively. A spectrum showing the same energy interval acquired on one of the pulleys without lead is reported in Figure 3b; in this case, the left shoulder on the sum peak of iron at 12.61 keV is not present.

In Figure 2c the spectrum acquired on the wheel of one of the metallic pulleys is shown. It is possible to describe the material as a lead bronze, i.e., an alloy containing copper, tin, and lead. Most of the peaks previously described for Figure 2a are present also in this spectrum, except for the escape and sum peaks of iron. Moreover, there is the additional presence of the characteristic peaks of lead (Lα-10.55 keV, Lη-11.35 keV, Lβ6-12.14 keV, Lβ4-12.31 keV, Lβ1-12.61 keV, Lβ5-13.01 keV, Lγ1-14.76 keV, Lγ6-15.18 keV), silver (Kα-22.16 keV), tin (Kα-25.27 keV, Kβ1-28.48 keV and Kβ2-29.11 keV), and antimony (Kα1-26.36 keV). The remaining peaks can be identified as sum peaks, e.g., 16.06 keV (Cu-Kα + Cu-Kα), 16.67 keV (Cu-Kα + Zn-Kα), 16.97 keV (Cu-Kα + Cu-Kβ), and 18.61 keV (Pb-Lα + Cu-Kα).

An interesting case study is then represented by the two turnbuckles, which are of great importance both from the technical and historical points of view. These tools constituted a great innovation that allowed to lift heavy loads in a smooth and controlled way. Moreover, they substituted steel rods for the stone positioning, reducing the risk of chipping them during this operation. Their historical importance is then testified by their representation in different collections of drawings in the Renaissance era, as an example in the 'Taccuino senese' by Giuliano da Sangallo [22].

As can be seen in Figure 1a and Figure 1b, turnbuckles are composed of different parts, namely the central screw, the nut, the hook, and two connecting rods. Threaded components are particularly important in this investigation as they can give new insights on the production routes typical of the Renaissance era and can provide hints to date the objects. During that period threaded parts were mainly realized in bronze, as this alloy has good machinability using steel tools. For this reason, threaded components made in iron should belong to a later period. The most representative spectra collected on the two turnbuckles are shown in Figure 4. The nut of the 'Turnbuckle1' (Figure 1a) is constituted by a bronze alloy. This was identified by the presence of the major elements as copper (Kα-8.05 keV and Kβ-8.90 keV), tin (Kα-25.27 keV, Kβ1-28.48 keV and Kβ2-29.11 keV), zinc (Kα-8.64 keV and Kβ-9.57 keV), and lead. Lead can be identified through several peaks in the spectrum: Mα-2.34 keV, Mγ-2.65 keV, Lι-9.18 keV, Lα-10.55 keV, Lη-11.34 keV, Lβ6-12.14 keV, Lβ4-12.30 keV, Lβ1-12.61 keV, Lβ5-13.01 keV, Lγ1-14.76 keV, Lγ6-15.17 keV. Other elements are present too, such as: iron (Kα-6.40 keV and Kβ-7.06 keV), nickel (Kα-7.48 keV), antimony (Kα1-26.35 keV and Kβ1-29.71 keV), arsenic (Kα-10.54 keV and Kβ-11.72 keV), manganese (Kα-5.90 keV), calcium (Kα-3.69 keV and Kβ-4.01 keV), and potassium (Kα-3.31 keV).

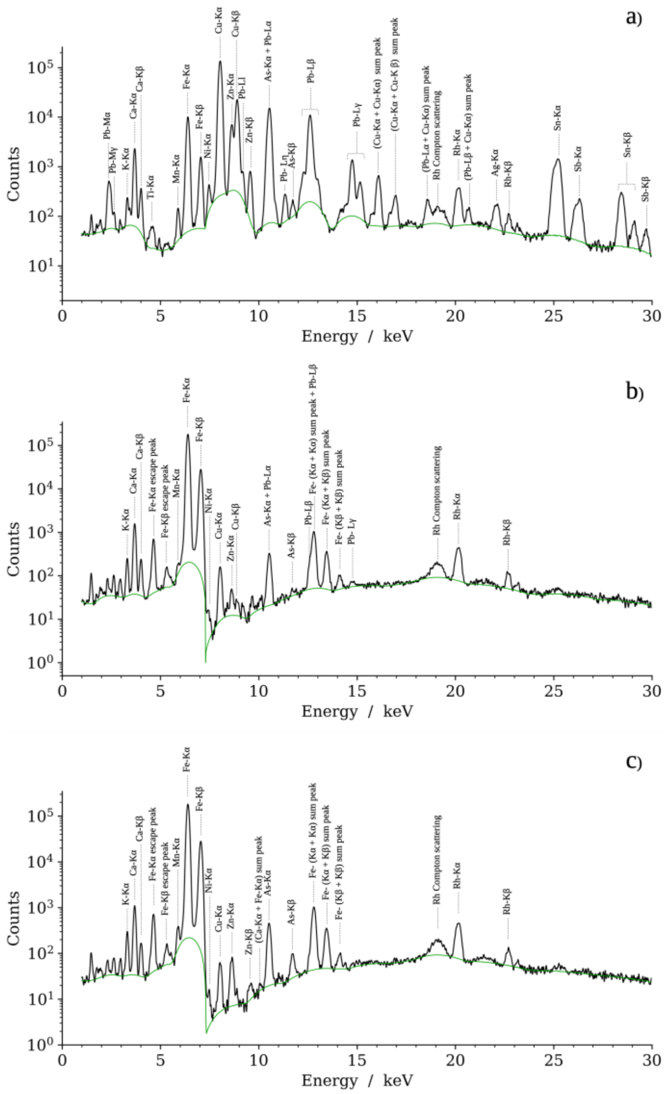

Figure 4. XRF spectra collected on the two turnbuckles: nut of Turnbuckle1 (a), one of rods on Turnbuckle1 (b), nut of Turnbuckle 2 (c). The black line is the acquired spectrum, while the computed baseline is in green.

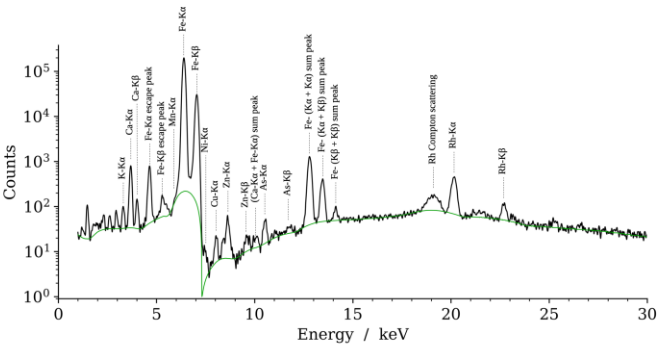

Figure 5. XRF spectrum acquired on the pincers. The black line is the acquired spectrum, while the computed baseline is in green.

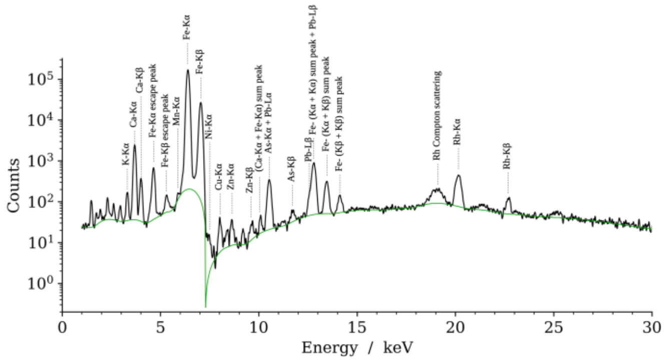

Figure 6. XRF spectrum acquired on one of the three-legged lewises. The black line is the acquired spectrum, while the computed baseline is in green.

Additional peaks are present at higher energies. In particular they can be identified as sum peaks, e.g. 16.06 keV (Cu-Kα + Cu-Kα), 16.97 keV (Cu-Kα + Cu-Kβ), and 18.61 keV (Pb-Lα + Cu-Kα). Moreover, the material of the anode, rhodium, can be identified by the following peaks: Kα-20.22 keV and Kβ1-22.72 keV. The broad peak at 19.06 keV can be attributed to the Compton scattering of the Rh characteristic photons.

Compared to the composition found for the pulley's wheels (Figure 2c), it is possible to notice a less intense peak of zinc and a higher relative concentration of antimony. It is not easy to compare these findings to previous literature because most of the studies investigating the bronze composition of that period are related to statuary art. Anyway, it is worth noticing that the presence of zinc, nickel, and iron in lead bronze was already reported in previous studies [23], [24]. Moreover, the presence of antimony was found in different artifacts dating back to the Renaissance period and also in the alloy used for the realization of the 'Porta del Paradiso' reliefs by Lorenzo Ghiberti, which were positioned in the East door of the Baptistery of San Giovanni Battista, in front of Santa Maria del Fiore cathedral [25]-[27]. This last point is of particular importance because, like also arsenic, these elements were not intentionally added by the founder, but they are impurities due to raw materials [26]. This can further confirm the dating of this turnbuckle to the Brunelleschi era. Apart from the nut, all other parts constituting the 'Turnbuckle1' are instead made of an iron alloy containing copper, zinc, arsenic, and lead (see Figure 4b). On the other hand, the 'Turnbuckle2' (Figure 1b) is entirely made of a similar iron alloy, with a higher content of manganese, zinc and arsenic (see Figure 4c).

Finally, spectra acquired analysing the pincers and the lewises are reported in Figure 5 and Figure 6, respectively. They are both tools used to lift stones; the use of pincers is straightforward, while lewises were used inserting this tool in a clearance realized on purpose in the stone. These objects were realized using an iron alloy, whose composition is mainly characterized by the presence of copper, zinc, nickel, and arsenic. Most of the peaks previously described for Figure 2a are present also in these spectra. The main difference between these last two objects is the presence of lead, which can be identified in the spectrum reported in Figure 6 by the left shoulder on the sum peak of iron at 12.61 keV, while is not present in the alloy constituting the pincers.

3.2. PCA and spectra classification

After identifying the main alloys constituting the different tools, Principal Component Analysis was used in order to discover possible similarities in the materials composition. Finding analogies in the alloys composition for different objects cannot be considered as a univocal proof that the two tools belong to the same historical period, but anyway can give additional useful indications to curators and scholars. So, three different processing were performed: in the first one, all pulleys were analysed in order to examine possible groups in this kind of objects, in the second one, all spectra identified as bronzes were investigated and then in the third one the spectra acquired on the two turnbuckles were taken into consideration.

PCA was performed using the acquired XRF spectra as input data. Actually, when dealing with XRF measurements, two strategies are possible. The first one consists in the computation of the material composition after identification of the elements by means of their characteristic peaks. In this case, the weight percentage of each element is used as input data for the PCA [28], [29]. The second approach, which is the one used in this study, directly uses the raw spectra as input data for the PCA, without computing elemental composition. The advantage of this second approach is that the result from the PCA processing is not influenced by the elements identification performed by the user, which could be in some cases questionable or at least not univocal [30], [31]. Thus, using XRF spectra for the PCs computation allows to reduce possible sources of error related to spectra interpretation. At the same time, particular care should be taken in order to exclude from the processing those parts of the spectra that do not carry useful information, because they could bias the PCA model without a significative reason from the compositional point of view. Because of this, the processed spectrum was limited to the range from 1 keV to 12.2 keV for iron alloys and from 1 keV to 15.5 keV and from 24.5 keV to 30 keV for bronzes. Regions of the spectrum not analysed by means of PCA are characterized by the presence of sum peaks or lines related to the anode material. Results from the PCA of spectra acquired on pulleys can be seen in Figure 7. In this biplot it is not possible to highlight a well-defined clustering among different objects, but anyway it is possible to give a primary interpretation. Spectra for 'Pulley1' (one of the wooden pulleys) and 'Pulley6' (one of the metallic pulleys) appear to be outliers, characterized by values of PC1 above 30. As can be seen from the loadings, this is due to a higher concentration in nickel, copper and lead (this last element was identified only in 'Pulley 6' spectra). All the other pulleys group in the left part of the graph where, even if it is not possible to draw confidence regions for two classes, it is possible to observe a separation related to the PC2 value. All wooden pulleys (as said before, the analysis was performed on the metallic frame) are in the upper part of the graph,

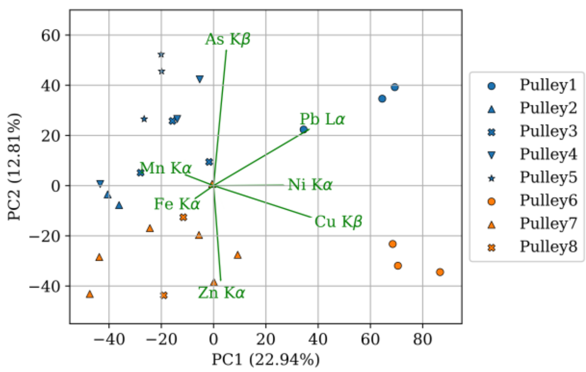

Figure 7. Score and loading plot of the first two components (PC1-PC2) calculated from XRF spectra acquired on pulleys. Pulleys labelled from 1 to 5 are 'wooden' pulleys (see Figure 1e), while those from 6 to 8 are the 'metallic' ones (see Figure 1d). Percent variance captured by each PC is reported in parenthesis along each axis.

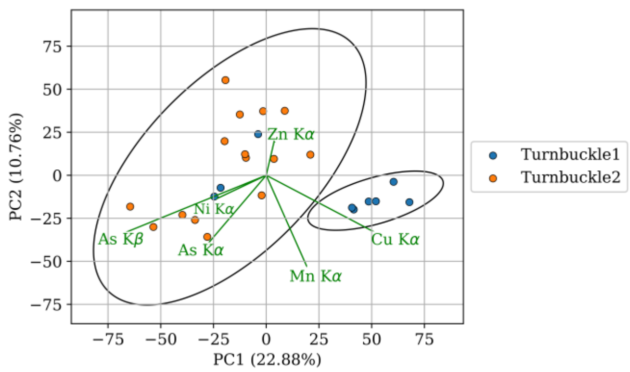

Figure 9. Score and loading plot of the first two components (PC1-PC2) calculated from XRF spectra acquired on iron parts of the two turnbuckles. Percent variance captured by each PC is reported in parenthesis along each axis.

characterized by higher values of arsenic and manganese. On the other hand, metallic pulleys are characterized by lower values for PC2, due to higher concentration of zinc.

PCA processing was then performed on spectra acquired on bronze components (see Figure 8). As it is possible to observe, in this case a clear clustering was found, as highlighted by the confidence ellipses drawn according to the Gaussian mixture model for probability distribution. Spectra acquired on the wheels of the metallic pulleys are characterized by a higher amount of zinc, tin and nickel. On the contrary the bronze used for the nut of the 'Turnbuckle1' has a higher concentration of lead, antimony and iron. This is an important finding because the drawing of a turnbuckle noticeably similar to 'Turnbuckle1' is present in the 'Taccuino senese' by Giuliano da Sangallo [22]. So, if we assume that the metallic pulleys presumably do not belong to the Renaissance era, as can be argued considering their design, this clear difference in the bronze composition can be taken as a confirmation for the attribution of this turnbuckle to the Brunelleschi era.

Finally, last PCA processing was performed on the iron alloy spectra collected on the two turnbuckles in order to investigate possible similarities or differences among their constituent materials; the result is presented in Figure 9. As can be seen, it is possible to draw two confidence regions. The first one, smaller, contains the spectra collected on 'Turnbuckle1' except those acquired on the hook and on the arch where the two connecting rods are nailed. Actually, these three spectra fall in the other confidence region, which includes all points of analysis taken on 'Turnbuckle2'. The alloy used for 'Turnbuckle1' is richer in copper and manganese, while the other has a higher relative concentration of zinc, arsenic and nickel. This particular clustering can be explained considering that investigated objects were tools used in everyday works, so it was not uncommon to perform repairs or to substitute broken parts. Thus, it is possible to conclude that the two components (the hook and the arch) belonging to 'Turnbuckle 1' but falling in the 'Turnbuckle 2' confidence ellipse could have been substituted in a more recent period, using an alloy similar to the one constituting 'Turnbuckle 2'.

Analysing by means of PCA also the remaining tools, it was not possible to highlight any relevant clustering; the only observable grouping was related to spectra collected on the same object. So, no other analogies were found among alloys.

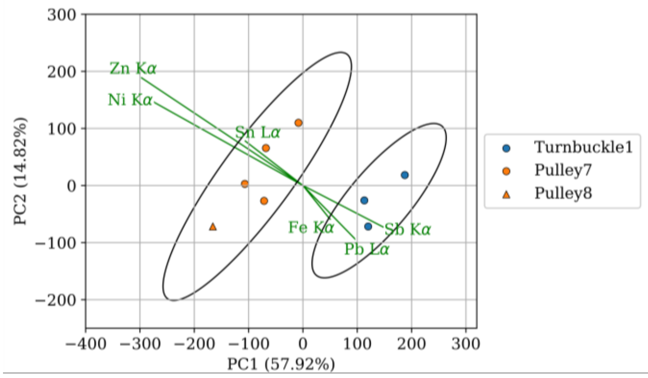

Figure 8. Score and loading plot of the first two components (PC1-PC2) calculated from XRF spectra acquired on bronze components. Percent variance captured by each PC is reported in parenthesis along each axis.

4. CONCLUSIONS

This study analysed some of the tools employed in the construction of the Santa Maria del Fiore Cupola. Thanks to X-Ray Fluorescence measurements, it was possible to investigate, for the first time and with a totally non-invasive approach, the composition of the alloys constituting these objects, which have a primary importance both from the technical and historical point of view. Then, thanks to chemometric analysis, analogies and differences among alloys were examined. It was possible to discriminate between the different iron alloys employed for the pulleys, which can be discriminated in two typologies belonging to different historical times. The use of PCA allowed also to highlight the presence of two bronze alloys (one used for threated components and one for the wheels of the metallic pulleys) and two iron alloys used for the turnbuckles. The use of XRF analysis does not allow to draw univocal conclusions on dating of these objects, as this technique is not even specifically intended for this purpose. Anyway, these findings, if supported also by historical sources and by the work of curators, can give new insights on the world of technology in the Renaissance era.

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