Material characterization and functional implications of a Claude Laurent Glass Flute

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Abstract

The Claude Laurent glass flutes (1805 - 1844) are singular elements that contributed to the transformation of musical instruments through the introduction of new styles and technologies. These flutes combine improved technical capabilities with aesthetic criteria, making them high-quality instruments and appreciated objects of art. Through the analysis of an 1823 flute, the present study is focused on the determination of their material characteristics and the relationship of these materials with the flute's structure and constructive process. The composition of the glass and metallic parts has been determined by XRF after establishing a specific calibration for each material and energy range. A potash-lime-silica glass, which shows similar composition to some previously analysed flutes conserved at the Library of Congress in Washington, was used for the glass parts of the flute. Composition of the metallic parts is presented for the first time. Regarding the larger parts, four different composition groups can be distinguished. The composition established can be related to the function of each group – for example, a silver-copper alloy serving aesthetic reasons was used for all visible metallic parts, while hidden parts that demand higher mechanical resistance were made with bronze - while also yielding information about the constructive process. Regarding the flute's smaller metallic parts, which consist of the keys and key levers and some mechanical pieces, such as screws or springs, the materials detected include a silver-copper alloy and steel.

Key Words: XRF, Glass Flute, Claude Laurent, Fundamental Parameters, Glass Analysis, Metal Analysis

1. Introduction

Musical instruments in Europe underwent an important transformation during the last decades of the 18th century, largely due to the new technology derived from the Industrial Revolution. One of the protagonists of this transformation was Claude Laurent (1774-1849), a Parisian watchmaker who, in 1806, patented one of the most innovative instruments of his time: a flute made of glass and silver. These flutes fitted perfectly into the aesthetic canons that pursued the romantic ideals of beauty, purity and singularity. The instruments were sophisticated works of art, lavish objects built with noble metals and high-quality clear, blue or green-coloured glass. The keywork and ferrules were plated with alloys or noble metals, and the keys could present, in the most luxurious models, incrustations of precious or semiprecious stones. The invention aroused great admiration and its creator quickly

acquired a great reputation and a distinguished clientele, which included professional and amateur musicians of the European aristocracy, such as Emperor Napoleon I and Tsar Alexander I of Russia.

The use of glass did not serve only decorative purposes. In his patent, Laurent states that given its inalterability before environmental variations, glass was the most appropriate material to solve the problem of sound and tuning variation present in wood or ivory flutes due to changes in temperature and humidity. In addition, it provided greater purity and sweetness to its sound and beauty to its design [1].

Laurent devised a flute that incorporated new procedures and elements in the manufacturing process, such as a new fastening system of the mechanism that would be crucial for the evolution of woodwind instruments and that is still used nowadays. Several innovative mechanical aspects, commonly attributed to other later manufacturers, have been shown to appear in the Parisian flute maker's work years in advance. One of the most important challenges that had to be faced was the fastening of the keys onto the glass body, something not feasible with the methods used in the existing wooden or ivory flutes. Laurent conceived a post-mounted key system that was fastened onto silver plates and screwed directly into the tube. The introduction of new materials, such as hardened steel, in some of the elements that make up the keys, which was traditionally used in watchmaking but not in the manufacture of wind instruments, must also be highlighted. Claude Laurent also introduced the use of completely metallic sockets and tenons to join the different parts of the tube, using various metals and alloys.

Currently 159 glass flutes made by Laurent have been found around the world [2]. Analysis of the composition of the flutes and determination of the materials used can offer more insight into how they were created and can also help with conservation and characterization matters. The composition of the flutes has been associated with their state of conservation, as flutes made with crystal glass rich in lead are better conserved than those with a higher K_2O concentration, which are less resistant to attack by moisture [3]. In alkali-rich glasses, moisture and changes in humidity can cause sodium or potassium ions to leach into the glass. This can lead to the hydration of the glass's silicate network, which deteriorates into a gel layer and can ultimately cause irreversible damage to the flute, such as microscopic cracking, which is known as crizzling. Absorption of alkali ions can also cause weeping or sweating, which is the formation of liquid droplets on the glass surface. The determination of the flutes' composition can offer valuable information into how each one of them should be conserved, in order to avoid deterioration or further damage [4–6].

As is the case with most cultural heritage objects, sampling is not allowed, thus making necessary the use of non-destructive analytical techniques to determine their composition. An appropriate technique for this purpose is X-ray Fluorescence (XRF), whose capabilities have already been demonstrated in the analysis of a wide range of art objects, such as paintings [7], manuscripts [8], sculptures [9], metallic [10] and glass artefacts [11] and musical instruments [12,13]. XRF is an atomic analytical technique that can be used alone or accompanied by other complementary techniques, such as Raman Spectroscopy or X-Ray Diffraction which can provide information on the sample's molecular

composition or crystalline structure respectively [14,15]. Chemometric techniques are also often used to process XRF results, when large batches of data have been obtained in order to reveal the most relevant information [16–18].

In a previous set of studies of the Laurent flutes conserved at the Library of Congress in Washington, small glass fragments resulting from previous damages of two flutes were used to quantitatively determine the composition of the glass via Direct Couple Plasma (DCP) and XRF [19]. The objective of this study is to obtain information about the composition of the glass and metallic parts of the flute, but also about the flute's structure and the functionality of each of its elements. In this study, an 1823 Claude Laurent flute (MG:Lau1823.01) has been analysed, without acquiring any sample of the flute, applying X-ray Fluorescence analysis. Furthermore, the composition of the metallic components of a Claude Laurent flute has been analysed for the first time, providing further knowledge about the fabrication process of these pieces and their mechanical and decorative purposes. In order to obtain reliable semi-quantitative results in a completely non-invasive method, multiple measurements on the glass and metallic parts of all the flute joints and a very precise calibration are necessary.

2. Material and methods

2.1. X-ray fluorescence

The XRF analysis was performed using a portable commercial XRF spectrometer (Elio, XGLAB Srl). The instrument is equipped with a Rh anode X-ray tube, a 12.5 μm thick Be window and a 25 mm^2 active area Silicon Drift Detector with an energy resolution of 135 eV at the Mn Kα line. The analysis range of the instrument lies between 1 and 40 keV, thus permitting the detection of elements from Na to U, when the air is purged with a Helium flux. If that is not the case, only elements from Si to U can be detected.

The measuring conditions for the analysis of the metal alloy samples and the metallic parts of the flute were maintained at 50 kV, 80 μA, with a 60 s analysis time. The distance between the detector and the sample is 1.4 cm. For the analysis of the glass samples and the glass parts of the flute, the air was purged with He (input pressure = 2.5 bar) and the conditions were adjusted to 20 kV, 200 μA and 300 s in order to allow the detection of Na, a main constituent of glass. Three measurements were obtained from all glass flute parts and larger metallic flute parts. Only one measurement was obtained from some smaller metallic parts, such as the flute keys or the interior of the metallic connecting pieces, due to limited sample surface or difficulties in the measurement achievement resulting from their cylindrical shape, respectively. The points analysed can be seen in Figure 1.

2.2. Glass dissolution

The dissolution of the glass control materials used for the calibration was based on the procedure described by Rauret et al. [20]. 100 mg of the control material were placed in a Teflon beaker, before adding 4 mL of water, 1 mL HNO_3 and 1 mL of HF (40%). The beaker was covered with a Teflon watch glass and was placed for 5 min in a sand bath which had been heated to approximately 300 ^oC. 4 mL of water were added to the solution, after it had slightly cooled down, and it was then heated for

another 5 min at 300 ºC. Following this procedure, the glass was completely dissolved. The solution was subsequently transferred to a volumetric flask and diluted to a final volume of 20 mL.

In order to be able to detect Si and avoid its volatilization, the same procedure was followed, with the difference that the dissolution took place in a Teflon beaker inside a pressure vessel, which was closed and heated at 300 ºC for 15 min. After that, when the vessel reached room temperature, it was shortly opened to add 1 g of solid H_3BO_3 – necessary to neutralise the excess HF and thus, prevent the volatilization of SiF_4 [21] – and 5 mL of water and quickly closed again and heated for another 15 min at 300 ºC, before finally cooling to room temperature.

2.3. Metal alloy dissolution

The metal alloy control materials were dissolved following the procedure described by Sessa et al. [22]. 20 mg of the metal alloy, 1 mL of HNO_3, 1 mL of double-deionized water and 0.25 mL of HF were added in a Teflon beaker. The solution was heated for 5 min in a sand bath at approximately 300 ºC and was then left to rest for 12 h in order to assure complete dissolution. Then, the solution was diluted to 50 mL.

2.4. ICP analysis

For the quantitative analysis of the glass and metal standards via Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), the solutions were diluted until reaching an adequate concentration for the measurements. The matrix of these solutions was adjusted to 1% HNO_3. In the cases where Si was measured, NH_3 was used as a matrix. The elements analysed were measured with ICP-OES (Perkin-Elmer Model OPTIMA 3200RL equipped with a Perkin-Elmer AS-90 Plus auto sampler) and ICP-MS (Perkin-Elmer ELAN 6000 ICP-MS equipped with a Perkin-Elmer AS-91 auto sampler), depending on the concentration present in each sample.

2.5. Calibration and semi-quantitative analysis

The XRF spectra were analysed using PyMCA (Software Group of the European Synchrotron Radiation Facility (ESRF)) [23], an open source software based on the “fundamental parameters” approximation. For this approximation, calibrations were carried out separately for the glass and metallic parts. A reference material (NIST SRM 610) and 8 other glass pieces were used for the glass calibration, whereas for the metallic parts, the calibration was carried out using 8 metal alloy pieces. The composition of both the glass and the metal alloy control materials had previously been determined by ICP-OES and ICP-MS. In order to use the “fundamental parameters” approximation, the characteristics of the XRF equipment, presented in section 2.1, must be introduced to the PyMCA software.

When three XRF measurements were available, they were used to calculate the composition of every flute part and the average of these concentrations was calculated. In the cases where only one XRF measurement could be carried out, the spectrum obtained was the one used.

3. Results and Discussion

3.1. Description of the flute

The flute analysed was made in Paris in 1823 and like all transversal flutes from that period, it consists of four parts that can be separated: the head joint, the upper joint, the lower joint and the foot joint. The parts are connected to each other with silver sockets and tenons. The top end of the head joint is closed with a mother-of-pearl cap that fits into the tube by means of a thread.

The flute is made of polished, clear glass, present on the flute's outer surface. On the inner surface, frosted glass is applied in order to achieve a more porous surface, an aspect that positively influences the flexibility and sound quality of the instrument. The total length of the flute is 629 mm, whereas the sounding length – which is the distance between the middle of the mouth hole and the end foot joint – is 538 mm. In the mouth hole area, which is the widest part of the instrument, the outer perimeter of the tube is 92 mm, whereas the narrowest section of the flute is 70 mm at the foot joint end.

The instrument consists of six open tone holes, intended to be covered directly with the fingers, and five keys (B♭, C, G♯, F and D♯) covering another five holes that cannot be reached with the fingers. The keys are mounted on pillars, welded on curved plates that follow the shape of the tube. The B♭, C, G♯ and F keys are screwed directly into the glass, whereas the D♯ key is screwed onto the silver foot joint socket. Each key has a hardened steel flat spring incorporated, allowing its opening and closing, in order to cover the corresponding hole and produce different notes. The keys are round and curved, adapting to the flute body and have levers of different shapes and sizes, used to operate the keys from a distance. The lower parts of the keys, designed to cover the tone hole when closed, are equipped with pads.

The head joint ferrule, the lower joint socket and the D♯ key present the guarantee hallmark of the silver used in Paris between 1819 and 1838, with the shape of a "rabbit head" (Fig. 2.a). Furthermore, the maker mark of Jean Dupin, the goldsmith Laurent usually collaborated with in the 1820s, also appears on these parts (Fig. 2.b). The lower end of the head joint has a main silver ferrule, on which the name of the flute maker, the year (Fig. 2.c) and place of manufacture and the word "Breveté" (which means patented) are stamped.

No documentation has been found regarding restoration undergone by the flute, which seems to have been widely used and presents small scratches and marks due to this fact. The superficial silver coating of some of the connecting metallic pieces of the flute has been scratched off, revealing the bottom bronze layer. Regarding the conservation state of the glass parts, the flute has suffered a small blow on the head joint, causing the superficial breaking of a small part of the edges of the carving of the glass without nonetheless affecting the integrity of the tube. Furthermore, the glass presents a certain opacity, which could be caused by a different type of polishing in some specific areas of the flute, or by some initial degradation process.

3.2. Calibration of XRF instrument

The “fundamental parameters” approximation used in this analysis takes into account the type of sample analysed, the measuring conditions, such as the emission energy, the analysis time and the detector-sample distance, and also the spectrometer’s characteristics, such as the detector type, the thickness of the Be window, the active area of the detector and the ingoing and outgoing angles [24,25]. The above mentioned factors, in combination with the relative areas between elements, allow the calculation of the concentration for each constituent based on the area of the corresponding peak and the fundamental equations that connect the two variables [26]. This approximation was chosen for its ability to provide trustworthy semi-quantitative results and has furthermore been proven to provide good inter-lab reproducibility, especially when calibrated with standards [27,28], as is the case in this study.

The use of standards or control materials of known composition is necessary for the calculation of the intensity of the X-ray radiation on the sample in relation to the concentration of each element, which in turn is necessary for the calculation of the concentration of samples with unknown composition. The determination of the intensity is only possible after having defined the matrix of the sample and correctly introduced the variables mentioned above. The photon flux must then be adjusted until the concentrations of the elements obtained by XRF match the known concentrations of the standards or control materials.

The comparison of the XRF results of the control materials and the glass and metallic standards with the results obtained via ICP-OES and ICP-MS demonstrates that the magnitude order of the concentrations of all elements can be trusted. However, taking into account the intrinsic difficulty associated to concentration determination using XRF and the caution derived from previous experience in this field analysing heterogeneous materials, greater standard deviations between measurements of the same samples might exist than those determined and presented in the following tables.

After achieving the calibration for both a glass and a metal alloy matrix, the conditions established can be used for the semi-quantitative determination of the composition of the glass and metallic parts of the flute.

3.3. Analysis of glass parts

3.3.1. Glass analysis and calibration challenges

Several factors must be taken into account when performing semi-quantitative analysis of glass, especially in the cases of historical glasses, as is the one analysed in this work. These factors include the material’s lack of uniformity and the fact that depth analysis and X-ray emission attenuation vary from element to element, meaning that certain elements are detected closer to the surface and others deeper inside the sample. Furthermore, it must be noted that XRF can only measure major constituents of glass that are up to approximately 30 μm deep, signifying that surface condition also greatly affects results [29]. In the case of the Laurent flutes, where the opacity observed in the glass

has been associated to crizzling, which in turn is associated to the formation of alkali depleted layers in the glass, the lack of knowledge regarding the depth of each measurement could lead to variability in the results.

Another issue regarding glass analysis stems from the fact that the emissions of light elements, such as Na, Al, Si, K and Ca, are strongly influenced by the environmental conditions, as they can be absorbed by the nitrogen and the oxygen in the air. This is particularly troublesome when analysing glass objects, as these elements are the main constituents of all glasses. Even while purging the air using a steady He flux during the glass measurements, detection of Na remains difficult and the intensities of other element emissions could also be affected.

A direct consequence of these issues is the difficulty to achieve a good XRF calibration for glass samples in comparison to other sample types. As mentioned by Kaiser and Shugar, low Z elements must be calibrated separately from high Z elements [29]. For this reason, a calibration was used for elements heavier than Ca, while the lighter ones were calibrated independently.

3.3.2. XRF Results

The XRF analysis of the glass parts of the flute has revealed that the composition of all points analysed is very similar, with only some small differences in the intensity of certain peaks (Figure 3). These differences are most likely related to the issues presented previously, such as the heterogeneity of historical glasses and the degradation effects. As can be seen in Table 1, the main constituents of the flute's glass are SiO_2, K_2O, CaO and Na_2O. The average semi-quantitatively calculated concentrations for these oxides, taking into account the four flute parts, are 84(4), 10(1), 3.7(0.1) and 1.3(1.1)% respectively, indicating that the glass used for the manufacturing of the flute is a potash-lime-silica glass. From these results it can be deduced that the same type of glass has been used for the four flute sections.

As has been mentioned previously, these results are semi-quantitative and the errors associated to them can be explained due to the aforementioned issues. Under such conditions, a relative standard deviation of around 5% can be expected for major elements, while an even higher one can be expected for minor elements. In the case of Na_2O, the very large standard deviation can be explained due to the difficulty to detect Na, even under specific conditions, such as the He purging.

3.3.3. Comparison to previous studies

Previous analyses of the glass composition of 21 Claude Laurent flutes and piccolos conserved at the Library of Congress in Washington, DC, USA have demonstrated that the term "crystal", used by Laurent to describe his flutes, is not always applicable, as only two of these flutes are made of leaded crystal glass and the rest are made of potash glass.

MG:Lau1823.01, the flute analysed in this work, belongs to the group of potash glass flutes elaborated by Laurent. Its composition is very similar to that of the two potash flutes conserved at the Library of Congress and analysed via XRF, SEM and DCP, with slight differences in the concentration of SiO_2 and K_2O, as can be seen in Table 2. The analysis of minor elements has proved that oxides

such as Fe_2O_3, MnO, BaO, Rb_2O, TiO_2 and ZrO_2, are also present in MG:Lau1823.01, in similarly low concentrations.

Regarding K_2O, high concentrations have been associated with a type of glass degradation called crizzling, which leads to an opaque glass effect. The lower K_2O concentration found in the MG:Lau1823.01 could be due to the fact that the glass areas where the XRF measurements were carried out were relatively transparent, a fact that can be associated with a limited amount of degradation and thus a lower K_2O accumulation in the glass surface.

As it is not known whether Laurent himself fabricated the glass used for the flutes, or if this work was carried out by expert glass blowers under his orders [2], the small differences in glass composition among the flutes could also be attributed to the use of different glass recipes or variations in the process. These differences could subsequently also be the cause behind the different conservation states the flutes are in.

The K_2O concentration cannot be directly associated with the age of each flute. DCM-0717 (1829), the flute with the highest concentration, was the last one of the three to be manufactured, whereas the flute analysed in this work has a lower concentration in comparison to DCM-1235 (1812), even though it was made later in time. Furthermore, it is interesting to note that the leaded glass flute DCM-1051 was elaborated in 1807, before making the other three flutes whose composition is presented here.

The differences in the composition of glass used for the Claude Laurent flutes, although relatively small, have to be established in order to be able to follow the most adequate conservation strategy for each one of them. In addition, the variations in the glass composition increase the interest to establish the composition of the metallic parts, as they too could vary from flute to flute, indicating the need for a different treatment and can also help to know better the creative process followed by Laurent.

3.4. Analysis of metallic parts

3.4.1. Larger pieces

The larger metallic pieces of the flute can be sorted into four different categories according to the structural information provided and their different composition:

(i) The head joint's top head, main ferrule and tuning slide, the lower joint's socket and tenon and the foot joint's socket and bottom end, which make up the majority of the flute's silver large pieces, form the first and most prominent category. These pieces present a fairly consistent composition of 95-97% Ag and 2-3% Cu (Table 3), a typical jewellery silver composition.

In order to better establish the composition of these pieces, measurements were acquired from the interiors of the head joint's tuning slide, and the lower and foot joints' sockets, displayed in Figure 4. The interior of the upper joint's tenon is also displayed in the same figure for comparison reasons, even though it belongs to another category. These measurements provide a more in-depth view of the flute's construction and the mechanical design of the instrument.

The tuning slide (Fig. 4.a), situated inside of the head joint's main ferrule, was found to have the same composition in the interior as in the exterior, indicating that a homogeneous piece of a silver-copper alloy was used to make it. Bronze was detected in the interior of the lower joint's socket (Fig. 4.b). The bronze thread can be found in the back side of the socket, attached to the glass, before being covered with a metallic piece, similar to the one used for the main ferrule and the tuning slide. The same material was also used for the foot joint's socket, although in this case, instead of bronze, a ring made of Sn can be found in the back of the piece, protecting the glass (Fig. 4.c).

The lower joint's tenon (Fig. 4.d) is a partially degraded piece, since it connects tightly into the socket of the foot joint. Multiple measurements were carried out on this part, which can be organized in 3 different groups: 3 measurements were made on the tenon "tube", 3 on the ring at the edge of the tenon and 2 in the area between the tube and the ring (Table 4). Higher concentrations of Cu (63%) can be found in this piece in comparison to the others. This difference could be attributed to the screwing of the tenon into the socket and its subsequent erosion, apparent by the visible scratch marks on the tenon's surface. The detection of Cu could be due to the exposure of the bottom layer of bronze. The perimeter of the ring at the edge of the tenon was found to have a composition very similar to most of the silver pieces of the flute (95% Ag, 4% Cu). The measurements of the most degraded areas of the tenon measurements (Border 1 and Border 2), found between the tenon tube and the ring, revealed the presence of Sn, which was probably used to weld the two metallic pieces together. The differences between the two border measurements are related to the size of the X-ray analysis area, which is bigger than the size of the area that needs to be analysed.

(ii) The upper joint tenon forms a category of its own. Although the interior of the piece is made of bronze (Fig. 4.e), it is the only flute part where no Cu can be detected on the exterior. Instead, a higher concentration of Ag and a varying amount of Hg is present. Mercury gilding was a common practice in the past, which included the application of an amalgam of powdered silver or gold and mercury onto metallic objects, before heating the object in order to evaporate the mercury [30]. Due to the fact that the mercury is not fully removed, the final result is a homogeneous layer of silver covering the metallic base with a fairly consistent concentration of Hg found in every part of the layer. However, the analysis of the flute tenon showed that the concentration of Hg varies in different parts of the piece, with differences of up to 24% between different points analysed. This would indicate that the technique of mercury gilding was not used in this case, but instead it is a silver foil that has been welded onto a copper piece with the help of Hg. This was an alternative welding method, where Hg was applied onto a part of the metallic object to be covered with a silver leaf. This means that Hg can only be found in certain spots, as it is not necessary to weld the whole surface of the silver foil onto the metallic object. The distribution of Hg concentration in the spots analysed can be seen in Figure 5. The remaining percentage in each measurement corresponds mainly to Ag.

Analysis of this piece begun on a straight line visible with the naked eye (Point 1 in Figure 5) and measurements were acquired from the three distinct areas of the piece: the part of the tube closer to the tenon ring, the incomplete ring that serves for connecting the piece to the head joint and the small part of the tube that is closer to the glass (Tenon A, B and C respectively in Figure 5). Measurements

were acquired perimetrically, turning the flute 45º after every measurement and thus covering the whole piece's surface. In the case of the Tenon B measurements, the flute was turned 90º every time.

In the case of Tenon A, the highest concentration was detected on top of the straight line and a similarly high concentration was also found in Point #5, located directly opposite Point #1. Relatively high amounts were also found in Points #2 and #8 that correspond to points situated at 45º left and right of the straight line. These concentrations lead to the hypothesis that a silver foil was placed and welded on the tube at Point #5, giving it stability and in continuation, the two ends of the foil were connected and welded at Point #1, thus explaining the presence of the straight line and of Hg.

The highest concentrations were detected in the Tenon C section and more specifically on and next to the straight line. The presence of Hg is wider, indicating that the foil was welded at several points perimetrically, possibly in order to achieve greater stability in an area with limited surface.

(iii) The tenon rings of the upper and lower flute joints form the third category. Their composition is made up mainly by Sn, Sb and Pb, as can be seen in Table 5, indicating the use of a tin-antimony alloy.

(iv) The thread that connects the upper joint to the lower one forms the fourth and last category. It is made of bronze, with a composition of 87(11)% Cu, 8(1)% Sn, 4.2(0.5)% Zn and 0.5(0.1)% Pb. The small thread situated in the back part in the interior of the lower joint socket could possibly also be part of this category, but its exact composition is not known, due to the difficulty to carry out a measurement because of the piece's position.

3.4.2. Smaller pieces

The analysis of the keys and other smaller mechanical parts showed similarities between elements with similar functions.

All the keys have a fairly consistent composition, with a concentration of ~97% Ag and ~2% Cu, as can be seen in Table 6. The silver alloy used is of similar nature to the one used for some of the major flute pieces, providing malleability at the time of the element's construction but also the sufficient hardness and stability in order to carry out specific functions.

The same alloy was also used for the construction of the posts and post balls that support the B♭, C. G♯ and F keys. However, the D♯ key post ball has a slightly different composition, as a higher Cu concentration was detected. Due to the singularity of this difference, multiple measurements (a total of 7) were carried out on the balls on the two sides of the support system (n=3 for each ball) and the post that holds one of the balls (n=1), assuring that the whole post ball piece has the same composition. It is difficult to explain the reason behind this compositional difference, as the D♯ key support system does not seem to offer any additional functions which would require extra hardness in comparison to the other keys. Two possible explanations could be a restoration treatment, which would include the change of the original support piece with another one made at a later time, or that

Laurent had pieces of different compositions in his workshop and just happened to use one with a higher Cu concentration for only this key.

Some smaller mechanical pieces used to hold the key support system together were also studied (Table 7). Both pieces analysed contain Fe, indicating the use of steel. However, without the use of a complementary technique that can detect C, it is not possible to be certain. The screw used to support the D♯ key contains 99.04% Fe, whereas the key spring contains 59.03% Fe and 40.0% Ag, indicating that it was painted, gilded or bathed in silver, which serves decorative purposes and gives visual homogeneity to the flute.

3.4.3. Composition and functionality relationship

Based on the results presented above, several conclusions can be drawn regarding the relationship between composition and functionality of the flute's metallic pieces.

The study of the interiors of these pieces is quite enlightening as it reveals that each connecting piece is fabricated in a unique way, using different materials every time. Bronze is used when more mechanical strength needs to be applied, giving the flute more stability. Its use is particularly apparent in the case of the connection between the upper and lower joint, where the upper joint's thread screws into the lower joint's socket. Its application can also be found in the pieces connecting the upper joint to the head joint. The tenon is a homogeneous bronze piece, covered in silver, whereas on the very back of the head joint's main ferrule's interior, bronze can also be found, making this piece sturdier. Bronze is also detected on the lower joint's tenon, the flute's most degraded piece.

Apart from bronze, it can be deduced that a silver-copper alloy of a relatively stable concentration is the most applied material in the flute, used for both larger cylindrical pieces and for smaller elements. This material serves decorative purposes when it is covering smaller bronze pieces, necessary to connect the flute parts between themselves, but also functional purposes, when it is used to form pieces such as the keys and the key levers. In the first case, it is most probable that a flat metallic piece is used, folded around a cylindrical object and welded in order to connect the two sides, as can be suggested by certain visible horizontal lines found on some of these pieces.

Analysis of these lines has shown that no Hg is present, unlike in the upper joint tenon, indicating that they have been welded together using different techniques. In the case of the tenon, the material used is not a silver-copper alloy, but instead, it is a pure silver foil welded onto the bronze piece using Hg. Since this is the only metallic flute piece that does not have a flat surface, but instead has an elevated ring running through it, it is probable that during the flute's fabrication it was necessary to fabricate the original piece using a different technique from the others. However, the differences between the composition of the two materials and the way they have been applied to the flute, could also generate the hypothesis that the foil was applied during an unknown conservation treatment. Due to the uniqueness of the piece in comparison to the rest of the flute metallic parts, it would be interesting to analyse more flutes made by Laurent in order to see if they have any pieces with a similar composition.

The tin-antimony alloy used for the construction of the tenon rings of the upper and lower flute joints was most likely used for its visual similarity to silver but with increased resistance.

Finally, the last material used in the flute is probably steel, found in the elements that provide support to the keys. The improbability, as has also been mentioned previously, is due to the fact that carbon cannot be detected via XRF. These pieces, when visible, are also decorated with silver, demonstrating once more the importance Laurent gave to the visual aesthetics of the flute and all of its elements.

4. Conclusions

The global study of the MG:Lau1823.01 has provided useful insights in the manufacturing process followed by Claude Laurent and has shone light on the composition of the materials used for the glass and metallic pieces, allowing a better understanding of the connecting mechanisms of the flute. The analysis of the glass parts of the flute has demonstrated that a potash-lime-silica glass was used for its elaboration, with a composition similar to that of the two flutes conserved in the Library of Congress in Washington. The small differences in the composition of the glass, that could be associated to the degradation of the flutes, indicate the importance of being able to establish the glass composition non-destructively, as knowledge of each flute's composition can help choose the best strategies for its correct conservation. The composition of the metallic parts has shown how the materials used depend on the functionality of each piece and how the visual aspect of the flutes was high on Laurent's priorities when making them: bronze was used for the structural parts of the flute that need more mechanical strength, a silver-copper alloy for the visible metallic parts, a tin-antimony alloy was used for the tenon rings and some smaller metallic elements were made with steel in order to have elasticity and provide support. From an analytical point of view, the importance of a precise calibration has been highlighted as it can provide trustworthy semi-quantitative results without requiring sampling.

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Figure Captions

Figure 1. Scheme of the principal XRF point analyses. The red arrows represent measurements in the internal sides of the metallic pieces.

Figure 2. Authenticity proofs photographed with the Olympus SZ61 Stereomicroscope. (a) “Rabbit head” guarantee hallmark, (b) Jean Dupin maker mark, (c) year of manufacture.

Figure 3. XRF spectra of the glass parts of the four flute pieces, indicating the major elements present.

Figure 4. Interior view of the four different pieces analysed. (a) Head joint main ferrule, (b) lower joint socket, (c) foot joint socket, (d) lower joint tenon and (e) upper joint tenon.

Figure 5. Distribution of Hg on the upper joint tenon’s surface. Concentrations expressed in (w/w)%. The remaining percentage in each case is attributed to Ag.

Table Captions

Table 1. Semi-quantitative results of the analysis of the four flute glass parts, expressed in (w/w)%.

Table 2. Comparison of the glass composition of MG:Lau1823.01 and the three flutes analysed by Buechele et al. [19] and Zaleski et al. [5], expressed in (w/w)%.

Table 3. Semi-quantitative results of the composition of the larger silver pieces, expressed in (w/w)%.

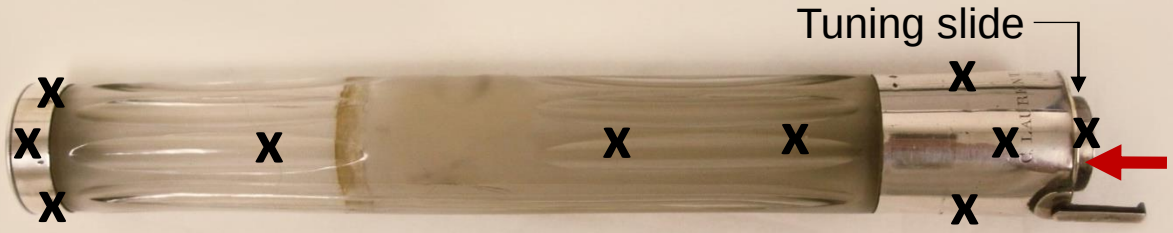
Table 4. Percentage of Ag, Cu and Sn in the chemical composition of the lower joint tenon, expressed in (w/w)%.

Table 5. Semi-quantitative results of the composition of the tenon rings, expressed in (w/w)%.

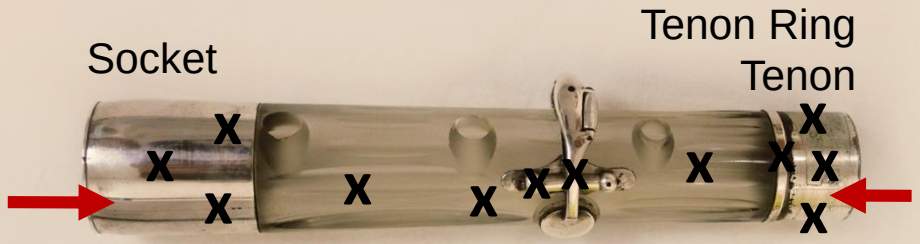
Table 6. Semi-quantitative results of the composition of the keys, expressed in (w/w)%.

Table 7. Semi-quantitative results of the composition of the D♯ key support elements, expressed in (w/w)%. Only one measurement has been acquired for each piece.

Head Joint

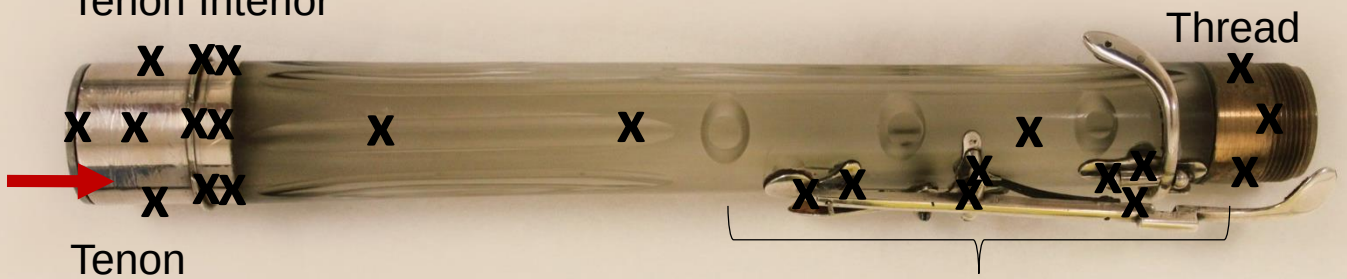


Lower Joint



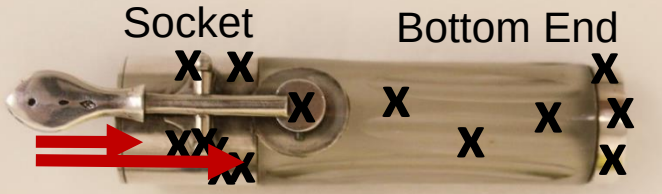
F key & Key Post Ball,
F Key Lever & Lever Roller

Upper Joint

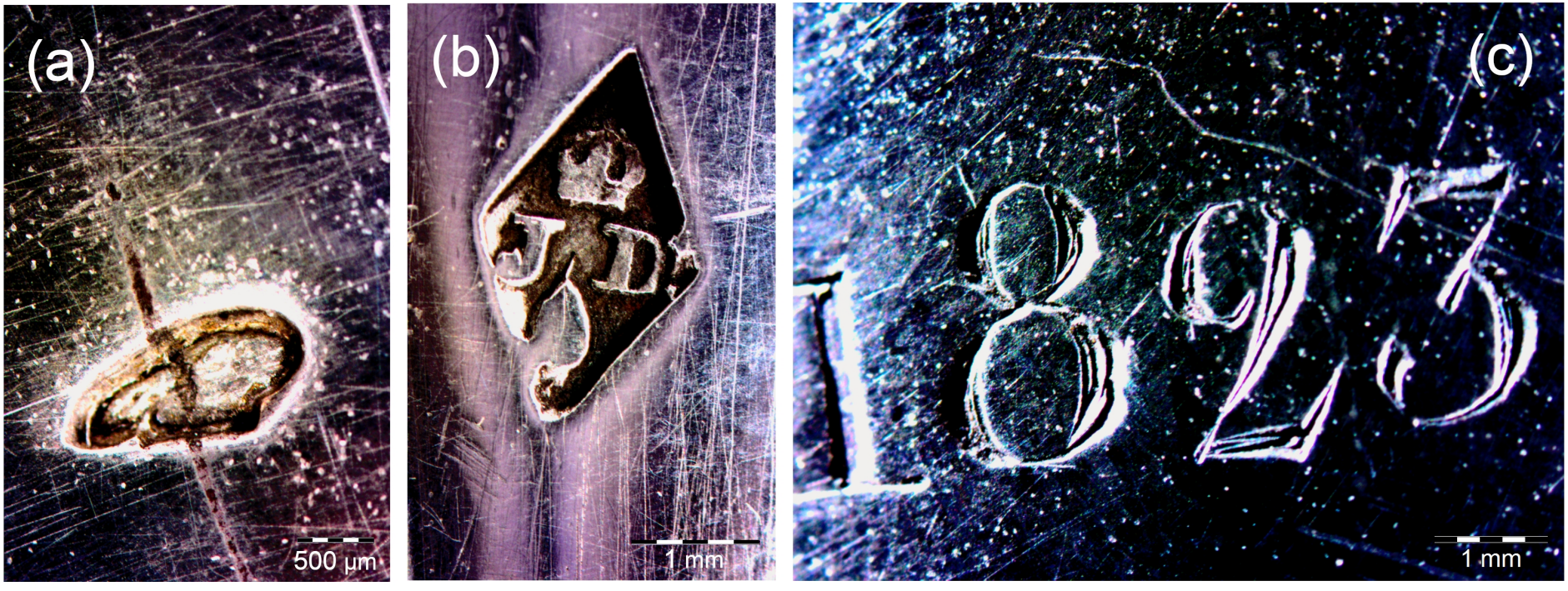


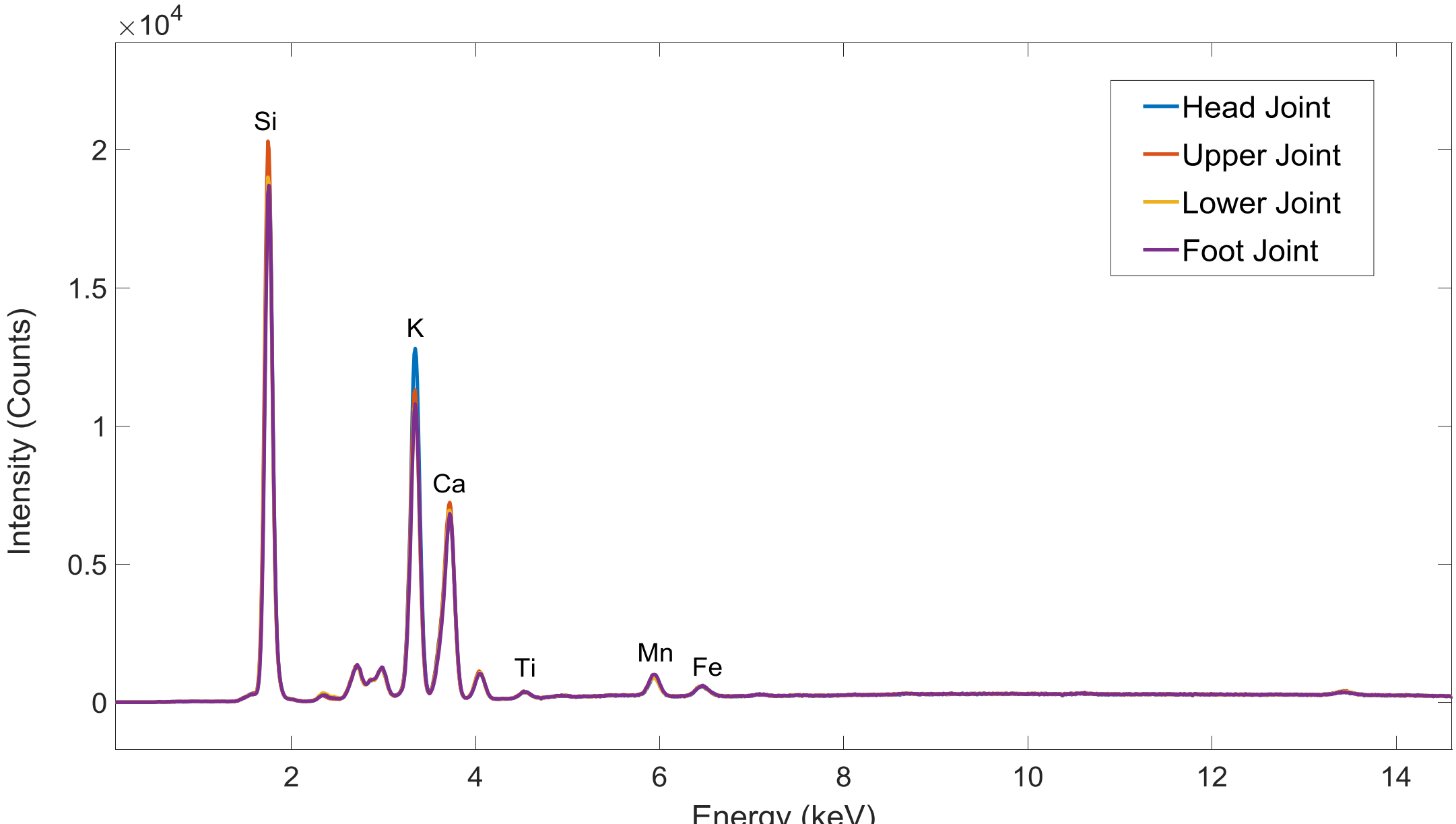
B♭, C and G♯ Keys & Key Post Balls,
C Key Lever

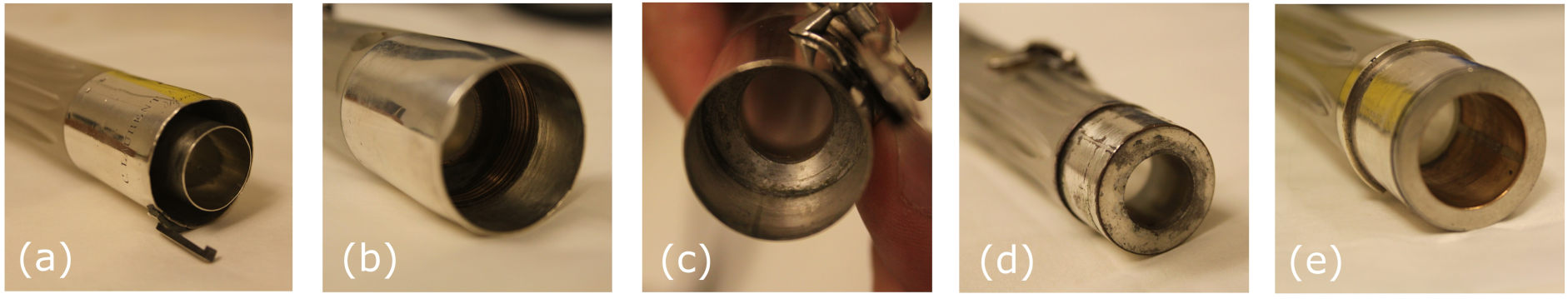
Foot Joint



D♯ Key,
D♯ Key Axis, Post Ball,
Spring & Screw


(a)
500 µm
(b)
1 mm
(c)
1 mm


×10^4
Intensity (Counts)
Energy (keV)
Si
K
Ca
Ti
Mn
Fe
Head Joint
Upper Joint
Lower Joint
Foot Joint
0
0.5
1
1.5
2
2
4
6
8
10
12
14


(a)
(b)
(c)
(d)
(e)

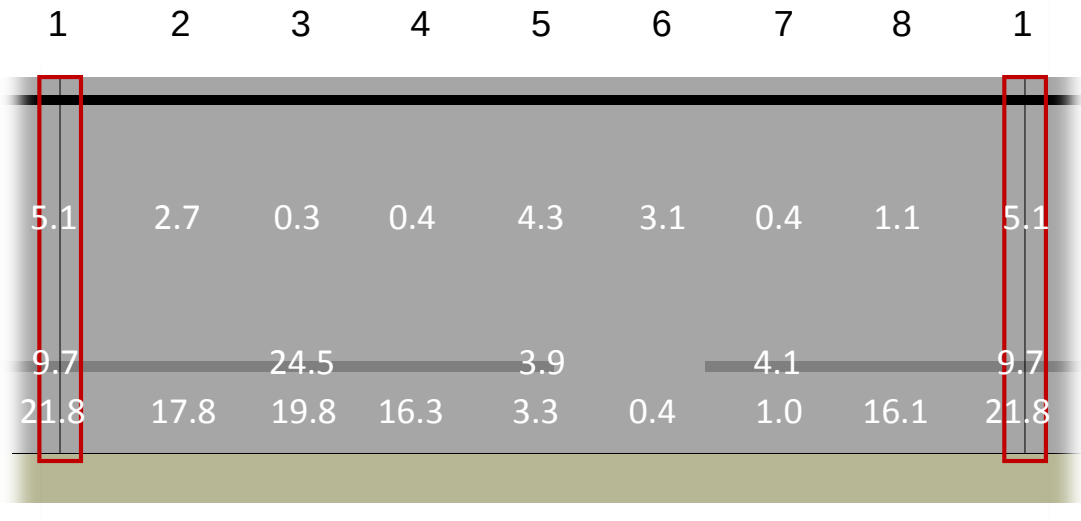
Tenon Ring

Tenon A

Tenon B

Tenon C

Glass

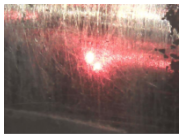
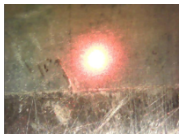
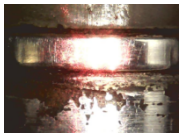
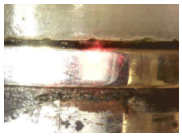
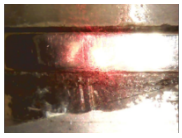
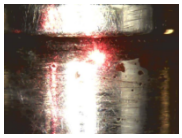


Flute Part	% SiO_2	% K_2O	% CaO	% Na_2O	% Al_2O_3	% TiO_2	% MnO	% BaO	% Fe_2O_3	% Rb_2O	Trace
Head joint (n=3)	83 (5)	11 (1)	3.5 (0.1)	1.2 (0.3)	0.57 (0.08)	0.140 (0.002)	0.162 (0.002)	0.136 (0.003)	0.072 (0.003)	0.0096 (0.0007)	NiO, SrO, ZrO_2
Upper joint (n=3)	85 (3)	9 (1)	3.7 (0.1)	0.9 (0.7)	0.59 (0.09)	0.140 (0.006)	0.168 (0.006)	0.139 (0.010)	0.074 (0.003)	0.0093 (0.0001)	NiO, SrO, ZrO_2
Lower Joint (n=3)	84 (4)	9 (2)	3.8 (0.2)	1.4 (1.8)	0.58 (0.05)	0.148 (0.003)	0.171 (0.003)	0.147 (0.009)	0.079 (0.004)	0.0093 (0.0008)	NiO, SrO, ZrO_2
Foot Joint (n=3)	84 (3)	9 (1)	3.7 (0.2)	1.7 (1.5)	0.59 (0.05)	0.147 (0.001)	0.199 (0.001)	0.140 (0.011)	0.078 (0.007)	0.0080 (0.0005)	NiO, SrO, ZrO_2
Total	84 (4)	10 (1)	3.7 (0.1)	1.3 (1.1)	0.58 (0.07)	0.144 (0.003)	0.175 (0.009)	0.140 (0.008)	0.076 (0.004)	0.0090 (0.0005)	NiO, SrO, ZrO_2

	Sample	Technique	% SiO_2	% K_2O	% CaO	% Al_2O_3	% Na_2O	% PbO	% Others
This work	**MG:Lau1823.01**	XRF	84 (4)	10 (1)	3.7 (0.1)	0.58 (0.07)	1.3 (1.1)	-	0.4
Buechele et al. (2015)	**DCM-1235**	DCP	79.04	15.54	3.38	0.36	0.77	-	0.92
		XRF	77.88	16.49	3.48	0.66	0.68	-	0.80
		SEM	78.03	17.18	3.69	0.34	0.63	-	0.13
	DCM-0717	SEM	74.45	21.02	3.49	0.00	0.68	-	0.36
Zaleski et al. (2019)	**DCM-1051**	XRF	56.030	10.583	0.100	0.111	0.883	31.142	1.008

Flute Piece		% Ag	% Cu	% Pb	% Ni	% Fe
Head Joint	**Main Ferrule**	96.8	2.46	0.6	0.090	0.019
(n=3)		(0.2)	(0.01)	(0.2)	(0.003)	(0.001)
	Top Head	95.8	3.7	0.38	0.09	-
		(0.4)	(0.4)	(0.01)	(0.01)	
	Tuning slide [a]	96.0	3.05	0.83	0.09	-
Lower Joint	**Socket**	96.3	3.30	0.36	0.074	-
(n=3)		(0.3)	(0.24)	(0.03)	(0.004)	
	Tenon	---------- See Table 4 ----------				
Foot Joint	**Socket**	97.9	1.74	0.28	0.075	-
(n=3)		(0.2)	(0.12)	(0.06)	(0.005)	
	Bottom End	97.52	2.04	0.4	0.089	-
		(0.07)	(0.04)	(0.3)	(0.002)	

a. Only one measurement acquired.

	% Ag	% Cu	% Sn	Photos
Tube (n=3)	36 (4)	63 (4)	0.12 (0.04)	  
Ring (n=3)	95 (2)	4 (2)	0.4 (0.5)	  
Border 1 (n=1)	24	54	20.8	
Border 2 (n=1)	83	10	6.5	

Flute Piece		% Ag	% Cu	% Sn	% Sb	% Fe	% Ni	% Pb	% As
Upper joint	**Tenon Ring**	0.026	0.20	81.3	17.8	0.024	0.035	0.55	0.026
(n=3)		(0.004)	(0.08)	(0.3)	(0.3)	(0.004)	(0.003)	(0.04)	(0.004)
Lower Joint	**Tenon Ring**	0.038	0.30	80	17.7	0.026	0.40	1.8	0.14
(n=3)		(0.005)	(0.07)	(1)	(0.3)	(0.004)	(0.005)	(0.7)	(0.01)

Flute Piece		% Ag	% Cu	% Fe	% Pb	% Ni
Upper joint	**B♭ key**	97.6	1.9	0.03	0.38	0.09
(n=1)	**B♭ key post ball**	95.4	3.5	0.02	0.95	0.07
	C key	97.8	1.8	0.02	0.30	0.07
	C key lever	97.8	1.8	0.02	0.28	0.08
	C key post ball	95.5	3.5	0.35	0.57	0.07
	G♯ key	97.8	1.8	0.02	0.31	0.10
	G♯ key post ball	95.5	3.6	0.08	0.72	0.08
Lower joint	**F key**	97.9	1.7	0.03	0.29	0.10
(n=1)	**F key lever**	96.9	2.6	0.03	0.37	0.09
	F key lever roller	96.2	3.2	-	0.49	0.09
	F key post ball	95.9	3.1	0.08	0.73	0.08
Foot joint	**D♯ key**	97.3	2.1	0.03	0.47	0.09
(n=1)	**D♯ key axis**	97.7	1.8	0.06	0.41	0.06
	D♯ key post ball	94.0	5.4	-	0.54	0.08
	(n=7)	(0.6)	(0.5)		(0.14)	(0.01)

Flute Piece		% Ag	% Cu	% Fe	% Pb	% Sb	% As
Foot joint (n=1)	**D♯ key spring**	40.0	0.5	59.03	0.42	Trace	Trace
	D♯ key screw	-	0.2	99.04	-	0.81	-

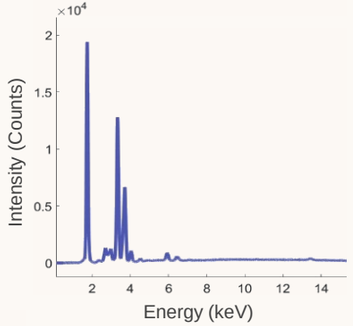
H. Bagán: Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Supervision, Project administration.

G. Magkanas: Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Visualization, Project administration.

M. Gascón: Resources, Writing - Review & Editing.

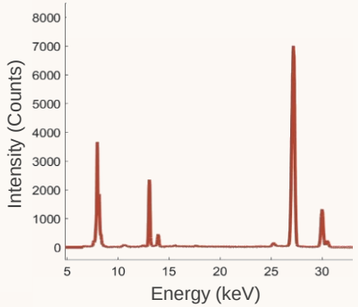
J.F. García: Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition.

Claude Laurent Glass Flute

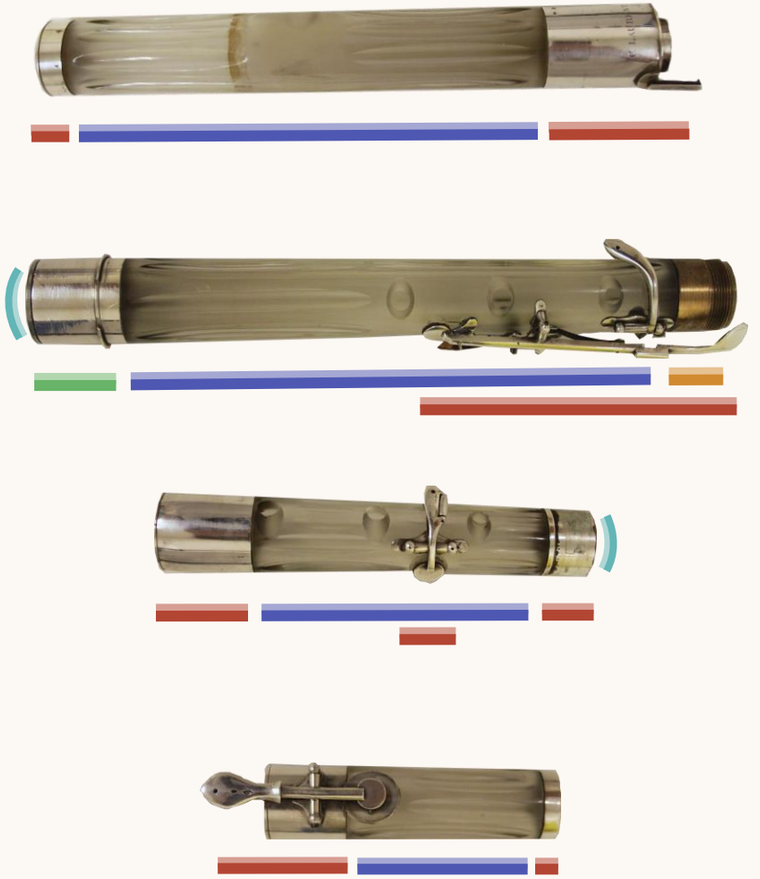


Glass Parts

XRF analysis



Metallic Parts



- Potash-Lime-Silica Glass
- Silver - Copper Alloy
- Bronze
- Silver - Mercury
- Tin - Antimony Alloy