Using characterization techniques for determining the history of a 2 millennia old kettle made of bronze alloyed with iron

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Abstract

A bronze kettle dating from the 1st to 2nd Century was found in a riverbed of the Kupa river in Croatia. After excavation it spent another 50 years in a depot of a museum in atmospheric conditions prior to starting the conservation treatment and our studies. A study on the surface layers development was performed to determine the history of the object. This study is a demonstration of how such analysis can be used to reconstruct what the object went through during its life span.

It was determined that the kettle is made of low-tin bronze, called *mild bronze*, with addition of iron, aluminum, calcium and nickel. Using iron for alloying copper is unusual since pure iron is generally not added to bronze, thus the presented case is a rare subject. Presence of cassiterite SnO$_2$ showed that the kettle was used for preparing food on open fire prior to ending up in the river. While being in the riverbed malachite formed on the kettle. After longer exposure to the river Si-oxides and CaCO$_3$ formed on the surface of the kettle, over malachite. It was shown that the kettle probably had a ferrous alloy handle which degraded and disappeared in time. After excavation, the kettle came again in an oxygen-enriched atmosphere and developed additional surface layers over the malachite layer.

1. Introduction

Objects made of copper and its alloys are often covered by layers of corrosion products called patina. These layers are an important factor that constitutes the historical and artistic value of the artifact. They are corrosion products that form naturally upon exposure of the object to its environment and have a specific composition, structure and color depending on the environmental conditions and type of alloy.

The characteristic green-blue patina color is caused by the Cu(II)-ion in compounds forming the outer patina layer, such as brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$) or atacamite ($\text{Cu}_2\text{Cl(OH)}_3$). The Cu(II) ion acts as a color forming ion, and is part of all compounds in the outer patina layer and as a consequence it is hard to distinguish different compounds by mere observation of the patina color [1]. On the other hand, the patina can be darkened by presence of copper sulphides or lead, lightened by lead carbonate or tin-oxide and reddened by an underlying layer of copper(I)oxide, cuprite [2]. There have been reported a large number of studies on different conditions and effects influencing patina formation, often in controlled conditions. Thus, it is known in which conditions it is possible to obtain different copper and bronze patinas [2, 3, 4, 5]. It is also known that after sudden or drastic changes of the environment the bronze object is exposed to, e.g. after excavation corrosion of bronze is restarted or accelerated that leads to formation of new layers of corrosion products [6]. If one understands the relationship and interaction between environments metals are exposed to and the formation and stability fields of corrosion products on metals, one may be able to tell under what sort of environmental conditions these materials have grown. This information should provide investigators with the possibility of writing the biography of ancient metal artifacts [5], i.e. by studying the corrosion products layering and composition it is possible to reconstruct the history of an object. The conclusions obtained from such studies are valuable both for the person performing the conservation treatment as well as for art historians.
There are numerous objects made of copper alloys that were found with no known history. The problem is that metals do not possess physical properties that can be expressed as a function of time and thus metallic artefacts cannot be directly dated. There are different approaches for authentication of ancient metals [7], but still the history of the artifacts is often not clear. When working with objects of historical or cultural importance it is possible to obtain samples of corrosion products from the artifact during the restauration treatment, but it is not possible to do studies that would use any destructible methods on the object itself. There are standard techniques used for analyzing corrosion products like X-ray radiography, or X-ray diffraction which is useful for validating hypothetical presence of unusual products. Yet, conservators are often limited by the number and/or quality of samples, as well as techniques that are accessible to them. Many conservators do not have access to sophisticated analytical techniques in their facilities and are forced to send samples for analysis to other institutions. This work presents how characterization of surface layers and corrosion products using elemental analysis in combination with Fourier Transform Infrared Spectroscopy can be used for determining the history of a bronze object on an example of an ancient artifact by joined collaboration of restorers and scientists.

A bronze kettle dating from the 1st to 2nd Century, Roman Empire period was found in a riverbed in the place of the Roman Empire city Siscia in Croatia. After excavation it spent another 60 years in a depot of a museum in atmospheric conditions prior to starting the conservation treatment and our studies. The item was received in a very bad condition and was covered with various corrosion products and remains of sand trapped in the corrosion products. Upon observing the exact state of the object, it was obvious that these very diverse surface layers were very interesting, not only because of their different structure and colors, but also because of their complexity. We intended to study which corrosion products had been created on the surface of the object, considering the environment in which the object was exposed to, as well as the chronological order of the corrosion products formation. In order to do so different analysis and instrumentation were used on a selected number of samples. This study is a demonstration of how studying the surface layers can be used as a tool for reconstructing the history of an object.

2. Materials And Methods

2.1. Materials

In the 1960s during dredging of the Kupa river in Sisak, a city located in central Croatia, a large group of objects was found, among which was the object of our investigations. A bronze kettle 22 cm high and 22 cm wide dating from the 1st to 2nd Century, Roman Empire period, probably from the Roman Empire city Siscia spent over a millennium in the riverbed. After excavation, the kettle was stored in the depot of the Sisak City Museum and was not processed until 2018 when it was sent for conservation-restoration treatment to the Art and Restoration Department of University of Dubrovnik, Workshop for conservation and restoration of metal. Prior to performing the conservation treatment different surface layers were visually distinguished and sampled. The investigations were performed on these samples.

2.2. Methods
Observation by optical microscopy

The samples were observed by a digital microscope Dino-Lite AM4113ZT under 60x and 240x magnification.

X-Ray Fluorescence (XRF) analysis

The samples were then investigated using a portable XRF instrument, which was developed at the Laboratory of the Academy of fine arts in Zagreb. It consists of a 50-kV Rh transmission excitation tube (Moxtek, USA) and a Peltier cooled silicon drift detector (Amptek, USA) with energy resolution of 145 eV at the Mn Kα excitation line. Depending on the analytical needs, the device can provide either mili or micro X-ray beam for sample excitation, by employing a motorized collimator interchanger to switch between a pinhole collimator (spot size ca. 1.5 mm) and a polycapillary lens (IfG, Germany, spot size ca. 65 µm). The operating parameters for tube voltage and anode current during the measurements were set to 40 keV and 150 µA, respectively, and the acquisition real time was 100 s. For these measurements the device was used in a micro mode and the diameter of the beam was set to ca. 65 µm. For easy and reproducible alignment of the sample in front of the X-ray source and the detector, a two-laser beam system is used. The lasers are aligned in such a way that the point of their beam intersection coincides with the cross-point of the X-ray tube and detector axes. On every sample two measurements were made and the results are a combination of the obtained data.

Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared spectroscopy (FTIR) was performed using Bruker’s Tensor II spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with Attenuated total reflection (ATR) module for checking presence of functional groups on the surface of the samples. FTIR spectra were recorded at room temperature in frequency range 500–4000 cm\(^{-1}\) at 4 cm\(^{-1}\) scan step and total 16 scans per measurement.

Scanning electron microscopy and X-ray energy dispersive spectroscopy (SEM/EDX) analysis

The samples were also inspected using the JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) equipped with the Oxford Instruments INCA-350 X-ray energy dispersive spectrometer microanalysis system (EDX). Computer program ImageJ was used in processing of FE-SEM sample images to obtain particle size distributions.

3. Results

3.1. Visual and optical observation of the surface layers

When the kettle was received at the Workshop for restoration treatment it was in a very bad condition and covered with various corrosion products and remains of sand trapped in the corrosion products. The
kettle seemed to be made by the embossing technique. No X-ray radiography was possible and no cross-section was allowed on the object, thus after the visual examination, six samples were taken from the kettle for further analysis. Two samples were broken fragments of the kettle found discarded within the object. They were covered with corrosion products and analyzed as Samples 1 and 2. Four samples (named Sample 3 to 6) were taken from the surface of the object as presented in Fig. 1. Each sample seemed to have a different surface layer based on the difference in color and structure.

Figure 2 presents the images of the studied surface samples taken by a digital microscope. The most prevalent corrosion product was greenish in color and was observed on various samples but was most expressed on Sample 3. Also, on the surface of the object, some other impurities have been trapped in corrosion products and there was accumulation of materials like sludge stones. Other black, brown, white-yellow and blue layers were also visible on the surface. Some of them covered the surface of the green areas, while some were close to the surface of the metal and degraded the metal until they made holes in the material itself. During the removal of the layers, it was observed that the black layers (Sample 6) were partially diluted in distilled water and 96% ethanol and were easily removed by mechanical cleaning with a scalpel. Below the black layers there was a layer of green corrosion products. The brown products (Sample 4 and 5) are more strongly adhered to the substrate itself. Below the brown layers, the green products only existed in traces and did not have such a uniformly covered surface as was the case under the black layers. Yellow-white layers observed on Sample 4 were fairly powdery and below them there was a layer of partially formed green corrosion products, while in other places a very thin layer of reddish-brown layers was observed.

### 3.2. The elemental composition of the samples determined by XRF

In order to distinguish the alloying elements from the elements embedded from other sources into the corrosion products X-Ray Fluorescence measurements were performed on all samples. The results are presented in Table 1. The results consist of three groups of elements: main elements are the elements with the highest intensity (proportional to their concentration); other elements are the elements with lower intensity and traces are the elements that are present only in traces. Sample 1 was one of the samples that had been discarded in the inside of the kettle. After performing measurements on the layers covering the surface, Sample 1 was cleaned manually and afterwards immersed into a 10% sulfuric acid solution for 3 minutes and consequently rinsed with distilled water. The cleaned Sample 1 was observed again by XRF to determine the composition of the alloy the kettle was made from. As the XRF analysis was carried out using a portable device, in air, with no reference materials and on corroded samples of unequal sizes and shapes, the measurements yielded only semi-quantitative results.
Table 1

| Sample          | main elements | other elements | traces           |
|-----------------|---------------|----------------|-----------------|
| Sample 1 cleaned| Cu, Sn        | Fe             | Al, Ca, Ni      |
| Sample 1        | Fe, Cu, Sn    | -              | Si, S, Ca, Ni   |
| Sample 2        | Fe, Cu, Sn    | -              | Al, Si, S, Ti, Pb|
| Sample 3        | Fe, Cu, Sn    | Ca             | Si, S, Ti, Mn   |
| Sample 4        | Ca, Fe, Cu    | Si, S, K, Ti   | Mn              |
| Sample 5        | Fe, Cu        | Si, K, Ca, Sn  | Al, K, Ti, Mn, Zn, As |
| Sample 6        | Fe, Cu        | Ca             | Si, P, S, K, As |

The results confirmed the kettle was made from bronze considering tin is next to copper a main element in the alloy. Since the kettle was made by the embossing technique the alloy is a low-tin bronze, probably *mild bronze* which contains up to 6 wt % tin because this type of bronze was used for embossing. Mild bronze was one of the two most commonly used antique bronze alloys that has been known since the Bronze Age, where *classic bronze* has a higher content of tin [8]. Low-tin antique bronze is mainly a single-phase alloy. Iron is the most notable alloying element in the kettle's bronze. Such high proportion of iron is not to be expected in a copper alloy, which is an interesting fact considering that pure iron is usually not added to bronze. Aluminum and nickel are also present in order to reinforce the structure of the alloy. Calcium was added to reduce the melting point of the alloy, which greatly facilitates the processing and as a deoxidizer for copper. [9]

The kettle was found in Kupa which is a karst river. This would explain the presence of calcium from calcium carbonate, CaCO$_3$, in all samples, although calcium was obviously also one of the elements present as *traces* in the bronze. According to Bilinski [10] the lower part of Kupa river where the kettle was found consist primarily of SiO$_2$ (81%) and the other compounds present in Kupa's sediments are Al$_2$O$_3$, CaO, Fe$_2$O$_3$, K$_2$O, Na$_2$O and MgO and in very small amounts of TiO$_2$, P$_2$O$_5$ and MnO. Silicon is present either as one of the *other elements* or as *traces* in all cases. The presence of silicon in large quantities was firstly thought to be an indication of alloying with silicon, but results on the cleaned Sample 1 have shown that silicon is not a part of the alloy that it obviously comes from the riverside sediment that has been deposited on the object due to a long period of time being buried in the river mud.

### 3.1. Surface layers analysis

IR spectra provide valuable information on the patina composition because IR spectroscopy senses the low crystalline and amorphous fraction and it has an extremely high detection limit for some species commonly found in the patina [11]. FTIR-ATR measurements were performed on all samples and
analyzed with SEM images and EDS results. The results are presented on samples grouped according to the similarities of the results.

**Sample 1**

Sample 1 shows a mostly greenish colored surface as can be seen in Fig. 2. SEM analysis of Sample 1 showed a unified structure, as well as a unified composition presented in Fig. 3.

The EDS results show a significant amount of carbon. As explained earlier presence of a form of calcium carbonate is also expected, but due to the green color of the sample also a green carbonate-based corrosion product could be present. Carbonate is presented by four normal modes of vibration peaks: \( \nu_1 \) symmetric C-O stretching, \( \nu_2 \) CO\(_3\) out-of-plane bending, \( \nu_3 \) asymmetric C-O stretching mode, and \( \nu_4 \) O-C-O bending (in-plane deformation) mode [4, 10, 12]. In the FTIR spectrum obtained on Sample 1 the bands characteristic for carbonate that are easiest to observe are the two broad bands in the region around 1500 – 1300 cm\(^{-1}\). The peak at 1488 cm\(^{-1}\) indicates that calcium carbonate is present in the form of vaterite on this sample, since it has been reported that different calcium carbonate phases can be identified using FTIR [13–15]. Presence of malachite, Cu\(_2\)CO\(_3\)(OH)\(_2\), is also observed through various peaks. The bands at \( \sim 1097 \) and \( \sim 1034 \) cm\(^{-1}\) are assigned to the CO symmetric and asymmetric stretching vibration. The two bands at 879 and 816 cm\(^{-1}\) are attributed to the out of phase and in phase bending modes of carbonate in malachite [16]. The spectrum also shows peaks in the OH stretching mode region, but although the different basic copper(II) salts developed on copper during corrosion may be identified by IR reflectance spectroscopy, the OH stretching mode region (above approximately 3000 cm\(^{-1}\)) cannot be used because of a large overlap observed for different components in the spectra of different compounds [17].

According to both XRF and EDS analysis Sample 1 contains a high amount of tin. Tin as a corrosion product on antient metals is usually found in the tin(IV)oxide form, i.e. cassiterite, SnO\(_2\). The FTIR spectrum obtained on Sample 1 showed different peaks in the fingerprint region presented in Fig. 3b. The spectrum showed a peak at 816 cm\(^{-1}\) which presents the Sn-O stretching vibrations, while the peaks at 533 and 480 cm\(^{-1}\) present the bending vibrations [18].

EDS showed clear presence of Si in some form in the sample. Inorganic silicates have Si-O bands at 1050 – 1000 cm\(^{-1}\) (strong) and they also absorb at 540 – 440 cm\(^{-1}\) (medium). Silica absorbs near 1100 cm\(^{-1}\) (strong), near 800 cm\(^{-1}\) (weak) and near 475 cm\(^{-1}\) (medium). The silica bands overlapped by other peaks are present in the spectra, as well as the band at \( \sim 419 \) cm\(^{-1}\) is related to the (O–Si–O) deformation mode [19, 20].

Both XRF and EDS analysis showed a significant amount of iron in this sample. There are various possibilities for iron to be present in bronze corrosion products. Presence of iron in the form of pyrite, FeS\(_2\), pyrrhotite, Fe\(_{(1-x)}\)S, and chalcopyrite, CuFeS\(_2\), is indicated by peaks around 1360, 1100, 1020 cm\(^{-1}\). It is hard to distinguish these compounds one from another [21, 22]. Fe\(_2\)O\(_3\) is also expected to be present
on the surface, if not formed on the bronze, then at least deposited from the river’s sediments as explained earlier. The two bands at 533 and 480 cm$^{-1}$ that are attributed to SnO$_2$ are overlapping bands of Fe–O which indicate the presence of Fe$_2$O$_3$ [23].

EDS and XRF analysis also showed that sulfur is present on the surface of Sample 1. The peak that is attributed to sulphates is around 1100 cm$^{-1}$. The peak at 1097 cm$^{-1}$ exists, but the peaks that would represent typical sulphate copper corrosion products like brochantite, Cu$_4$SO$_4$(OH)$_6$, antlerite, Cu$_3$(SO$_4$)(OH)$_4$, or posnjakite, Cu$_4$SO$_4$(OH)$_6$·H$_2$O, are not present in the spectra. So, it can be assumed that the sulphate is present in an inorganic form on the sample [24, 25].

The peak attributed to cuprite, Cu$_2$O, at around 625 cm$^{-1}$ [26] is not observed on this sample or any of the other samples.

**Samples 2 and 3**

Sample 3 was the sample with the most expressed green color with small presence of light blue hues. The surface layers used for the analysis of Sample 3 were prevalent in green. Sample 2 was also green, although its color was uniform. The SEM image of the surface of Sample 3 showed two different structures presented in Fig. 4. The main difference between the two structures is that the composition of the second structure shows presence of tin, while the first composition does not. Sample 2 showed presence of only one composition that is similar to the composition in Point 1 with slightly higher content of calcium and lower content of aluminum and magnesium, indicating that the oxides composition is the only difference.

The FTIR spectra obtained on Samples 2 and 3 were very similar as can be seen in Fig. 5. Presence of malachite, Cu$_2$CO$_3$(OH)$_2$, was observed through various peaks. The bands at ~ 1097 and ~ 1034 cm$^{-1}$ are assigned to the CO symmetric and asymmetric stretching vibration. The two bands at ~ 879 and ~ 821 cm$^{-1}$ are attributed to the out of phase and in phase bending modes of carbonate in malachite [16]. The two bands clearly present at ~ 3403 and ~ 3319 cm$^{-1}$ are assigned to O–H groups bound to intramolecular H-links [20], but as said earlier they cannot be used for distinguishing presence of different copper patinas.

EDS and XRF analysis showed presence of Si in these samples. The peak at ~ 1097 cm$^{-1}$ which is also attributed to malachite in combination with the rest of the peaks explained earlier indicated presence of Si-oxides. Presence of calcium carbonate in the form of vaterite is again presented by peaks at 1489, 879 and 743 cm$^{-1}$ on Sample 3, while in the spectrum of Sample 2 the peak at 712 cm$^{-1}$ represents calcite [13]. SnO$_2$ is presented by 533 and 480 cm$^{-1}$. These samples showed presence of iron only in the form of Fe$_2$O$_3$ with very small peaks at 786 cm$^{-1}$ and 462 cm$^{-1}$.

The broad peak at 1097 cm$^{-1}$ could also be attributed to a sulphate compound. Although by EDS analysis sulfur was not found, XRF indicated its presence on both Samples 2 and 3. Upon observing the
FTIR spectra it can be seen that the main peaks that present sulphate copper corrosion products are present \[17, 24, 25, 27\]. They show the internal vibrational modes of sulfate ions at 1097 and 1034 cm\(^{-1}\) (v3), 879 cm\(^{-1}\) (v1), 605 cm\(^{-1}\) (v4), the signals below 500 cm\(^{-1}\) are assigned to the v2 internal mode of \(\text{SO}_4^{2-}\) and to Cu-O vibrations, while the peaks at 3403 and 3319 cm\(^{-1}\) are attributed to v(OH). Samples 2 and 3 were the only samples were sulphate patina was detected, and considering the intensity of the peaks compared to the peaks of malachite it was not the main type of patina on the samples. It is hard to distinguish which sulphate copper patina is present on bronze, brochantite, \(\text{Cu}_4\text{SO}_4(\text{OH})_6\), antlerite, \(\text{Cu}_3(\text{SO}_4)(\text{OH})_4\), or posnjakite, \(\text{Cu}_4\text{SO}_4(\text{OH})_6\cdot\text{H}_2\text{O}\), using FTIR, but posnjakite is not normally found on archaeological bronzes. On the other hand, brochantite mainly forms in exposed areas and it is a common corrosion product on bronze sculptures located in urban areas where atmospheric sulfur dioxide is present \[28\]. On bronze objects exposed to freshwater antlerite is most commonly found \[5\]. The presence of sulphate patina does not exclude presence of inorganic sulphates that were found on Sample 1.

**Sample 4**

Sample 4 has a blackish color, as can be seen in Fig. 2. The main color is not green/blue pigmented, so it is expected that this sample is not a sample where copper corrosion products prevail. The SEM image obtained on Sample 4 is presented in Fig. 6. It shows presence of two different structures pointed by numbers 1 and 2. The structure in Point 1 has a rougher structure, while the structure in Point 2 is smoother. EDS analysis were performed in these two points and the results are also presented in Fig. 6. It is clear that in Point 1 iron is a dominant element, while in point 2 silicon is.

FTIR results obtained on Sample 4 show clear peaks only in the region up to 1500 cm\(^{-1}\) presented on Fig. 7. Metal oxides of various types have bands from the metal-O-metal group that can absorb throughout the 800 – 200 cm\(^{-1}\) region \[19\]. As stated earlier, various metal-oxides are expected to be present according to the composition of the traces of river Kupa. According to the EDS analysis presence of \(\text{Al}_2\text{O}_3\), MgO and NaO is most likely and the other peaks in this region are most likely attributed to their presence. In the spectrum of Sample 4 the bands representing \(\text{Fe}_2\text{O}_3\) are observed as on the other samples with peaks at 796 and 468 cm\(^{-1}\).

EDS showed significant amount of Si in the sample. The band at around \(~ 1000\) cm\(^{-1}\) that presents silica is not present on this sample, but the bands at 1050 – 1000 cm\(^{-1}\) (strong) and at 540 – 440 cm\(^{-1}\) (medium) presenting inorganic silicates are present in the spectra.

The broad wide peak at \(~ 1001\) cm\(^{-1}\) is much more expressed in this spectrum compared to the spectra of Samples 1 – 3 and it again indicates presence of \(\text{SO}_4\) vibrations. As in the case of Sample 1 there are no peaks indicating copper sulphate patina, so it can be assumed that the inorganic sulphates are present here as well.
The spectrum of Sample 4, unlike the spectra of Sample 1 indicates that calcium carbonate is present in the form of calcite rather than vaterite. This is due to only one band at $\nu_3 \sim 1418$, $\nu_2 \sim 877$ and the peak at $\nu_4 \sim 695$ cm$^{-1}$ which is specific for calcite [13].

Sample 4 was the only sample that did not show presence of tin on its surface.

Samples 5 and 6

Samples 5 and 6 seem to have a similar appearance by the bare eye and this can be seen from the images in Fig. 2. They are both multicolored. The SEM results showed a similar structure as can be seen in Fig. 8a and the FTIR spectra obtained on the two samples are also very similar as can be seen on Fig. 8b. On the other hand, EDS analysis (Table 2) on the two samples showed quite different results. It seemed each measured point had a different composition as can be seen in Table 2. Sample 5 showed a significant amount of iron and copper while Sample 6 showed higher content of tin and silicon, depending on the position. Also, the content of carbon in Sample 6 is significantly higher than on the other examined samples. Sample 6 also showed very small content of copper indicating that just like in the case of Sample 4 in this sample copper corrosion products do not prevail. As for Sample 5 the copper content is somewhat higher.

| Element | Sample 5 | Sample 6 |
|---------|----------|----------|
|         | Position 1 | Position 2 | Position 1 | Position 2 | Position 3 |
| C       | 22.0      | 23.7      | 47.9      | 52.8      | 66.1       |
| O       | 58.5      | 55.5      | 42.8      | 39.3      | 29.7       |
| Cu      | 14.7      | 8.0       | 0.6       | 1.7       | 2.1        |
| Fe      | 1.3       | 9.6       | 0.3       | 0.7       | 0.5        |
| Sn      | -         | 0.6       | -         | 4.1       | -          |
| Ca      | 0.4       | 0.3       | 0.7       | 0.8       | 0.9        |
| Si      | 1.9       | 1.5       | 4.4       | 0.3       | 0.4        |
| Al      | 0.8       | -         | 2.3       | -         | 0.2        |
| Mg      | 0.4       | -         | 0.6       | -         | -          |
| S       | 0.1       | 0.4       | 0.2       | 0.2       | 0.1        |
| P       | -         | 0.6       | -         | 0.2       | -          |
The FTIR spectra in the metal-oxide region, i.e. at lower wavenumbers, show very many peaks that are close to each other. It can be assumed that some of the peaks representing different metal-oxides are overlapping. When we look at EDS results, we can assume presence of different metal oxides. The peak at 1002 cm\(^{-1}\) presents Si-O bands, while the peak at 796 cm\(^{-1}\) represents quartz, i.e. SiO\(_2\). The peak at 796 cm\(^{-1}\) overlaps with the peak of SnO\(_2\) which is also indicated by peaks at 527 and 465 cm\(^{-1}\). The peak at 527 is also presenting Fe\(_2\)O\(_3\). The two peaks at around 1571 and 1375 cm\(^{-1}\) indicate presence of carbonate in some form. The peaks at 796, 750 and 1375 cm\(^{-1}\) indicate presence of malachite, although it is clear from the size of the peaks that its quantity is small as on sample 4. The peak at 778 cm\(^{-1}\) presents overlapping peaks presenting both quartz and malachite. As in the case of Sample 4, the FTIR spectra shows presence of chalcopyrite, CuFeS\(_2\), with peaks at 1008 and 471 cm\(^{-1}\).

4. Discussion

The kettle was made was made by the embossing technique from mild bronze which contains up to 6 wt % tin, with iron being the most notable alloying element in the bronze. The presence of iron in a copper alloy is not common since pure iron is generally not added to bronze. Iron in the alloy may originate from impurities of the raw material for making the object, but it would be expected if it is present, it would be found only in traces which was not the case in our examination, thus it can be concluded that it was intentionally used as an alloying element.

The kettle was an object for everyday use, and the damage began to form while it was still in function. After that, it was buried for almost 2000 years, which led to the creation of various corrosion products and production of beautiful patina which was intermittently interrupted by active products of corrosion. After excavation, drastic and sudden changes in environmental conditions of surrounding environment, especially the increase of oxygen concentration, induced restarting and accelerating the corrosion of the bronze substrate [4, 6] and new layers of corrosion products were created on the kettle. There were no interventions at the kettle after it was excavated until the moment it arrived at the Workshop, which means it had been waiting for restoration while being exposed to atmospheric conditions of the Museum's depot for more than 50 years.

Table 3 presents the different compounds that were found present on the examined samples. The characteristic green-blue appearance of the patina layer is due to the color forming Cu(II)-ion in the outer patina layer which needs to be 12 ± 2 µm to fully cover the inner oxide layer [1]. The patina on the kettle was identified as malachite, Cu\(_2\)CO\(_3\)(OH)\(_2\). It was formed over most parts of the object's surface, but it is not everywhere in equal amount and thickness. Figure 9 presents the presence of malachite on the kettle. The schematic image was made by isolating only the color of the malachite from the image of the kettle. It is the corrosion product that was created on the surface of the kettle while the object was buried in the mud of the Kupa River. It was the first corrosion product that covered the surface during this period. When copper alloys are buried in damp places, they tend to form green corrosion products such as georgite, which forms before malachite. Also, the blue-colored mineral azurite may appear, however, in little less
humid places, but it is also prone to creation under buried conditions. Neither georgite or azurite were found in our case.

**Table 3.** Overview of the different compound's presence on the examined samples.

| Sample                                      | 1 | 2 | 3 | 4 | 5 | 6 |
|---------------------------------------------|---|---|---|---|---|---|
| Malachite, Cu$_2$(CO$_3$)(OH)$_2$           | H | H | H | L | L | L |
| Cassiterite, SnO$_2$                        | H | H | H | - | - | L |
| Calcium carbonate, CaCO$_3$                 | H | H | H | L | - | - |
| Ferric oxide, Fe$_2$O$_3$                   | L | L | L | H | H | H |
| Fe sulfides (pyrite, FeS$_2$, pyrrhotite, Fe$_{(1-x)}$S, and chalcopyrite, CuFeS$_2$) | L | L | L | L | L | L |
| Inorganic sulphates                         | L | L | L | H | - | - |
| Sulphate patina (antlerite)                 | - | L | L | - | - | - |
| SiO$_2$                                     | L | - | - | - | H | H |
| Si-oxides                                   | - | L | L | H | - | - |

H – high content; L – low content

The samples had several other compounds present on the surface. Presence of SnO$_2$ which is black in color in the form of cassiterite was observed on most of the samples. Tin oxides form when tin is exposed to fire in presence of air [29]. This indicates that the kettle was probably used to prepare food on open fire. Thus, we can assume that some of the SnO$_2$ was created before the kettle was buried in the river mud and remained on the kettle as it is not soluble in water. We assumed that beneath malachite a layer of cuprite, Cu$_2$O, is present. Such a layer when formed in atmospheric conditions is fully attained at thickness of 0.8 ± 0.2 µm [1]. We were not able to identify cuprite on the kettle. This was either because the layer was well covered by other compounds or because SnO$_2$ was present in a large amount.

Si-OH, SiO$_2$ and SiO, as well as CaCO$_3$, were also observed on most samples. We can conclude that they are a result of the sediment of the river Kupa. These layers were present over malachite and they are a result of longer exposure to the river environment. These Si and Ca based layers have a large volume and are porous, thus sediment like soil and stones located in the riverbed in the proximity of the object were captured in the corrosion products. All other trace elements that were found can also originate from the structure of the sediment in Kupa River or be part of the corrosion products produced while the object was buried.
The three samples (Samples 4, 5 and 6) which were not predominant in green color, but rather brown/blackish showed presence of a higher quantity of ferric oxide, \( \text{Fe}_2\text{O}_3 \). Iron does not have to originate only from the bronze alloy. The assumption is that the bronze kettle had a ferrous alloy rim and a handle which was attached while forging, so there was no need to solder it to the kettle. The sample was taken at the top of the kettle, where the handle would have been located. Unfortunately, no part of the handle was preserved, however, most of the kettles found in that period had one. Part of the \( \text{Fe}_2\text{O}_3 \) creation may have been caused by the degradation of the ferrous alloy handle. As ferrous alloy degraded, ferrous corrosion products were created locally. Vicinity of the ferrous objects such as rim or some other objects can also be the case of the formation of the Fe oxides, but there was no evidence if other ferrous objects were found in such vicinity of the kettle itself. At the same time iron also degraded from the bronze alloy itself and thus also created this corrosion product. This would explain the inability to form malachite below this layer of corrosion products, since galvanic corrosion occurred and the iron dilution rapidly accelerated, while in these areas the copper was cathodically protected.

Below two samples a layer of malachite was found: Sample 5 is brown in color and Sample 6 is black. Analyzes have shown that these are, Fe, Sn and Si oxides. The brown sample (Sample 5) showed a greater presence of iron, and it can be concluded that it consists mainly of iron oxides. The black surface layers (Sample 6) indicated the presence of tin oxides, which is black, as well the presence of SiO. At the areas on the kettle where Sample 5 was taken, the surface layers were brown. The layer of malachite beneath the brown surface layers is slightly thinner, i.e. on every part of the metal surface on which a layer of a stable surface layer is not formed, there is a possibility of later oxidation to occur when exposed to air, and the result is the creation of new corrosion products after the excavation of the object. There is a higher percentage of Fe oxide formation which can be explained by the fact that these surface layers were partly created after excavation, since the surface of the metal was not completely protected by malachite. On the same sample Sn oxides are found to be in smaller percentage, as are Si oxides that originate again from the sediment of the river Kupa. In Sample 6, the same compounds were found, however, Sn oxide prevails, which explains the black color of the surface layers. In this case these oxides were also formed after the formation of malachite, since by removing the powdered black colored product underneath the already formed green malachite layer was found. On the same sample, compounds such as \( \text{Fe}_2\text{O}_3 \) were found and the presence of carbonates was detected.

5. Conclusions

The kettle is made of low-tin bronze with the addition of iron, aluminum, calcium and nickel. Such low-tin bronzes were called *mild bronzes* and were used for manufacturing by embossing because of their resistance to mechanical and corrosion resistance. This alloy has a large content of iron and as a result there are plenty of ferrous products like iron oxides on the surface of the kettle. The presence of iron in a copper alloy is a unique case since pure iron is generally not added to bronze. Addition of calcium reduced the melting point of the alloy, while addition of aluminum and nickel can be attributed to the reinforcement of the bronze.
The layers of corrosion products were formed according to the conditions the object was exposed to. The kettle was used for preparing food so it was exposed to fire. Thus, the first product that was formed on the kettle’s surface was tin(II)oxide, SnO$_2$. SnO$_2$ is insoluble in water and the oxides stayed on the surface during its exposure to water in the Kupa river. The kettle was buried for almost two millennia in the mud of the Kupa River. Since no chlorides are present in such waters, the subject has remained fairly well preserved. The limited oxygen presence and very humid conditions in which the object was found almost completely covered it with a malachite layer that gave it a greenish-blue color. Surface layers, such as iron oxides, formed from iron found in the alloy, but also most likely from dissolving the iron rim and handle which have not been preserved until today, as they have completely degraded, probably while the kettle was still underground.

The item was excavated in the 1960s and stored in a museum depot. After excavation, the object came again in an oxygen-enriched atmosphere and it developed additional layers of corrosion products over the malachite layer. The analyzed samples showed that the upper layers are mainly iron oxides and tin oxides, which are brown and black. Also, calcium carbonate and silicon oxides are present on the kettle. They are compounds that remained trapped in the corrosion products from the mud of the Kupa river.

**Abbreviations**

XRF - X-Ray Fluorescence

FTIR - Fourier transform infrared spectroscopy

ATR - Attenuated total reflection

SEM - Scanning electron microscopy

FE-SEM - Field emission scanning electron microscope

EDX - X-ray energy dispersive spectroscopy

**Declarations**

**Ethics approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

**Availability of data and materials**
The raw data presented in this manuscript are in the possession of the authors. Since the amount of data is large the authors will present the data upon request.

**Competing interests**

The authors declared that there is no conflict of interest.

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**Authors' contributions**

MS and KM conceived this research. MS performed the conservation-restoration operations of the object and sampling. KM organized the analytical investigations and interpretation of analysis. MS interpreted the results of analysis according to the history of the object. VD performed XRF analysis. NM performed FTIR analysis.

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**Figures**

**Figure 1**

Image of the bronze kettle and the surface layers’ sampling positions
Figure 2

Images of the examined samples taken by a digital microscope: Samples 1 and 2 which are fragments under 60x and the rest of the samples under 240x magnification
Figure 3

a) SEM image, b) FTIR-ATR spectrum and c) elemental composition obtained by EDS on Sample 1.
Figure 4

SEM image of two different positions on Sample 3 and elemental composition in atomic-% obtained on the two positions.

| Element | Position 1 | Position 2 |
|---------|------------|------------|
| C       | 23.5       | 13.1       |
| O       | 57.8       | 68.6       |
| Cu      | 13.3       | 6.5        |
| Fe      | 0.4        | 1.5        |
| Sn      | -          | 7.8        |
| Ca      | 0.3        | -          |
| Si      | 2.9        | 1.8        |
| Al      | 1.4        | 0.4        |
| Mg      | 0.4        | -          |
| K       | 0.2        | -          |
| P       | -          | 0.3        |
Figure 5

FTIR spectra observed on Samples 2 and 3.

| Element | Point 1 | Point 2 |
|---------|---------|---------|
| C       | 14.9    | 4.5     |
| O       | 59.2    | 64.4    |
| Cu      | 5.4     | 0.6     |
| Fe      | 10.9    | 2.0     |
| Ca      | 1.8     | 0.2     |
| Si      | 5.0     | 28.3    |
| Al      | 0.9     | -       |
| Mg      | 1.3     | -       |
| S       | 0.3     | -       |
| P       | 0.4     | -       |

Figure 6
SEM image of Sample 4 and elemental composition in atomic-% obtained by EDS analysis on the two points marked on the SEM image.

**Figure 7**

FTIR spectrum obtained on Sample 4.

**Figure 8**
(a) Typical SEM image of Samples 5 and 6, and (b) FTIR spectra observed on the samples.

Figure 9

Prevalence of the malachite on the bronze kettle.

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