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A non-destructive in-situ approach to monitor corrosion inside historical brass wind instruments☆

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ABSTRACT

Brass instruments of the 19th and early 20th centuries get more and more used to be played in historically informed performance practice. Monitoring of the corrosion state inside these historical brass instruments before and after being played is essential to check the efficiency of preventive conservation protocols. As corrosion of metal artifacts is an electrochemical process, electrochemical techniques are the method of choice, especially since nowadays these measurements can be carried out in situ and are not destructive.

In this work open circuit potential (OCP) and polarization resistance (Rp) measurements were carried out. A special electrochemical sensor combining an Ag/AgCl (pseudo) reference electrode and a small platinum grid as counter electrode, both embedded in a thin cylindrical sponge mounted on a flexible tube, was developed for the in-situ measurements. The sensor had a surface of about 2 cm^2 and could be pressed against the inside of the brass tuning slides by a small balloon that could be pumped or emptied.

The inside of nine different tuning slides of four ancient brass instruments (horns) was characterized by OCP and Rp measurements; in addition photographs of inner walls were taken with an endoscope.

A very promising representation for diagnostic purpose is the polarization resistance (log Rp) vs open circuit potential (OCP) plot, which allows assign groups of OCP/Rp data from the tuning slides to different surface conditions that were established on laboratory experiments. As a result, the surface condition at the point of measurement is more important than the bulk alloy composition.

1. Introduction

Brass is used as material for wind instruments since the 16th century, mainly due to its very good acoustic properties, the ease of manufacturing of the instruments and its good corrosion resistance [1]. The brass alloys used for historical instruments show a continuously changing composition with time: early instruments had less zinc and more lead [2], in the 19th century the zinc content was between 30 and 35 wt.% [3]. Note that the brass instruments do not show usually a homogeneous composition because the manufacturer used various alloys for the construction of different pieces [3].

Historical or "period" musical instruments usually are conserved in private or public collections in museums, e.g., the Burri Museum in Bern (Switzerland) with more than 1200 brass wind instruments [4]. Usually instruments are exposed and never played; nevertheless an increasingly dominant trend in contemporary musical practice, the 'historically informed performance practice' (HIP) [5], intends to play these original instruments in concerts. So the criteria for the use of period instruments negotiate between the two extremes: being displayed only in museum cases, or being subjected to 'normal' concert use. Private and public instrument collections are more and more being forced to confront such issues. A research project entitled "Brass instruments of the 19th and early 20th centuries between long-term conservation and use in historically informed performance practice" has a clearly defined object of research, the brass instruments used in a Parisian theater orchestra on a specific evening in May 1913 — namely for the world première of Igor Stravinsky's "Le Sacre du Printemps". The overall goal of the project is to examine the corrosion phenomena in historical instruments currently being used, and to present an appropriate set of recommendations for their conservation and usage [6]. An interdisciplinary methodology is being developed for the evaluation and monitoring of the corrosion state inside historical brass instruments before and after being played in order to establish the efficiency of preventive conservation measures.

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The corrosion resistance of copper and brass is due to the formation of stable and protective layers of corrosion products, which reduce the deterioration rate. The main concern of museums and conservators besides mechanical damage is however corrosion of the brass instruments due to the high humidity inside the instruments during playing [7–9]. Measurements have shown that after 5 min playing the relative humidity (RH) inside the instruments exceeds 90% and it takes several days to reach ambient RH again [10]. Thus conditions for atmospheric corrosion, the formation of a very thin film of liquid water at the surface [7–9] are in principle present for quite a long time when the instruments are regularly played and damage of the artifacts (brass instruments) could be possible on long-term. The scientific approach to this conservation problem according to the Conservation Committee of the International Council of Museums (ICOM-CC) is preventive conservation, defined as "*all measures and actions aimed at avoiding or minimizing future damages*" [11–13]. Understanding the mechanism of corrosion is thus the starting point in order to propose preventive measures able to control the conditions that might cause damage.

Non-destructive techniques to assess the conservation state of the artifacts by means of in-situ measurements are thus very important tools for conservators to obtain the important information on the corrosion state and rate and to control the efficiency of preventive conservation measures. As corrosion is an electrochemical process [14], electrochemical techniques are the methods of choice. The simplest way is to measure the open-circuit potential, also known as corrosion potential. Quantitative information on the instantaneous corrosion rate can be obtained from polarization resistance (Rp) measurements (see the Experimental section).

In this work a small non-destructive electrochemical sensor for in-situ measurements (inside the instruments) is used to assess corrosion potentials and corrosion rate on several tuning slides of different brass instruments.

2. Experimental

2.1. Materials

Brass alloys with a zinc content ranging from 15 to 38% zinc (Table 1) were produced as thin sheets with a special technology in order to get similar metallurgical structure as found in the artifacts from the 19th century [3]. Nominal composition and those obtained by EDX and XRF (see Section 2.3) are provided. These model alloys were tested both in "as received" conditions and after mechanical polishing with diamond paste in ethanol.

2.2. Brass wind instruments

In the project, 16 historical brass wind instruments, trumpets, horns and tuba, from French and German manufacturers are used. The condition of the critical parts of the instruments, especially the tuning slides, was assessed in order to determine their conservation state. In this work the results of four horns are presented (Table 2). For each instrument, detailed investigations are performed on two tuning slides (named .1 and .2).

Three of the historical horn instruments (HKB 5004, HKB 5009, HKB 5025) were in a cleaned state: the cleaning was performed in a workshop by immersion of the instruments in a citric acid bath (Cuproten®), accompanied by fine brushing with a nylon brush and finally followed by a neutralization in a sodium carbonate (Na_2CO_3) solution. It is expected that the citric acid primarily dissolve calcareous deposits.

Table 1
Nominal, EDX and XRF composition of the brass model alloys examined in this work.

Alloy	EDX composition	XRF composition
CuZn15	Cu84 Zn16	Cu86 Zn14
CuZn28	Cu73 Zn27	Cu74 Zn26
CuZn30Pb1	Cu58 Zn35 Pb1	Cu68 Zn32 Pb0.1
CuZn37	Cu63 Zn37	Cu67 Zn33
CuZn38Pb2	Cu60 Zn39 Pb1	Cu63 Zn36 Pb1

Table 2
The four instruments (horns) used in the investigation. The range of compositions (wt.%) determined by XRF is provided.

Instrument	Manufacturer	Year	condition	XRF composition (wt.%)
HKB 5004	Cousenon Monopole, Paris (F)	1922	Cleaned in 2011–2012	Cu: 60–76 Zn: 22–37
HKB 5009	Raoux–Millerau, Paris (F)	1900	Cleaned in Dec 2012	Cu: 64–69 Zn: 30–35
HKB 5024	Cousenon Monopole, Paris (F)	1932	no cleaning	Cu: 61–74 Zn: 22–38
HKB 5025	Cousenon Monopole, Paris (F)	1910	Cleaned in 2013–2014	Cu: 62–73 Zn: 26–38

2.3. XRF measurements

XRF measurements were performed directly on the instruments with ARTAX 800 (Bruker) working in atmospheric pressure. The operating conditions were 50 kV, 600 μA, and aluminum filter. In order to access the possible heterogeneity of the alloy composing the different parts of an instrument 10 to 20 analysis areas were chosen. On each area a 2 mm^2 area scan, composed of 6 measuring points, was performed. Duration of the total area scan was 5 min. The diameter of the X-ray beam is 80 μm. Calibration of the spectrometer in the specific operation conditions was performed on 4 external certified brass standards. The uncertainty in the determination of copper and zinc concentration is estimated to be 6.5 and 11% respectively. The uncertainty on minor elements can reach value as high as 50%. For these elements the concentrations are only representative of the differences existing between different instruments. The composition of the different model alloys and instruments are reported in Tables 1 and 2.

2.4. Measurements with the endoscope

The endoscope measurements were performed with an endoscope with rigid optic and an angle of view prism of 45°. Photos were taken with a digital camera (Nikon Coolpix P7000) every 0.5 cm on the left and right side of both ends of the tuning slides; each photo covers a distance of 1.0–1.5 cm. The adopted procedure is illustrated in Fig. 3.

2.5. In-situ measurements with the sensor

2.5.1. Sensor

The electrochemical in-situ sensor (Fig. 1) combines a tiny Ag/AgCl electrode that is used as reference electrode (RE) and a thin, flexible platinum grid as counter electrode (CE). Both electrodes are mounted in a thin sponge. The size of the sensor is ca. 2 cm^2. For the use inside the instruments (tubular tuning slides) the sensor was mounted on a thin flexible tube (Fig. 1). This tube allowed to slightly inflate a small balloon mounted at the end of the tube and to press the sensor gently against the inside of the tuning slide. In terminating the measurement at one point air pressure was released and the sensor was moved to the next measurement position without scratching the inside of the instrument part.

2.5.2. Electrolyte

The electrolyte used to soak the in-situ electrochemical sensor was a diluted solution (1:10) of a phosphate buffer pH 7 (Fluka®) with 0.001 M NaCl in order to get a stable reference electrode potential of the Ag/AgCl electrode. The response of the same Ag/AgCl sensor