

How Surface Analysis Can Contribute to an Understanding of the Preventive Conservation of Brass Instruments¹

Abstract Historical brass instruments can suffer corrosion during and after playing due to the high degree of humidity inside – but the surface chemistry inside the tuning slides remains essentially unknown. Based on a series of previously published works of the present authors, this paper describes in a comprehensive way how ex-situ XPS surface analytical measurements can shed light on this topic. On freshly polished brass samples exposed to model solutions such as artificial saliva, a thick, polycrystalline surface film composed of copper-thiocyanate and zinc phosphate is formed, whereas in a phosphate buffer solution only a thin film composed of copper and zinc oxy-hydroxide and zinc phosphate is present. ‘As received’ brass samples from old instruments showed quite a thick surface film of copper and zinc oxy-hydroxide that protects the alloy beneath from corrosion. In combination with the in-situ electrochemical results, a first, tentative identification of the surface film inside the tuning slides can be offered.

Introduction Brass instruments of the nineteenth and early twentieth centuries are being played more and more often for purposes of historically informed performance practice. In the case of a brass instrument, a musician’s hot, wet breath could worsen the instrument’s interior corrosion, but little is known about this danger. The corrosion state inside these historical brass instruments before and after being played has been monitored using electrochemical methods in order to check the efficiency of preventive conservation protocols.² The measurements inside the tuning slides, however, lack any

- ¹ The Swiss National Science Foundation (SNSF) is acknowledged for financing the project “Brass instruments of the 19th and early 20th centuries between long-term conservation and use in historically informed performance practice” CRI2IL_146330/I. The Italian Ministry of University and Research (MIUR) is thanked for financing the PRIN project prot. 2010329WPF_005 “Sustainability in cultural heritage: from diagnosis to the development of innovative systems for consolidation, cleaning and protection”. The Regional Government of Sardinia is gratefully acknowledged for financial support (P.O.R. Sardegna F.S.E. Operational Program of the Regione Autonoma della Sardegna, European Social Fund 2007–2013 – Axis IV Human Resources, Objective 1.3, Line of Activity 1.3.1 “Avviso di chiamata per il finanziamento di Assegni di Ricerca”).
- ² Bernhard Elsener/Marion Alter/Tiziana Lombardo/Martin Ledergerber/Marie Wörle/Federica Cocco/Marzia Fantauzzi/Silvia Palomba/Antonella Rossi: A Non-Destructive In-Situ Approach to Monitor Corrosion Inside Historical Brass Wind Instruments, in: *Microchemical Journal* 124 (2016), pp. 757–764, <https://doi.org/10.1016/j.microc.2015.10.027>; Bernhard Elsener/Federica Cocco/Marzia Fantauzzi/Silvia Palomba/Antonella Rossi: Determination of Corrosion Rate Inside Historical Brass

information on the surface state and composition at the point of measurement (except for endoscope images). In order to correlate the results of electrochemical measurements with the surface state and composition, information from surface analytical experiments on model alloys in controlled environments is required.

In this chapter, we report on the results of an x-ray photoelectron spectroscopy (XPS/XAES) surface investigation of brass (Cu-Zn alloy) model samples that have been exposed both to a mild environment (phosphate buffer pH 7) and to a quite aggressive solution (artificial saliva) that represent the two extremes of liquids that can be present in the tuning slides after playing. Brass alloys exposed to the phosphate buffer solution show a rapid formation of a thin film composed of copper and zinc oxide that limits the corrosion rate but is not protective. With the artificial saliva solution, the corrosion rate of brass is initially very high, but decreases rapidly to values below $1 \mu\text{m}/\text{year}$. XPS surface analysis has shown the formation of a thick protective film of CuSCN (thiocyanate) and zinc phosphate.³

Combining electrochemical and surface analytical data obtained on model brass alloys allows us to rationalise the different corrosion behaviour found in the tuning slides of the brass instruments.⁴ We here investigate the link between electrochemical behaviour and the surface composition of brass alloys exposed to the atmosphere or to the environment present in the tuning slides.

XPS surface analysis X-ray photoelectron spectroscopy (XPS) has its roots in nuclear physics research and attracted major interest in 1964 when it was first demonstrated that chemical-state information could be obtained by measuring the kinetic energy of electrons emitted by a sample irradiated with soft x-rays. Since then, enormous progress has been made to improve the quality of spectrometers, standards of operation, and procedures for quantification. XPS is a non-destructive technique that combines high sensitivity with chemical-state identification. This technique is well suited for obtaining the quantitative composition of nanometre thick surface films.

The principle X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect: photons of an adequate energy $h\nu$ ionise atoms in the sample, resulting in the

Wind Instruments. Proof of Concept, in: *Materials and Corrosion* 67 (2016), pp. 1336–1343, <https://doi.org/10.1002/maco.201608996>; and the article by Bernhard Elsener et al. in this volume, pp. 61–72.

- 3 Federica Cocco/Marzia Fantauzzi/Bernhard Elsener/Antonella Rossi: Dissolution of Brass Alloys Naturally Aged in Neutral Solutions. An Electrochemical and Surface Analytical Study, in: *RSC Advances* 6 (2016), pp. 90654–90665, <https://doi.org/10.1039/c6ra18200c>.
- 4 See the article by Bernhard Elsener et al. in this volume, pp. 61–72.

emission of core-level electrons. Photo-ionisation comprises (Figure 1): (1) photon absorption, (2) electron emission, (3) move of the electron within the solid toward the surface, and (4) escape of the electron from the solid into the vacuum of the spectrometer.

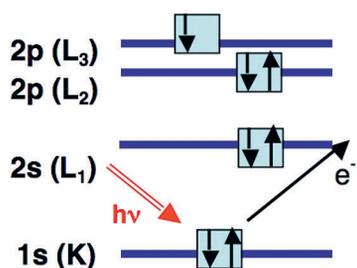


FIGURE 1 Schematic of the photoemission process. The x-radiation of energy, $h\nu$, ejects a photoelectron from the κ level (XPS notation is)

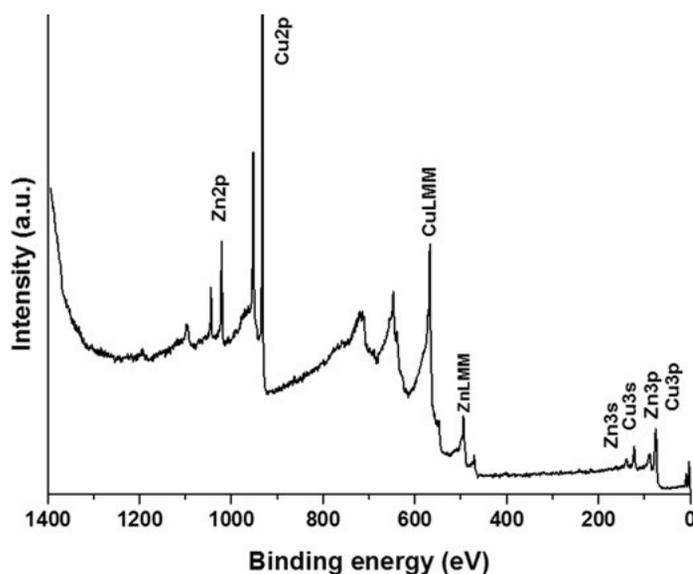


FIGURE 2 Survey spectrum of a CuZn₃₇ brass model alloy after sputtering in UHV. Core levels: copper Cu_{2p}, zinc Zn_{2p}. Outer levels: Zn_{3p}, Zn_{3s}, Cu_{3p}, Cu_{3s}. X-ray excited Auger electrons: CuLMM and ZnLMM (reproduced with permission from the Royal Society of Chemistry)

According to the principle of conservation of energy, the sum of the energy of the initial state E^i plus the photon energy, $h\nu$, is equal to the sum of the energy of the final E^f state plus the kinetic energy of the emitted photoelectron, KE . Rearranging this, one obtains the binding energy, BE , of the photoelectron from equation (1) (the difference in energy between the final and the initial state) as the difference between the energy of the incident beam minus the kinetic energy of the emitted photoelectron.

$$BE = h\nu - KE = E^f - E^i \quad (1)$$

As each element has characteristic core-electron binding energies, it will emit photoelectrons with a characteristic kinetic energy for a given photon energy. Element identi-

fication can thus be accomplished by recording the photoelectron energy distribution (spectrum), which will show peaks corresponding to different elements. As an example, the survey spectrum of a CuZn₃₇ brass alloy after ion etching is shown in Figure 2. The spectrum recorded exhibits photoelectron signals attributable to photoemission from core levels of copper (Cu2p), zinc (Zn2p), to photoemission from outer levels (Cu3s, Cu3p, Zn3s, Zn3p), from the valence region (Cu3d and Zn3d with Cu4s and Zn4s) and peaks due to x-ray-excited Auger emission (CuLMM, ZnLMM). Filling the core vacancy with an electron originating from an outer level generates other electrons, known as Auger electrons, that emit no radiation. It should be noted that the photoelectron peaks are narrower and simpler than the Auger signals. The background increases on the low-kinetic-energy side (high-BE side) of the peaks due to the occurrence of inelastic photo-emission. The acronym ESCA (electron spectroscopy for chemical analysis) emphasises the fact that both photoelectron and Auger electron peaks appear in the 'XPS' spectrum.

Chemical State Information The difference in binding energy between the same atom, either in two chemically different sites in the same compound or in two different compounds, is referred to as the 'chemical shift'. Many factors can contribute to the chemical shift, and usually its interpretation is accomplished on an empirical basis. A description of chemical shift theory is given in the literature.⁵

From an analytical point of view, it is very useful to compare the measured binding energy for the unknown element with the binding energy of a reference compound, measured under the same experimental conditions. Tables of peak positions may be found in the literature and a database is available from NIST.⁶ However, as in the case for copper and zinc, the identification of the chemical state of an element based on binding energy alone is not always possible.⁷ Other features of the XPS spectra have to be examined, such as the presence of shake-up satellites or the chemical shift of the x-ray-excited Auger lines combined with that of the correspondent photoelectron peak binding energy in a two-dimensional Wagner plot.⁸

- 5 See William F. Egelhoff: Core Level Binding Energy Shifts at Surfaces and in Solids, in: *Surface Science Reports* 6/6–8 (1987), pp. 253–415, [https://doi.org/10.1016/0167-5729\(87\)90007-0](https://doi.org/10.1016/0167-5729(87)90007-0).
- 6 Alexander V. Naumkin/Anna Kraut-Vass/Stephen W. Gaarenstroom/Cedric J. Powell: NIST Standard Reference Database 20, Version 4.1, <https://doi.org/10.18434/T4T88K>, accessed August 2019.
- 7 Federica Cocco/Bernhard Elsener/Marzia Fantauzzi/Davide Atzei/Antonella Rossi: Nanosized Surface Films on Brass Alloys by XPS and XAES, in: *RSC Advances* 6 (2016), pp. 31277–31289, <https://doi.org/10.1039/C5RA23135C>.
- 8 Ibid.; see also Giuliano Moretti: Auger Parameter and Wagner Plot in the Characterization of Chemical States by X-Ray Photoelectron Spectroscopy. A Review, in: *Journal of Electron Spectroscopy and Related Phenomena* 95 (1998), pp. 95–144, [https://doi.org/10.1016/S0368-2048\(98\)00249-7](https://doi.org/10.1016/S0368-2048(98)00249-7).

Instrumentation A basic block diagram of an x-ray photoelectron spectrometer is given in Figure 3. It consists of an ultra-high vacuum chamber equipped with an x-ray source, usually $\text{MgK}\alpha$ (1253.6 eV) and/or $\text{AlK}\alpha$ (1486.6 eV), which can also be monochromatic, a lens system that collects the photo-ejected electrons, an energy analyser, a detector, and a system suitable for displaying signal intensity as a function of the kinetic or binding energy. The electron-energy analyser is the heart of the system; its task is to measure the electron energy spectrum.

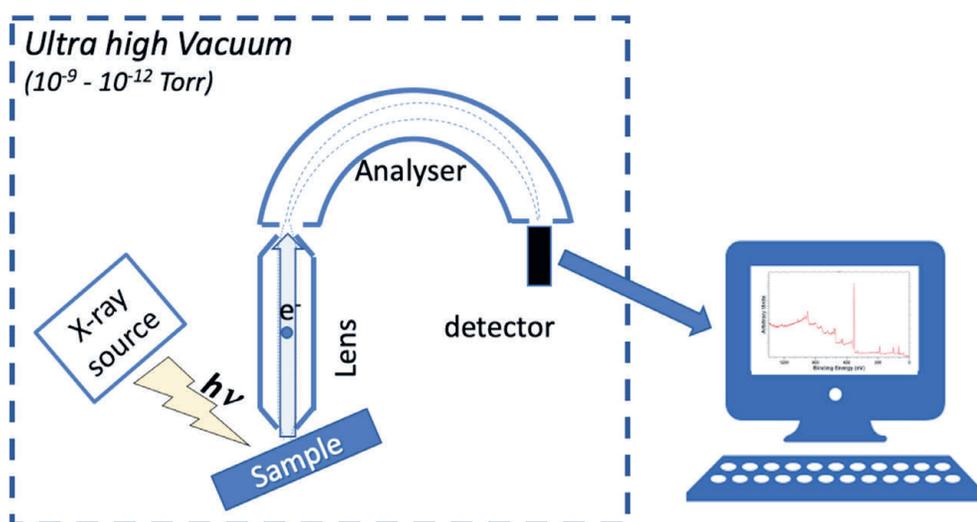


FIGURE 3 Block diagram of a basic XPS instrument

Older spectrometers have poor lateral resolution; however, with recent generation imaging photoelectron spectrometers, lateral resolution down to about $3\ \mu\text{m}$ can be achieved. XPS imaging offers new opportunities compared to existing surface-analysis techniques.

Copper, zinc and brass alloys For copper, zinc and brass alloys, the above outlined approach based on the binding energy to determine the chemical state is very difficult because the chemical shift between the metallic state and the oxidised one is very small.⁹ A close inspection of the shape of the x-ray-induced Auger signals $\text{CuL}_3\text{M}_{4,5}\text{M}_{4,5}$ and $\text{ZnL}_3\text{M}_{4,5}\text{M}_{4,5}$, together with the use of the Auger parameter, greatly improves the

9 See Mark C. Biesinger/Leo W. M. Lau/Andrea R. Gerson/Roger St. C. Smart: Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Sc, Ti, V, Cu and Zn, in: *Applied Surface Science* 257 (2010), pp. 887–898, <https://doi.org/10.1016/j.apsusc.2010.07.086>.

assignment of the chemical state for both copper and zinc.¹⁰ A detailed study analysing sputter-cleaned, mechanically polished and ‘as received’ copper, zinc and Cu₃₇Zn brass alloys¹¹ provides the basis for the surface analysis of model brass alloy samples and samples from old instruments used in this work.

Auger signals of pure elements copper and zinc (metal and oxide) The Auger signals of metallic copper and copper oxide Cu₂O show a chemical shift of about 1.7 eV and the shape of the spectra are different (Figure 4); the same holds for metallic zinc and zinc oxide ZnO with a chemical shift of 4.0 eV. Thus, based on the Auger signals, it is possible to distinguish and identify metallic and oxidised components on the same sample.

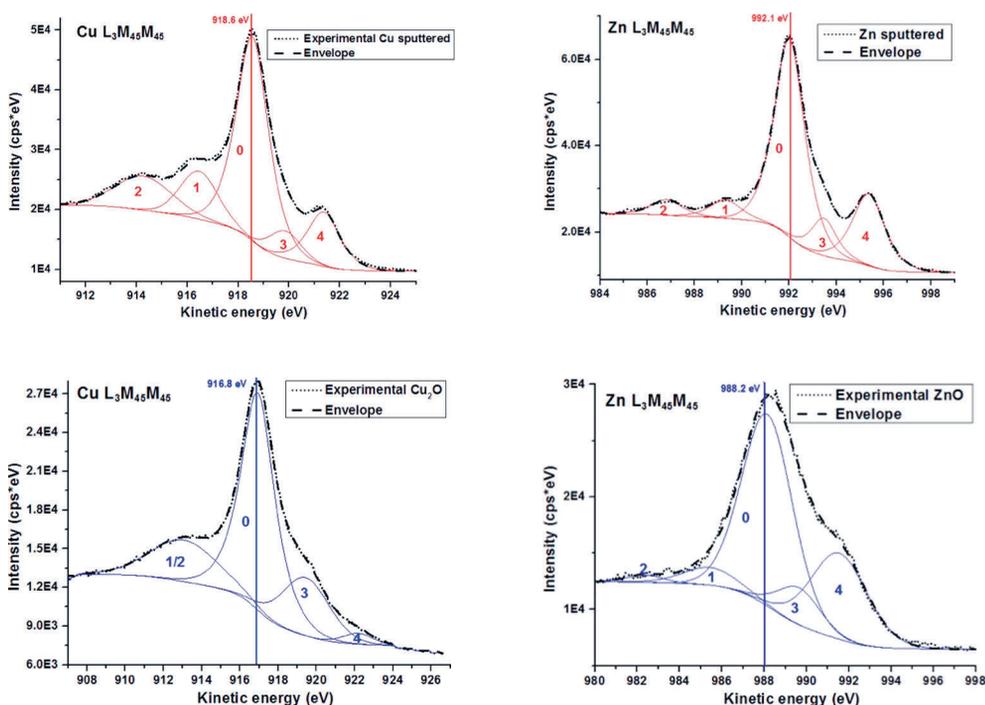


FIGURE 4 Auger spectra CuL₃M_{4,5}M_{4,5} of metallic copper and Cu₂O copper oxide (left) and ZnL₃M_{4,5}M_{4,5} of metallic zinc and ZnO zinc oxide (right)¹²

Brass Cu₃₇Zn model alloy mechanically polished In mechanically polished brass alloys, the signals from copper and zinc are present in the metallic and oxidised state. The most intense photoelectron peaks Cu_{2p}_{3/2} and Zn_{2p}_{3/2} showed only one single peak with the

¹⁰ Cocco/Elsener/Fantauzzi/Atzei/Rossi: Nanosized Surface Films on Brass Alloys.

¹¹ Ibid.

¹² The multicomponent Auger signals are given in detail in *ibid.*

same binding energy as in pure copper (932.5 eV) and zinc (1021.7 eV), confirming that these signals do not allow for the identification of the chemical state of copper and zinc. The XAES spectra of $CuL_3M_{4,5}M_{4,5}$ (Figure 5a) and $ZnL_3M_{4,5}M_{4,5}$ (Figure 5b) have a clearly different shape with two maxima compared to those of pure metals or pure oxides (Figure 4). This indicates the simultaneous presence of the metal and oxide component due to the presence of a thin oxide layer on the brass surface. The curve fitting of the two Auger peaks (Figure 5) was performed using the envelopes of the metallic state and the oxidised ones (Figure 4). The kinetic energy in the XAES spectrum of metallic and oxidised copper was 918.5 eV and 916.8 eV respectively, of metallic and oxidised zinc 992.3 eV and 988.0 eV respectively.

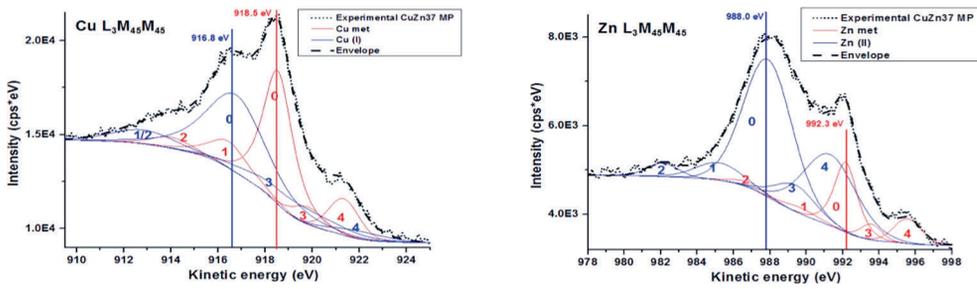


FIGURE 5 High resolution XAES spectra of mechanically polished brass model alloy $Cu_{37}Zn$, left: copper $CuL_3M_{4,5}M_{4,5}$, right: $ZnL_3M_{4,5}M_{4,5}$

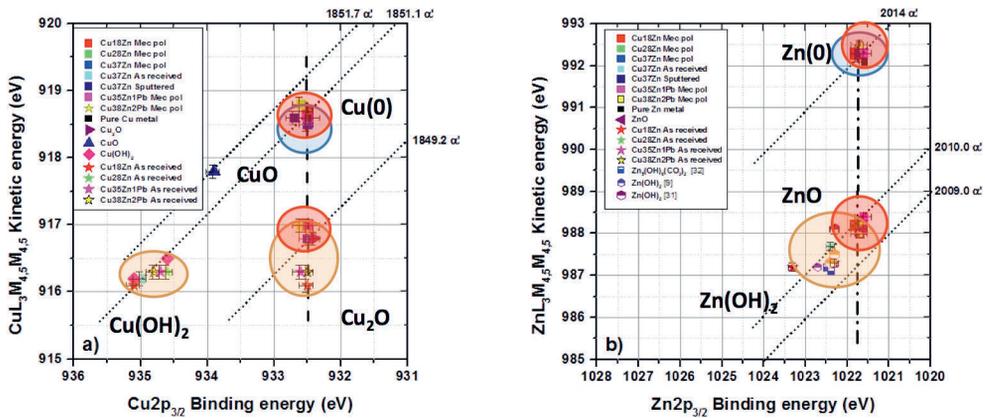


FIGURE 6 Wagner chemical state plot of a) copper compounds and b) zinc compounds (light blue: sputtered alloy, red: mechanically polished alloy, brown: 'as received' alloys)

Wagner chemical state plot The chemical state plot, a two-dimensional plot of XAES kinetic energy, KE, versus photoelectron binding energy, BE, of the same compound, allows for a more accurate assignment of the chemical state, especially in the case of copper and zinc and their alloys.¹³

The chemical state plot for copper compounds (Figure 6a) shows that for sputter-cleaned alloys, only the signal of the metallic copper is revealed for all alloys (BE/KE of 932.6 eV/918.6 eV). By contrast, for 'as received' alloys, no metallic signal is detected due to the thick surface film consisting of Cu(OH)₂ and Cu₂O. Mechanically polished alloys show a thin film of Cu₂O, beneath the signal of metallic copper.

The chemical state plot for zinc compounds (Figure 6b) shows for sputter-cleaned alloys only the signal of metallic zinc for all alloys (BE/KE 1021.7 eV/992.3 eV). For the 'as received' alloys studied, a thick surface film composed of ZnO is found and no metallic signal is detected. Mechanically polished alloys show a thin film of ZnO, beneath the metallic signal of zinc.

Brass model alloys exposed to solutions Mechanically polished brass alloys were exposed for up to 16 hours to solutions and the electrochemical and surface analytical data were recorded.¹⁴ In the more aggressive artificial saliva solution,¹⁵ the corrosion rate at the beginning was high but diminished to values <1 μm/year after 16 hours due to the progressive formation of a polycrystalline surface film of copper thiocyanate (CuSCN) and zinc phosphate (Zn₃(PO₄)₂). In the phosphate buffer solution, the electrochemical and corrosion behaviour did not change depending on the duration of immersion, and surface analysis revealed a thin surface film composed of copper and zinc oxy-hydroxide.¹⁶

Applying the technique to samples from old brass instruments After we had elaborated the scientific basis for the XPS/XAES surface analysis using brass model alloys, the XPS surface analytical technique was applied to samples from old brass instruments that were no longer in use. The 'as received' samples showed quite a thick hydrocarbon contamination layer, and after washing in organic solvents a thick surface film com-

13 See Moretti: Auger Parameter and Wagner Plot.

14 Cocco/Fantauzzi/Elsener/Rossi: Dissolution of Brass Alloys; Cocco/Elsener/Fantauzzi/Atzei/Rossi: Nanosized Surface Films on Brass Alloys.

15 Composition according to G. Tani/F. Zucchi: Valutazione elettrochimica della resistenza alla corrosione dei metalli di uso corrente nelle protesi dentarie [Electrochemical Evaluation of the Corrosion Resistance of Commonly Used Metals in Dental Prosthesis], in: *Minerva Stomatologica* 16 (1967), pp. 710–713.

16 Cocco/Fantauzzi/Elsener/Rossi: Dissolution of Brass Alloys; Cocco/Elsener/Fantauzzi/Atzei/Rossi: Nanosized Surface Films on Brass Alloys.

posed of copper oxide (Cu_2O), zinc oxide (ZnO) and hydroxides ($\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$) was revealed.

On these samples, the same electrochemical tests were performed with the dedicated sensor¹⁷ as inside the tuning slides, and the open circuit potential (corrosion potential) and the polarisation resistance (corrosion rate) were measured.¹⁸ The ‘as received’ samples from old brass instruments showed a corrosion potential between -50 and 0 mV Ag/AgCl, similar to brass samples after mechanical polishing or after immersion in phosphate buffer solution (Figure 7), the polarisation resistance instead is in the range of 200 $\text{k}\Omega\text{cm}^2$ to 1 $\text{M}\Omega\text{cm}^2$, indicating a very low corrosion rate between 1.5 and 0.3 $\mu\text{m}/\text{year}$.

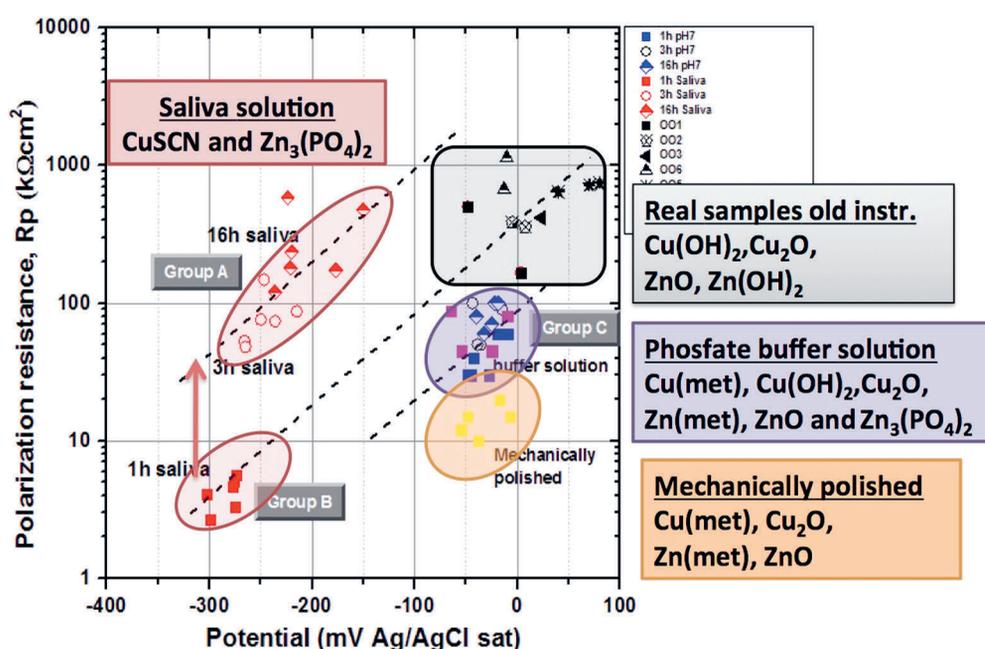


FIGURE 7 Diagnostic plot combining the electrochemical and surface analytical data obtained on brass samples with different surface conditions

Combining electrochemical and surface analytical results (Figure 7), it can be concluded that old samples from brass instruments show a very low corrosion rate due to the presence of a thick ‘as received’ surface film composed of copper oxide (Cu_2O), zinc oxide (ZnO) and hydroxides ($\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$). By contrast, samples where this native oxide

¹⁷ Elsener/Alter/Lombardo/Ledergerber/Wörle/Cocco/Palomba/Fantauzzi/Rossi: A Non-Destructive In-Situ Approach to Monitor Corrosion; Elsener/Cocco/Fantauzzi/Palomba/Rossi: Determination of Corrosion Rate.

¹⁸ See also the article by Bernhard Elsener et al. in this volume, pp. 61–72.

film has been removed by mechanical polishing (resulting in a brilliant brass surface appearance) show a low polarisation resistance (thus the corrosion rate is very high). Indeed, at the beginning of immersion into the solutions, the corrosion rate is 50–100 times higher than the corrosion rate on real samples with a protective oxide film. This can be explained by the electrochemical mechanism of the oxygen reduction reaction where the redox couple $\text{Cu}_2\text{O}/\text{CuO}$ play a key role.¹⁹

Based on this information (Figure 7), it is possible to link the electrochemical information obtained from measurements inside the tuning slides²⁰ with the composition of the surface determined ex-situ on the same materials exposed to different solutions – and thus to make tentative, indirect conclusions regarding the (unknown) surface composition inside the tuning slides.

Conclusions The novel analytical strategy based on a combination of XPS and XAES signals allowed chemical state identification and full quantification of complex systems with copper and zinc such as the brass alloys.

The natural patina formed on old instruments, analysed in the ‘as received’ condition, was identified as a thick surface film composed of copper and zinc oxides and hydroxides that protects the alloy from corrosion. Freshly polished brass alloys instead showed a thin, non-protective surface film.

Combining the ex-situ surface analytical results with results from electrochemical measurements performed on the same samples allowed for a tentative interpretation of the corrosion behaviour of brass alloys in neutral solutions, which in turn enabled us to get information on the interior of tuning slides of brass instruments.

19 Elsener/Alter/Lombardo/Ledergerber/Wörle/Cocco/Palomba/Fantauzzi/Rossi: A Non-Destructive In-Situ Approach to Monitor Corrosion.

20 Ibid.; see also the article by Bernhard Elsener et al. in this volume, pp. 61–72.

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TO PLAY OR NOT TO PLAY

Corrosion of Historic Brass Instruments

Romantic Brass Symposium 4 • Edited

by Adrian von Steiger, Daniel Allenbach

and Martin Skamletz

MUSIKFORSCHUNG DER
HOCHSCHULE DER KÜNSTE BERN

Edited by Martin Skamletz
and Thomas Gartmann

Volume 15



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