Original Article

Easy-to-use, low-cost electrochemical open-source hardware to analyse heritage metals: possibilities and limits

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ABSTRACT

Open-source hardware (OSHW), as low-cost and easy-to-use instrumentations, are particularly suited to the needs of the conservation field. This paper presents two OSHWs developed for the diagnosis of heritage metal artefacts. The *DiscoveryMat* application allows the qualitative analysis of slightly oxidised metals such as copper and aluminium-based alloys, through the standardized monitoring of the variation of their corrosion potential (Ecorr) with time. The *Pleco* allows the local identification of corrosion products through linear sweep voltammetry (LSV) plots and this contributes to a better adjustment of conservation treatments on metal artefacts covered with heterogeneous corrosion layers through the selective intervention on some corrosion products and the preservation of others. If the Pleco can already be found in the toolbox of some conservation professionals, the DiscoveryMat application is still in its infancy and needs to be developed in the future as a participatory tool.

KEYWORDS: OSHW, electrochemistry, conservation, metal artefacts, Ecorr, LSV, Pleco, DiscoveryMat, analysis.

INTRODUCTION

Electrochemistry is used in the conservation field to assess the risk of corrosion of metal artefacts or components of composite objects. By monitoring their corrosion potential (Ecorr) versus time when in contact with a specific solution, conservation professionals can immediately assess the electrochemical behaviour of metals (either passivation or corrosion) [1]. Moreover, corrosion forms are often investigated electrolytically using linear sweep voltammetry (LSV) such as in the case of silver tarnish or active lead corrosion where characteristic reduction peaks can be identified [1, 2]. These parameters are then used to develop conservation treatments mostly carried out in chronoamperometric conditions. Furthermore, impedance spectroscopy has proved to be an efficient technique to assess the efficiency of protection systems [3].

Electrochemical devices, such as potentiostats only recently gained use in conservation laboratories although voltammetric studies are invaluable in studying oxidation and reduction processes. Indeed, the sensitivity of metal artefacts to certain forms of corrosion can be deduced from the study of the number and importance of oxidation and reduction peaks. However, the available instrumentation is expensive, at least for conservation professionals, and the range of possible measurements with existing portable hardware is limited (few tens of mA). Furthermore, the software developed by the suppliers is complex and offers many functions that are not always relevant to field work.

Therefore, there is a need for suitable portable, low-cost, easy-to-use instrumentation as a technical

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support for the diagnosis of cultural heritage assets. It is our objective to develop this instrumentation within the framework of the EU COST Action PortASAP (http://portasap.eu).

METHODS

The open-source hardware association (OSHWA) defines open-source hardware (OSHW) as 'hardware whose design is made publicly available so that anyone can study, modify, distribute, make, and sell the design or hardware based on that design' [4]. Due to the democratization of 3D printers, the availability of low-cost open-source electronic platforms such as Arduino and of low-cost, small, single-board computers (Raspberry Pi), many research groups and enthusiasts are developing OSHW to complement classical research instrumentations. Pearce mentions that OSHW allows building your own instrumentation at a fraction of the cost of the commercial alternative [5]. However, provision of what is needed to replicate a given project online, as well as providing explicit permission for users to use, improve, and share it with others are not always guaranteed as suggested by Bonvoisin [6]. Each scientific community must adapt with the resources available, as in analytical chemistry where Dryden has proposed best practices for doing so (e.g. software and hardware licensing) [7].

While there is a need in the conservation field, for open-source tools to address the lack of funding as well as to tailor the instrument to specific requirements, only a few instrumentations are currently available. The two open-source analytical instruments presented below have been developed by conservation professionals of the Research Unit of the Conservation Department of Arc school (UR-Arc CR), HES-SO University of Applied Sciences and Arts Western Switzerland, Neuchâtel, Switzerland in collaboration with the Engineering Department of the same university. They clearly reflect what conservation professionals usually require from an analytical instrument: the qualitative analysis of the metal under study and the determination of the nature of the corrosion products which developed with time on the metal surface and may be affected by conservation treatment(s).

DiscoveryMAT application

The DiscoveryMat application is dedicated to the qualitative analysis of metal artefacts (http://157.26.64.17:8080/bilat-discoveryMat-user/index.html). It is based on the standardized monitoring of the corrosion potential (Ecorr) of an unknown metal object versus (vs) time using a reference electrode inserted in a junction protection tube (JPT) and a drop of solution (see below) placed between the tip of the JPT and the metal surface [8]. The data acquired by a voltmeter are exploited by DiscoveryMat application through analysis algorithms and a database of more than 150 entries of known compositions and electrochemical behaviour. The metals from the database matching the best with the electrochemical behaviour of the unknown metal investigated are then proposed to the operator (Figure 1).
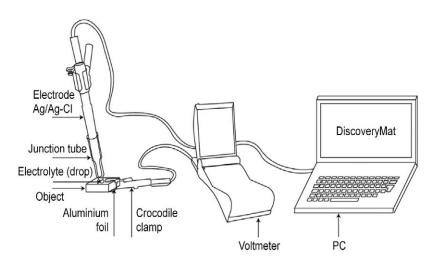

Figure 1. Schematic representation of the DiscoveryMAT device; drawing made by C. Despland.
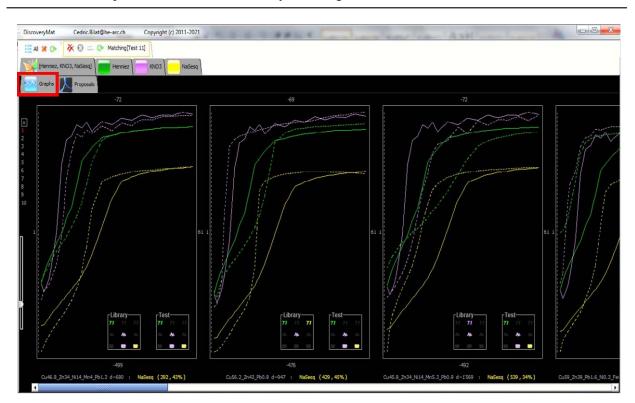
Figure 2. Comparison of the three plots of an unknown metal or Test (solid lines) with those of three metals of the DiscoveryMat database or Library (dotted lines) using the application's 'Graphs' mode. Inserts under the plots provide information on the lack of reproducibility (𝌀) and fluctuation of the plots (⋀⋁) as well as the presence of stains after the test (∎).

Figure 3. Classification of the database entries according to their distance of similarity to the unknown metal under investigation using the application's 'Proposals' mode.

The analysis is slightly invasive since the metal surface has to be polished (with silicon carbide paper of grade 4000) prior to each measurement. Discrete areas are chosen though and must be approved by the person responsible for the object. As a result, the analysis is only possible on metals such as copper and aluminium-based alloys that are covered by thin corrosion layers which can be removed easily. The same electrolyte volume and the same measuring surface are systematically used. Three solutions are considered: KNO_3 1% (w/v) pH = 5.8, mineralised water (Henniez®) pH = 7.5 and sodium sesquicarbonate 1% (w/v) pH = 9.5. The monitoring is carried out over a period of 5 min at least twice in order to check the reproducibility of the measurements. In case the results are reproducible, the monitoring is extended to 15 min. Only the last measurement is used for the qualitative analysis. The same procedure is followed for the three solutions.

The 'Graphs' mode of the DiscoveryMat application allows to compare the three Ecorr vs time plots of an unknown metal object or 'Test' (solid lines, Figure 2) and those of the metals in the database or 'Library' (dotted lines). To have a good matching, the plots of the unknown material and those of the database entry should be parallel at the end of the monitoring period as shown in the first graph of Figure 2. Crossing of plots at their start is very common though due to differences in surface preparation prior to the experiment. Additional information collected during data acquisition (fluctuation of the plots during both 5 min and 15 min of monitoring, lack of reproducibility and presence of stains after the test) provided in the inserts below the plots are a second way to appreciate the good matching between the Test material and the corresponding Library entry.

Another way to visualise any possible matching is to use the 'Proposals' mode of the application. It classifies by increasing order the distance of similarities (DS) calculated from algorithms, of all entries of the database versus the unknown metal under investigation. The distance of similarity for the three solutions is the sum of the distance between the two plots (that of the unknown metal and that of the metal in the database) for each solution used. By convention, a distance of similarity lower than 500 corresponds to a good match while

values above 1000 illustrate poor matching. In Figure 3, only the first ten proposals, the most probable, have their background highlighted in blue.

Clearly the operator must use both modes ('Graphs' and 'Proposals') of analysis as well as his/her knowledge of the material under investigation before accepting/discarding the proposals made and come up with what is from his/her point of view the most relevant composition.

The *Pleco*

The electrolytic pencil Pleco is used to analyse locally, corrosion layers on metal artefacts (http://www.fablab-neuch.ch/pleco/plus.php?id=1& lang=en). It is assembled from a kit of elements fabricated in a FabLab (small-scale digital fabrication workshop operating in many countries all around the world) using flat rate computer-controlled technologies such as 3D printing and laser cutting [9].

The Pleco is equipped with a three-electrodes cell containing a vitreous carbon (VC) rod as the reference electrode (Metrohm® 0.3 V/SHE - Standard Hydrogen Electrode) and a platinum rod as the counter-electrode. It is closed by a micro-porous polyvinyl formal (PVFM) foam pad which is put in contact with the metal surface to analyse (working electrode) and the electrolyte is supplied and extracted continuously using diaphragm pumps [10, 11]. Electrical contact with the working electrode is achieved using an aluminium strip attached to it with adhesive tape.

Local electrochemistry using the Pleco is particularly suitable for the investigation of corrosion products of metal components on composite artefacts which cannot be immersed in solution. The silver tarnish of the painted gilded silver object represented in Figure 4 was analysed using LSV with the Pleco connected to a potentiostat (Origalys®, Origastat e200), the potential of the material being scanned from Ecorr to -2.5 V/VC. The electrolyte is $NaNO_3$ 1% (w/v) and the scanning rate is 10 mV/s. The plot shows two reduction peaks: I (AgCl→Ag) and II (Ag_2S→Ag).

RESULTS AND DISCUSSION

As an illustration of the possibilities of the DiscoveryMat application, the top bell of a lantern
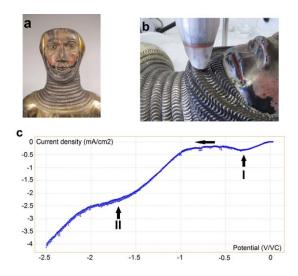
Figure 4. Local analysis of silver tarnish using the Pleco on a painted gilded silver reliquary bust (saint Victor of Saint-Maurice Abbey, 15th c., detail) (**a**) and linear voltammetry in progress (**b**), photographs taken by R. Jeanneret; LSV plot in NaNO$_3$ 1% (w/v), scanning rate: 10 mV/s (**c**).
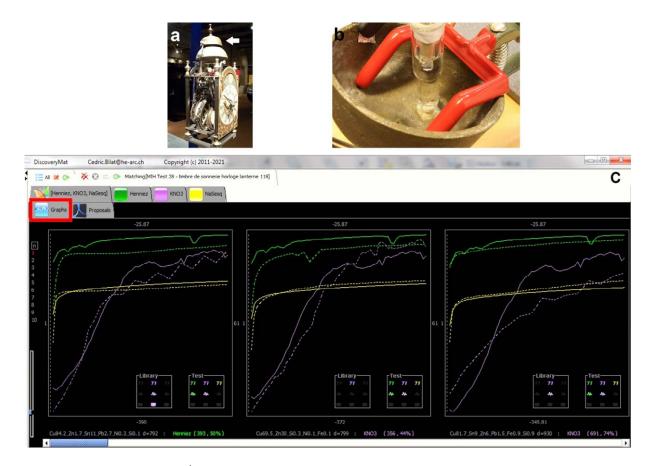

Figure 5. The lantern clock, 18th c., of the International Museum of Horology, La Chaux-de-Fonds, Switzerland (**a**), the back side of the top bell during the DiscoveryMat analysis (**b**) and the comparison of the plots obtained for the bell with those of the first three proposals of the database (**c**).

clock dating from the 18th century, from the International Museum of Horology at La Chaux-de-Fonds, Switzerland was analysed (Figure 5a). It was shown first to a metal conservator who specialised in clocks. Based on his knowledge, he identified it as bronze with high tin content (15-20% by weight). The analysis was carried out on the back side of the bell (Figure 5b) and the DiscoveryMat application ('Proposals' mode) suggested as a first choice, a quaternary alloy with nominal composition by weight of Cu 84.5%, Sn 11%, Zn 1.7%, Pb 2.7% and traces of Ni and Si. The comparison of the Ecorr vs time plots gives a relatively good match in 'Graphs' mode: the ends of the plots for each solution are parallel and as expected, the presence of lead in the metal provokes significant fluctuations with KNO_3 after a few minutes of monitoring. The comparison of the inserts for the Test material and the Library entry which are showing different results, allows us to understand the poor matching revealed by the high DS (around 800) obtained. It is certainly due to the lack of reproducibility of the results caused by the high porosity on the back side of the cast alloy (Figure 5c).

The compositions of the bell suggested by the conservator and provided by the DiscoveryMat application were compared to the elementary analysis of the metal using a portable X-ray fluorescence spectrometer (NITON XL3t 950 Air GOLDD+ analyser, ThermoFischer®). It gave a nominal composition by weight of Cu 82.7%, Zn 8.3%, Sn 5.0%, Pb 2.1%, S 1.8% and traces of Fe, Ni and Sb. Due to the absence of a material similar to that of the bell in the database, the concentration of the elements of the Test material (the bell) and the Library proposal are different. By identifying the metal of the bell as a quaternary alloy, DiscoveryMat provides qualitative but important analytical information for conservation professionals. Furthermore, the application suggests the presence of impurities (Ni, Si) in the metal, which is confirmed by XRF (Ni, Sb). This result supports the idea that the metal of the bell could be authentic as compared to the hand of the clock which is made with a clean metal of nominal composition by weight of Cu 63.4%, Zn 35%, Pb 1.6%. The absence of impurities is once again confirmed with XRF which gives a nominal composition by weight of Cu 68.9%, Zn 31% and traces of Pb. It indicates that the handle had certainly been replaced recently.

Aluminium alloys covered with very thin corrosion layers can be easily investigated using DiscoveryMat. We are currently building the database for the family of aluminium alloys and hopefully conservation professionals should soon have the ability to analyse heritage aluminium-based artefacts. An interesting result already observed with the current entries concerns the possibility to detect the presence of impurities in the metals studied which would indicate their recycling origin.

Among the possible applications of the Pleco is its use in matching the visual observation of heterogeneous silver tarnishes and their electrochemical responses before the cleaning of the metal surface. Such heterogeneous tarnishing had developed on the silvered brass coffee filter from the Lausanne Historical Museum, Switzerland shown in Figure 6a. Four zones ranging from a very slight (Z1) to a thick, black tarnish (Z4) can be distinguished (Figure 6b).

Preliminary voltammetry studies were carried out on copper and silver-based coupons artificially tarnished with boiled eggs in a sealed container (production of H_2S) and fingerprints. They were used to determine the starting potentials of characteristic reduction peaks in sodium sesquicarbonate 1% (w/v) with the Pleco whose pad had been sharpened to limit the size of the area studied to the minimum (Table 1). The potentials obtained were then compared with the results from the literature to identify the corresponding corrosion products [12, 13].

Table 1. Starting potentials of the reduction processes of characteristic corrosion products constituting the artificial tarnish formed on silver and copper-based alloys in sodium sesquicarbonate 1% (w/v) determined using the Pleco and identified from the literature. The compounds in bold are the most probable.

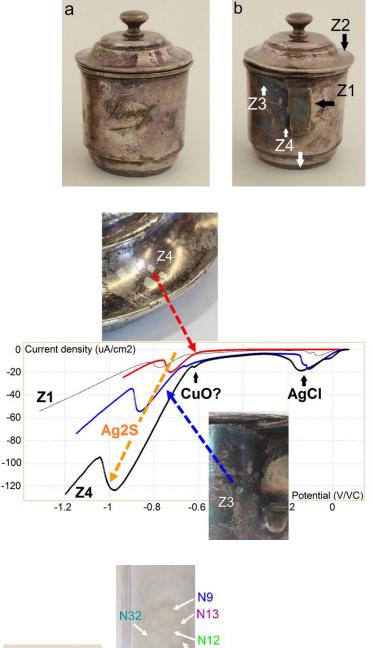| Starting potentials (V/VC)	Reduction processes
>0	**AgCl**
#-0.1	**Cu-O** (or Cu-Cl)?
#-0.35	**Cu-O**?
#-0.45	**Cu-O** (or Cu-Cl)?
#-0.55	**Ag₂S** (or Ag-Cu-S?)
#-0.65	Cu-O?
#-0.8	**Cu₂S** (or **Ag-Cu-S**?)

Figure 6. Heterogeneous silver tarnish observed on a coffee filter, Lausanne Historical Museum, Switzerland (**a**) and the four zones showing different levels of silver tarnish (**b**); photographs taken by L. Leuenberger.

Figure 7. Voltammetric plots for the different zones of the heterogeneous tarnish observed on the coffee filter, in sodium sesquicarbonate 1% (w/v), scanning rate: 10 mV/s; photographs taken by L. Leuenberger.
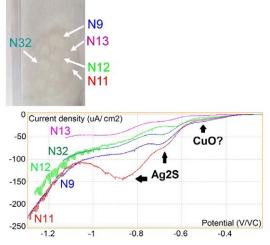

Figure 8. Voltammetry studies in the same area of a heterogeneously tarnished silver object (enriched Ag-Cu Tea caddy, 20th c., Lausanne Historical Museum) in sodium sesquicarbonate 1% (w/v), scanning rate: 10 mV/s; photographs taken by L. Leuenberger.

The same approach was used on the coffee filter and the four different tarnished zones observed visually (see Figure 6b). We clearly see that the peak of the reduction of Ag_2S grows with the thickness of the tarnishing. In addition, other peaks corresponding to the reduction of AgCl and possibly CuO appear as the tarnishing thickens (Figure 7). These results show that visually different silver tarnishes give different electrochemical signatures.

We also studied the variety of electrochemical responses from the zones of an area, that were visually judged to be similar, on a silver object with overall heterogeneous tarnishing. Figure 8 shows that they are the same although with different current densities.

These promising results give new perspectives for the electrolytic cleaning of the tarnishing on silver-based alloys in sodium sesquicarbonate 1% (w/v). A preliminary macro observation of the metal surface, accompanied by a few voltammetry studies should allow the conservator-restorer to identify the nature of the tarnish and assess its extent. It would also allow one to reduce it at the most adequate potential. Overcleaning caused by the application of a too-negative potential would be avoided. When the presence of Cu-based corrosion products is revealed by reduction peaks, a pre-treatment in chelating agents such as ethylenediaminetetraacetic acid (EDTA) salts would be needed to prevent the formation of black reduced Cu on the metal surface.

The work on the Pleco is currently pursued through the design of a pumping system which follows the same open-source philosophy as the Pleco itself.

CONCLUSION

Although open-source hardware has a lot of potential in the conservation field, the community is not yet proactive in the development of suitable instrumentation. The Pleco described in this paper has already found its place in the toolbox of professionals. As for the DiscoveryMat application, its development will largely depend on the active contribution of conservation professionals who should enrich the existing database with new entries which will make the analytical tool more relevant.

It is expected that both tools will benefit from the input of experts engaged within the EU COST action PortASAP.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

REFERENCES

1. Degrigny, C. 2010, J. Solid State Electrochem., 14(3), 353.
2. Degrigny, C. and Le Gall, R. 1999, Stud. in Conservation, 44, 157.
3. Letardi, P. and Luciano, G. 2007, Survey of EIS Measurements on Copper and Bronze Patinas, C. Degrigny, R. Van Langh, B. Ankersmit and I. Joosten (Eds.) METAL07. Proceedings of the ICOM-CC Metal WG interim meeting, Rijksmuseum, Amsterdam, 3, 44.
4. https://www.oshwa.org/definition/ [Accessed 21.09.2018].
5. Pearce, J. 2013, Open-Source Lab, Elsevier, Amsterdam.
6. Bonvoisin, J., Mies, R., Boujut, J-F. and Stark, R. 2017, J. Open Hardware, 1(1), 5.
7. Dryden, M. D. M., Fobel, R., Fobel, C. and Wheeler, A. R. 2017, Anal. Chem., 89, 4330.
8. Degrigny, C., Guibert, G., Ramseyer, D., Rapp, G. and Tarchini, A. 2010, J. Solid State Electrochem., 14(3), 425.
9. Jeanneret, R., Bussy, G., Degrigny, C., Baudin, C. and Carrel, H. 2014, WAAC Newsletter, 36(3), 37.

10. Degrigny, C., Jeanneret, R. and Witschard, D. 2015, e-preservation science, 12, 20.

11. Degrigny, C., Jeanneret, R., Witschard, D., Baudin, C., Bussy, G. and Carrel, H. 2016, Stud. in Conservation, 61(3), 162.

12. Costa, V. and Dubus, M. 2006, Evaluation of the environmental impact on metal artifacts using electrochemistry and grazing incidence XRD. Indoor Air Quality Conference Braunschweig.

13. Costa, V. and Dubus, M. 2007 Impact of the environmental conditions on the conservation of metal artifacts: an evaluation using electrochemical techniques, T. Padfield and K. Borchersen (Eds.). In Museum Microclimates. National Museum of Denmark, 63.