Report on the outcomes of a Short-Term Scientific Mission

Action number: IG16215

Grantee name: Pablo Andrés General Toro, Research Centre for Science and Technology of the Arts – Catholic University of Portugal

Details of the STSM

Title: **Combining user-friendly electrochemical hardware and a freely accessible application for the chemical analysis of modern copper-based alloys**

Start and end date: 05/06/2023 to 09/06/2023.

Location: Haute Ecole Arc Conservation – Restauration (HE-Arc CR), Neuchâtel, Switzerland

Scientific support: Christian Degrigny (HE-Arc CR).

Technical Support: Haute Ecole Arc Conservation – Restauration: Reference electrode Ag/AgCl (RE), junction tubes and syringes per solution (Evian, KNO_3, NaSesq), stand, clamps, Yoctopuce voltmeter and consumables (polishing paper, Teflon band).

General programme: Implementation of the DiscoveryMat analytical tool to study the chemical composition of copper alloy samples from the casting of 20th and 21st century sculptures from the northern region of Portugal. Training on the operation of the DiscoveryMat hardware and software; data collection; interpretation of results obtained and discussion.

Description of the work carried out during the STSM

Several activities have been conducted, focusing on the application of DiscoveryMat to characterize the chemical composition of copper alloy samples by the monitoring of their corrosion potential (E_{corr}) over time.

A particular characteristic of the samples to be studied is their significant size and roughness. Although DiscoveryMat has been proven effective in studying small samples, it has not been previously utilized to examine larger specimens with irregular surfaces, which more closely resemble the characteristics of sculptural pieces. Additionally, it is noteworthy that these samples necessitate a different approach to handling and securing during the measurements compared to smaller pieces.

The first stage of this STSM (Short-Term Scientific Mission) involved assembling the DiscoveryMat analytical tool. It comprises the following components: a Metrohm Ag/AgCl reference electrode (RE) model 6.0733.100 (Fig. 1a) inserted in a Radiometer junction tube filled with one of the solutions used to perform the measurements. A layer of Teflon tape is applied around the glass tube of the RE to ensure that the junction tube is properly secured (Fig.1b).

The Yoctopuce voltmeter (Fig. 1c) is connected to the RE using the white banana plug (Fig. 1d), while a crocodile clamp is attached to the brown banana plug (Fig. 1e). This clamp is then connected to an aluminium

foil underneath the copper alloy sample to analyse, which makes electrical contact with it. The weight of the sample ensures this contact. The DiscoveryMat hardware is controlled by software of the same name (only available for Windows) (Fig. 1f). The Yoctopuce voltmeter is connected to the computer using a USB cable.

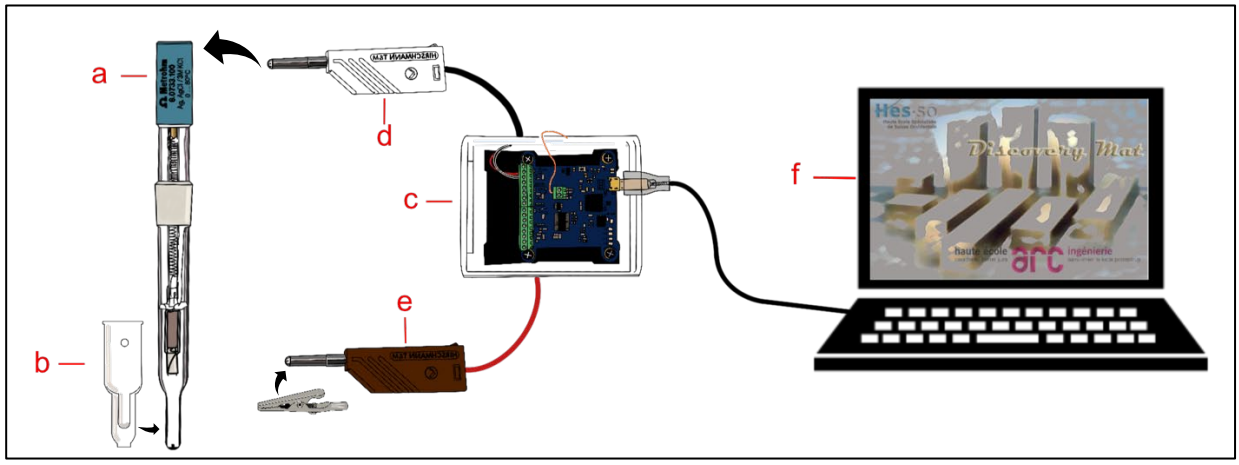


***Fig. 1**. DiscoveryMat instrumentation and setup: a) Ag/AgCl reference electrode, b) junction tube, c) Yoctopuce voltmeter, d) white plug, d) brown plug and crocodile clamp, e) DiscoveryMat software.*

The samples analysed come from four reverberation tubes of sculptures cast in the 1970s, as well as in 2022 and 2023 (Fig. 2). These samples were taken from a foundry in Vila Nova de Gaia, northern Portugal. Due to the irregular surface of the specimens, it was necessary to polish it to improve the results of the analysis (Fig. 3).

***Fig. 2**. Samples studied during the ENDLESS Metal STSM, after cutting them from the reverberation tubes. Samples 1 and 3 correspond to casts from the year 2023, sample 2 is from a sculpture cast in 2022 and sample 4 corresponds to a sculpture cast in the 1970 decade. © Pablo General.*

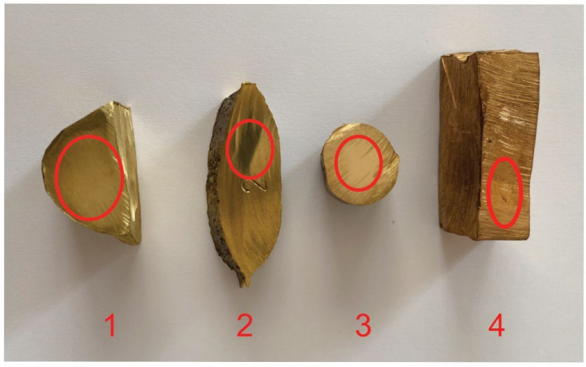
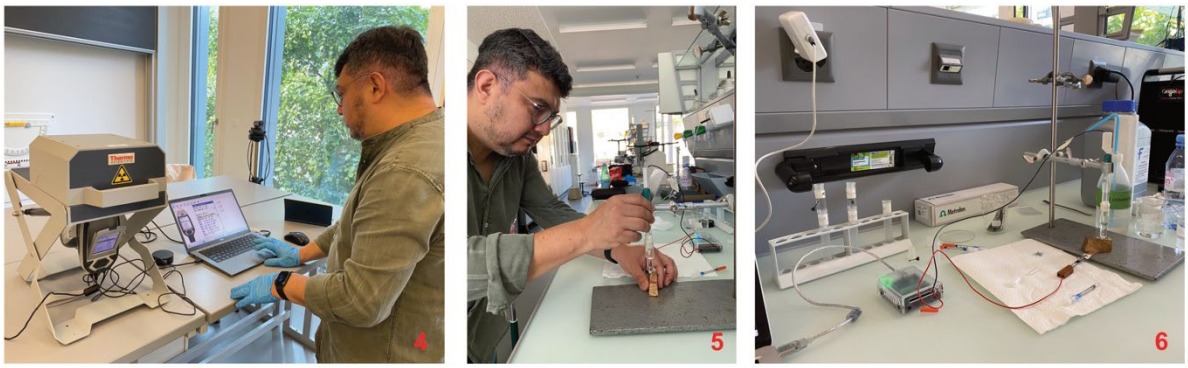


Fig. 3. *The surfaces of the samples were polished (marked with the red circles) to improve the measurement reproducibility with DiscoveryMat. © Pablo General.*

To achieve the smooth surface appearance for each coupon as depicted in Figure 3, medium-grit SiC papers (240, followed by 360 and 500) were employed to refine the surface, followed by fine-grit SiC papers (1000, followed by 1500) to further diminish roughness, and extra-fine grit SiC paper (4000) for achieving a precise finish. Polishing was carried out under tap water stream to prevent overheating and potential alteration of the metal microstructure.

The four specimens were analysed using X-ray fluorescence (XRF – ThermoFischer Niton XL3t GOLDD with X-ray tube 50kV 2W) to determine the concentrations of elements in the metal alloys (Fig. 4). This information is crucial for integrating the results obtained with DiscoveryMat into the software database.

The DiscoveryMat measurements were carried out using Evian mineral water (pH around 7), a 1% (w/v) solution of KNO_3 in deionized water (pH around 5-6), and a 1% (w/v) solution of sodium sesquicarbonate (equimolar $NaHCO_3$ + Na_2CO_3) in deionized water (pH=10). The system RE + junction tube + selected solution must be left to rest for twenty minutes. The RE + junction tube system is then placed in a clamp fixed to a stand and connections of the voltmeter both to the measuring system and the metal surface to investigate are ensured. An external voltmeter can be used to confirm the electrical contact. The tip of the junction tube coupled to the RE is positioned approximately 3 to 5 mm away from the metal sample (Fig. 5). Figure 6 depicts the DiscoveryMat hardware set up and ready to commence the E_{corr} measurements.



Figs. 4, 5 and 6*. Preparation for the measurement of* E_{corr} *with DiscoveryMat: fig. 4, analysis of the metals composition to be studied using XRF; fig. 5, placing the RE + junction tube system in the clamp and positioning it over the sample to be measured; fig. 6, DiscoveryMat hardware prepared for the measurement. © Pablo General.*

For the measurement, a drop of solution is introduced using a syringe between the polished surface of the sample and the tip of the junction tube. The operator must then wait a short time (about 3 seconds, necessary to ensure good data communication between the Yoctopuce voltmeter and the DiscoverMat application) before starting the measurement by activating the "scan" button on the DiscoveryMat control panel. The measurements are repeated three times for each solution, two over 5 minutes and one over 15 minutes. A 15-minute scan is deemed successful if the data for the first 5 minutes are between those of the two preliminary 5-minute scans.

Between each measurement, the metal surface needs to be polished with 4000 grit SiC paper under running water, to eliminate any residue from the previous measurement's reactions.

In this study, the results of the measurements of the copper alloy samples in the three solutions showed many differences. The measurements carried out with Evian and KNO_3 were often not reproducible and had to be repeated several times, as shown in Table 1. On the other hand, the measurements with NaSesq went smoothly, with only minor fluctuations, and only three measurements were taken (two over 5 minutes, followed by one over 15 minutes).

Table 1. *Detail of the number of DiscoveryMat measurements performed on the four samples, using the Evian, KNO_3 and NaSesq solutions.*

Sample	Solution	Number of plots
1	Evian	7 (3 = 5 min, 4 = 15 min)
	KNO_3	15 (11 = 5 min, 4 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)
2	Evian	8 (7 = 5 min, 1 = 15min)
	KNO_3	4 (3 = 5 min, 1 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)
3	Evian	4 (2 = 5 min, 2 = 15 min)
	KNO_3	7 (4 = 5 min, 3 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min
4	Evian	4 (3 = 5 min, 1 = 15 min)
	KNO_3	5 (2 = 5 min, 3 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)

The disparity in the number of measurements conducted with the solutions Evian, KNO_3, and NaSesq is linked to the reaction of these solutions with the copper alloy, producing irregular behaviour in the data acquisition but also the irregularities of the metal surface at the beginning of the polishing process (Fig. 7). Samples 1 and 3 exhibited more irregular measurements when using Evian and KNO_3, in contrast to samples 2 and 4. Conversely, the measurements using NaSesq, when the metal surface was homogeneously polished, demonstrated consistent regularity in all four samples.

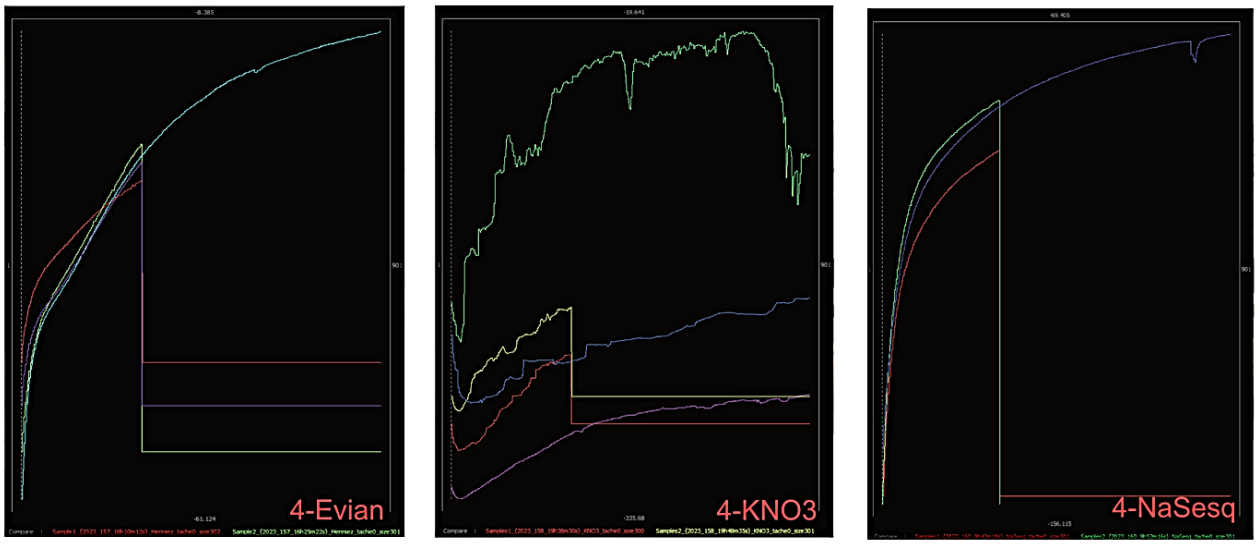


Fig. 7. *Example of distinct plots obtained from sample number 4 using DiscoveryMat in Evian, KNO_3, and NaSesq. Each plot demonstrates the diverse shapes obtained during the measurement process. For KNO_3, only the 15-minute plot in the middle was considered in the data processing. © Pablo General.*

After the measurements, the plots obtained from the four samples, and selected as relevant, were compared using DiscoveryMat algorithm with the entries of DiscoveryMat database. It is important to note that the DiscoveryMat database/library is made up entirely of measurements from previous analyses carried out using DiscoveryMat, following the same protocol as the one described in this report. Over time, the database has been enriched by contributions from various projects. This participatory approach aims to ensure its relevance.

Before this step, additional information is provided to the algorithm about the lack of reproducibility of the plots, the fluctuation of potential values, and the presence of stains on the metal surface at the end of the 15-minute recording, in each solution.

The algorithm then calculates the distance of similarity (dSim) between the plots of the material studied and the plots of the entries in the database, resulting in a ranking of the "proposals". These results are also represented in "graphs", where the plots obtained and those of the entries from the DiscoveryMat library are superimposed by the algorithm.

In the "proposals" ranking, attention should be given to the first ten entries that have the lowest distance (dSIM) between the input and the compared entry. They indeed give a preliminary idea of the nature of the material under study. Graphs are then examined, and proposals whose plots intersect at the end of the recording with those of the studied material or follow different slopes are discarded.

By convention we consider that a dSim inferior to 500 corresponds to a good match while if it is between 500 and 1000, it is medium and beyond 1000, it is not a good match. On this basis, the results are as follows:

Sample 1

A good match has been found between the sample plots and those of entries 1 and 3 provided by the database. In entry 1 (Fig. 8), the dSim is 395 and the composition given is Cu 77.5%, Zn 15.7%, Sn 2.4%, Pb 2.4, Fe 1%, Si 05%, Sb 0.3% and Ni 0.2%. Entry 3 (Fig. 9), with a dSim of 824 gives a composition of Cu 81.1%, Zn 16.1%, Pb 1.3%, Sn 1.2% and Fe 0.3%.

As observed in Figures 8 and 9, the parallelism between the plots of sample 1 and those of DiscoveryMat database entries can be seen, particularly at the end of the measurement. The fluctuations of potentials in the KNO_3 plot indicate that the presence of Pb is higher than 1%. The KNO_3 plot is the one that highlights a distinct difference between the two selected entries. While in entry 3, the plot follows a different trajectory compared to sample 1 and intersects with it, in entry 1, the plot follows a similar trajectory to the sample plot, despite the aforementioned fluctuations. Fluctuations in NaSesq. of sample 1 at the end of the plot is not understood yet. Fluctuations in Evian water indicated in the inset below the plots seem to be very limited compared to those in KNO_3.

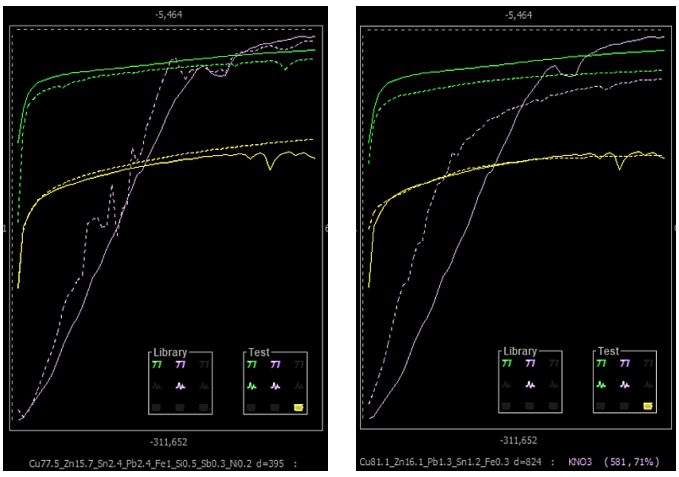


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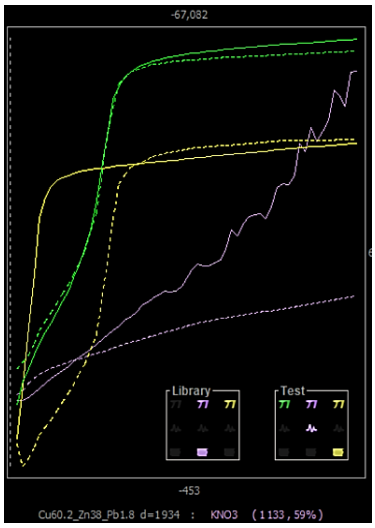
Fig. 8 and 9. *Matching results for sample 1. © DiscoveryMat.*

The composition of the sample according to XRF is Cu 81.7%, Zn 13.9%, Sn 1.9%, Pb 1%, Fe 0.6%, Ni 0.6% and Si 0.3%. When comparing these percentages with the selected entries from the DiscoveryMat database, it can be observed that the closest similarities are found between sample 1 and entry 1, as suggested above.

Sample 2

In contrast to sample 1, the matching for sample 2 is not good. Although none of the entries offered by the database provide a satisfactory match for the sample, entry number 3 (dSim 1934 and a composition of Cu 60.2%, Zn 38%, and Pb 1.8%) (Fig. 10) shows a significant match in the Evian plot and coincides at the end of the NaSesq record. However, there is a distinct difference in the KNO_3 measurements, where the entry exhibits fluctuations due to the Pb content exceeding 1% and a different plot profile.

On the contrary, in entry number 7 (Fig. 11) (dSim 2199 and a composition of Cu 58.1%, Zn 38%, Pb 2.5%, Sn 0.5%, Fe 0.5%, and Ni 0.7%), the match is observed for the KNO_3 measurement and runs parallel in the NaSesq plot. However, the match is not as strong for Evian, as the entry plot shows fluctuations that are not present in the sample plot. It is also interesting to observe that the insets characterising the behaviours of sample 2 and entry 7 are similar.



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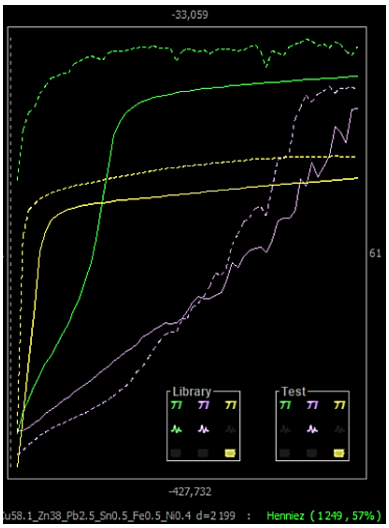

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Fig. 10 and 11. *Matching results for sample 2. © DiscoveryMat.*

The XRF analysis reveals that the composition of sample 2 consists of Cu 58.7%, Zn 38.8%, Pb 1.5%, Sn 0.4%, Si 0.2%, Ni 0.2%, and Fe 0.2%. These results closely resemble the concentrations of major elements in both entries, but they are more comparable to entry 7 in terms of the types of elements present in the alloy.

The presence of Sn in sample 2, determined by XRF, seems to influence the slope shape in the KNO_3 plot.

Sample 3

Four of the entries given by the DiscoveryMat database have a dSim below 1000, most of them being quaternary alloys. With entry number 2 (Fig. 12) (Cu 77.5%, Zn 15.7%, Sn 2.4%, Pb 2.4% Fe 1%, Si 0.5%, Sb 0.3% and Ni 0.2%, dSim 954), the match is correct in KNO_3 but not in Evian. On the contrary, with entry number 10 (Fig. 13) (Cu 90.4%, Sn 5.2% Zn 2.4%, Pb 1.5%, Sb 0.2%, Fe 0.2% and Ni 0.1%, dSim 1365) the match is with Evian, but not so good with KNO_3.

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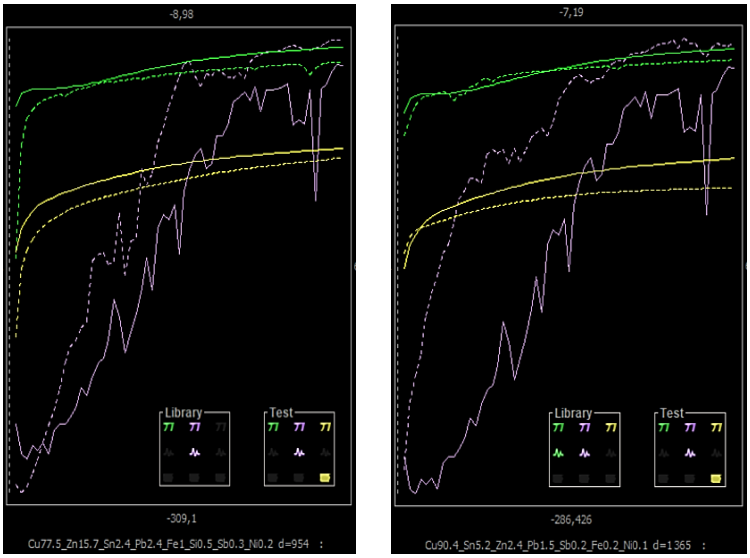

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Fig. 12 and 13. *Matching results for sample 3.© DiscoveryMat.*

This sample, analysed by XRF, shows a composition of Cu 86.2%, Zn 7%, Sn 4.5%, Pb 1.1%, Fe 0.4%, Ni 0.3% and Si 0.4%. Sample 3 is located in between the two entries. However, the matches are not as close as those observed for samples 1 and 2.

Sample 4

In this case, the lowest dSim value is slightly above 1100. Only one match has been found, being entry number 10 (Fig. 14), (dSim 2319; Cu 89.5%, Zn 2.4%, Sn 5.6 and Pb 2.5%). Despite being far apart, the plots are parallel for all three solutions. Only in the case of KNO_3 fluctuations are observed in the analysed metal, but not in the database input. The inserts comparing the characteristics of both sample 4 and entry 10 are rather different. Therefore, we expect a composition of sample 4 different from entry 10.

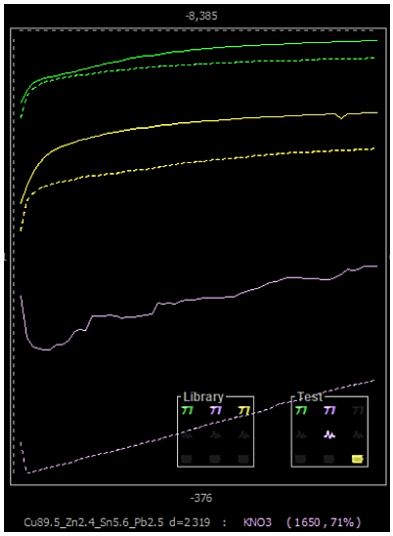

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Fig. 14. *Matching results of sample 4.© Christian Degrigny.*

The XRF results for sample 4 are: Cu 91.7%, Zn 5.5%, Sn 0.7% Pb 0.7%, Si 0.6%, S 0.5% and Fe 0.3%. As indicated above, if the presence of major elements are recognized by DiscoveryMat, their concentration is not correct.

Other activities carried out in the context of STSM:

- Visit to the Olympic Museum in Lausanne. The STSM participants attended a DiscoveryMat demonstration by Rayan Ammon, HE-Arc CR BA student, on artifacts related to the history of the Olympic Games made of aluminium-based alloys (Fig. 15 and 16).

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Fig. 15 and 16. Rayan Ammon, BA conservation student at the Olympic Museum. Lausanne, attaching the junction tube to the reference electrode (Fig. 15) and injecting the solution between the tip of the junction tube and the sample to initiate the measurement (Fig. 16).

Observing the use of the analytical tool in the context of a museum enabled us to experience the advantages of using DiscoveryMat over any other expensive analyser. However, it is important to understand that DiscoveryMat is a sensitive analytical tool that requires adequate space for operation, which may not be available in many museums. This space is essential for ensuring precise measurements and obtaining reproducible results.

Additionally, the unique physical characteristics of each piece, coupled with their significance in the museum's collection, requires a meticulous examination when selecting the area to be polished and analysed. This careful approach ensures that the visual aspect and readability of the object are not compromised.

- Visit to the Haute Ecole Arc Engineering, at Microcity in La-Chaux-de-Fonds. During this visit, samples of a monumental bronze sculpture, cast in Portugal in 1887, were analysed by optical microscopy and Scanning Electron Microscopy (SEM). With the results of this analysis, which clearly show the stratigraphic layers of metal and patina, as well as a mapping of the elements present in these areas, a MiCorr sheet will be generated. This report will also be included in my PhD thesis, as the analysed sample corresponds to one of the sculptures studied for this purpose.

Description of the STSM main achievements and planned follow-up activities

Although some archaeological bronze samples were initially considered, this STSM focused on modern ones corresponding to sculptures made in the 1970s, in 2022 and 2023 in the Vila Nova de Gaia region of Portugal. The reason for this choice was the physical properties of the latter and possible diversity and proportion of elements present in the samples.

The purpose of the STSM was to acquire proficiency in the use of the DiscoveryMat hardware and software. Some experience is required for the handling of this tool, which is quickly gained through practical application. The software is intuitive and has a guide that makes it easy to use.

The use of larger samples than those usually analysed, of smaller size, allowed the use of DiscoveryMat to be tested on materials with irregular surfaces. It was observed though that it is necessary to polish well the

metal surface to get reproducible results. Although it may seem to be an impediment, this could be done on non-visible or barely visible areas.

The use of three different solutions: Evian, KNO_3 and NaSesq, showed variations in the monitoring of E_{corr}. It was found that NaSesq plots were less irregular compared to the other solutions in the measurements carried out. The lack of reproducibility is partly explained by the fact that the measurements with the first solutions were performed on a recently polished surface, which may have retained some irregularities on the metal and, consequently, generated irregular results in the measured values. In contrast, the NaSesq measurements were carried out on a surface that has been polished many times, reducing the probability of irregularities, and contributing to more consistent results.

The analysis of the four samples using DiscoveryMat allowed us to compare the results obtained with those of the database and gather information about the alloys they are composed of. Furthermore, their XRF analysis make them as new entries in the DiscoveryMat database. Expanding this library will enable other users to find more precise matches when analysing their metal objects with DiscoveryMat.

This STSM has been a great opportunity to get to know and experience first-hand a low-cost electrochemical instrument that can be very useful for the chemical determination of metallic materials.

In addition, the opportunity to work in parallel with two other colleagues in STSM was very beneficial. It also provided me with an on-site insight into the assembly system and operation of Pleco, as well as the process of accurately creating a MiCorr sheet.

The experience gained in using DiscoveryMat will make it easier to disseminate this knowledge to the academic community and to conservator-restorers. This STSM should also be the first in a series of scientific collaborations between HE-Arc CR and the Research Centre for Science and Technology of the Arts - CITAR - UCP in the field of conservation-restoration and the application of low-cost, portable and easy-to-use devices like DiscoveryMat and other devices such as Pleco and MiCorr, which HE-Arc CR is currently developing.