Report on the outcomes of a Short-Term Scientific Mission

Action number: IG 16215

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Details of the STSM

TITLE: Training in the analytical possibilities of the electrolytic pencil Pleco and comparison with a similar, self-made pencil

START AND END DATE: 05/06/2023 to 09/06/2023

LOCATION: Haute École Arc Conservation-Restauration (HE-Arc CR), Neuchâtel, Switzerland

SCIENTIFIC SUPPORT: Christian Degrigny (HE-Arc CR), and Romain Jeanneret (HE-Arc CR & Abbey of Saint-Maurice, Switzerland)

GENERAL PROGRAMME: The assembly of the Pleco and training in its use, as well as its comparison with a homemade pencil made in Vienna, were the focus of this STSM. Initially, artificially tarnished pure silver (Ag999) and sterling silver (Ag925) coupons were used as test surfaces; subsequently, original historical objects were also examined using Pleco.

Description of the work carried out during the STSM

Pleco is a tool designed by HE-Arc for local electrolytic analysis and treatment of historical metal, mainly silver-based and lead-based alloys. Pleco is equipped with a glassy carbon (GC) electrode supplied by Metrohm® (rod: L 76mm and Ø 2mm) and used as a reference electrode and 1 platinum counter-electrode (rod: L ~40mm and Ø 2mm). AION® (clean room sponge D-3) microporous PVFM foam is used to make the nozzle pads. AION foam absorbs moisture very well thanks to its microfine structure, which is optimal for use with Pleco. When the foam is removed from its plastic protection, it must be thoroughly washed in tap water to remove all traces of the biocide used to preserve it. Only then the suitable nozzle pads for Pleco can be cut and shaped.

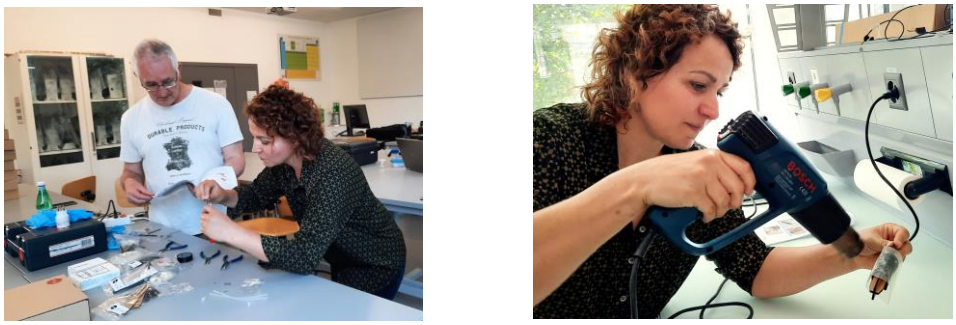
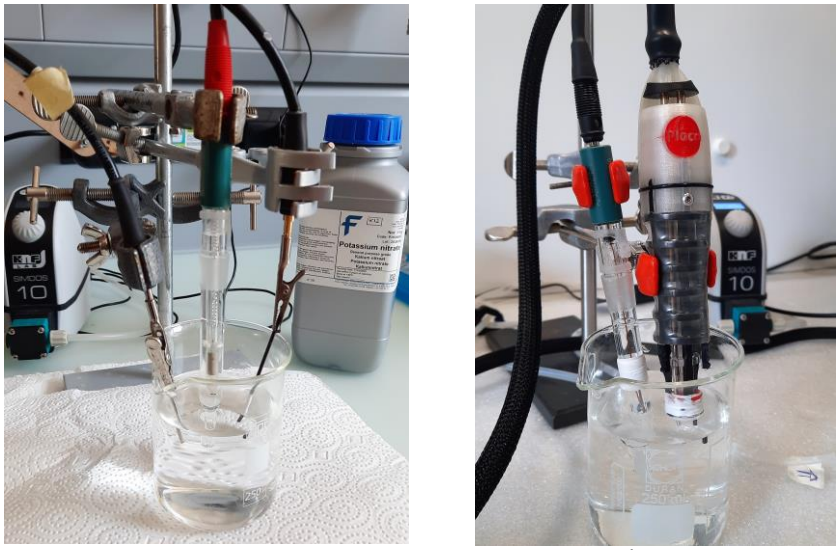


Figure 1. First steps in assembling a new Pleco (left) and making the envelope of Pleco from the heat-shrink tube with a heat gun (right).

The first task of my STSM was to assemble a new PLECO electrolytic pencil from its components. Once this was done, the open circuit potential (OCP) of the GC had to be checked. Both the Pleco GC and platinum electrodes as well as an Ag-AgCl reference electrode (Metrohm®, ref. 60726100 6.0726.100) were held by clamps on a laboratory stand and placed above a beaker containing a 1% KNO_3 (w/v) electrolyte. The three electrodes were then connected to an *OrigaStat 200* potentiostat, controlled by Origamaster 5 corrosion software. The electrodes were immersed in the electrolyte before starting OCP monitoring for 5 minutes (Fig. 2a). Another possible setup is shown in Figure 2b. The GC potential value was entered into the software settings.



a b

Figure 2. Setups to measure the OCP of the GC electrode: a/ the Pleco platinum and GC electrodes together with the Ag/AgCl electrode are immersed in 1% (w/v) KNO_3 (left, after Christian Degrigny); b/ the Pleco nozzle is removed and the GC and platinum electrodes already inserted in the head are immersed in the electrolyte together with the Ag/AgCl electrode placed aside (right, after Romain Jeanneret).

The GC and platinum electrodes were then inserted into the Pleco head. Any gaps between the electrodes and the head had to be sealed with layers of Teflon. A strip of Teflon (10 cm) was wound in several layers over the head. This thickness was made compact by manually smoothing it with the fingers, before inserting the nozzle. A pad cut and shaped (~Ø 1 cm with a rounded tip) from the soft humidified AION foam, using a pair of scissors, was inserted between the teeth of the nozzle. The Pleco hoses were connected to the two *SIMDOS*® Diaphragm Liquid Dosing Pumps and the electrolyte was primed in the Pleco electrolytic cell. It is essential at this stage to check that the cell is properly sealed. If so, the extraction of electrolyte is accompanied by the production of air bubbles in the cell from the pad and not from the upper part of the nozzle. These air bubbles can also be seen in the extraction hose. It took several attempts to make the newly assembled Pleco watertight. The Teflon seals had to be checked and replaced several times, and the position of the pad inside the nozzle had to be adjusted.

By optimising the pumps parameters (in particular, the extraction flow rate), the pad was kept sufficiently wet for the electrolyte to reach the metal surface without running off. If too much electrolyte is extracted, the pad remains dry and no electrochemical reaction can take place. In general, the supply flow of Pleco was kept constant at 10 mL/min and the extraction was varied between 20 mL/min and 90 mL/min.

It should be noted that an extraction flow of 90 mL/min is a sign of poor sealing. The maximum extraction flow should be around 50ml/min. The key point is to optimise the electrolyte flow so that the reduction peaks are clearly visible. To do this, we start with a relatively dry pad and a high extraction rate. If the Linear Sweep Voltammetry (LSV) plot on the materials under investigation shows no peak, the extraction flow is reduced until reduction peaks appear. At this stage, we fine-tune the extraction flow so that the reduction peaks remain visible while limiting the current fluctuations that could mask the small reduction peaks to investigate.

Some measurements were first carried out on artificially tarnished silver-based coupons to check that the expected reduction peaks actually appeared. Pure Ag coupons (Ag999) exposed to boiled egg vapours for 45 minutes, and sterling silver coupons (Ag925) exposed in the presence of vapours released by an egg white albumin solution boiled at 90° were used. The surfaces of the coupons simulated those of historical objects to be cleaned. Although the coupons were tarnished under controlled conditions, an edge effect was observed. The orange/brownish tarnish is slightly thinner than the blue-violet areas. This should be taken into account during the data processing.

A potentiostat was used to scan the OCP of the coupons over time and perform LSVs in the cathodic field, starting at E_{corr}, at a scan rate of 10 mV/second. Reduction reactions are identified through the potential corresponding to the intersection of the first tangent of the reduction peak and the potential axis: on tarnished Ag999 only Ag_2S was reduced and the size of the reduction peak depends on the thickness of the tarnish layer (Fig. 3 left). LSV plots on tarnished sterling silver showed two reduction peaks, i.e. both Ag_2S and Cu_2S were being reduced (Fig. 3 right).

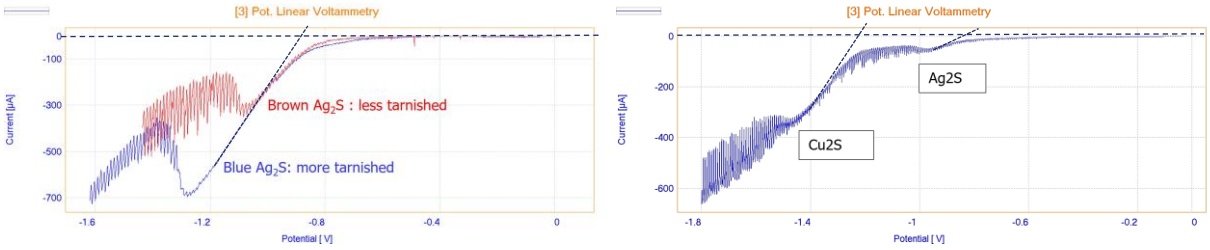


Figure 3. LSVs using Pleco on tarnished Ag999 (left) and Ag925 (right) coupons.

By means of chronoamperometry it was possible to determine, for a given potential, the duration of tarnish reduction. In the chronoamperometry plot below, the cleaning is complete (current is constant) after about 200 seconds at a potential of -1.2 V/GC.

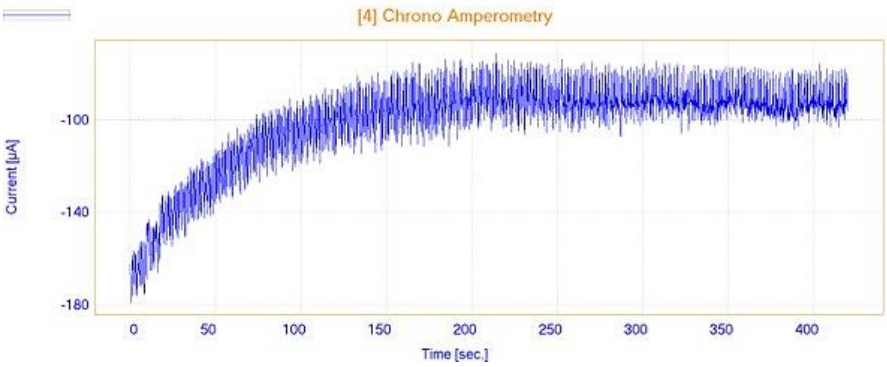


Figure 4. Chronoamperometry at -1,2 V/GC on tarnished pure Ag.

⇒ **Comparison of the two electrolytic pencils – newly built Pleco versus Vienna pencil**

An important part of the STSM work was the comparison of Pleco and the electrochemical pencil which was modelled after Pleco in Vienna. Two essential differences must be noted here:

1. instead of the auxiliary platinum electrode used in Pleco, a gold electrode was used in the Vienna pencil;
2. instead of the GC-electrode used in Pleco, cheaper graphite leads from the Faber-Castell company were tested in different degrees of hardness in the Vienna pencil and a lead of hardness 3B was installed in the pencil.

In order to check whether the GC electrode and the Faber-Castell graphite leads are comparable in their behaviour, OCP measurements were carried out with the GC electrode and the 3B and 5H hardness leads in 1%(w/v) KNO_3. It was observed that the 3B lead is stable and very comparable to the GC electrode, while the 5H lead required a much longer time to give a stable OCP due to its high clay content (Fig. 5).

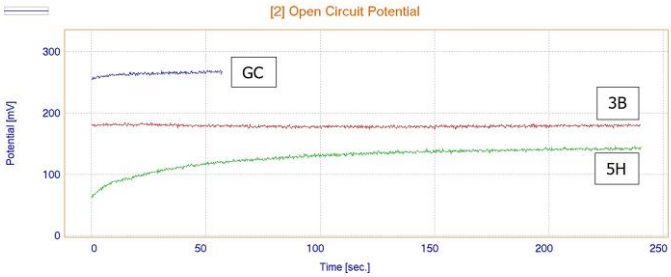


Figure 5. Comparison of OCP for all three electrodes GC, 3B and 5H leads in 1%(w/v) KNO_3, before polarization.

Furthermore, the LSV using Pleco with the GC electrode was compared with the LSV using Vienna pencil with the 3B electrode (Fig. 6). Although both pencils showed Ag_2S reduction, in the case of Pleco this occurred more delayed, which may also depend on the thickness of the tarnish layer. Most importantly, the tangents of the peaks in Fig. 6 show that the reduction peak remains the same for both pencils. The OCP for GC after polarisation took more time to come back to its original value than OCP for 3B lead.

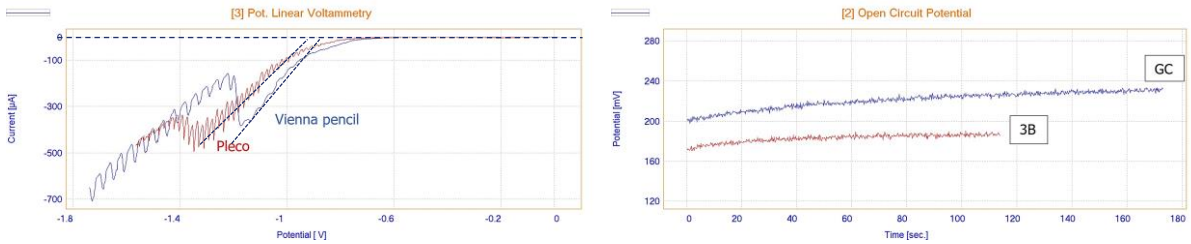


Figure 6. LSV measurements on tarnished pure Ag using Vienna pencil in blue and Pleco in red (left); Comparison of OCP for GC and 3B after polarization – the 3B comes back pretty fast to its original potential while it takes longer time for GC (right).

Since the Faber-Castell leads showed similar results to the GC electrode, a comparative measurement with Pleco was carried out on tarnished Ag925 coupon, once equipped with GC and once with 3B lead. Although the plots are slightly different, the same reduction peaks showed up (Fig. 7).

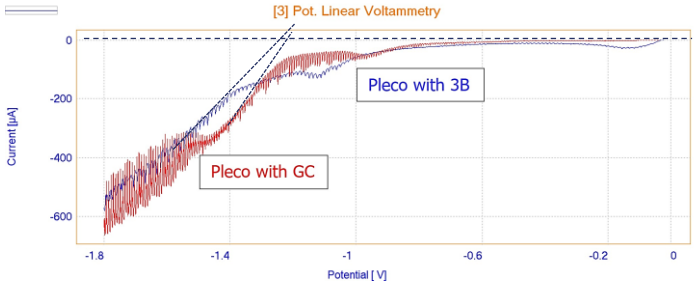


Figure 7. LSV on tarnished Ag925 coupon with Pleco equipped with a GC (red) and with a Faber-Castell lead 3B (blue) RE.

⇒ Tests on historical objects

LSVs were carried out with the newly built Pleco on several historical silver objects of unknown composition from the collections of the Musée historique Lausanne. Discrete analysis points were always chosen, for example on the narrow edge, so that the cleaned measurement point did not attract attention (Fig. 8). Before measuring historic objects, the surface was degreased. Although the fluctuation of currents is quite high, only the Ag_2S reduction peak is observed, suggesting that the Cu concentration in the silver-based alloy is less than 3% (w/v) (Fig. 9). In addition, the level of tarnish is much less than on the tarnished Ag999 coupon.

Figure 8. OCP measurement on a silver plate of Musée Historique Lausanne (VL83A100) with the newly built Pleco connected to the potentiostat controlled by the OrigaMaster 5 software, Supply flow of 10mL/min. and extraction flow of 20mL/min.

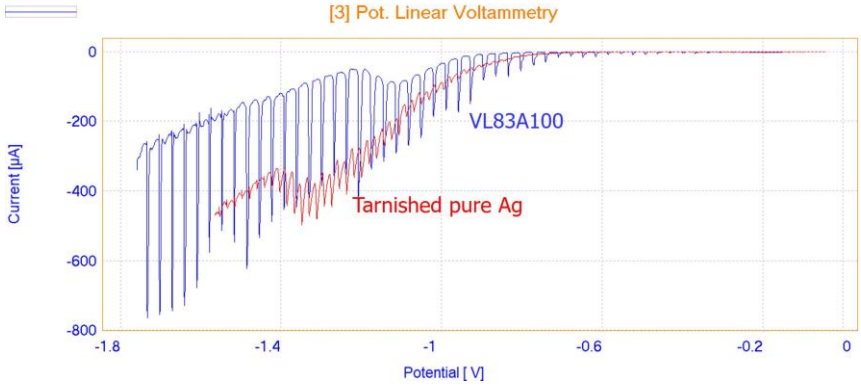


Figure 9. LSV using Pleco on silver plate VL83A100 compared with the voltammogram on tarnished pure Ag999 coupon (Fig. 3).

Additional tests were carried out with Romain Jeanneret, still with the newly built Pleco, in the conservation workshop of St. Maurice Abbey. Initially, the poorly sealing mentioned in p.2-3 had to be fixed, but it was not clear where exactly it came from. The Pleco pencil was partially disassembled, all Teflon seals were replaced, and the pad was repositioned. Romain Jeanneret assumed that the hoses might be too long and take up too much electrolyte, which the Pleco cannot process as quickly, or that it is difficult to bring the pump system into line with the correct dosage of liquid in the pad. Furthermore, the expansion of the hoses and the elasticity of the material were observed. If there is too much expansion, the hoses would accommodate more electrolyte than the pencil and would interfere with the measurement and cleaning procedures.

Once the problem was fixed, Pleco was tested on the surface of a naturally tarnished silver chalice by silversmith Marcel Feuillat (1930-1935, Geneva). The surface was first degreased with acetone and LSV and chrono-amperometry plots were performed with a potentiostat (OrigaLys®, Origaflex 1A) (Fig. 10, left).

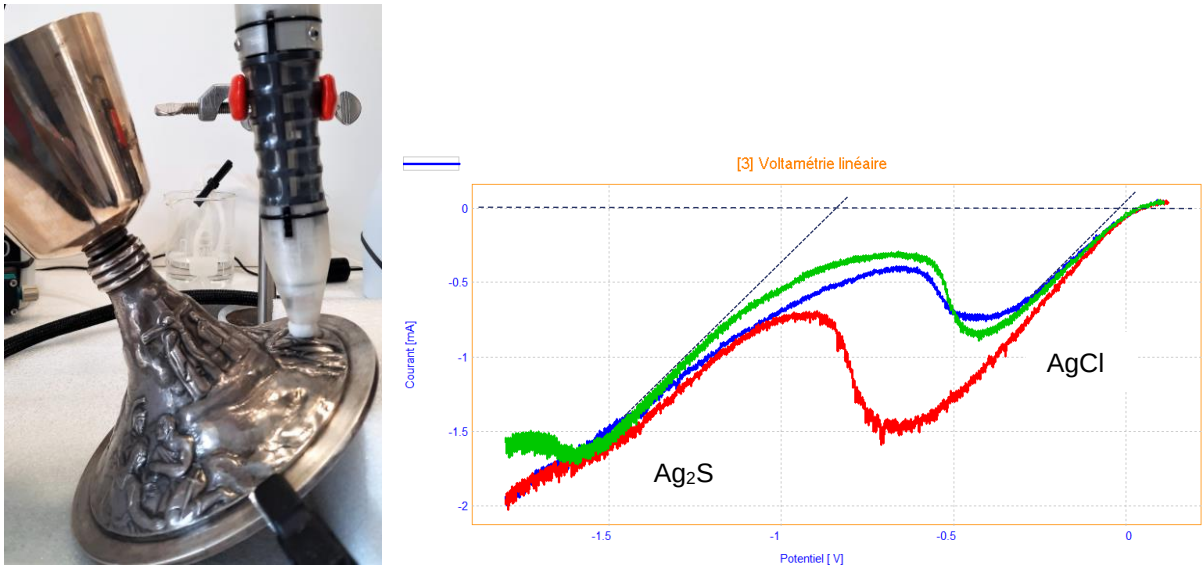


Figure 10. Set-up of the chalice during the LSV measurements using Pleco (left). Three LSV plots measured at the base of the chalice showing strong AgCl compounds and Ag_2S.

Three areas at the base of the chalice were investigated (Fig. 10, right):

1. The slightly lighter elevation of the relief at the shoulder of the female figure (red) - this spot is rich in silver chlorides, probably due to frequent handling with bare hands.
2. A chiselled relief depression with dark tarnish/dirt accumulation (green) - the results show that depressions contain both AgCl and Ag_2S.
3. Dark area at the edge of the foot (blue) - strong AgCl is also measured in this area.

With the help of chronoamperometry it was possible to determine the duration of the cleaning at a certain potential. When the tarnish reduction is complete, the curve flattens out and the pencil can be relocated. The two chronoamperometry curves of Fig. 11 show the cleaning of two approximately 2x2 cm areas at the base of the chalice. For the first area, the pencil had to be moved 8 times (completed after about 50

seconds at a potential of -0.5 V/GC), for the second area only 5 times because the surface was flatter (completed after about 30 seconds at a potential of -2.0 V/GC). The metal surfaces were cleaned better at -2V/GC than at -0.5V/GC, but no overcleaning was evident.

Historical silver objects are rarely made from pure silver, but from silver-copper alloys. In this case, pre-treatment with EDTA salts to remove copper corrosion products is recommended, followed by electrolytic cleaning of the silver tarnish.

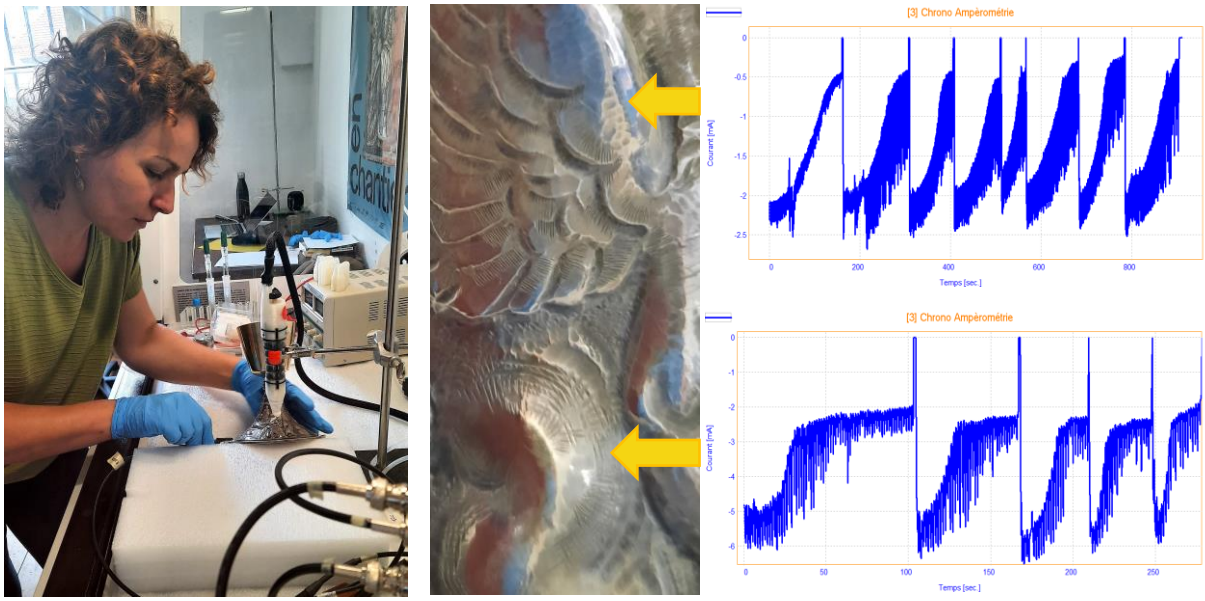


Figure 11. Chronoamperometry measurements on the base of the chalice at St. Maurice Abbey workshop at -0.5V/GC (top) and -2V/GC (bottom).

Parallel to my STSM, two other STSMs took place at the HE-Arc CR:

- one on MiCorr application (Ahmad Abu Baker, Jordan).
- another on DiscoveryMat (Pablo General Toro, Spain).

Even though we each had our own focus of work, there was a good collegiality and exchange of knowledge, and we were able to gain an insight into the other techniques.

⇒ Visit of SEM/EDX laboratory in Microcity, La Chaux-de-Fond

The metal samples brought by my two colleagues Ahmad Abu Baker (archaeological copper alloys) and Pablo General Toro (contemporary bronzes) to work on the MiCorr application were examined under an optical microscope and SEM/EDX at Microcity, a laboratory of the Haute Ecole Ingénierie Arc (Fig. 12). The importance of sample preparation, grinding and polishing on the quality of the images obtained was clearly demonstrated.

Figure 12. SEM/EDX examinations at Microcity in La Chaux-de-Fond

⇒ Visit to The Olympic Museum in Lausanne

Together with my colleagues Ahmad Abu Baker and Pablo General Toro and our host Christian Degrigny, I had the opportunity to visit the Olympic Museum in Lausanne, where a bachelor student from HE-Arc CR carries out his diploma work using DiscoveryMat. A selection of Olympic torches, mainly made of aluminium alloys, is being studied. DiscoveryMat results are being compared with XRF and will be entered into the database of the application. We got an impressive, guided tour in the depot, and could have a close look at the storage conditions, but also at the very interesting museum objects (Fig. a-c).

Figure 13. The Olympic torches in the depot of the Olympic Museum in Lausanne (left); discussion and introduction to the problem of the analysis of aluminium alloys (center); all three STSM fellows in front of the Olympic Museum (right).

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

STSM fully met and even exceeded its objectives and expected results. By acquiring a Pleco kit, I not only had the opportunity to assemble it as part of my STSM, but also to test it in intensive cooperation with Christian Degrigny and Romain Jeanneret. In addition, the STSM enabled me to gain experience in its practical use. The Pleco electrochemical pencil is a very important tool for surface analysis and cleaning of silver and its alloys.

My main concern during the STSM was to gain experience and strengthen my knowledge so that I could use Pleco myself, but also to disseminate and promote it in Austria among conservators-restorers. Inspired by the ENDLESS Metal training school in Ljubljana in February 2023 and this STSM, a training school is planned with Christian Degrigny in Vienna in September 2023. The training school entitled "INTRODUCTION TO THE USE OF ELECTROCHEMICAL / ELECTROLYTIC TECHNIQUES IN METAL CONSERVATION" will be advertised through the Austrian Association of Conservators and is planned for 10 participants. Our host will be the Austrian Federal Office for Monuments. This will enable us to continue our collaboration and initiate a joint publication.

Compared with the Viennese pencil, Pleco is technically more advanced. Like the Viennese pencil, it requires a certain amount of practical experience to operate correctly. By planning new trials with graphite leads produced by the Faber-Castell company, it would be possible to reduce the cost of the Pleco still further, and thus make it genuinely affordable for end-users.

This STSM also strengthened the cooperation between Haute École Arc Conservation-Restauration in Neuchâtel, Switzerland, the University of Vienna, where the Vienna pencil was constructed, and the TU Wien, where the Pleco and Vienna pencil will be further used and developed as part of the Heritage Science project PHELETYPIA of the Austrian Academy of Sciences.

Thank you!