Report on the outcomes of a Short-Term Scientific Mission

Action number: IG16215

Grantee name: Christian Degrigny, Haute Ecole Arc Conservation-restauration, IG16215 chair

Details of the STSM

Title: "Application of ENDLESS Metal analytical tools in the context of Polish Cultural institutions: National Museum, Second World War Museum and the National Maritime Museum, Gdansk"

Start and end date: 19/06/2023 to 23/06/2023

Locations: National Museum Gdansk; 2nd WW museum Gdansk; National Maritime Museum Gdansk and Tczew

Technical support: Potentiostat Gamry Ref 600 borrowed from Prof. Kazimierz Darowicki, head of Electrochemistry, Corrosion and Material Engineering Faculty, Gdansk University of Technology and prof. Stefan Krakowiak.

General programme: dissemination of ENDLESS Metal analytical tools to respond the needs of three museums.

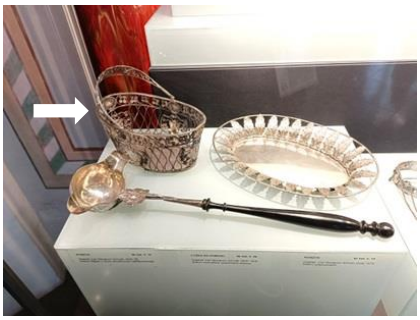
Description of the work carried out during the STSM

- **Location1: National Museum Gdansk (NMG)**

Contact person: Catia Viegas Wesołowska (CVW - head of conservation)

Day 1 (19.06.2023): testing Pleco on objects of the Silversmiths' gallery to detect the presence of copper in silver through Linear Sweep Voltammetry (LSV) plots

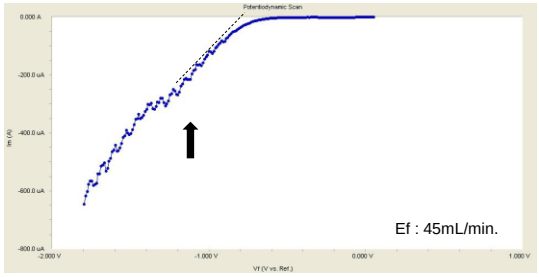


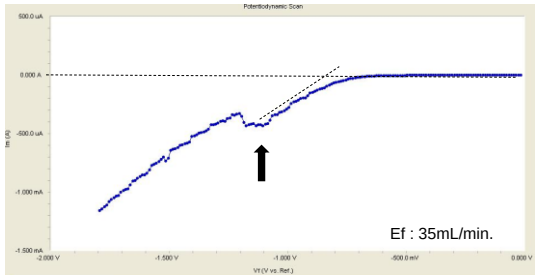


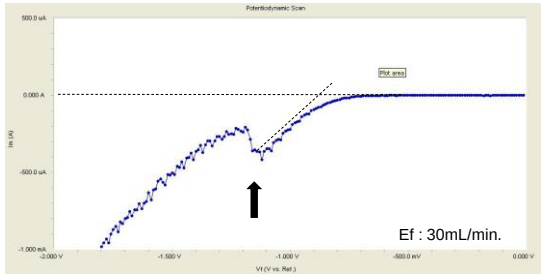

A few objects from the Silversmiths' gallery (see pictures above) were kindly proposed by Anna Baranowska-Fietkiewicz (ABF - Metals curator) and documented by CVW using Dinolite microscope. These objects were:

- A silver-based plate from Augsburg (Inv. Kat.VIII.1, Johann Andreas Thelot, mid. 17th c.)
- A gilded silver-based goblet from Nuremberg (Inv. Kat. VIII.3, Hans Bertolt, 17th c.)
- A silver-based wire basket with filigrees (Inv. Kat.V.15, Carl Benjamin Schultz, 1834-1836)
- A partly gilded silver bowl from Augsburg (Inv. Kat. VIII.4, Johan Baptist Biller, 1665)

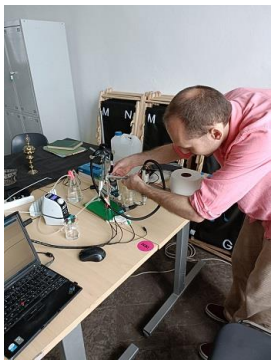
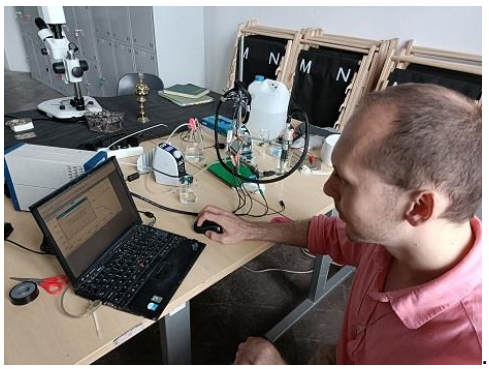

The experiments parameters were determined using the Gamry 600 potentiostat equipped with Gamry Instruments Framework, v.5.67 software and a silver 99.9% coupon tarnished artificially with boiled eggs. After checking the glassy carbon (GC) electrode in 1% KNO_3 (45mV/Ag-AgCl) and sealing properly the Pleco electrolytic cell, we adjusted the extraction flow of the electrolyte to visualise properly the Ag_2S->Ag reduction peak (-0.85V/GC). It appeared that the best results were obtained for an extraction flow of 30mL/min. (supply flow of 10mL/min.). A lower extraction flow would lead to leakage of the solution.





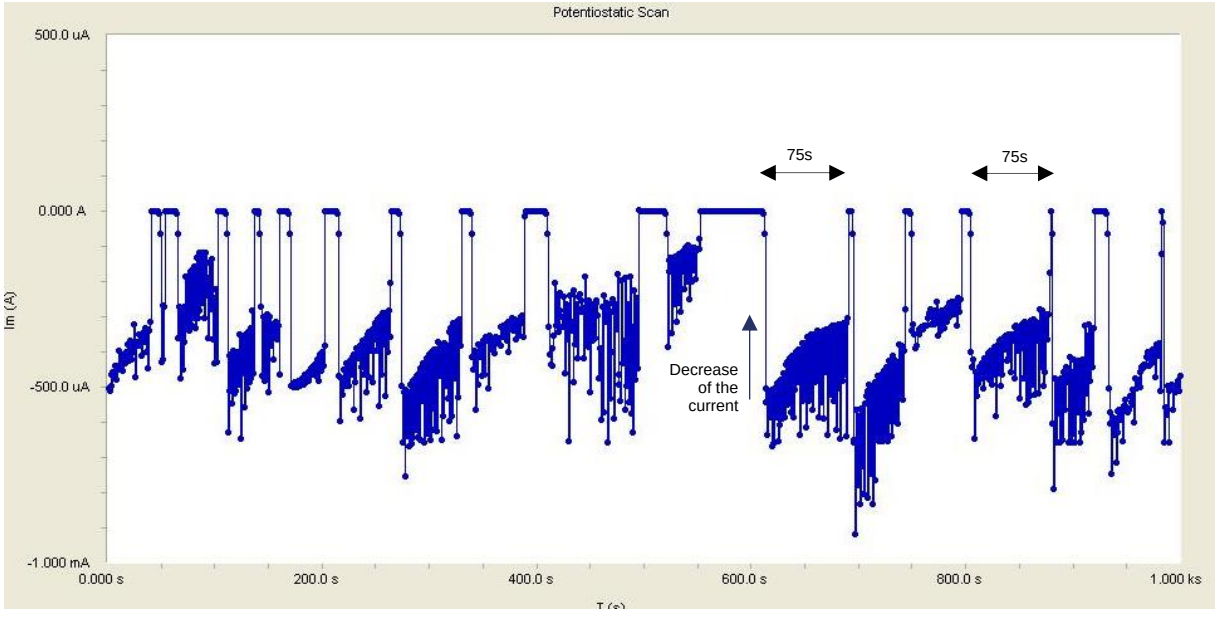


The conditions of the experiments set, we could pursue our measurements on the objects selected, degreased with acetone. Milan Charytoniuk (MCH – objects conservator) was trained so to carry out the next experiments.

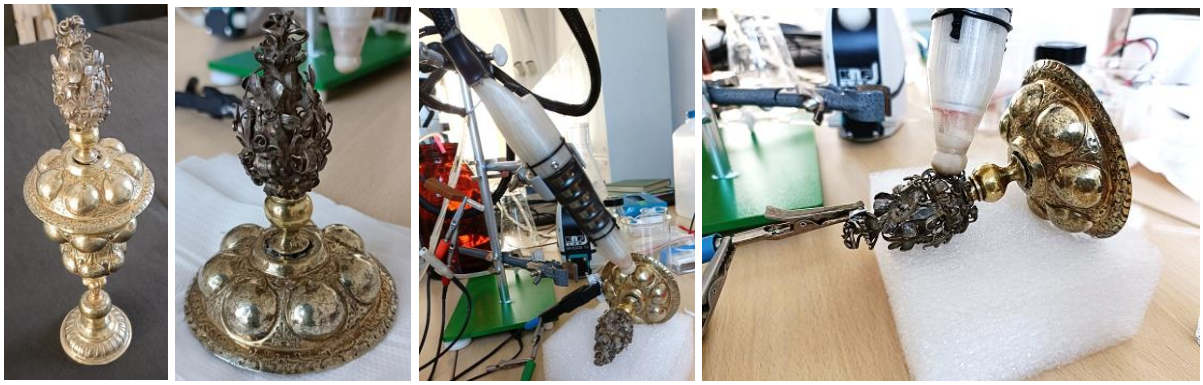
- *Silver-based Augsbourg plate*

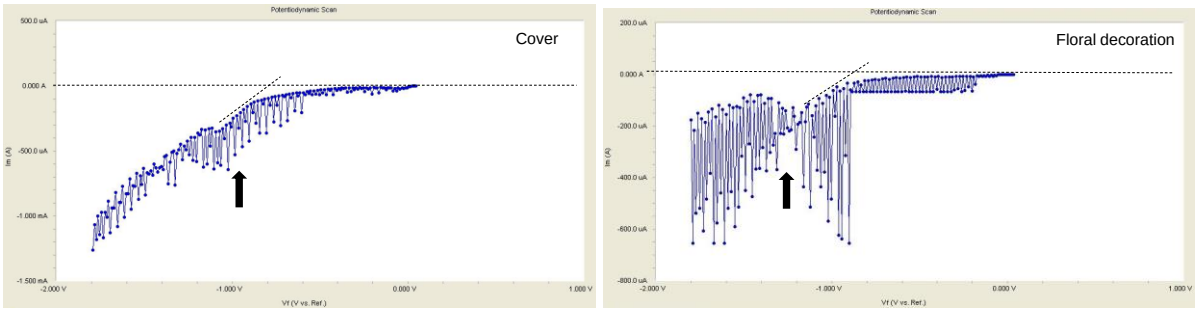
No reduction peak could be seen on LSV plots even by decreasing the extraction flow to 20mL/min. Still the area investigated looked cleaned (2nd picture from the left below). These areas were clearly visible on purpose since CVW wanted to test the cleaning abilities of Pleco. Therefore, potentiostatic plots were performed first at -1V/GC (middle of the reduction peak) and then at -1.2V/GC (see the plot below) to speed up the reduction process (max. of the reduction peak on artificially tarnished Ag coupon, see above). The reduction is efficient after 30 to 75s. Most of the tarnish of the front plate could be cleaned using Pleco dynamically (3rd picture from the left below). Some black spots remained after cleaning which could be due to the presence of copper corrosion products (1st picture from the right).



- *Gilded silver-based goblet*

Only the cover was considered and LSVs were performed as discreetly as possible both on the gilded cover and its silver-based floral decoration (extraction flow of 20mL/min.).

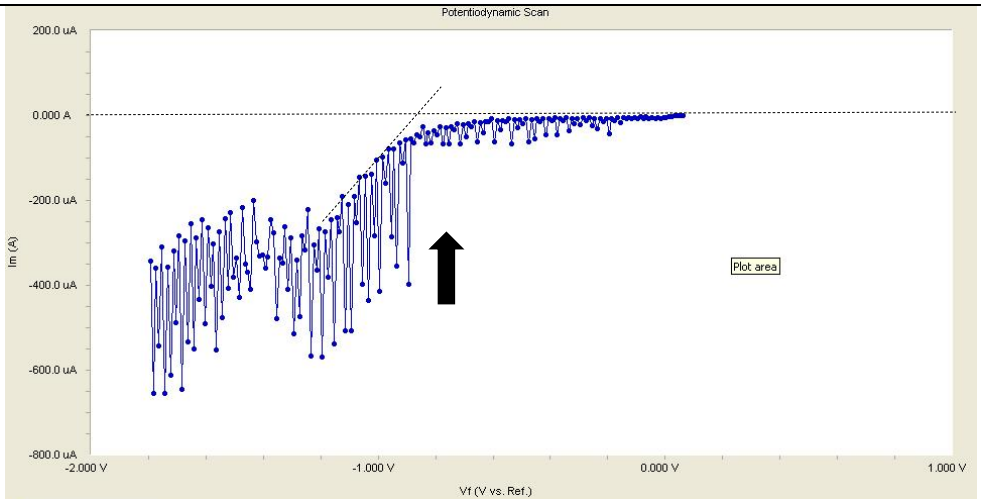




In both cases only the Ag_2S -> Ag reduction peak could be identified (see the LSVs above). This seems to indicate the presence of a low concentration of copper in the silver-based alloy (< 3% ?) but due to the slight tarnish, this result should be validated by X-ray fluorescence (XRF) analysis.

- *Silver-based wire basket with filigrees*

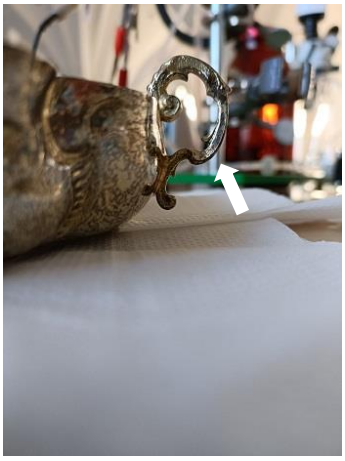
Again, an LSV was performed as discreetly as possible on one of the tarnished wires and again only Ag_2S -> Ag reduction peak could be identified (see the LSV below), indicating, apparently, that the wires are made in a silver alloy containing less than 3% wt Cu.

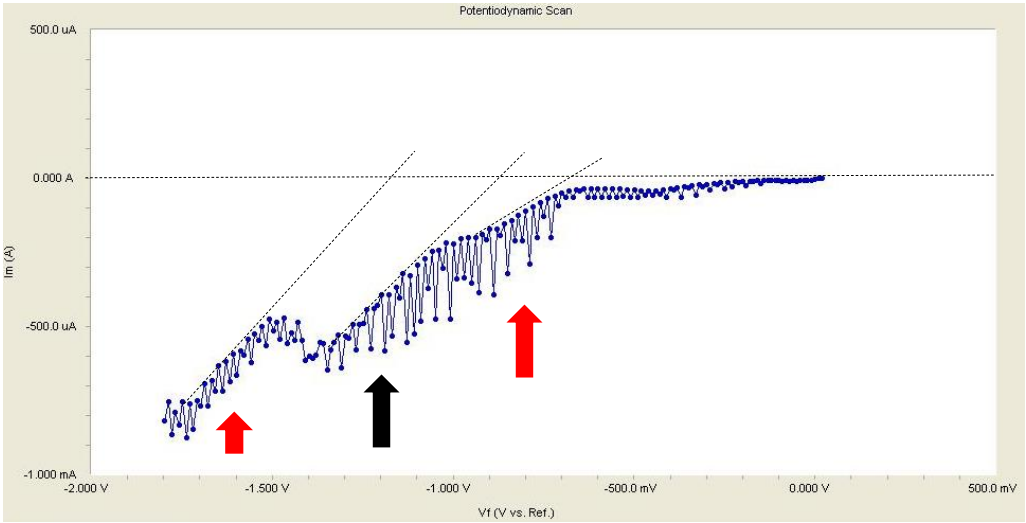


The fluctuations of current being quite large, we could have increased the extraction flow (from 20mL/min.) to make the reduction peak clearer.

- *Partly gilded silver-based bowl*

Once again, an LSV was performed as discreetly as possible on one of the handles of the bowl (see the right picture and plot below). This time three reduction peaks were observed. In addition to Ag_2S -> Ag reduction peak, a first small peak could be attributed to the reduction of a Cu-O compound, while the peak with a max. at -2V/GC could be due to the reduction of a Cu-S compound. These two Cu-based reduction peaks indicate, apparently, that the silver-based alloy contains more than 3% wt Cu.





As said above, the fluctuations of current being quite large, a higher extraction flow would have made the reduction peaks clearer.

As a conclusion of these tests, we clearly see the possibilities of Pleco to identify the presence of not of large amounts of copper (around 3% in weight) in the silver-based alloys.

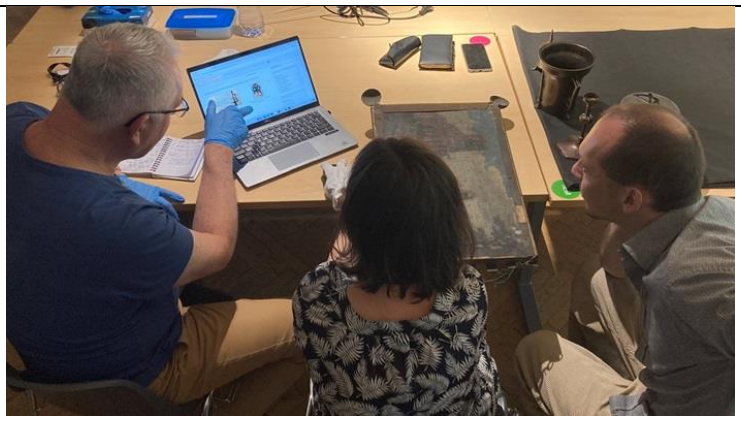
Day 2 (20.06.2023 - morning): Use of MiCorr as an identification tool for metals

A few objects were selected by Anna Baranowska-Fietkiewicz (ABF) and we questioned the MiCorr application and its search engine “By visual inspection” to identify them.

The following table describes the objects (information provided by ABF) and gives the results proposed by MiCorr. Three objects are questionable (highlighted in yellow) and would need to be analysed by XRF. Their core metal is supposed to be zinc-based alloys.

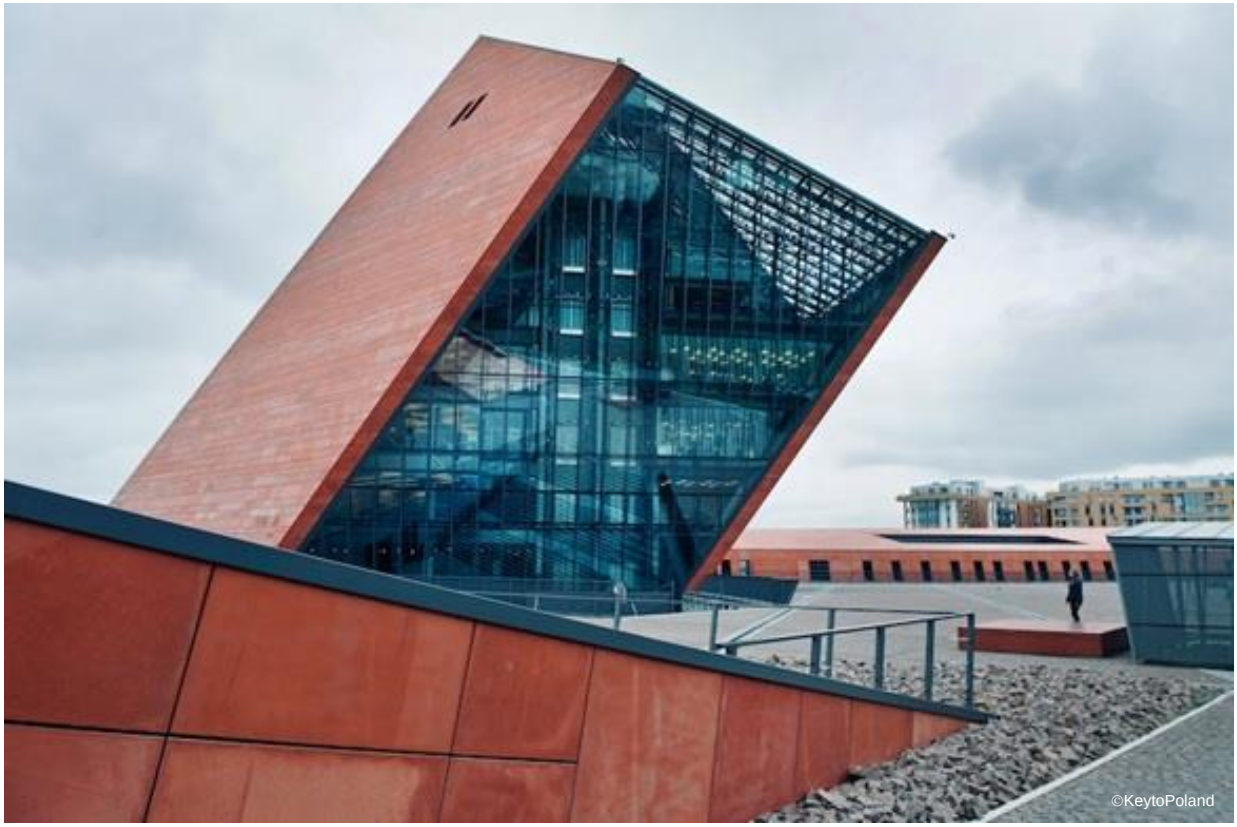
N°	Objects	MiCorr proposal
1	Nuremberg plate, 16th c.?, fake? pewter?	Zinc-based alloy with tin coating?
2	German mortar, 18th c.?, Gothic style	Bronze
3	Cu-based mortar, 1567	Bronze
4	Candle stick	Bronze
5	Reliquary base, gilded copper alloy?	Gilded copper
6	Container, Baroque period, Pb-based?	Pb-Sn alloy
7	Asiatic box	Artificially patinated zinc-based alloy?
8	Two copper-based dragons	Not investigated
9	Box, beginning of the 20th c.	Zinc-based alloy with tin coating?
10a	Plate of the Guild of brush makers	Painted iron plate
10b	Bottom decorations of the plate 10a	Brass

The questioning of MiCorr was the occasion of interdisciplinary exchanges between the applicant and the conservation staff of NMG (curator and conservators). Most identifications were successfully carried out by ABF.



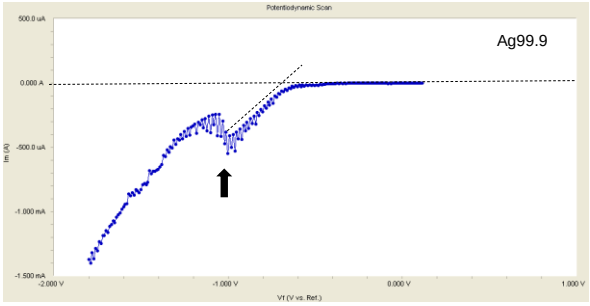
- **Location2: 2nd World War Museum Gdansk**

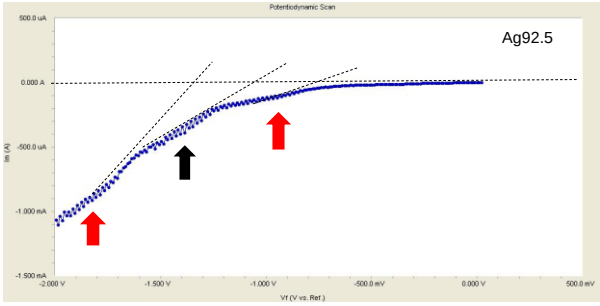
Contact person: Mateusz Rutkowski (MRU – Objects conservator)



Day 2 (20.06.2023 - afternoon): Testing Pleco on a tarnished Ag-Cu cup to define the concentration of copper in the alloy

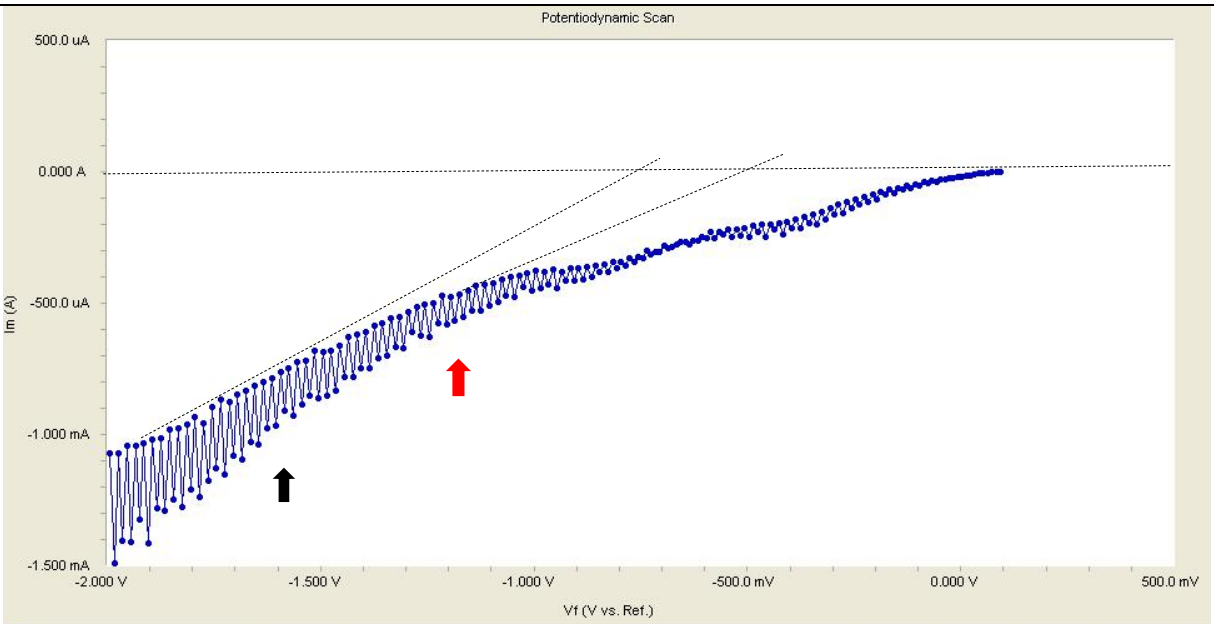
Similarly to the first day, the experimental parameters were determined using LSV plots on silver 99.9% and silver 92.5% coupons tarnished artificially with boiled eggs. After checking the glassy carbon (GC) electrode in 1% KNO_3 (21mV/Ag-AgCl) and sealing properly the Pleco electrolytic cell, we adjusted the extraction flow of the electrolyte to visualise properly the Ag_2S->Ag reduction peak (-0.85V/GC) on Ag 99.9 coupon. We passed then to the detection of the additional Cu compounds reduction peaks on Ag 92.5% coupon. It appeared that the best results were obtained for an extraction flow of 20mL/min. (supply flow of 10mL/min.).





LSVs were then performed on the cup.

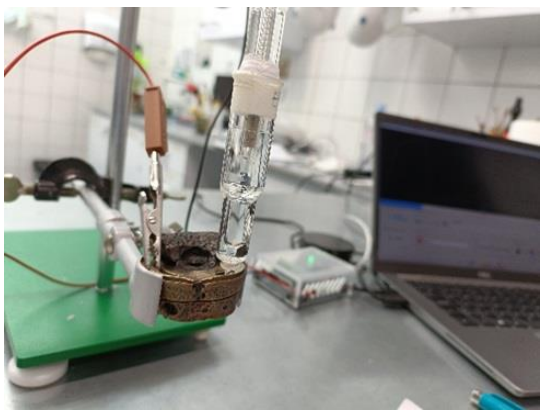
The first Cu-compound reduction peak (Cu_2O, red arrow) is difficult to visualise. The next reduction peak is probably the reduction of Ag_2S (black arrow). Reduction peaks starting at a potential just below Ecorr could be attributed to silver chloride (?).

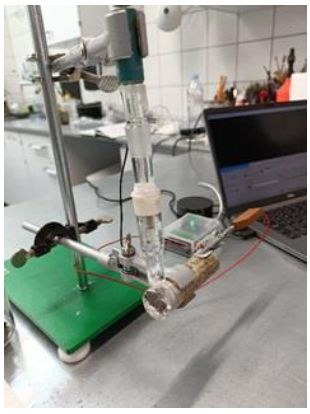


Day 3 (21.06.2023 - afternoon): Use of DiscoveryMat to define the composition of copper and aluminium-based objects

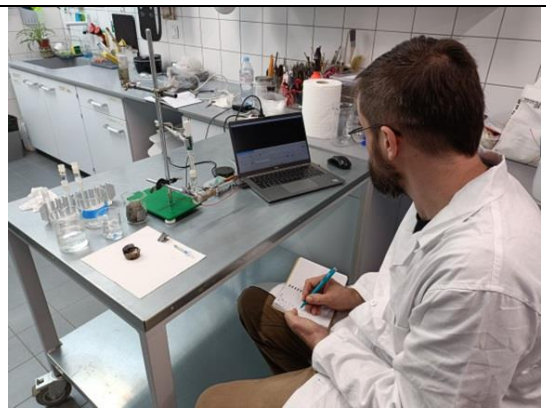
Two objects were selected by MRU: a copper-based part of a Soviet missile or bomb fuse from World War II found by archaeologists in Westerplatte, Poland (left picture, below) and an aluminium-based used box with salt pills from World War II (or before the war), also found in Westerplatte (right picture, below).

The metal surfaces were polished in a discreet area. In the case of the pill box, we realised during the measurement that the cap was not in electrical contact with the tube of the box. Therefore, the contact was modified (right picture, below) and put next to the measuring area on the cap.

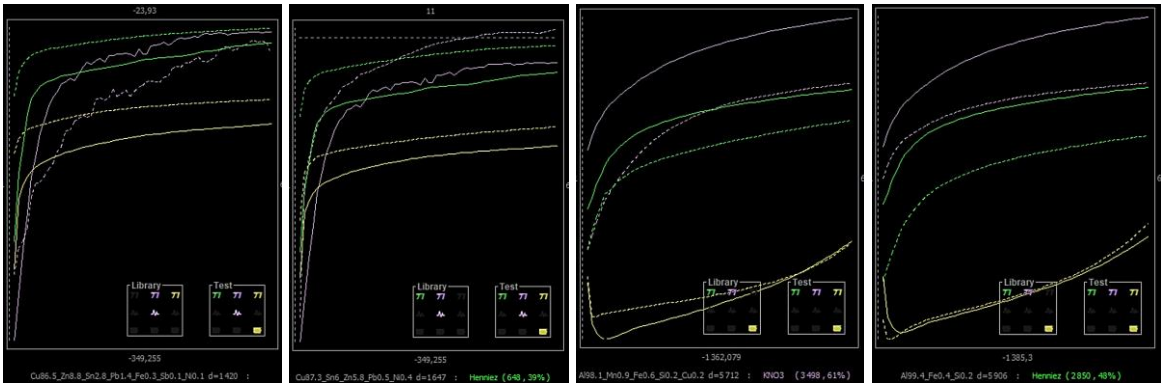




After a reminder of the different steps of the measurement protocol, Mateusz Rutkowski carried out most of the measurements himself.

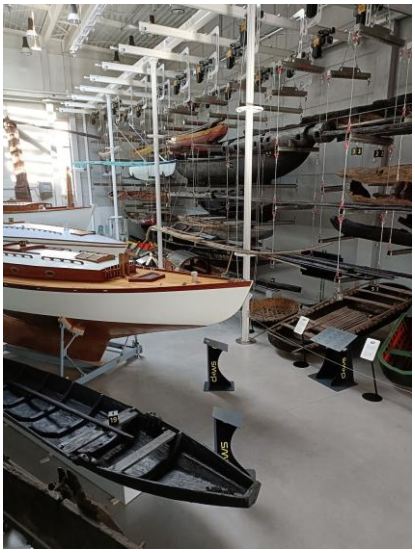



Interpretation of the data using the MiCorr database (135 entries) seems to show (fairly good matching: first proposal with a distance of similarity – Dsim. of around 400) that the part of a Soviet missile or bomb fuse is a quaternary alloy with low concentrations of Zn and Sn (below 10%) and Pb (not below 1% however, due to the instability of the corrosion potential measurements, see the two proposals on the left below). At this stage, it is difficult to determine whether Zn or Sn is more important. As for the pills box, the matching is not good (first proposal with a Dsim. of more than 3000) but it seems that the metal is made of a relatively pure aluminium sheet (see the two proposals on the right below).



- **Location3a: National Maritime Museum Gdansk – Shipwreck conservation centre, Tczew**

Contact person: Katarzyna Schaefer-Rychel (KSR - Deputy Head of Conservation Department)



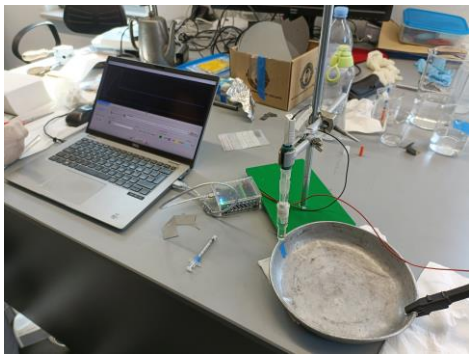
Day 4 (22.06.2023 - afternoon): Use of DiscoveryMat to define the composition of aluminium-based objects

KSR had prepared a few objects to analyse using DiscoveryMat application. CDE recommended to work on two objects only. KSR preferred to limit the analysis to one object to give us time for discussion around data processing.

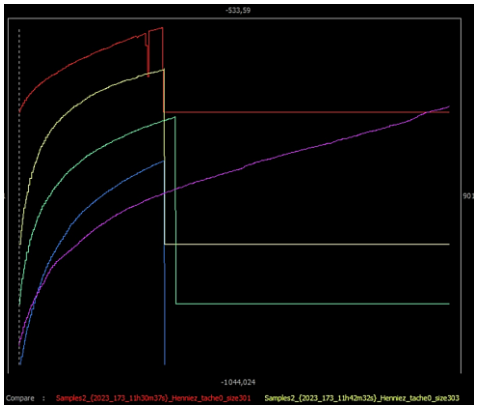
The team present (Dagmara Bojar (DBO, object conservator), Piotr Felkier (PFE, object conservator), Piotr Dziewanoski (PDZ, object conservator) and Artur Fonżychowski (AFO, curator in the marine ethnology department) experimented the use of DiscoveryMat themselves.

Preliminary tests were carried out on a piece of aluminium alloy, the top surface of which was clearly anodised (see picture above). A discussion with AFO about the best measurement area led us to work on the edge of the tube, but we were unable to obtain the electrical contact required for our measurements.

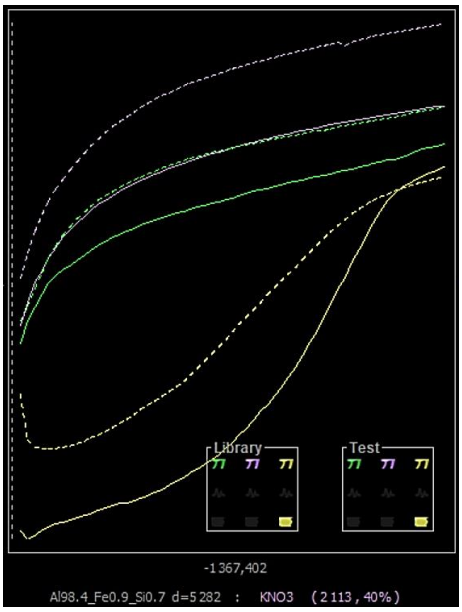
Another aluminium-based object was selected: a plate without anodisation treatment.

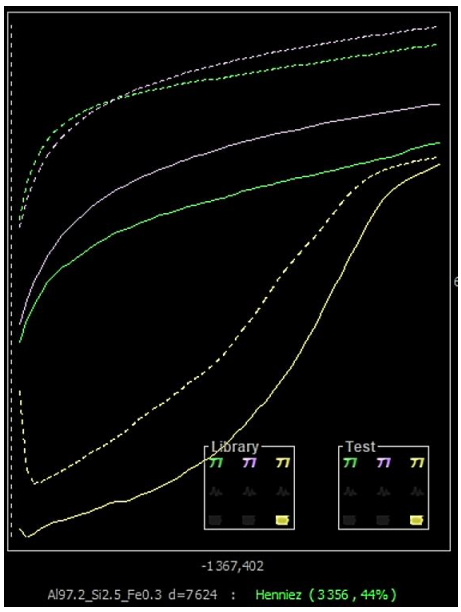


The first results in Evian mineralised water were not reproducible (see the series of plots on the left below). CDE explained that this was due to the presence of a corroded metal surface which electrochemical behaviour changed after each polishing step. A discussion followed then on how far to go with the polishing process so to get reliable results. Obviously, a better reproducibility of results was obtained with 1% KNO_3 during the second series of measurements (series of plots on the right below).



Interpretation of the data using the MiCorr database (80 entries) seems to show (mediocre matching: first proposal with a distance of similarity – Dsim. of around 2000) that the metal of the plate is made of a relatively pure aluminium sheet or an alloy Al-Si with a small amount of Si (see the proposals below).





- **Location3b: National Maritime Museum Gdansk – Maritime Culture Centre**

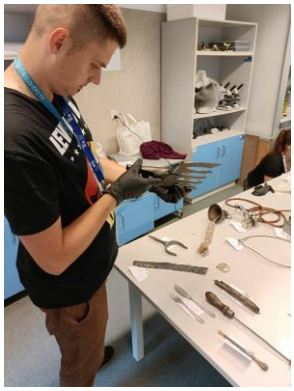
Contact person: Katarzyna Schaefer-Rychel (KSR - Deputy Head of Conservation Department)

Day 5 (23.06.2023 - morning): Use of MiCorr as an identification tool for metals

Katarzyna Schaefer-Rychel (KSR) had prepared a corpus of representative objects of the museum collection (see below).

Artur Fonżychowski (AFO, curator in the marine ethnology department) was introduced by CDE to the general proprieties of metal artefacts: colour, magnetism, weight, their elaboration and corrosion. Some objects could then be easily identified based on these proprieties:

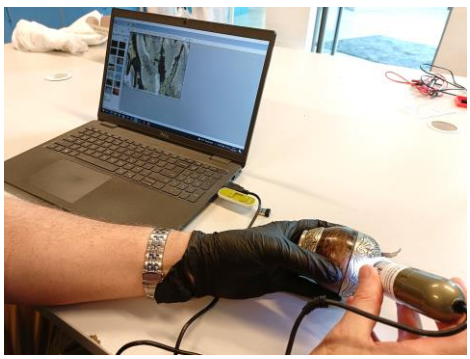
- Magnetic iron-based objects: 1 & 2 (steel), 3 & 4 (wrought iron), 5 (white (?) cast iron)
- Non-magnetic iron-based objects: 6 (austenitic stainless steel)
- Red and yellow alloys: 7 (pure copper), 8 (bronze ?), 9 (brass ?), 10 (mixture of brass and bronze ?) and 11 (mixture of brass and copper)
- Weight: 12 (lead)



Other metals required to look at MiCorr application:

- 13 appeared to be tin-based
- 14 could be a tin-plated cast brass
- 15 could be a nickel-plated brass

16 and 17 were the most challenging objects. They work together. A closer look at 16 and the assistance of MiCorr revealed that the decorated tube was a heavily tarnished silver-plated brass with a copper-based spout. The accompanying vessel (17) also seemed to be made of silver-plated brass, but closer examination under a Dinolite microscope revealed an untarnished whitish-yellowish metal covered, locally with black deposit (see pictures below). We then hesitated between German silver (Cu-Zn-Ni alloy) and nickel-plated brass. But Catia Viegas Wesołowska, who turned up at the beginning of the afternoon, immediately recognised in these two objects a Yerba Maté set (cup or maté and its filtering straw or bombilla), certainly from Argentina. Similar Yerba Maté set can be found on the web. Often, they are mentioned to be made in Alpaca (German silver). Objects 18 and 19 were not considered.



Beyond fully visible and partially visible metals, AFO was introduced to non-visible metals such as marine wrought iron as shown below.

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

Day 5 (23.06.2023 - afternoon): Outcomes of the STSM

CVW, MCH, MRU, AFO and KSR attended CDE presentation of STSM outcomes and results were discussed. The main outcomes are the following:

- Use of Pleco, DiscoveryMat and MiCorr can easily be transferred to conservation staff knowledgeable or not in metal conservation;
- All analytical tools were used successfully in the three institutions visited;
- If the collection of data does not raise too much problem, their interpretation remains complicated and requires the support of an expert, at least at the beginning. The user needs to practise and only through this process, he.she will build his.her expertise;
- The combination of the three tools allows to complete the diagnosis of metal artefacts: the analysis of silver tarnish on a silver-based object identified by MiCorr, using Pleco, provides information on the content of copper in the silver alloy and the analysis of copper-based alloys also identified by MiCorr with DiscoveryMat allows to detect the presence of lead.

We could see during the STSM that the use of additional instrumentations such as a multimeter and a Dinolite microscope allowed us to check the conductivity of metal surfaces, required between the contact and measurement areas when using DiscoveryMat, and appreciate the presence of coatings non-visible with naked eyes when questioning MiCorr.

It also appeared that non-metal conservation professionals might lose some time in using systematically MiCorr application and its search engine by visual inspection to identify metal artefacts. Preliminary observation of metal artefacts and the appreciation of their physical properties (colour, magnetism, weight) clearly help to propose almost immediately metal families. MiCorr application is then used for objects which are more complicated to analyse.

Finally, we have proved once again that collaboration between different communities (curators, conservators and conservation scientists) can speed up the diagnostic process. The examination of the two elements of the Yerba Maté set of the National Maritime Museum clearly demonstrated this. All the participants recognised this essential contribution, which should encourage us to systematically promote these partnerships, which unfortunately are all too rare because of everyone's workload.