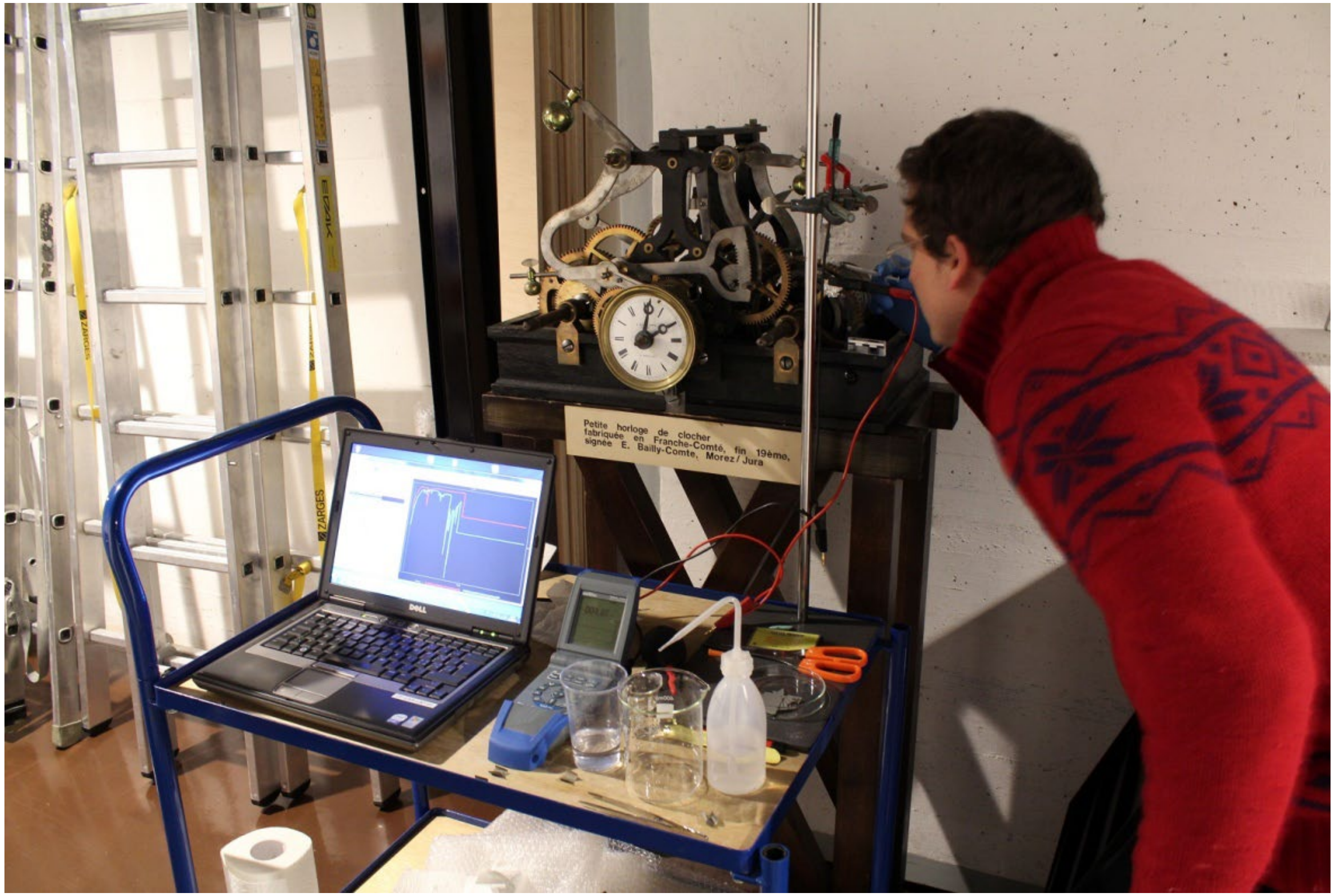
Protocol for data collection and processing with the Discovery Mat software



Prior to any measurement...

Preparation of the system Reference electrode-RE (Ag-AgCl 3M) / junction tube : checking the correct functioning of the RE (immersion for 1/4h in tap water (or conductive solution) and monitoring the potential with another RE serving as a control), filling the junction tube (after rinsing) with the test solution, inserting the RE into the junction tube and blocking it with Teflon tape so that the frit of the RE is 2mm from the frit of the junction tube, immersing the RE / junction tube assembly in a test tube containing the test solution, holding it in place for 20min. (stabilising the system). For more information, see the file "Equipment for measuring potentials".

At the time of measurement...

a. Attach the RE / junction tube system to a stand with a clamping nut, rinse the junction tube externally with deionised water and dry the junction tube glass. Apply absorbent paper to the frit end of the junction tube to absorb any drip.

b. Polishing (locally) the test metal with silicon carbide paper (final grade: Struers 4000). The polishing protocol depends on the object under consideration (whether or not it can be placed under a stream of water). The polished surface should be slightly larger than the diameter of the junction tube frit, i.e. about 1cm in diameter.

c. Position the RE / junction tube system and the metal so that they are about 5mm distant and check the connections (the COM output of the multimeter is connected to the RE / junction tube system and the V output to the metal for the Metrix B3282, the red cable with its brown banana plug connected to the metal and the black/white cable with its white banana plug connected to the RE / junction tube system for the Yoctopuce voltmeter). Contact with the metal is made with an alligator clip and the contact point is protected from scratching with aluminium foil.

d. Apply a drop of solution (20µL) between the junction tube frit and the metal surface with a syringe (rinsed with the test solution before use).

1. Data collection

The operator collects the data automatically (Fig. 1) with an interfaced multimeter (Chauvin-Arnoux Metrix range, model M3282 or Yoctopuce voltmeter) and driven by the "Discovery Mat" software.

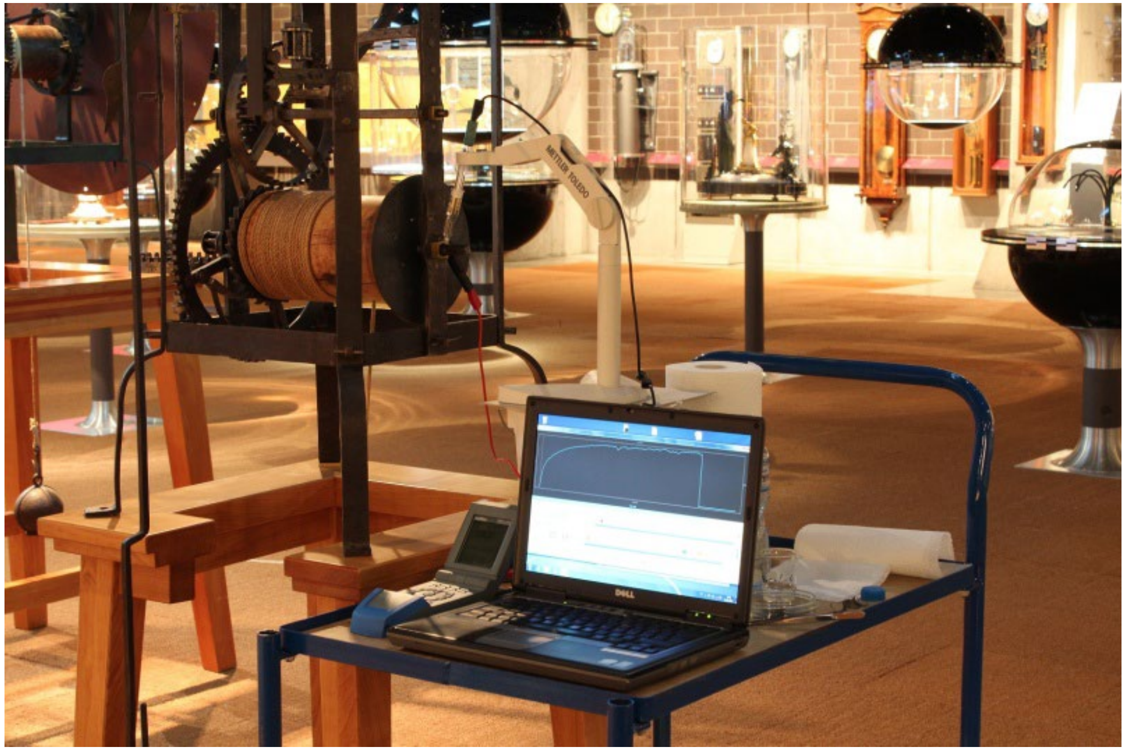


Fig. 1: Automatic data collection with an M3282 multimeter controlled via the laptop by the "DiscoveryMat" software.

1.1. Pre-checking the connections between the laptop and the multimeter (Fig. 2)):

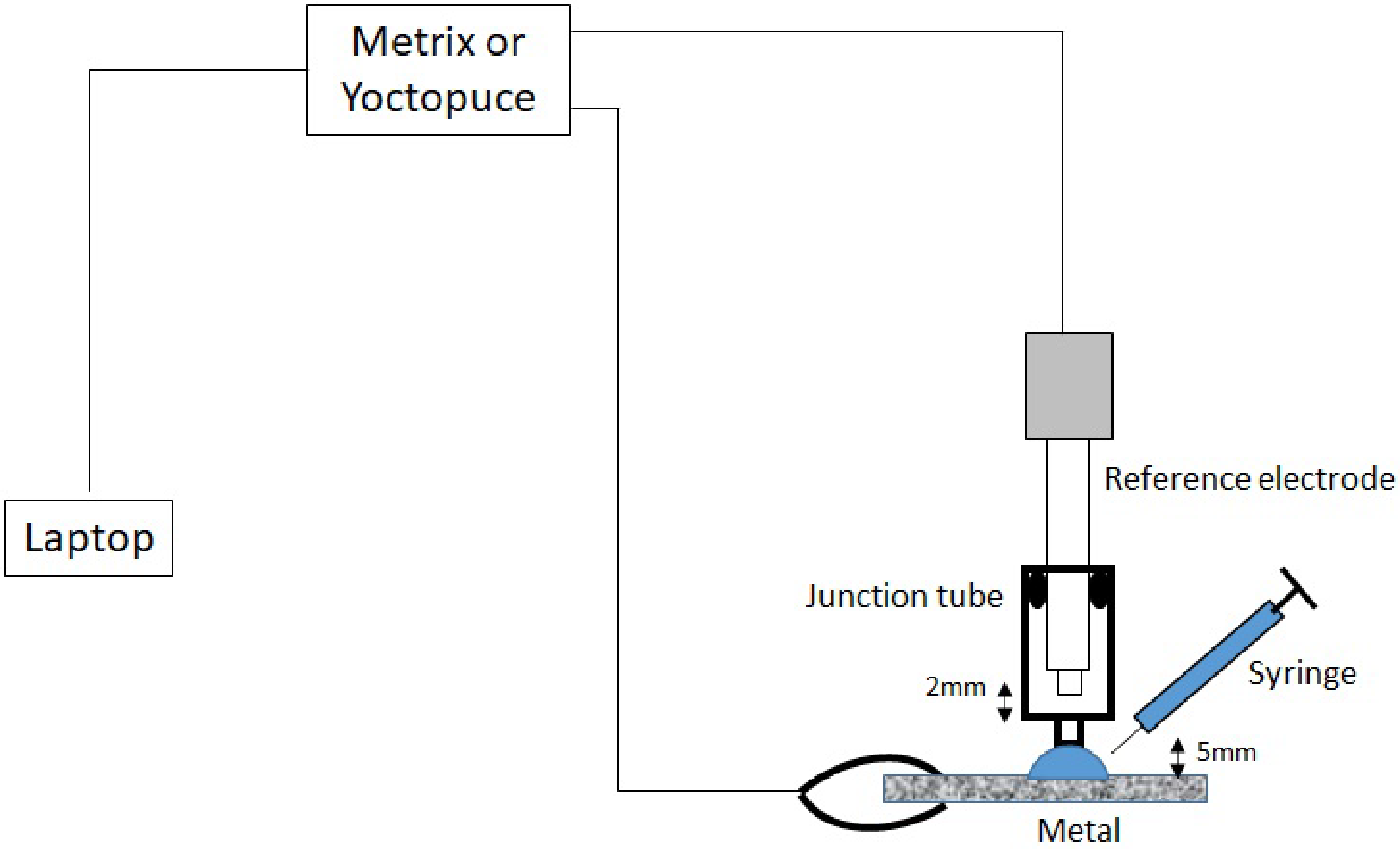


Fig. 2: Connection between multimeter and laptop for automatic data collection.

1.2. Starting the Scanning tool of the DiscoveryMat software for data collection (Fig. 3):

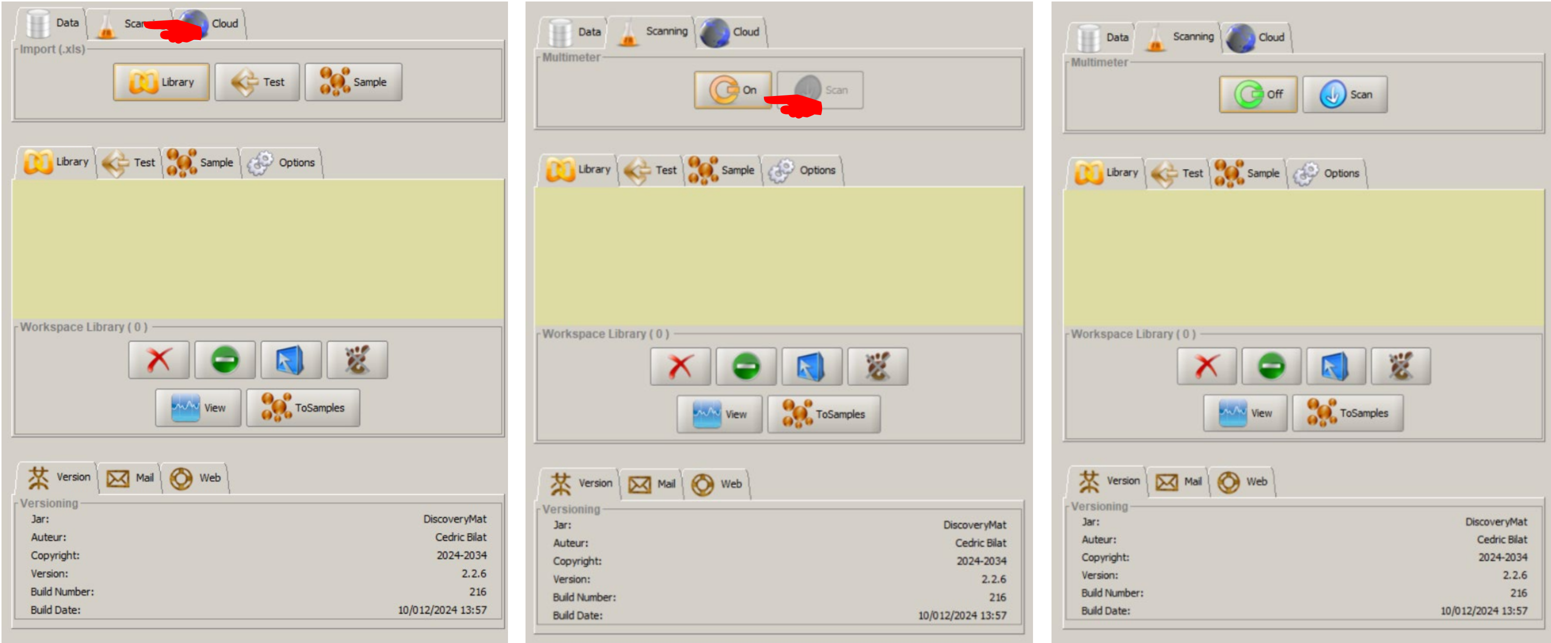
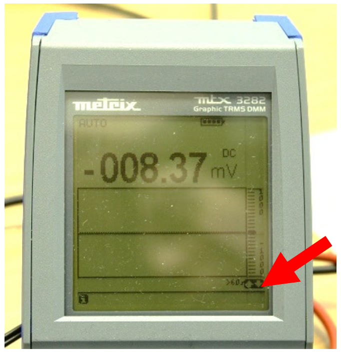
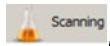
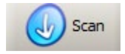


Fig. 3: Data collection control operations.



In the settings window, click on the button , then on the button . The settings window will appear as above (right) and the Scanning tool is ready for measurement (on the Metrix B3282 multimeter screen, the flashing symbol appears at the bottom right, see opposite). If the setting window does not appear as expected, check the connections. If necessary, switch off the multimeter and switch it on again, and the same with the laptop.

As for the Yoctopuce voltmeter, it starts up immediately after the connections are made.

1.3. Once the drop of solution has been inserted between the frit of the junction tube and the metal surface, click on the 

button of the "DiscoveryMat" software settings window (it is better to wait a few seconds to ensure that the multimeter is correctly driven by the software).

The corrosion potential versus time plot then appears on the screen in Figure 4.

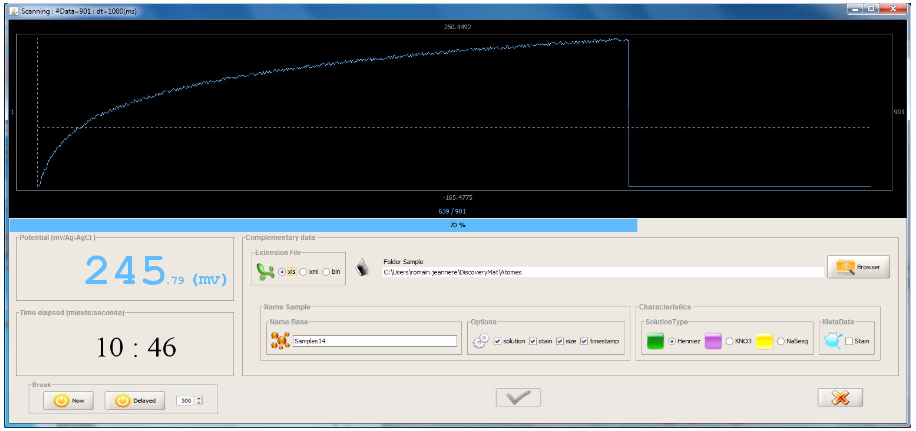
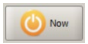
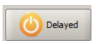


Fig. 4: Visualisation of the monitoring of the corrosion potential versus time.

The plot is in the upper part of the window. At the bottom left, the measured potential (mV/relative to the potential of the Ag-AgCl reference electrode) is shown in blue and the elapsed time (seconds) is shown in black. The x-axis is represented by the blue cursor below the plot. Specify at the bottom of the window in which format you wish to recover the data (Excel (xls) or other), the name of the file (if no name is proposed, the software automatically gives the name Sample, the year, the number of the plot as it is carried out, the time, the test solution and number of measurement points), its destination (recording folder), the nature of the solution considered and the presence (or not) of a stain left by the solution during the measurement (this last piece of information can be corrected at the end of the measurement). In the Options box, tick the information (nature of the solution, number of points on the plot, date and time of the measurement, presence or absence of a stain) that you wish to associate with the name of the Sample. The first measurement is carried out over 5 minutes (300s, i.e. 300 measurement points). After 5 minutes, click on the 

button or on 

button, once you have inserted the number 300 in the box on the right.

1.4. The save plot window appears - Fig. 5:

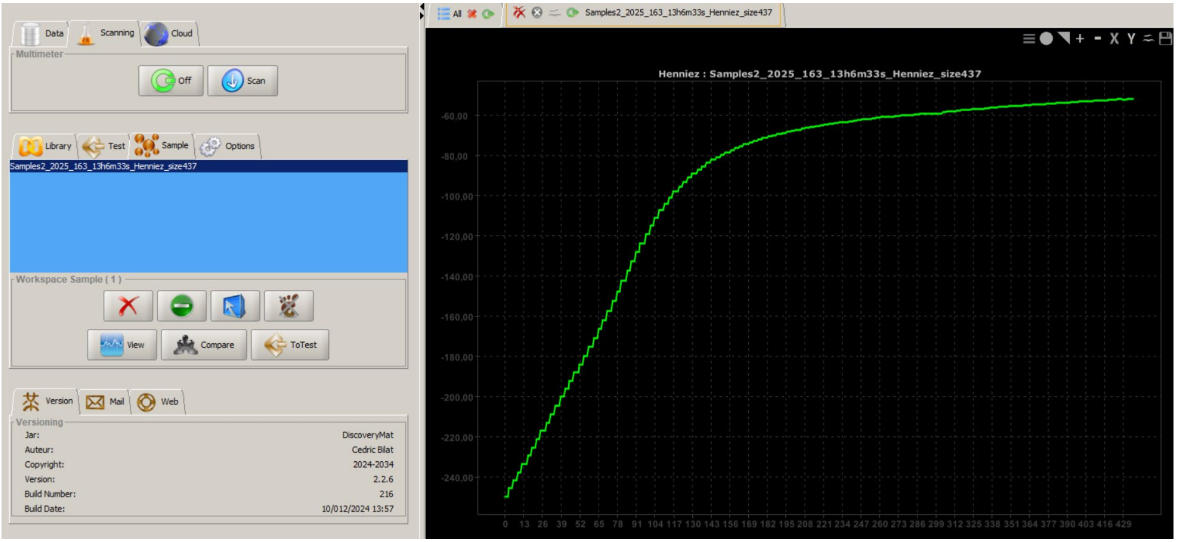
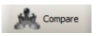


Fig. 5: Saving of the 1st plot made on 5min.

The plot name appears in the Sample workspace (blue area of the settings window). Note that the plot is saved in the hard disk folder mentioned above.

1.5. Cleaning the measuring system

After wiping the surface of the metal with an absorbent paper, observe it to detect or not the presence of a stain left by the tested solution and repeat the previous steps in order to carry out the 2nd plot over 5 minutes. At the end of the measurement, highlight the 2 plots made over 5 minutes and click on the 

button to assess the reproducibility of the plots obtained (Fig. 6).

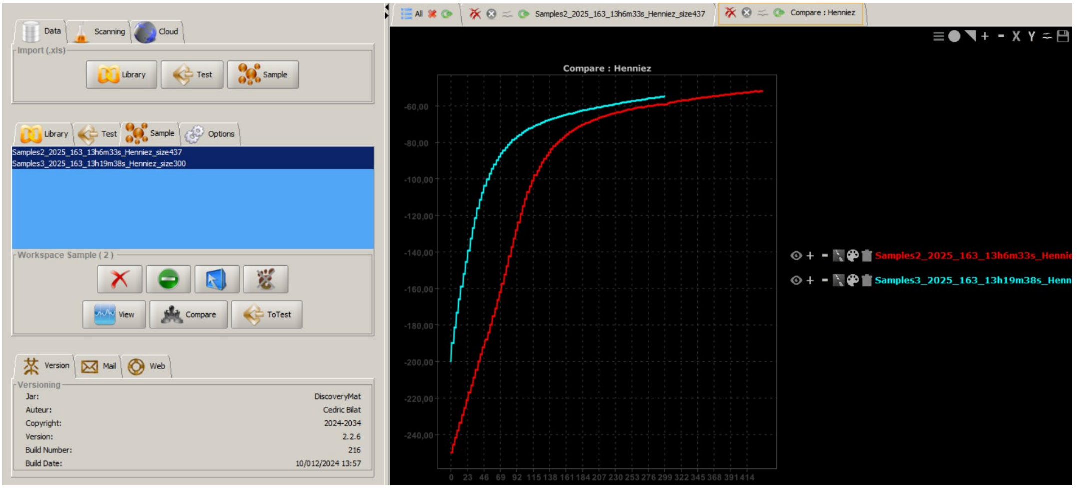
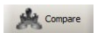


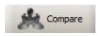
Fig. 6: Comparison of two plots to check their reproducibility.

Note the possibility to modify the characteristics of each plot (thicker, thinner, dashed points, colour)

1.6. Cleaning the measuring system and repeating the previous steps in order to carry out the 3rd plot

If the potential values written down are similar (to within 5-10mV) to the previous ones (which are themselves identical), continue with the 15min plot.

At the end of the measurement, highlight the 3 plots made and click on the  button to evaluate the reproducibility of the plots.

If during the 5 minutes of measurement the potential values are different from the previous ones (themselves identical or not), stop the measurement at 5 minutes, validate the non-reproducibility of the measurements by clicking on the  button and repeat the measurements again. If during the 4th plot the potential values are again different but within the range defined by the values of the 3 previous plots, continue the plot until 15min (Fig. 7).

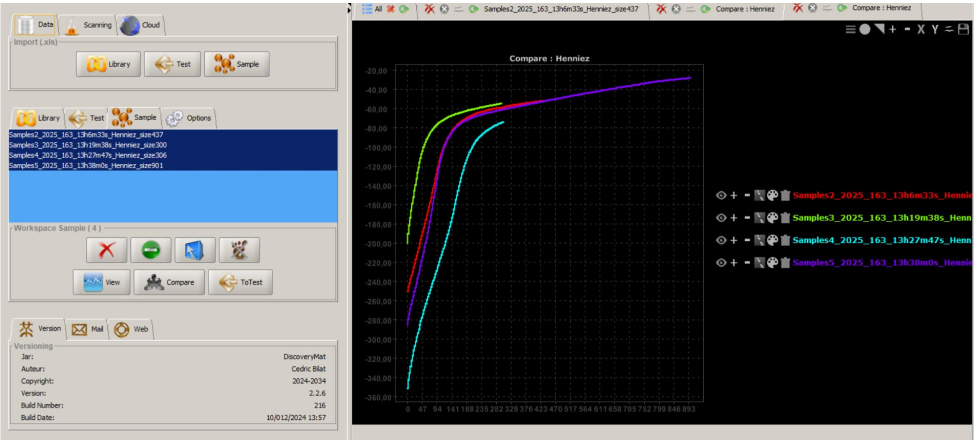


Fig. 7: Comparison of four plots to check their reproducibility.

If the potential values are different from the previous plots and outside the range defined by these same plots, a decision can be made to perform a 5th plot. Any new plot must be obtained by highlighting previous plots, to make it easier to compare the different plots. The new plot shows up as the “Live” plot (Fig. 8).

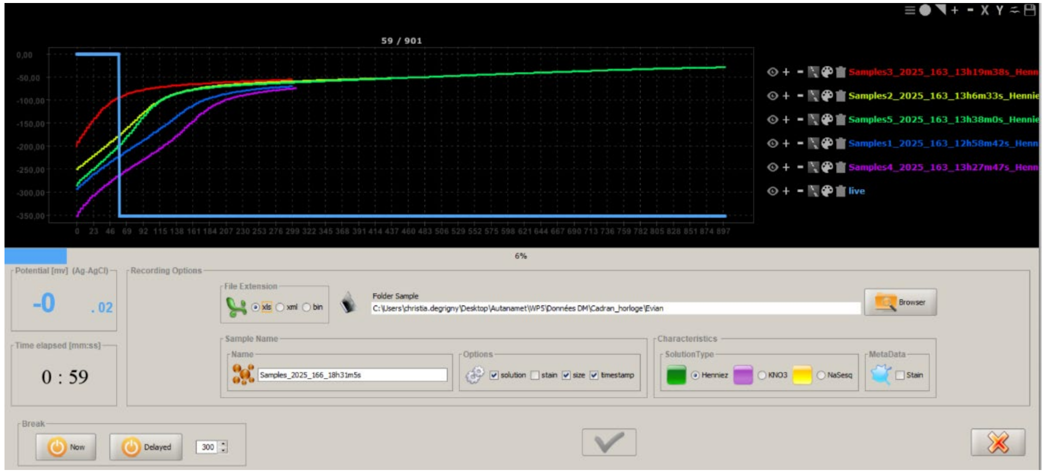


Fig. 8: Plotting of a new plot (Live) and comparison with the previous plots to check their reproducibility.

1.7. Selection of the 15-minute plots in the Sample workspace of the settings window from the set of plots obtained in each of the 3 solutions considered for the metal of unknown composition tested using the Ctrl key on the laptop keyboard and transfer to the Test folder by clicking on the ToTest button (Fig. 9).

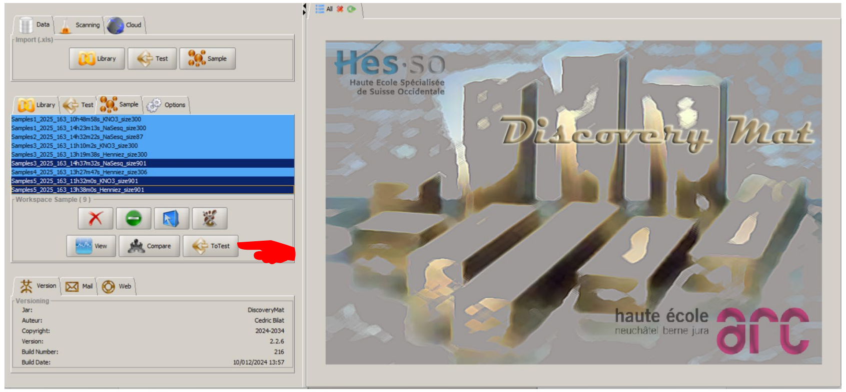


Fig. 9: Selection in the workspace Sample of the 3 plots over 15min. of the unknown metal being tested.

1.8. The test material

A new window opens (Fig. 10). Here again, specify the format in which you wish to save the data, the saving folder, the name of the Test material associated or not with the date and time of compilation of the plots (Options box) and the 3 characteristics (existence or not of a horizontal shift between the plots made in the same solution (2 plots 5 min and 1 plot 15 min), fluctuations or not of the potentials and presence or not of a stain) of the plots in the 3 solutions considered. Use the Compare files for the 3 solutions to help you. Once the data has been filled in, click on the button.

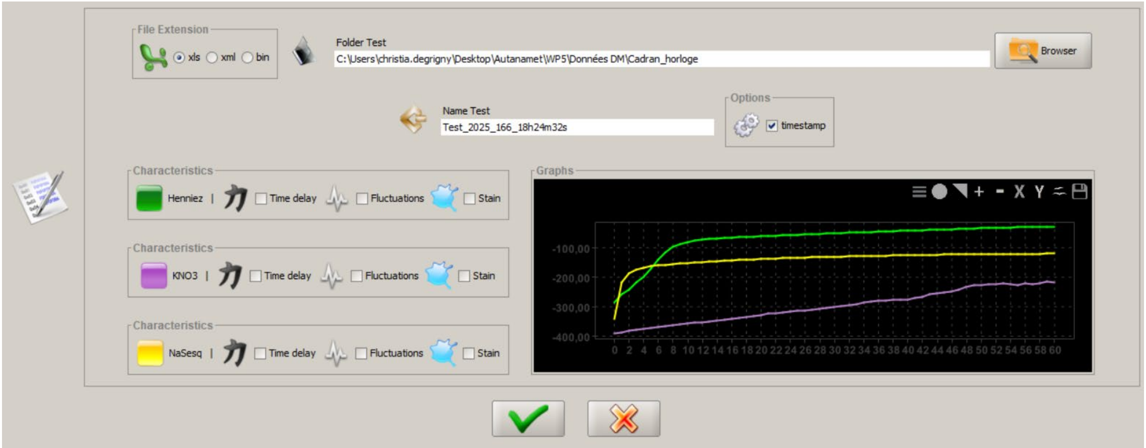


Fig. 10: Recording of the compilation of the three plots of the unknown metal tested, their characteristics and a rough visualisation of all the plots.

The window shown in figure 11 appears with the name of the Test material in the Test workspace in the settings window and on the right its plots in the three solutions considered with the box indicating the characteristics of the plots at the bottom right.

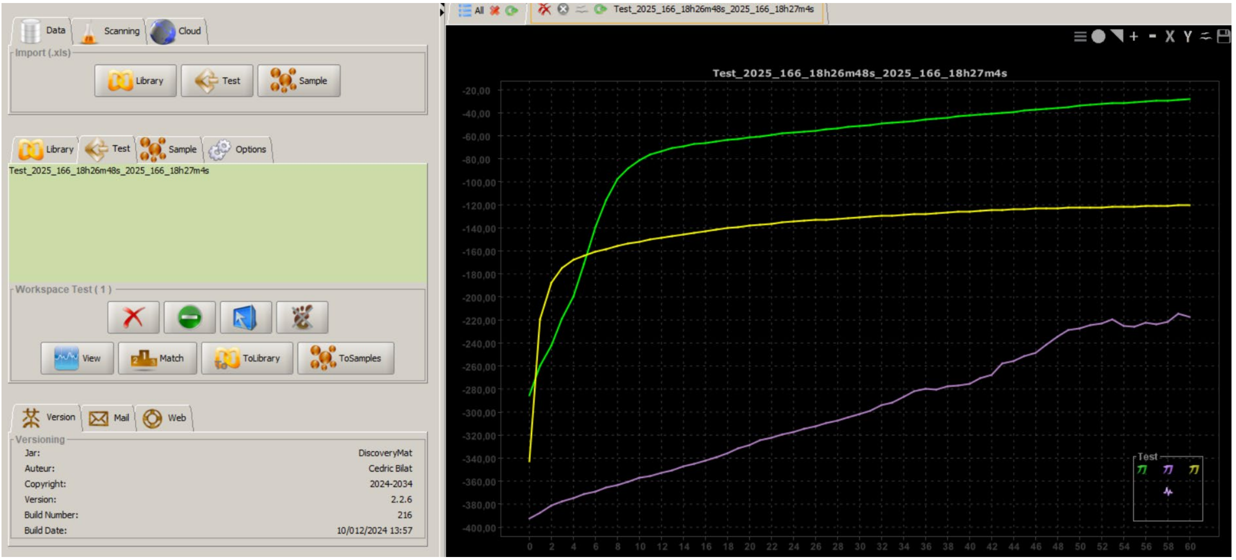


Fig. 11: Visualisation of the three plots of unknown metal tested and their characteristics.

1.9. Important remarks

Start the measurements with neutral solutions (Henniez / Evian water or KNO3) and continue with sodium sesquicarbonate (the reference electrode may be affected by the pH of the solution, especially for alkaline solutions). Record the pH and conductivity values of the solution tested (a new solution is prepared daily) and compare them with the values usually obtained:

Solutions	pH	Conductivity (µS/cm-1)
Henniez / Evian water	7.55 ± 0.25	640 ± 90
KNO3 1% (w/v)	6.6 ± 0.6	$12 \pm 0.8 \times 10^3$
Sodium sesquicarbonate de 0.44NaHC+0.21Na2Cg/100mL	9.6 ± 0.25	$7.2 \pm 1 \times 10^3$

Before each measurement on a new material, make a preliminary blank with a copper coupon and check that the plot obtained (over 5 minutes) corresponds to the previous plots obtained by yourself. The plot in NaSesq medium is the most reproducible and that in KNO3 medium the least. The order of magnitude of the potentials is shown below:

Solutions	Starting potentials vs the Ag/AgCl RE (0.2V/ENH)	Potentials after 5min. versus the Ag/AgCl RE
Henniez / Evian water	-70 à -30	-10 à +10 (with some variations)
KNO3 1% (w/v)	-80 à -10	+30 à + 50 (avec de nombreux écarts)
Sodium sesquicarbonate (NaSesq) 0.44NaHC+0.21Na2Cg/100mL	-170 à -130	-85 à -75 (avec quelques écarts)

Change the solution in the junction tube every 3 hours (beyond this time, problems have been observed with pollution of the solution in the junction tube by that contained in the RE).

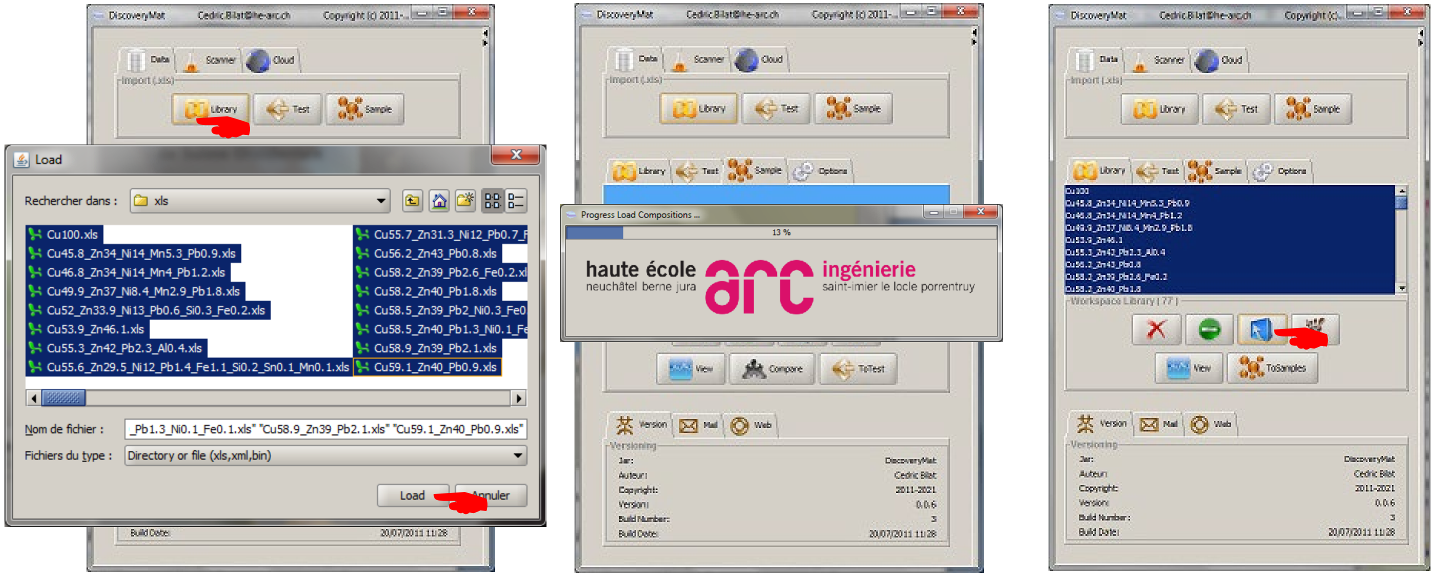
Always make the 3, 4 or 5 plots with the same solution and the same material in succession to limit the problems of lack of reproducibility due to the variation of the operating conditions.

2. Processing of the plots obtained

The operator starts from data obtained automatically and processed as above.

Selection of the database to identify the Test material. Click in the settings window on the 

button and download the selected database from the laptop by clicking on the corresponding folder and selecting the files to be considered (Fig. 12a). The download % window appears (Fig. 12b). When the download is complete, the database files appear in the settings window. Select them all by clicking on  button (Fig. 12c).

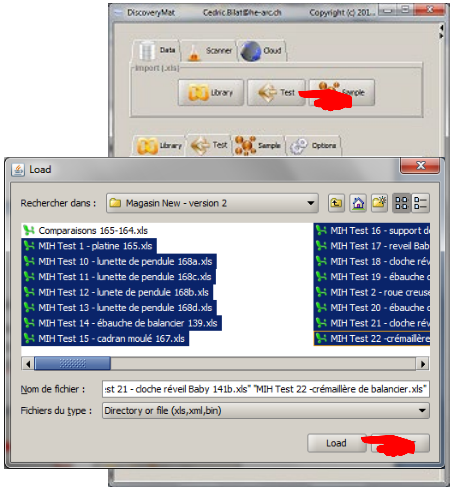


a/ b/ c/

Fig. 12: Control operations for downloading database files from the laptop to the Library workspace.

2.1. Selection of the Test material (file obtained by automatic data collection (Fig. 13) by clicking on the 

button – Fig. 13a. If there is more than one Test material, the material to be analysed more specifically is highlighted (Fig. 13b).


a/

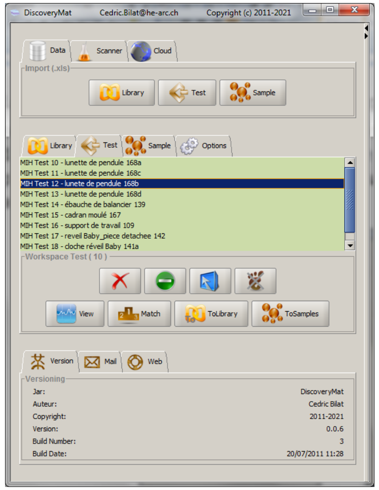

b/

Fig. 13: Control operations for downloading a test material file from the laptop into the Test workspace.

2.2. Comparing the plots of the test material with those of the materials in the database by clicking on 

button Fig. 14).

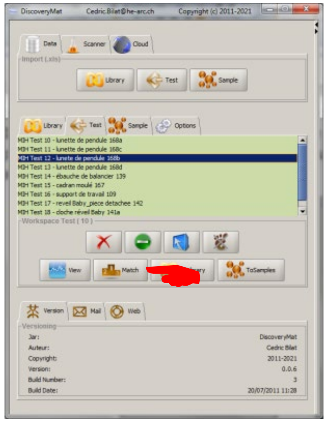
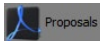
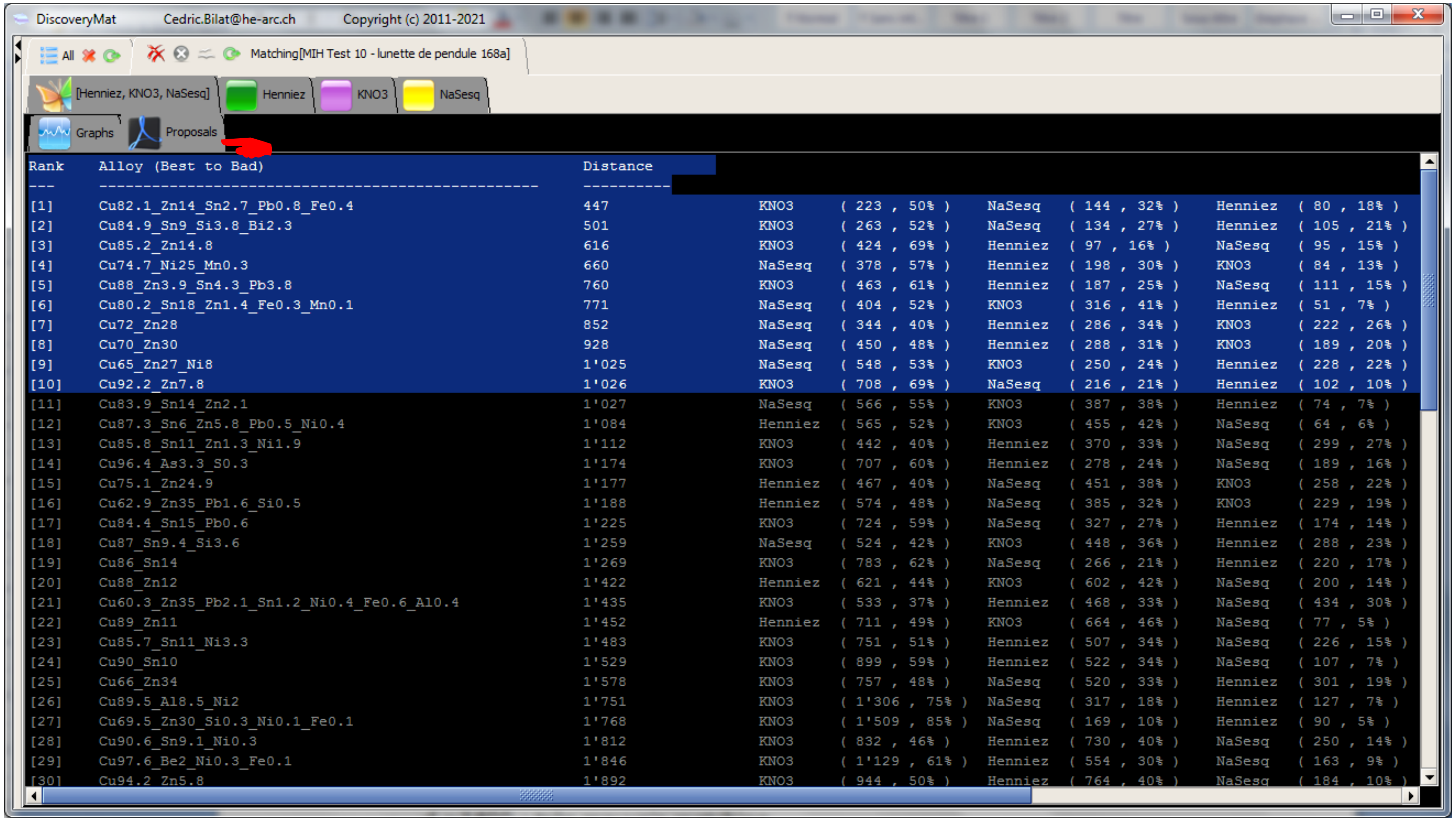


Fig. 14: Control operation of the comparison of the plots of the unknown metal tested with those of the materials in the selected database.

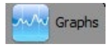
2.3. The graphical interface shows two types of information: the proposal of compositions based on the calculation of distances between the different plots (click on the 

on the right-hand window of the graphical interface). The smaller the distances indicated, the more plausible the matching. Thus proposal 1 in the list is the most plausible, the last the least (Fig. 15).



Rank	Alloy (Best to Bad)	Distance						
[1]	Cu82.1_Zn14_Sn2.7_Pb0.8_Fe0.4	447	KNO3	(223 , 50%)	NaSesq	(144 , 32%)	Henniez	(80 , 18%)
[2]	Cu84.9_Sn9_Si3.8_Bi2.3	501	KNO3	(263 , 52%)	NaSesq	(134 , 27%)	Henniez	(105 , 21%)
[3]	Cu85.2_Zn14.8	616	KNO3	(424 , 69%)	Henniez	(97 , 16%)	NaSesq	(95 , 15%)
[4]	Cu74.7_Ni25_Mn0.3	660	NaSesq	(378 , 57%)	Henniez	(198 , 30%)	KNO3	(84 , 13%)
[5]	Cu88_Zn3.9_Sn4.3_Pb3.8	760	KNO3	(463 , 61%)	Henniez	(187 , 25%)	NaSesq	(111 , 15%)
[6]	Cu80.2_Sn18_Zn1.4_Fe0.3_Mn0.1	771	NaSesq	(404 , 52%)	KNO3	(316 , 41%)	Henniez	(51 , 7%)
[7]	Cu72_Zn28	852	NaSesq	(344 , 40%)	Henniez	(286 , 34%)	KNO3	(222 , 26%)
[8]	Cu70_Zn30	928	NaSesq	(450 , 48%)	Henniez	(288 , 31%)	KNO3	(189 , 20%)
[9]	Cu65_Zn27_Ni8	1'025	NaSesq	(548 , 53%)	KNO3	(250 , 24%)	Henniez	(228 , 22%)
[10]	Cu92.2_Zn7.8	1'026	KNO3	(708 , 69%)	NaSesq	(216 , 21%)	Henniez	(102 , 10%)
[11]	Cu83.9_Sn14_Zn2.1	1'027	NaSesq	(566 , 55%)	KNO3	(387 , 38%)	Henniez	(74 , 7%)
[12]	Cu87.3_Sn6_Zn5.8_Pb0.5_Ni0.4	1'084	Henniez	(565 , 52%)	KNO3	(455 , 42%)	NaSesq	(64 , 6%)
[13]	Cu85.8_Sn11_Zn1.3_Ni1.9	1'112	KNO3	(442 , 40%)	Henniez	(370 , 33%)	NaSesq	(299 , 27%)
[14]	Cu96.4_As3.3_S0.3	1'174	KNO3	(707 , 60%)	Henniez	(278 , 24%)	NaSesq	(189 , 16%)
[15]	Cu75.1_Zn24.9	1'177	Henniez	(467 , 40%)	NaSesq	(451 , 38%)	KNO3	(258 , 22%)
[16]	Cu62.9_Zn35_Pb1.6_Si0.5	1'188	Henniez	(574 , 48%)	NaSesq	(385 , 32%)	KNO3	(229 , 19%)
[17]	Cu84.4_Sn15_Pb0.6	1'225	KNO3	(724 , 59%)	NaSesq	(327 , 27%)	Henniez	(174 , 14%)
[18]	Cu87_Sn9.4_Si3.6	1'259	NaSesq	(524 , 42%)	KNO3	(448 , 36%)	Henniez	(288 , 23%)
[19]	Cu86_Sn14	1'269	KNO3	(783 , 62%)	NaSesq	(266 , 21%)	Henniez	(220 , 17%)
[20]	Cu88_Zn12	1'422	Henniez	(621 , 44%)	KNO3	(602 , 42%)	NaSesq	(200 , 14%)
[21]	Cu60.3_Zn35_Pb2.1_Sn1.2_Ni0.4_Fe0.6_Al0.4	1'435	KNO3	(533 , 37%)	Henniez	(468 , 33%)	NaSesq	(434 , 30%)
[22]	Cu89_Zn11	1'452	Henniez	(711 , 49%)	KNO3	(664 , 46%)	NaSesq	(77 , 5%)
[23]	Cu85.7_Sn11_Ni3.3	1'483	KNO3	(751 , 51%)	Henniez	(507 , 34%)	NaSesq	(226 , 15%)
[24]	Cu90_Sn10	1'529	KNO3	(899 , 59%)	Henniez	(522 , 34%)	NaSesq	(107 , 7%)
[25]	Cu66_Zn34	1'578	KNO3	(757 , 48%)	NaSesq	(520 , 33%)	Henniez	(301 , 19%)
[26]	Cu89.5_Al8.5_Ni2	1'751	KNO3	(1'306 , 75%)	NaSesq	(317 , 18%)	Henniez	(127 , 7%)
[27]	Cu69.5_Zn30_Si0.3_Ni0.1_Fe0.1	1'768	KNO3	(1'509 , 85%)	NaSesq	(169 , 10%)	Henniez	(90 , 5%)
[28]	Cu90.6_Sn9.1_Ni0.3	1'812	KNO3	(832 , 46%)	Henniez	(730 , 40%)	NaSesq	(250 , 14%)
[29]	Cu97.6_Be2_Ni0.3_Fe0.1	1'846	KNO3	(1'129 , 61%)	Henniez	(554 , 30%)	NaSesq	(163 , 9%)
[30]	Cu94.2_Zn5.8	1'892	KNO3	(944 , 50%)	Henniez	(764 , 40%)	NaSesq	(184 , 10%)

Fig. 15: List of proposed compositions of the unknown metal tested proposed by the "DiscoveryMat" software.

2.4. The second type of information consists of graphs that allow you to better appreciate the difference in appearance between the plots of the Test material and those of the materials in the database (click on the 

button on the right-hand window of the software – Fig. 16).

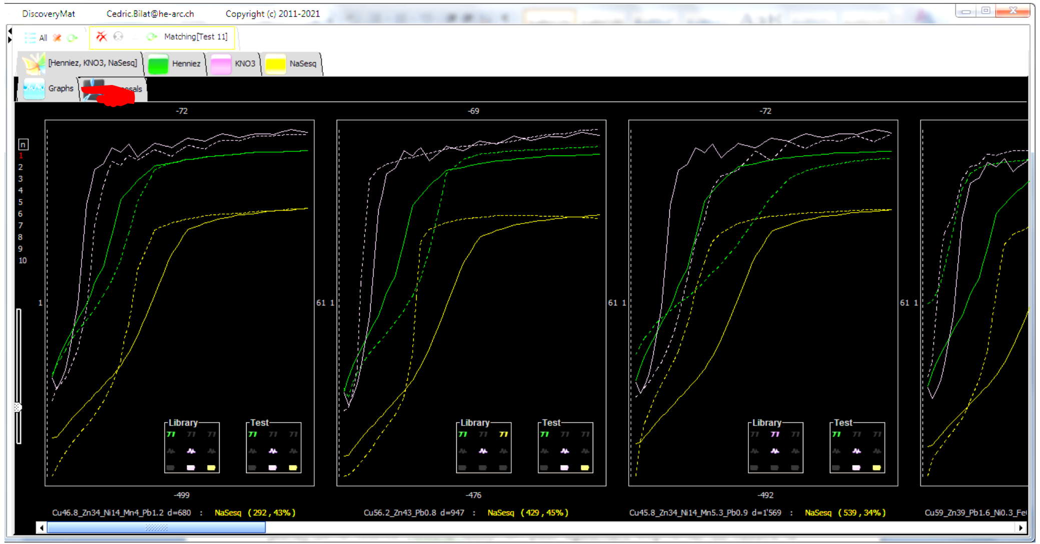


Fig. 16: Visual comparison of the plots of the unknown material tested with those of each of the materials in the selected database.

There are several options for viewing a selection of plots or all of them. The plots can also be zoomed in (see the "Discovery Mat software user manual" file).

In addition to the plots, there are boxes in the bottom right-hand corner for each proposal giving the characteristics mentioned above (horizontal shift between the plots, fluctuations of potentials in the plots and presence or absence of a stain), which make it possible to refine the comparison between the Test material and the material considered in the selected database.

2.5. At the end of this analysis and of the preliminary condition report carried out on the unknown material, the operator is in a position to make proposals for composition.