REVIEW

Use of E_{corr} vs time plots for the qualitative analysis of metallic elements from scientific and technical objects: the SPAMT Test Project

**Christian Degrigny · Geoffroy Guibert ·
Stephan Ramseyer · Guillaume Rapp · Antonin Tarchini**

Abstract A new analytical tool for copper alloys based on the monitoring of E_{corr} vs time is presented. This tool is particularly adapted to condition surveys carried out on-site by conservators on historic objects and was optimised so to respond to the needs of the conservation field such as the minimal impact on the artefacts, the portability of the instruments and its ease to use. A database constituted of 66 reference alloys representative of the materials found on technical artefacts with their electrochemical behaviour in three different solutions (Henniez mineral water, KNO_3 and sodium sesquicarbonate) was realised. The validation of the tool and the relevance of the database were assessed on two Swiss collections of technical, scientific and horology artefacts.

Keywords Corrosion potential monitoring ·
Qualitative analysis · Copper-based alloys ·
Technical objects · Scientific objects · Horology objects

C. Degrigny (✉) · G. Rapp · A. Tarchini
Haute Ecole de Conservation-restauration Arc,
60, rue de la Paix,
2300 La Chaux-de-Fonds, Switzerland
e-mail: christian.degrigny@he-arc.ch

G. Guibert · S. Ramseyer
Haute Ecole Arc Ingénierie,
Institut des microtechnologies appliquées IMA-Arc,
NEODE / Eplatures grise 17,
2300 La Chaux-de-Fonds, Switzerland

Introduction

Conservators use a quite empirical way to determine the composition of archaeological and historic metal objects when examining them. It is based on the shape of the artefact, its condition state and the nature and colour of corrosion products. To confirm their hypothesis and in the absence of any analytical tool, they use spot tests [1]. Quite corrosive chemicals (acids, chelating agents) are employed. Furthermore, interference problems between metallic species might occur and a thorough cleaning of the metal after the test is required.

Qualitative analyses of artefacts are often needed during the condition survey carried out on-site. The validity of the condition survey depends on these analyses as well as on the definition of the conservation treatment. This is particularly true for technical objects which are often constituted of several metallic elements of different compositions that are not always dismountable and require interventions that are not always compatible to each other. As usual in conservation, the best option is to have at disposal an easy-to-use, non invasive, portable and not a costly instrument that can give almost immediately a preliminary idea of the composition of the materials.

These issues have been at the origin of the SPAMT Test[1] Project. The main objective was to assess the possibilities of a new analytical tool adapted to the preliminary diagnosis of scientific, technical and horology objects. The principle is simple since it consists in measuring the potential (E_{corr}) taken by a metal artefact when a drop of

---

[1] SPAMT stands for Suivi du Potentiel d'Abandon des Métaux au cours du Temps.

solution (non-aggressive towards the material) is deposited on its surface and to monitor it vs time. A clean metal surface representative of the metal core is required as well as a reference electrode with the tip in contact with the drop. Both the metal and the reference electrode are connected to a voltmeter measuring the potential difference on a short period of time (5 to 15 min). The plot obtained is characteristic of the electrochemical behaviour of the material considered in this solution.

Within the SPAMT Test Project, a large number of reference materials (with known compositions) were used to plot E_{corr} vs time curves in different solutions. These results were compiled in a database that could be used for the qualitative analysis of any unknown metallic material whose electrochemical plots are close to those of the materials of the database. This technique was first tested and optimised in laboratory conditions on reference copper-based alloys that are often encountered in collections of technical objects. It was then validated on a group of objects representative of two collections of scientific, technical and horology objects.

Background and the methodology of the SPAMT Test Project

Recent studies carried out between 2004 and 2007 have shown the possibilities of E_{corr} vs time plots for the preliminary diagnosis of copper-based metals [2]. These studies performed first on brass alloys and then on 16 reference copper-based alloys indicated that the materials considered have a specific electrochemical behaviour in certain solutions like sodium sesquicarbonate and a common mineral water (Maltese origin for these preliminary tests). Sodium sesquicarbonate is commonly used by conservators for the stabilisation of active copper-based artefacts since the 1970s [3] and is known to passivate clean copper-based alloys. Mineral water, although having a low ionic strength that makes measurements less reproducible and a composition slightly different from one trademark to another, is cheap, safe and easily available.

The results obtained were quite promising since it was possible to differentiate one material from another, but several problems were noted:

- The variety of copper-based materials found on archaeological and historic objects is such that the electrochemical behaviour of the different materials of the main families of alloys is requested to produce a trustful database.
- The reproducibility of the results depends greatly on the preparation of the materials surface and then on the

operator. Therefore, a detailed experimental protocol must be defined to get reproducible results not only between two measurements but also between two operators. Besides, the level of reproducibility must be assessed to determine precisely the range of errors considered as acceptable between several measurements.

- Plots obtained on different materials in the same solution are sometimes so close to each other that errors of diagnosis might occur. The use of a third solution in addition to sodium sesquicarbonate and common mineral water should precise the electrochemical behaviour of the copper-based alloys listed in the database and refine then the diagnosis.
- The plots are obtained on bare or slightly oxidised metal surfaces. The technique developed cannot be used on objects covered partly or fully with thick corrosion layers (archaeological context). The presence of an artificially or naturally formed patina brings additional problems since these ones are often aesthetical and should not be damaged by the solutions considered within these tests.

The SPAMT Test Project was set up to respond to some of these questions. It comprised the following steps:

- Collection and analysis of 66 copper-based reference materials and electrochemical testing of the third solution selected
- Production of the database (plotting of E_{corr} vs time for the 66 reference materials in the three solutions selected) set up of a precise procedure for the collection of data and reproducibility tests (carried out between the different members of the research team)
- Application of the technique developed to the qualitative analysis of a group of ten objects representative of scientific, technical and horology collections (plotting of E_{corr} vs time curves, comparison with the results of the database, composition(s) proposal and checking through the noninvasive analysis of the objects)

Collection and analysis of reference materials

Copper-based standard reference materials can be purchased but their cost is in most cases prohibitive, at least within the SPAMT Test Project.[2] Furthermore, they do not correspond fully to the materials traditionally found on heritage objects. We collected then several materials from

---

[2] BAM certified reference materials (http://www.bam.de/pdf/service/referenzmaterialien/crm_catalogue.pdf. Accessed 17June 2009); Goodfellow standards (https://www.goodfellow.com/pdf/2906_1111010.pdf. Accessed 17 June 2009) and Swissmetal materials (http://www.swissmetal.com/fr/products-services/products/alloys.html. Accessed 17 June 2009).

colleagues involved in national, European and international research projects and programmes on the diagnosis and conservation of archaeological and historic copper-based artefacts. The list is given below:

– A series of four alloys (Cu/As, brass, lead bronze and quaternary bronze) produced within the European IMMACO [4] project and representative of metals used in Europe from the Bronze Age to the Roman period
– A series of bronze coupons produced within the European EUREKA E2210! BronzArt project [5] by the Venturi Arte foundry
– A series of one-phase tin bronzes produced by the Centre of Metallurgical Chemistry Studies of the Institute of Chemistry and Materials of East Paris (ICMPE-CECM, France)
– Other alloys lent by the National Institute of Nuclear Sciences and Techniques (INSTN, France), the research laboratory of the Victoria and Albert Museum (London, UK), the Canadian Conservation Centre (CCI, Ottawa, Canada), the Fraunhofer Institute for Silicate Research (ISC, Bronnbach, Germany) and the Swissmetal company (Switzerland)

Additional materials were provided by private collectors (PCs) and the collection of the Foundation of historic materials of the Swiss army HAM–Foundation HAM (Thun).

Table 1 gives a selection of 14 materials representative of the 66 reference materials finally considered. A more detailed table (Electronic supplementary material, Table S3) with all 66 materials is provided as supplementary information with the composition, when provided, in red. All materials on this list have been analysed (or reanalysed) by energy-dispersive spectroscopy associated to a scanning electron microscope (EDS-SEM–Jeol JSM 6400).[3] Our results (in black) are in most cases (except for coupon BronzArt 1) close to the compositions provided to us. It is noteworthy that the Swissmetal coupon indicated as CuZn16Si2Pb1 is in fact an aluminium–copper coupon of the following composition: CuAl11Ni1.5Fe1.2. Since no metallography study was carried out on the materials, only hypothesis on their microstructure could be done.

Experimental conditions for plotting E_{corr} vs time curves

The protocol defined previously [2] was optimised. Originally, both neutral 1% (w/v) Na_2SO_4 (pH=6.2–6.3) and

KNO_3[4] solutions (pH=5.7–6.2) commonly used in corrosion [6, 7] and conservation studies [8, 9] were assessed in addition to mineral water (Henniez[5], pH=7.4–7.8) and 1% (w/v) sodium sesquicarbonate[6] (pH=9.5–9.7) solution. Neutral KNO_3 solution only was finally considered due to the good reproducibility of the results and the specific (different) electrochemical behaviours obtained in comparison with the two other solutions. Preliminary tests were carried out on pure metal plates (Ag, Cu, Pb, Sn, Zn) and a brass (Cu 64/Zn 36) to precise the optimal conditions to get reproducible measurements. These tests showed that the reference electrode had to be inserted in a liquid junction protection tube[7] to prevent any diffusion of chlorides from the reference electrode in the drop of solution. Such diffusion could otherwise provoke some disruption of the curve corresponding to particular corrosion phenomena. The protection tube was filled with the same solution as the one of the drop (except for Henniez water where a more conductive solution (KNO_3) was used instead) and the potentials measured with a high-resistance multimeter.[8]

The following protocol of measurement was finally considered and is illustrated on Fig. 1:

– Checking of the reference electrode (RE, with a new reference electrode) and rinsing with fresh deionised water
– Stirring of the test solution, rinsing of the junction protection tube (JPT) with it (except for Henniez water where KNO_3 is used instead) and filling
– Overtightening of the RE in the JPT with Teflon sealing tape (the tip of the RE is at 5 mm from the membrane of the JPT) 30 min before the starting of the measurements to get a stable system
– Handling of coupons with latex or vinyl gloves
– Polishing of the metallic surfaces before each test with a new Struers 4000 paper. Drying of the coupons held vertically with alcohol (from the top to the bottom, starting on the side tested)
– Positioning of the system RE/JPT at 2 mm from the metal surface

---

[3] Analysis conditions: beam current, 1 nA; acceleration voltage, 25 kV; starting angle, 35–40°; tilt angle, 0°; azimuth angle, 45°; surface analysed from 100 × 200 μm to 10 × 10 mm.

[4] Merck (http://www.merck.de. Accessed 17 June 2009) product. Conductivity comprised between 11.7 and 12.4 S.
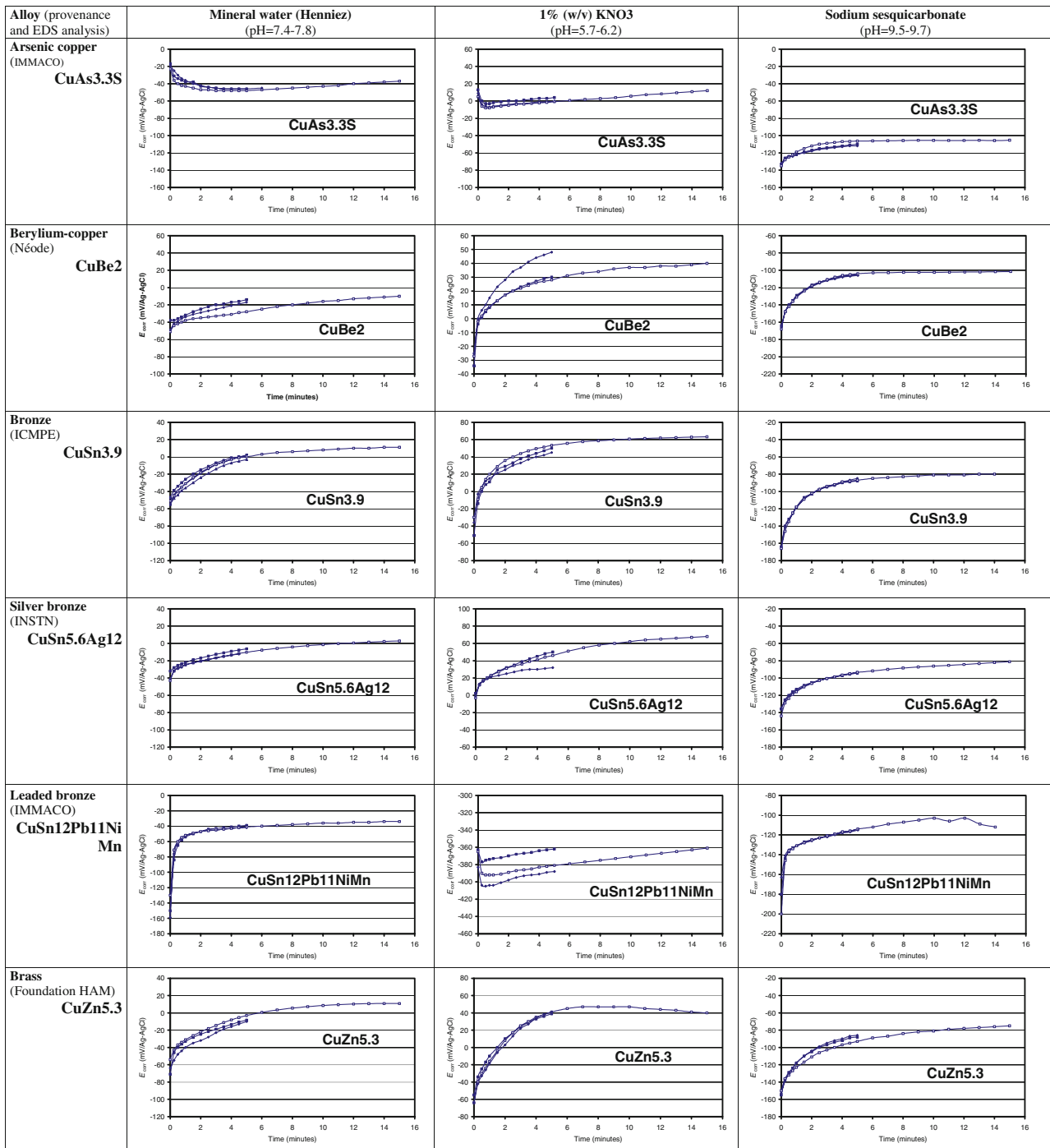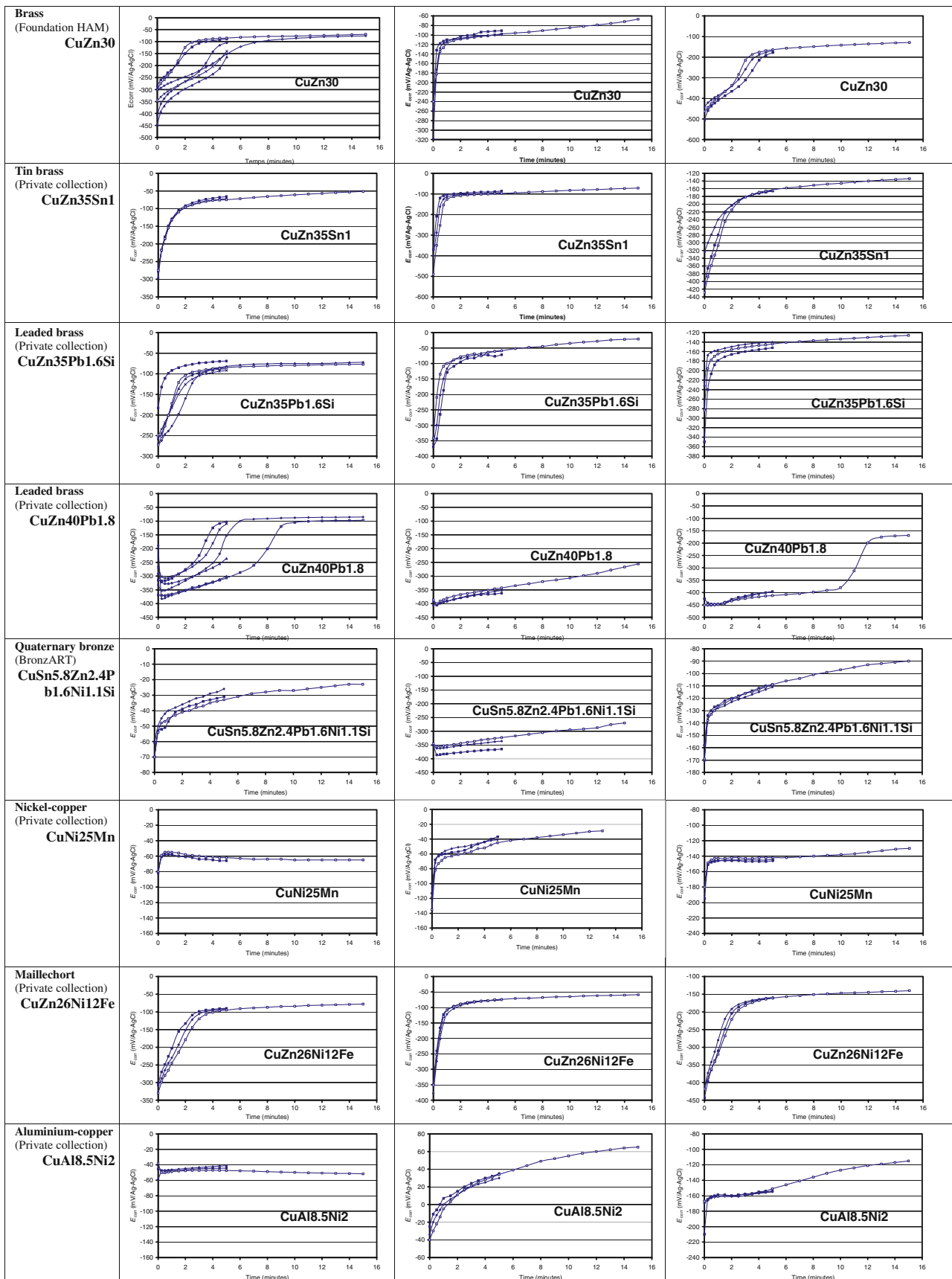
[5] Containing 106 ppm Ca; 19 ppm Mg; 7 ppm Na and 1 ppm K with a conductivity comprised between 610 and 670 mS. More information is available on the Henniez website (http://www.henniez.ch. Accessed 17 June 2009).

[6] Equimolar mixture of $NaHCO_3$ and Na_2CO_3, Merck). Conductivity comprised between 7.2 and 7.5 S.

[7] Radiometer AL100 (http://www.radiometer-analytical.com/en_volta lab_electrodes.asp. Accessed 17 June 2009).

[8] Mhit 1+ (Gossen Metrawatt, www.gossenmetrawatt.com/. Accessed 17 June 2009) certified according to the protocol DKD-K-19701 under the accreditation of the Deutsches Kalibrierdienst (DKD).

Table 1 E_{corr} vs time plots of a selection of copper-based alloys in the three solutions considered

Alloy (provenance and EDS analysis)	Mineral water (Henniez) (pH=7.4-7.8)	1% (w/v) KNO3 (pH=5.7-6.2)	Sodium sesquicarbonate (pH=9.5-9.7)
Arsenic copper (IMMACO) **CuAs3.3S**	CuAs3.3S	CuAs3.3S	CuAs3.3S
Berylium-copper (Néode) **CuBe2**	CuBe2	CuBe2	CuBe2
Bronze (ICMPE) **CuSn3.9**	CuSn3.9	CuSn3.9	CuSn3.9
Silver bronze (INSTN) **CuSn5.6Ag12**	CuSn5.6Ag12	CuSn5.6Ag12	CuSn5.6Ag12
Leaded bronze (IMMACO) **CuSn12Pb11NiMn**	CuSn12Pb11NiMn	CuSn12Pb11NiMn	CuSn12Pb11NiMn
Brass (Foundation HAM) **CuZn5.3**	CuZn5.3	CuZn5.3	CuZn5.3

- Stirring of the test solution and application of the drop (40 μL) with a syringe (rinsed before with the solution) in between the JPT and the metal surface
- E_{corr} measurement on a period of 5 min and/or 15 min
- Change of the solution in the JPT every 3 h and monitoring of the pH and conductivity of the solutions before and after the tests

The impact of the measurements on the materials tested is minimal. No trace was left by Henniez water and only Pb was stained by sodium sesquicarbonate. The KNO$_3$ solution left marks on Pb, Cu and brass.

Between each series of measurements (3 h of measurements), the JPTs were filled with the testing solution and inserted themselves in tubes containing the same solution.
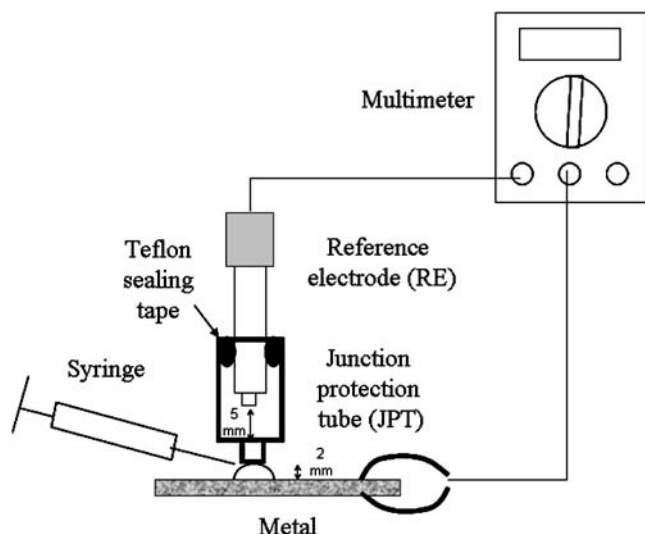
Table 1 (continued)

Brass (Foundation HAM) **CuZn30**			
Tin brass (Private collection) **CuZn35Sn1**			
Leaded brass (Private collection) **CuZn35Pb1.6Si**			
Leaded brass (Private collection) **CuZn40Pb1.8**			
Quaternary bronze (BronzART) **CuSn5.8Zn2.4Pb1.6Ni1.1Si**			
Nickel-copper (Private collection) **CuNi25Mn**			
Maillechort (Private collection) **CuZn26Ni12Fe**			
Aluminium-copper (Private collection) **CuAl8.5Ni2**			

Fig. 1 Experimental conditions for E_{corr} measurements: the system RE/JPT is positioned 2 mm from the metal surface and the drop of solution is applied with a syringe. The E_{corr} monitoring starts as soon as the drop is in contact with the metal surface

Fig. 2 Electric contacts between the objects and the crocodile clamp: directly on the object protected locally with an aluminium foil (**a**) and indirectly with a conductive material inserted in the object and to which the crocodile clamp is attached (**b**)

Furthermore, each series of measurements was preceded and terminated by an E_{corr} vs time plot on a reference metal surface so to check that the plots obtained in between the 3 h of testing were correct. Copper was used because of the very good reproducibility of the results obtained.

Constitution of the database: results

The conditions of the electrochemical measurements being established, the E_{corr} vs time plots were carried out on the 66 reference materials with the three solutions considered. Due to the complex shapes of the materials, the electric contacts were adapted from one object to another (see Fig. 2).

Practically, the whole series of plots on the 66 materials were performed with the same solution before moving to the two others. We studied first the binary alloys (tin bronzes, brasses, nickel–copper and aluminium–copper) and continued then with the ternary and quaternary alloys. For each family of alloys, we considered first the alloy with the lower concentration of the added element and studied then the next alloy listed on Electronic supplementary material, Table S3. By doing so, we had a good understanding of the effect of each element on the other and could easily detect any anomaly in the plots that would require repeating the test.

When reproducible results (a difference of max. 5 mV is accepted between each plot) were obtained on two plots carried out on a period of 5 min and one plot on 15 min, we moved to the next coupon. The following materials, CuAs3.3S (IMMACO), CuSn3.9 (ICPME), CuZn5.3
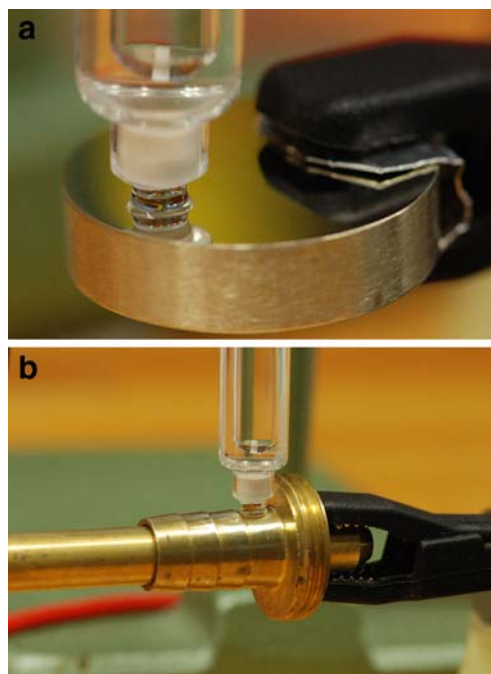
(HAM), CuZn35Sn1 (PC), CuNi25Mn (PC), CuZn26-Ni12Fe (PC) and CuAl8.5Ni2 (PC), whose electrochemical behaviour in mineral Henniez water (HW), KNO_3 and sodium sesquicarbonate (SS) is given in Table 1, are a good illustration of this approach. Results for CuBe2 (Néode), CuSn5.6Ag12 (INSTN), CuSn12Pb11NiMn (IMMACO) and CuSn5.8Zn2.4Pb1.6Ni1.1Si (BronzArt) are less reproducible but were still considered as acceptable. If problems of reproducibility were observed, the operator was changed and additional plots were realised to confirm that the lack of reproducibility was due to the specific composition of the material. The electrochemical behaviour of the following materials, CuZn30 (HAM), CuZn35Pb1.6Si (PC) and CuZn40Pb1.8 (PC), in the same solutions illustrates these problems.

At the end of this time-consuming work, it appeared that when we compared the electrochemical behaviours of the different alloys in the three solutions considered, they corresponded quite well to those expected from their composition (and microstructure) and predictions made from the theoretical Pourbaix diagrams [10]. This is particularly true for behaviours in KNO_3 and SS solutions for which the materials were either corroding or passivating on the Pourbaix diagrams. The theoretical behaviours in HW being more uncertain, it was not surprising to observe practically many differences with our preliminary hypothesis.

In the following, we have summarised the main trends observed on the reference materials tested, starting first with the binary alloys and continuing with more complex materials:

– E_{corr} vs time plots for binary bronzes and brasses show specific features. If in both cases we observe a passivation (increase of potential) behaviour in HW and SS (parallel plots with one (CuSn3.9, see Table 1) or two slopes (CuZn30 (see Table 1)), the behaviour is really different in KNO$_3$. Indeed, we observe first an increase of the potential (similar to the behaviour of pure Cu) for brasses with a Zn content inferior to 13 wt.% that is followed by a decrease after 10 min (CuZn5.3, see Table 1). Such a phenomenon is not observed on bronzes (see Fig. 3a). Beyond 7–10 wt.% Sn in bronzes and 30–35 wt.% Zn in brasses, a passivation in two steps is observed both in HW and SS (see Fig. 3b and Table 1 CuZn30). This might be due to the change of microstructure (one phase to two phases), but the first step is quick for bronzes whilst the second is slow, and the opposite is observed for brasses. In SS, E_{corr} obtained at 15 min decreases steadily with the concentration of Sn and Zn (see Fig. 4, with a different slope beyond 35 wt.% for Zn).
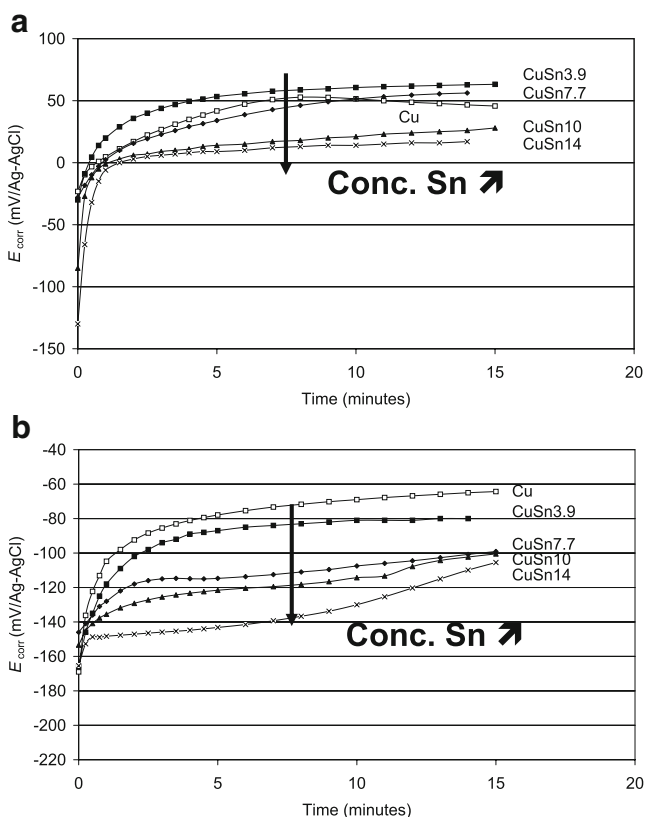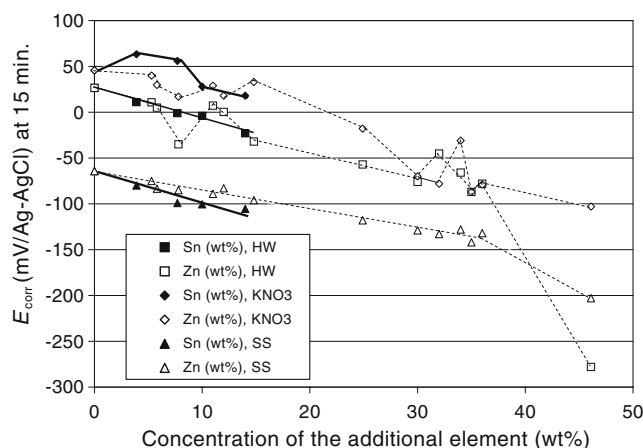

Fig. 4 E_{corr} vs concentration of the additional element (Sn or Zn wt. %) in HW, KNO$_3$ and SS

Such decrease appears less clearly in HW, at least with brasses and even less in KNO$_3$, particularly around 10% and beyond 30% of Zn.

– If the potentials continue increasing with time for bronzes in all solutions, they quickly reach (between 5 and 10 min) a stable value for brasses. When comparing the potentials in the different solutions, we have after 2 min for bronzes $E_{KNO3} > E_{EH} > E_{SS}$, whilst the same distribution is obtained for brasses after a longer period of time. E_{corr} vs time plots for Cu–As in KNO$_3$ solution and HW are specific: the potential decreases first and increases again (CuAs3.3 S, see Table 1). The Cu–Ni alloy studied corrodes in HW since its potential decreases steadily (CuNi25Mn, see Table 1). For the two latter alloys, the potentials are more negative than for Cu after 15 min.

– The addition of Ag to bronzes has almost no effect. Therefore, the presence of this element in these alloys is difficult to determine using the SPAMT Test measurements. On the other hand, the addition of tin to brasses with a Zn content superior to 35 wt.% seems to accelerate the passivation process, and the potentials in KNO$_3$ and HW are almost identical after 15 min. Similarly, the addition of Pb to the same materials tends to accelerate the passivation process in SS and HW, but this phenomenon is inverted when this concentration increases. Furthermore, the potentials of these alloys are constant in HW and SS after 12 min (between −75 and −103 mV/Ag–AgCl in HW (the values decreasing according the concentration of Zn (35 to 43 wt.%) and between −125 and −175 mV/Ag–AgCl in SS).

– The cumulative addition of Pb and Zn to binary bronzes gives immediately quite negative potentials (around −300 to −400 mV/Ag–AgCl) in KNO$_3$ (CuSn5.8Zn2.4Pb1.6Ni1.1Si, see Table 1), and a more or less slow passivation process is observed (depending

Fig. 3 E_{corr} vs time (15 min) for tin bronzes in KNO$_3$. Note the specific behaviour of Cu (a) and in sodium sesquicarbonate (b)

on the ratio C_{Pb}/C_{Zn}). For these alloys, the distribution of potentials in the three solutions is as follows: $E_{HW} > E_{SS} > E_{KNO3}$.

– The addition of Al to Cu–Ni alloys favours the passivation of the metal in HW. The higher this concentration is, the faster the passivation proceeds. The addition of Ni to brasses with a Zn content between 24 and 37 wt.% seems to slow down the passivation processes. The change from a one-phase to a two-phase alloy provokes a double passivation phenomenon (slow followed by a quicker one).

The reproducibility of the results was quite good (difference of potentials inferior to 5–10 mV) for most alloys except for those containing Pb (bronzes, brasses, quaternary bronzes and Cu–Ni–Zn alloys). These alloys were often stained by KNO_3. Both phenomena are used to detect the presence of Pb in the alloy studied.

Validation

A group of ten copper-based artefacts from the International Museum of Horology (MIH) located at La Chaux-de-Fonds and the collection of the Foundation of historic materials of the Swiss army HAM located at Thun were selected to validate the use of the electrochemical tool developed as well as the relevance of the database constituted. These artefacts are representative of the objects found in these technical collections.

After a preliminary diagnosis based on the manufacturing of the artefacts, electrochemical plots were performed according to the protocol given in "Experimental conditions for plotting E_{corr} vs time curves." Figures 5a and 6a illustrate two of the objects considered: a watch frame (MIH E78) and a cartridge case (HAM E83). Due to the cultural value of these objects, the polishing of the metal surface was as discrete as possible (see Figs. 5b and 6b) and done on the
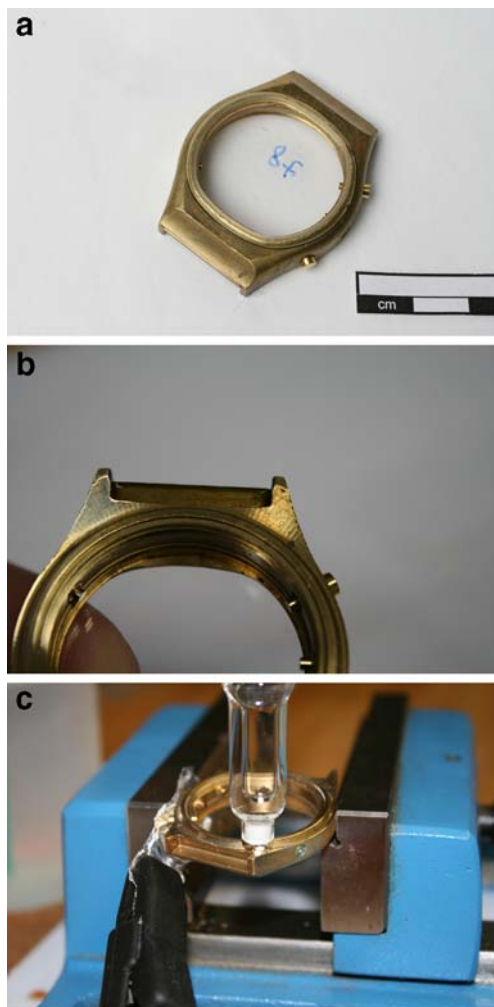

Fig. 5 Watch frame MIH E78 (**a**) used to validate the electrochemical tool with a closer view on the area tested (**b**) (*left top* section). Position of the object in the vice during the E_{corr} vs time monitoring (**c**)
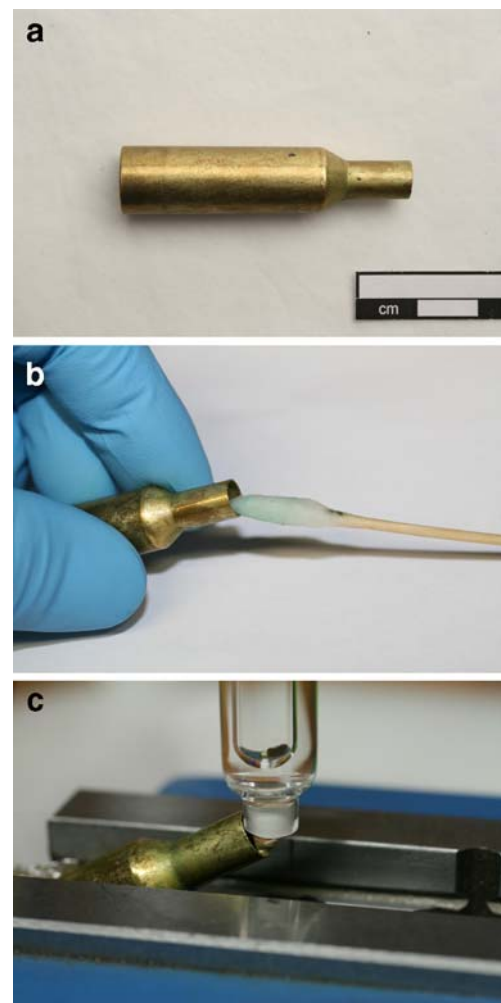

Fig. 6 Cartridge case HAM E83 (**a**) used to validate the electro-chemical tool and cleaning of the inside (**b**). Position of the object in the vice during the E_{corr} vs time monitoring (**c**)
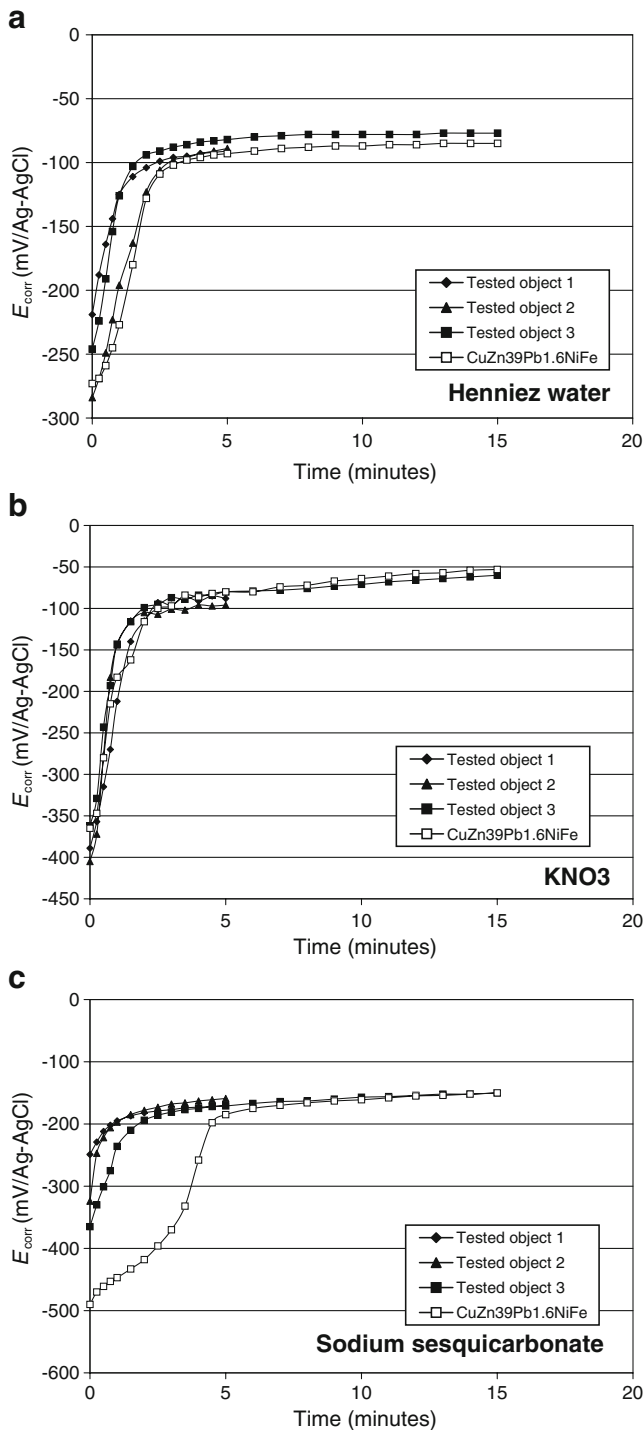
Figures 7 and 8 show the electrochemical plots obtained for these two materials in HW, KNO₃ and SS. Once again, the values were rather reproducible and the plots (monitored on a period of 15 min) of the reference materials that are the closer to our electrochemical data are indicated. On the basis of these comparisons, we could suggest that MIH E78
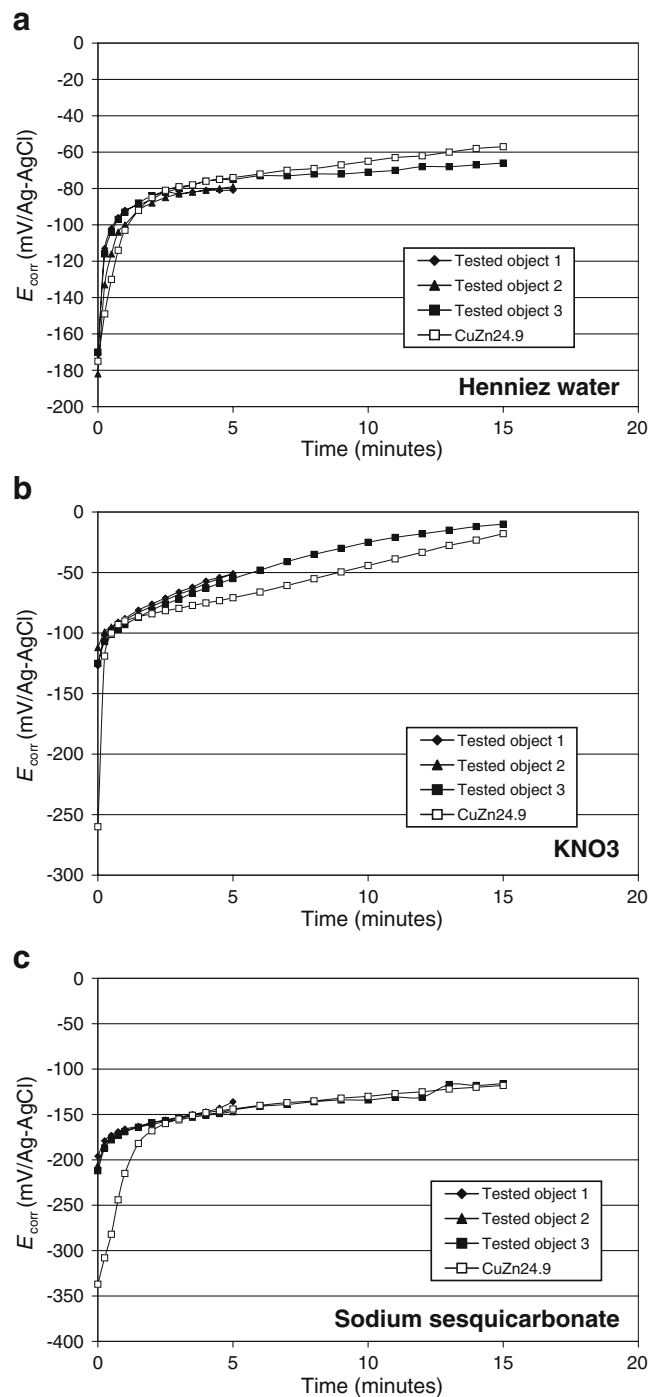

Fig. 7 E_{corr} vs time plots on MIH E78 (with additional plot of HAM E36 (CuZn39Pb1.6NiFe) monitored during 15 min) in HW (**a**), KNO₃ (**b**) and SS (**c**)

Fig. 8 E_{corr} vs time plots on HAM E83 (with additional plot of V&A Museum E82 (CuZn24.9) monitored during 15 min) in HW (**a**), KNO₃ (**b**) and SS (**c**)

back of the artefact or in internal parts. The objects were then positioned correctly into a vice so as to offer a surface large enough for E_{corr} measurements (see Figs. 5c and 6c). Once again, an aluminium foil attached to the artefact was used for electric contact.

should have a composition similar to HAM E36 (CuZn39Pb1.6NiFe) and HAM E83 a composition similar to V&A Museum E82 (CuZn24.9). Often, the potentials measured at the beginning of the monitoring were less negative than for the reference materials due to the limited polishing we applied on the real artefacts.

The electrochemical measurements being completed, the different artefacts were analysed on the same spots as the electrochemical testing by EDS-SEM using the same protocol as in "Collection and analysis of reference materials." Table 2 gives for each artefact considered in the left column the composition proposed from the electrochemical measurements and the use of the database and in the right column the actual composition obtained by EDS.

It appears that for the binary alloys (essentially brasses), the compositions suggested are quite correct. Important differences were observed though when more than one element of addition is present. The electrochemical plots still inform us on the presence of major elements and this much better than a simple observation of the artefacts and knowledge of the manufacturing process. For example, we could demonstrate that artefact MIH E77 is a ternary bronze (Cu–Sn–Zn) with a high Sn content and a lesser Zn content. Similarly, artefact MIH E80 is a quaternary bronze (Cu–Sn–Zn–Pb) and the difference observed with the reference material is certainly due to the high Zn content of the tested alloy. Artefact MIH E86 is a ternary alloy too (Cu–Sn–Zn) with quite similar Zn and Sn contents but a low Pb content. Finally, artefact HAM E85 is a Cu–Zn–Ni alloy close to reference material CuZn26NI12Fe.

If the five binary alloys and the leaded brass (MIH E78) correspond more or less to materials already listed in the database and confirm its relevance for the qualitative analyse of unknown materials, the other materials analysed but not listed yet can be inserted in the database to complete it. Indeed, we have now electrochemical plots for a quaternary bronze with a high Zn content (MIH E80). Furthermore, the electrochemical effect of a low Zn content

on bronzes with a high Sn content (MIH E77) is precised as well as the effect of a variation of Ni content on the one-phase Cu–Zn–Ni (HAM E85) alloy. Finally, we have clarified the effect of the increase of the Sn content on ternary bronzes with a low Pb content (MIH E86).

The electrochemical tool developed seems then to perfectly fulfil the conditions of a "spot-test." If in general the latter analytical tool can only give one element per test, with the SPAMT Test tool, we can detect the presence of the major elements in the alloy considered. Therefore, the tool developed provides a qualitative analysis, at least for copper-based alloys. Besides, it respects most of the ethical principles requested in the conservation field since it is an easy-to-use, almost non invasive, portable and not a costly instrument.

The SPAMT Test electrochemical tool needs to be optimised if we want it to become a common instrument used by conservators during condition surveys of artefacts carried out on-site. The level of polishing of the metal surface before the measurement must be better defined to limit the impact to the minimum whilst getting still interpretable results. Some suggestions have been proposed to position properly the materials surface in front of the tip of the JPT in order to have almost non invasive measurements. More testing is required though to limit even less the damage to the metal surface. Undoubtedly, the level of polishing plays a major role on the reproducibility of the results and the first potentials of the monitoring process. We have seen though that this effect is less prominent after 15 min.

Conclusion and perspectives

The SPAMT Test electrochemical tool responds well to the needs listed at the beginning of the paper. It is an easy-to-use, almost non invasive, portable and not a costly instrument that can provide a qualitative analysis of slightly oxidised copper-based surfaces (that can be easily

Table 2 Composition of the ten artefacts selected to validate the electrochemical tool developed and the relevance of the database constituted: the left column gives the suggested compositions from the electrochemical measurements and comparison with the database whilst the right column gives the actual composition obtained by EDS

	Composition proposed from the electrochemical measurements and comparison with the database	Composition obtained by EDS
MIH E77	CuSn14Zn2.1	CuSn18Zn1.4FeMn
MIH E78	CuZn39Pb1.6NiFe	CuZn39Pb1.7
MIH E79	CuZn30–34	CuZn30SiNiFe
MIH E80	CuSn5.3Zn5.5Pb1.5NiFe	CuSn4.3Zn24Pb2.9Fe
MIH E86	CuSn6Zn5.8PbNi	CuSn9Zn6Pb1.5FeSi
HAM E37	CuZn30	CuZn30
HAM E81	CuZn5.3–7.8	CuZn8
HAM E82	CuZn30	CuZn30
HAM E83	CuZn24.9	CuZn28
HAM E85	CuZn26Ni12Fe	CuZn27Ni8

cleaned). It is then adapted to the investigation of technical and scientific artefacts that are often covered with a thin corrosion layer.

All measurements were carried out by conservators specialised in the conservation of technical, scientific and horology objects. Not only these ones made a point in choosing really discrete zones and in limiting the impact of the measurement to the minimum, but as future users of the electrochemical tool, they tried to optimise it to get the best reproducible results they could. Their contribution was essential too for the validation of the tool on real artefacts. Their good knowledge of the manufacturing of the objects helped them to make preliminary proposals for the composition of the materials. These proposals were still imprecise and it is at that stage that the SPAMT Test electrochemical tool and its database were particularly useful.

If globally we are satisfied with the results obtained, some improvements are needed to make the tool particularly efficient:

- The level of polishing should be precised and it should be as limited as possible.
- The position of the tool vs the surface of the artefact should be optimised.
- The number of materials listed in the database should be increased to improve the coverage of the copper-based alloys that can be encountered on real artefacts.

In the long term, we plan too to computerise the database. With an appropriate software, we could quickly get with the electrochemical plots obtained and by comparison with those of the database some composition proposals.

Finally, the design of the tool could be optimised to make it more user-friendly. For instance, we should improve the way to attach it properly to the metal surface and the system RE/JPT/drop should be isolated from the outside to prevent any pollution that could influence the results obtained.

References

1. Odegaard N, Scott C, Zimmt WS (2000) Materials characterization tests for objects of art and archaeology. Archetype, London
2. Degrigny C, Crawford J, DeBattista R (2007) The "drop" E_{corr} vs time monitoring technique: a possible spot test for metal artefacts? In: Degrigny C, Van Langh R, Ankersmit B, Joosten I (eds) METAL07, Proceedings of the ICOM-CC Metal WG Interim Meeting, vol 3. Rijksmuseum, Amsterdam, p 71
3. Oddy WA, Hughes MJ (1970) Stud Conserv 15:183
4. Ingelbrecht C, Adriaens A, Maier EA (2001) Certification of arsenic, lead, tin and zinc (Mass Fractions) in five copper alloys CRM 691. In EUR 19778/1, Office for Official Publications of the European Communities, Luxembourg, 53 pp
5. E!2210–EUROCARE BRONZART. http://www.eureka.be/inaction/AcShowProject.do;jsessionid=7f0000011f9064ad9ec497414a5fa410d47bf568b3a0?id=2210. Accessed 17 June 2009
6. Abdel-Hakim Ali HA, Abdel Gwad SA, Al Masri AN, Baraka AM (1998) Materialwiss Werkstofftech 9(2):80
7. Bae DH, Cho SY (2003) Int J Mod Phys B 17(08–09):1594
8. Degrigny C, Baron G, Christodoulou P, Tran K, Hiron X (2002) Conservation of a collection of waterlogged composite rifles dating from the 17th century recovered from the Brescou II marine site. In: Per Hoffmann et al (eds) Proceedings of the 8th ICOM-CC WOAM Conference, Bremerhaven, pp 399–411
9. Degrigny C, Le Gall R (1999) Stud Conserv 44:157
10. Pourbaix M (1963) Atlas d'équilibres électrochimiques à 25 °C. Gauthier-Villars, Paris