

International workshop and training school on

## **Electrochemistry in Historical and Archaeological Conservation**

**11-15 January 2010**

**Lorentz Center, Leiden, Netherlands**

### **Organized by:**

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L.M. Abrantes (University of Lisbon, Portugal)

V. Argyropoulos (T.E.I. Athens, Greece)

V. Costa (CONSERVARE, France)

C. Degriigny (Haute Ecole de Conservation-restauration, Switzerland)

M.G. Dowsett (University of Warwick, UK)

P. Letardi (CNR- ISMAR, Italy)

D. Thickett (English Heritage, UK)

The workshop was sub-divided in six sessions over 5 days. Each session dealt with a different topic and started with an introductory talk presenting the most recent knowledge in the field, which was then followed by other presentations, laboratory experiments/technique demonstration and a general discussion. For the experiments, we could rely on the generosity of Professor Ludo Juurlink and Professor Marc Koper (Leiden University of Chemistry), who offered us laboratory space.

The first session of the workshop was dedicated to the presentation of “Analytical techniques” used for identification and characterization of corrosion products. Especially voltammetry of micro-particles (VMP) appears to be a very practical tool. The use of a paraffin impregnated graphite electrode (PIGE) makes sampling easy, as micro-particles stick to the electrode surface simply by rubbing the metal graphite electrode over the object under study. It was highlighted that the correct choice of the electrolyte is essential to obtain a good separation between the oxidation and reduction peaks of different materials. VMP can further be improved by using different working electrodes, such as the cavity microelectrode which allows micro-sampling (about ten nanograms) or treating samples by square wave voltammetry, which allows a better characterization of corrosion products in complex systems such as patinas.

The second session dealt with “Cleaning and stabilization treatments” using electrochemical techniques. The presentations made clear that informing conservators of electrochemical techniques for conservation treatments is the first step in correct dissemination of these techniques; the second dissemination step being their evaluation by conservators and the latter’s engagement with electrochemists for furthering applications specific to their artefacts’

circumstances. Regarding electrolytic reduction of lead and silver plate, several speakers and participants acknowledged the need for complementary techniques such as surface finishing via physical means – an under considered issue that requires further experimental evaluation and discussion relating to ethical considerations of such procedures. Masking of multi-component artefacts also needs to be evaluated in terms of its efficacy. In addition remote monitoring of electrolysis of marine artefacts has permitted regional engagement and support of cultural heritage preservation by regional community councils and public populations.

The “Protection” session on the third day of the workshop could be divided into two subjects: the use and evaluation of electrochemical techniques as a tool for testing the anti-corrosion efficiency of protective coatings, and metal protection using self-assembled monolayers (SAMs) as a surface modification.

Electrochemical tests were presented as new techniques and very valuable tools for research on the protectiveness of coatings and films applied to metal objects and artefacts.

Electrochemical impedance spectroscopy (EIS) and polarization resistance measurements ( $R_p$ ), for instance, are simple and inexpensive techniques, which have a lot of advantages to other more commonly used (in the automotive industry) techniques such as natural exposure and climatic chamber tests. Electrochemistry is used to obtain a high sensitivity, follow the corrosion rate of an object and measure this in real conditions on real artefacts. For the protection of metals, organic products can be used which have the possibility to react with the metal or metal oxide surface (e.g. dodecanethiols on gold surfaces). These ultrathin organic films are called self-assembled monolayers (SAMs). The protectiveness of the film depends on the functional group, the chemical reactivity of the head group, the surface pre-treatment and the solvent.

The fourth day of the workshop began with a session titled “Testing and Monitoring”. This session focussed on the development and use of in-situ techniques for the monitoring of chemical processes affecting cultural heritage materials, primarily via the use of simulant samples. The first three presentations concerned a portable electrochemical and environmental cell apparatus designed for in-situ use with various analytical techniques. The final presentation in the session concerned the application of a variety of techniques to materials which may be of interest to conservators. The techniques included grazing incidence X-ray diffraction (GIXD), Fourier transform infrared spectroscopy (FTIR), and laser techniques.

The first part of the final morning began with a series of talks that were intended to give an overview of the current “Educational programmes and standards” involving the application of electrochemical techniques to cultural heritage conservation. Topics such as can conservator-restorers be trained at a bachelor level in application of electrochemical techniques? and the different approaches curators, conservators and scientists have towards the conservation and treatment of cultural heritage artefacts were discussed. The final talk of the session concerned the CEN/TC 346 technical committee on conservation of cultural property. The need for standards in the field of cultural heritage conservation was emphasized, a point which most participants were in agreement with.

The final session of the workshop “Applications” began with a talk concerning the use of electrochemical techniques at the Rijksmuseum in Amsterdam. This was followed by an overview of the work carried out during the ETIC (Use of electrolytic techniques in metal conservation) project from 2003 to 2006. Finally, there was a talk concerning work being carried out in Qumran in Israel, the location of the Dead Sea Scrolls. A significant outcome of the final session was that a suggestion was also made to apply for a new COST action in the application of electrochemical techniques to heritage metals.

## Final programme

**Monday 11 January 2010**

08:45-09:45	Registration and coffee
09:45-10:00	Welcome by the Lorentz Center and the scientific organizers
10.00-11:00	<b>Session 1: Analysis</b> <ul style="list-style-type: none"> <li>– Characterization of cultural artefacts and their environment using electrochemical techniques, V. Costa</li> <li>– Evidence of tin-coating on archaeological ferrous artefacts by voltammetry of microparticules, E. Ottenwelter, A. Texier, V. Costa</li> </ul>
11:00-11:30	Coffee break
11:30-12:30	<b>Session 1: Analysis</b> <ul style="list-style-type: none"> <li>– Local investigation of corrosion processes by coupled electrochemical and spectroscopic techniques, V. Vivier, M.C. Bernard, S. Joiret</li> <li>– Layer-by-layer identification of bronze alteration products using Tafel analysis of square wave voltammetric responses, A. Doménech Carbó, M.T. Doménech Carbó</li> </ul>
12:30-14:00	Lunch break
14:00-15:30	<b>ECORR – lab experiments</b> ( <i>Maximum number of participants: 10</i> ) Use of Ecorr vs time as a spot test for copper based alloys, C. Degryny <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– Experiments</li> <li>– Discussion on the limits and possibilities to extend the technique to other metals</li> </ul>
14:00-15:30	<b>Group discussion moderated by D. Thickett</b>
15:30-16:00	Coffee break
16:00-17:30	<b>VMP – lab experiments</b> ( <i>Number of participants is not limited</i> ) Voltammetry of micro particles (VMP/PIGE), V. Costa <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– Experiments</li> </ul>

16:00-17:30	<p><b>ECORR – lab experiments</b> (<i>Maximum number of participants: 10</i>)</p> <p>Use of <math>E_{\text{corr}}</math> vs time as a spot test for copper based alloys, C. Degriigny</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– Experiments</li> <li>– Discussion on the limits and possibilities to extend the technique to other metals</li> </ul>
17:30	Wine and cheese party

## Tuesday 12 January 2010

09:00-09:30	<p><b>Summary of Monday’s experiments and group discussions</b></p> <p>C. Degriigny, V. Costa and D. Thickett</p>
09:30-10:30	<p><b>Session 2: Cleaning and stabilization</b></p> <ul style="list-style-type: none"> <li>– Cleaning of cultural heritage artefacts: an overview, C. Degriigny</li> <li>– Remote monitoring of electrolytic treatment: application to the conservation of marine artefacts, E. Guilminot</li> </ul>
10:30-11:00	Coffee break
11:00-12:00	<p><b>Session 2: Cleaning and stabilization</b></p> <ul style="list-style-type: none"> <li>– De-chlorination of industrial metallic monuments from a marine environment using electrochemical methods, E. Siova</li> <li>– Stabilization of cultural heritage artefacts: an overview, C. Degriigny</li> </ul>
12:00-13:30	Lunch break
13:30-15:00	<p><b>CLEAN – lab experiments</b> (<i>Maximum number of participants: 10</i>)</p> <p>Cleaning and stabilization of cultural heritage artefacts, C. Degriigny, E. Guilminot</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments,</li> <li>– Application to the cleaning of slightly oxidised metals (tarnish removal) and heavily corroded metals (removal of sediments)</li> <li>– Application to the stabilisation of metals (extraction of chlorides, consolidative reduction on lead)</li> <li>– Discussion on other applications: electrophoresis, local cleaning and stabilisation, protection of metals</li> <li>– Remote monitoring of electrochemical treatment</li> </ul>
13:30-15:00	<b>Group discussion moderated by K. Stemann</b>
15:00-15:30	Coffee break
15:30-17:00	<p><b>SENSOR – lab experiments</b> (<i>Number of participants not limited</i>)</p> <p>Metals as environmental sensors, V. Costa, D. Thickett</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– Experiments</li> </ul>

15:30-17:00	<p><b>CLEAN – lab experiments</b> (<i>Maximum number of participants: 10</i>)</p> <p>Cleaning and stabilization of cultural heritage artefacts, C. Degryny, E. Guilminot</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments,</li> <li>– Application to the cleaning of slightly oxidised metals (tarnish removal) and heavily corroded metals (removal of sediments)</li> <li>– Application to the stabilisation of metals (extraction of chlorides, consolidative reduction on lead)</li> <li>– Discussion on other applications: electrophoresis, local cleaning and stabilisation, protection of metals</li> <li>– Remote monitoring of electrochemical treatment</li> </ul>
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### Wednesday 13 January 2010

09:00-09:30	<p><b>Summary of Tuesday’s experiments and group discussions</b></p> <p>C. Degryny, E. Guilminot, V. Costa, D. Thickett and K. Stemann</p>
09:30-10:30	<p><b>Session 3: Protection</b></p> <ul style="list-style-type: none"> <li>– Electrochemical assessment of protection systems on metal artefacts, E. Cano</li> <li>– Metal Protection by Ultra-thin Organic Films - Surface Modification with Self-Assembled Monolayers (SAMs), L.M. Abrantes, A.S. Viana</li> </ul>
10:30-11:00	Coffee break
11:00-12:00	<p><b>Session 3: Protection</b></p> <ul style="list-style-type: none"> <li>– New Routes for Metal Protection – Combining Conducting Polymers with SAMs, L.M. Abrantes</li> <li>– EIS measurements for the performance evaluation of organo-silane in the protection of outdoor monumental bronzes, P. Letardi, E. Joseph, S. Prati, R. Mazzeo</li> </ul>
12:00-13:30	Lunch break
13:30-15:00	<p><b>PROTECT 1 – lab experiments</b> (<i>Number of participants not limited</i>)</p> <p>Electrochemical assessment of protection systems on metal artefacts, P. Letardi, E. Cano</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– EIS for testing protection systems (Module 1)</li> </ul>
13:30-15:00	<p><b>ECORR – lab experiments</b> (<i>Maximum number of participants: 10</i>)</p> <p>Use of Ecorr vs time as a spot test for copper based alloys, C. Degryny</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments</li> <li>– Experiments</li> <li>– Discussion</li> </ul>
15:00-15:30	Coffee break
15:30-17:00	<p><b>PROTECT 2 – lab experiments</b> (<i>Maximum number of participants: 20</i>)</p>

15:30-17:00	<p>Electrochemical assessment of protection systems on metal artefacts, P. Letardi, E. Cano</p> <ul style="list-style-type: none"> <li>– EIS for testing protection systems (Module 2)</li> </ul> <p><b>CLEAN – lab experiments</b> (<i>Maximum number of participants: 10</i>)</p> <p>Cleaning and stabilization of cultural heritage artefacts, C. Degriigny, E. Guilminot</p> <ul style="list-style-type: none"> <li>– Introduction to the equipment and the conditions of the experiments,</li> <li>– Application to the cleaning of slightly oxidised metals (tarnish removal) and heavily corroded metals (removal of sediments)</li> <li>– Application to the stabilisation of metals (extraction of chlorides, consolidative reduction on lead)</li> <li>– Discussion on other applications: electrophoresis, local cleaning and stabilisation, protection of metals</li> <li>– Remote monitoring of electrochemical treatment</li> </ul>
15:30-17:00	<b>Group discussion moderated by V. Argyropoulos</b>
17:00-21:00	Workshop dinner

### Thursday 14 January 2010

09:00-09:30	<p><b>Summary of Wednesday’s experiments and group discussions</b></p> <p>P. Letardi, E. Cano, C. Degriigny, E. Guilminot and V. Argyropoulos</p>
09:30-11:00	<p><b>Session 4: Testing and monitoring</b></p> <ul style="list-style-type: none"> <li>– In-situ time-resolved monitoring of metal surfaces through spectroelectrochemical experiments using an automated electrochemical cell with demonstration of the cell, M. Dowsett, A. Adriaens</li> <li>– An in-situ X-ray absorption spectroelectrochemistry study of the response of artificial chloride corrosion layers on copper to remedial treatment, A. Adriaens, M. Dowsett</li> </ul>
11:00-11:30	Coffee break
11:30-12:30	<p><b>Session 4: Testing and monitoring</b></p> <ul style="list-style-type: none"> <li>– In-situ spectroelectrochemical study of the growth of lead carboxylate coatings for protection and corrosion inhibition, M. Dowsett, A. Adriaens</li> <li>– In-situ diagnostics and dynamic protection studies by novel Laser-electrochemical, GIXD and FTIR approaches, W. Kautek</li> </ul>
12:30-14:00	Lunch break
14:00-17:00	Visit to the Museum Boerhaave (Leiden) – contact person Hans Hooijmaijers

## Friday 15 January 2010

09:00-10:00	<p><b>Session 5: Standards and education</b></p> <ul style="list-style-type: none"> <li>– An examination of education programmes (Bachelor and Masters) offered by European Conservation Departments in offering learning outcomes involving the application of electrochemical techniques to conservation. What is the level of competences needed by the profession and practice of the conservator-restorer and do the current education programmes meet this need?</li> </ul> <p>Participants at the meeting that teach the application of electrochemical techniques to C-Rs in training will be asked to present their course(s) to the audience. 10 minutes will be allotted to each presentation. Following these presentations, a group discussion will take place to examine how in depth education in the application of electrochemical techniques to conservation is needed for the education of C-Rs and at what level should this training take place in terms of European Qualifications Framework (EQF). If further development is needed, how can the Lifelong Learning Programme help in obtaining funds for this need?</p> <p>Selection of not more than 4 possible speakers (10 minutes each) so that there can be a 20 minute discussion afterwards.</p> <p>V. Argyropoulos, C. Degrigny, V. Costa</p>
10:00-10:30	<p><b>Session 5: Standards and education</b></p> <ul style="list-style-type: none"> <li>– The need for standards in metals conservation under the CEN/TC 346 <i>Conservation of Cultural Property</i> framework, V. Argyropoulos</li> <li>– Discussion</li> </ul>
10:30-11:00	Coffee break
11:00-12:30	<p><b>Session 6: Future activities and collaborations</b></p> <ul style="list-style-type: none"> <li>– Conservation and electrochemistry in the Netherlands, A. Pappot</li> <li>– ETIC activities, C. Degrigny</li> <li>– A scientific dialogue between copper and iron at Qumran: a case study with a sustainable future?, J. Gunneweg</li> <li>– Group discussion</li> </ul>
12:30	Lunch break

# Electrochemistry in Historical and Archaeological Conservation



Workshop January 11 – 15 2010, Leiden, The Netherlands

Scientific  
Organizers

- A. Adriaens, Ghent
- L.M. Abrantes, Lisbon
- V. Argyropoulos, Athens
- V. Costa, Compiègne
- C. Degryny, Chaux-de-Fonds
- M.G. Dowsett, Warwick
- P. Letardi, Genova
- D. Thickett, London

Invited  
Speakers

- M.C. Bernard, Paris
- E. Cano, Madrid
- A. Domenech Carbo, València
- M.T. Domenech Carbo, València
- E. Guilminot, Nantes
- J. Gunneweg, Jerusalem
- S. Joiret, Paris
- R. Mazzeo, Bolonga
- F. Mirambet, Paris
- E. Ottenwelter, Prague
- A. Pappot, Amsterdam
- E. Siova, Athens
- P. Storme, Antwerp
- S. Szunerits, Grenoble
- F. Urban, Brussels
- V. Vivier, Paris



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