Editor:
Christian Degrigny
Christian_degrigny@hotmail.com

METAL*Consn*-info

Metal working group

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BROMEC4

Editorial

Major events have happened during this Autumn. The most important was the triennial meeting of ICOM-CC in Rio de Janeiro at the end of September. Some national correspondents of BROMEC attended it: Vasilike Argyropoulos (Greece), David Thickett (UK), Gerhard Eggert (Germany) and myself (Finland).

I have been nominated the new coordinator of the Metal Working Group at that occasion and Janet Hughes, head of conservation at the National Gallery of Australia will help me as the assistant coordinator. This support will be very precious since the next interim meeting will take place in Canberra in October 2004.

I presented the BROMEC in Rio and Latin American conservators were very positive about it. I met there Johanna Theile who organised the last Metal 2001 conference in Santiago de Chile. Very fruitful discussions have started between us.

Since the beginning BROMEC has benefited from the support of the ICOM-CC Metal Working Group but its diffusion depended on national correspondents. From now on this bulletin will be sent to all the Working Group members to allow colleagues from countries not involved yet to be informed on our activities and efforts in conducting research in metal conservation. With time they might participate to this general effort.

Because the directories of the Metal Working Group and the BROMEC are now combined you might have received a message from Janet and I where we give already some ideas on our future policy for the next triennial period. With this message I have sent a questionnaire to know your wishes on research programmes and projects we could support during that time. Your answers are absolutely necessary if you want us to give the Directory Board of ICOM-CC a programme that reflects what you expect from the Working Group.

- National correspondents supporting my task as the editor of BROMEC are essential to the existence of BROMEC since they know their colleagues and where to collect the needed information. The team of national correspondents is increasing continuously. **Johanna Theile**, conservator and teacher at the Facultad de Arte - Universidad de Chile Las Encinas in Santiago de Chile, will represent Latin America in the future. **Dorin Barbu**, head assistant at the Zonal Restoration and Conservation Laboratory of the Brukenthal National Museum in Sibiu will represent Romania, **Jaco Boshoff**, Maritime archaeologist at Iziko Museums of Cape Town will represent South Africa and finally **Andrey Chulin**, conservator at the State Hermitage Museum in St Petersburg will represent the Russian Federation. Welcome to both Johanna, Dorin, Jaco and Andrey.

In September I received very sad news from Dusan Perlik, conservator at the Museum of Central Bohemia in Rostoky U Prahy (Czech Republic). His museum and conservation department have suffered tremendously during the floods in August (www.muzeum-roztoky.cz). Dusan like all his colleagues did a wonderful job in trying to save what could be saved. We are deeply concerned by the situation in Central Europe.

The organisation of seminars on new technologies applied to conservation is always welcome in conservation schools. On October 18, we organised at EVTEK Institute of Art and Design a seminar entitled “Conservators and the use of laser cleaning in conservation”. This seminar was funded by the European Commission and the COST Action G7 (“Artwork conservation by laser”, see the website on page 13). 50 delegates, experts and scientific contributors from 17 countries attended the seminar to give the up-to-date knowledge in the field to Finnish conservators and students from the Conservation department. Metals were considered as well as many other materials. The abstracts of the seminar can be sent by electronic means to the people interested (please contact the editor).

The last news is that I have resigned from my position as the principal lecturer at the Conservation Department of EVTEK Institute of Art and Design and I am leaving Finland too. This explains why you receive this issue of the BROMEC in advance. I hope to inform you of my new position in the next issue. Please note that my e-mail address has changed.

The Editor
Christian DEGRIGNY

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Applied research projects

 Comparison of quantitative methods of chloride measurement for metal conservation and desalination (***CWOCL/MAC Lab/NHC/VDHP***)

A group of archaeological conservators from the US Mid-Atlantic States met on July 19, 2002 for the second of a series of informal workshops. This meeting was hosted by Emily Williams and the staff at the CWOCL. Also present were Betty Seifert, Howard Wellman, Maret Warner, and Gareth McNair-Lewis of the MAC Lab, Claire Peachey and Melanie Periera of the NHC, and Melba Myers of the VDHP.

A variety of methods for measuring chlorides were tested, and the results of tests on standards and unknowns were compared. The NHC staff demonstrated LaMotte titration tests, Quantab® strips, and a Hach titration kit. MAC Lab staff demonstrated a Chloride Specific Ion Electrode connected to an Accumet® pH/mV meter. Emily Williams demonstrated Colonial Williamsburg's Jenway Chloride Meter. Melba Myers brought a Total Dissolved Solids meter, to see if results of TDS would be comparable to chloride-specific measurements. Other titration methods were not tested, as no one had the equipment or materials, and no one likes the additional trouble of disposing of mercury compounds.

The standards tested were provided by the MAC Lab, and were the same used to calibrate the Accumet meter. Commercial 1000ppm sodium chloride standard from Fisher Scientific was diluted with de-ionized water (and an aliquot of potassium nitrate Ionic Strength Adjuster) using calibrated pipettes and volumetric flasks to make 100 and 10ppm standards. The unknowns were provided by Emily Williams, and consisted of wash water from desalinating artifacts. All standards and samples were approximately neutral (pH 7). If the samples are alkaline (i.e., sodium hydroxide electrolyte, pH>13), they would be neutralized by adding 10% nitric acid (in deionized water), monitoring the change in pH with the Accumet meter, or pH test strips.

Results of the different methods were compared, and the relative speed and ease of tests were discussed. Each method had its benefits and problems; individual choice depended on the number of samples to be tested and how often, the accuracy and repeatability desired, the range of expected chloride levels, and the portability or field-readiness of the instrument.

- Quantab strips are a one-use chromatography test – the strip is dipped into the sample, and the solution is absorbed up through the reagent column. The concentration is read by comparing the location of a color boundary in the reagent against a calibration table. The strips provide a quick first test in the field or laboratory to determine the general range of chloride levels, and readings are close to those from other methods. They are extremely portable, have a good shelf-life, and are available from most laboratory suppliers. At approximately one US dollar per strip, however, they are too expensive for repetitive testing.

- The LaMotte and Hach titration kits are both designed for water quality testing in the field, but determining the titration end point (based on color change) can be a matter of personal judgement, especially if the sample is contaminated or cloudy. The LaMotte test requires the careful addition of reagents (potassium chromate and silver nitrate) by a hand-held dropper into an aliquot of sample. The number of drops must be counted until the color change occurs. The number of drops is compared to a calibration table to obtain the concentration. If the sample is too concentrated, the color change will not be obvious, and the sample must be

diluted, and the test run again. The test is relatively cheap and easy to use, but there is the potential for significant error if the drops are not dispensed evenly, and the endpoint can be a subjective judgement. The waste products contain silver compounds, which are considered hazardous materials in the USA.

- The Hach titrator dispenses known volumes of mercuric nitrate into a prepared sample aliquot. When the color change is achieved, the amount of reagent dispensed is compared to a calibration table to determine the concentration of chloride. The dispenser itself is awkward to use and there is a waste disposal issue with mercury compounds. The NHC staff have been performing numerous tests with this system to determine its accuracy and repeatability.

- The Jenway Chloride Meter measures the consumption of silver ions in the chloride sample, and is very simple and fast to use. It releases silver ions at a fixed rate from an electrode into an aliquot of sample. Chloride ions bond with the silver ions, and the overall conductivity of the solution is reduced. When all the chloride ions have reacted, conductivity ceases to change, and the device calculates chloride concentration from the amount of silver consumed. It is principally designed for clinical work and it is sensitive to contaminants and other ionic species, which would probably exclude samples from electrolytic or chemical reduction baths. The silver electrodes also require frequent polishing. The waste products contain silver compounds.

- The Accumet pH/mV meter with a specific ion electrode requires extensive sample preparation (pH must be neutral, and samples should be filtered), and frequent calibration with precisely made standards. Sample preparation and meter calibration can take twice as long as sample measuring, and the addition of neutralizers (nitric acid) and Ionic Strength Adjusters can dilute the sample. Once prepared, measuring is fast and easy by dipping the electrode into the solution, and reading the result. The Accumet meter performs calibration calculations, and you can connect this meter to the computer and download the data directly to a spreadsheet or database. There are various types of electrodes, most require regular maintenance including the changing of internal solutions and keeping the sensor polished. The initial cost of meter and electrode are high, and you must have a supply of calibration standards available. There are both bench-top and portable field meters. Waste products are sodium and potassium nitrates and chlorides.

- The Total Dissolved Solids meter is a standard conductivity-based test that is calibrated to calculate the total salts dissolved in the solution. While it gave consistent results on all the standards and unknowns used to test the other systems, there was no way to directly compare those results with any other device, especially since most of the other systems required the addition of reagent salts for titration or neutralization, which would increase the readings on the TDS.

In conclusion, the simple chromatography and titration methods are good for field and general ballpark determinations. They suffer though from interference if other halide elements (bromine, fluorine) are present in the sample. The Accumet meter with a specific ion electrode is very useful for day-to-day laboratory monitoring of chloride removal, although there is a large initial cost. There can be some interference from halide contamination. It also produced the least toxic waste. The Jenway would work well for wash samples without high concentrations of other dissolved salts. We all agreed that the issues of toxic waste disposal kept us from using mercuric titration tests. All the tests require samples to be approximately neutral pH.

Contact: Howard Wellman (CWOCL)
Funding: no external funding

Applied research projects

 Conservation research has started on the Civil War submarine H.L *Hunley* (***WLCC***)

The H.L. *Hunley* submarine made history 138 years ago on the night of February 17, 1864, when it rammed an explosive spar torpedo into the Union blockade ship *Housatonic* off the coast of Charleston. The *Housatonic* sank, and mysteriously, so did the *Hunley* with 8 crewmembers on board. The hand-cranked submarine was raised in 2000 and brought into the Warren Lasch Conservation Center (WLCC) to be excavated and conserved (for further information please consult www.hunley.org).

After the completion of the archaeological excavation of the interior and the removal of the remains of the crewmembers last year, the Hunley Project has entered a new phase. This submarine represents an extraordinary challenge to the conservators because it is basically made of hundreds of riveted wrought-iron plates and cast-iron fittings assembled together. The single most challenging aspect of conserving the *Hunley* is that “we don’t want to take it apart unless there is no other alternative".

The principal goal of our research is to identify which of the existing conservation techniques as well as any experimental methods will hold the greatest promise to minimize the disassembly of the submarine and ensure its stabilization.

The four (4) main objectives for the year to come are:

1. The characterization of the current state of corrosion of the submarine. As part of this process we are evaluating the literature on the determination of chloride ion concentration in liquids and on solids. We have also started to try and differentiate free and bound chloride in iron samples and concretions from the *Hunley* and other shipwrecks from the same period.

2. The evaluation of advantages and disadvantages of treatments that have been applied to stabilize marine iron artifacts. We are focusing on electrolysis in caustic and plasma thermal treatments. We will be conducting experiments in our Center and in other Laboratories as part of our evaluation.

3. The evaluation of experimental techniques including the use of sub and super critical fluids in the stabilization process.

4. To implement a conservation plan for the long-term stabilization of the *Hunley* to be peer-reviewed.

To address the scientific issues and questions to be answered before a decision can be made regarding the ultimate stabilization of the *Hunley*, a scientific team has been assembled at the WLCC. The 2002/2003-core team includes Paul Mardikian Senior Conservator for the Hunley Project, Philippe de Vivies conservator at the WLCC, Prof. Michael Drews, School of Materials Science & Engineering, Clemson University, Nestor Gonzales, Chemical Engineer. Dr. Ian MacLeod from the Western Australia Maritime Museum, personnel from the Smithsonian Institution in Washington DC and other scientists and supportive corporations from around the world have and will continue to be active participants in the research.

Once long-term stability is successfully achieved on the submarine, the *Hunley* will then be put on permanent public display as a historic and technological educational tool in a facility designed specifically to house this unique artifact.

We welcome comments, suggestions, ideas and contributions from anyone interested in assisting us in the conservation of the H.L. *Hunley* submarine. We are specifically interested in any research related to riveted plates.

Contact: Paul Mardikian (WLCC)
Funding: US Department of Defence (Legacy Resources Management Program), Friends of the Hunley, Clemson University.

Applied research projects

Treatment of corroded painted iron surfaces with chelating reagents (***ICN/SRAL/Stedelijkmuseum***)

Iron objects which are covered with an historic important paint layer that shows corrosion spots on the surface are typical examples of a complex conservation problem. In this student project (1 year) a modern object, made by the artist Soto was investigated. After analysis of cross sections of the paint layers with microscopy and SEM-EDS it could be shown that the corrosion, visible at the objects surface, arose via two mechanisms: through pores in the polymer layer and through migration of corrosion into the polymer matrix.

Treatment of these spots proved to be difficult. Model plates, with identical paint layers when compared to the object, were made and treated. Treatments chosen involved the use of chelating reagents such as EDTA. It was found that extracting iron ions from the polymer matrix gave extended paint disruption after ageing.

A new approach was chosen: dissolving free iron ions at the surface and blocking the excess of ions inside the polymer layer by phytate anions (phytic acid was in fact used). After ageing the paint layer was in a much better state than the EDTA treated ones.

Contact: Bart Ankersmit (ICN)
Funding: ICN and Stedelijkmuseum

Applied research projects

 Removal of chlorides from enamelled medallions (***IRPA***)

Three enamelled medallions under conservation treatment at the Institut Royal du Patrimoine Artistique (IRPA) show similar corrosion problems. The first one named "Fabri" is dating from the 12th century and belongs to the treasury of the church 'Notre Dame' in Huy (Belgium). The two others named "Sun" and "Moon" are dating too from the 12th century but belong to the Museum of the old abbey in Stavelot (Belgium).

The first medallion, with a diameter of 9.4 cm and presenting the tree of life, has been kept in inappropriate conditions. Besides a humid environment in the treasury, the showcase, in which the medallion was exposed, contained a fibreboard shelf covered with textile. The showcase itself was not hermetically sealed. Furthermore, the medallion has, in the past, been treated with waxes and other non-identified products. The two other medallions, with a diameter of 2.5 cm and excavated near the abbey of Stavelot in 1999, are archaeological objects still partly covered with a crust of copper corrosion products.

Although the history of the three medallions is completely different, they do show the same structure (a support of gilded copper with 'champlevé' enamel) and the same problems: the presence of chlorides. These chlorides can be found all over the medallions (front side, back side, under the enamel).

A literature survey on the way to stabilise the copper base without damaging the enamel showed that little information has been published so far on this delicate question. The use of benzotriazole has been mentioned but its effect on enamel is not known. Subjecting some treated reference enamels to accelerated ageing tests could inform us on the safe use of benzotriazole for the long term conservation of the medallions.

Once the medallions treated, an improved presentation environment will be provided.

Contacts: Gilberte Dewanckel and Marina Van Bos (IRPA)
Funding: no external funding

Ongoing research projects

 Use of multipulse Q- switched solid state lasers for art objects restoration (***NILPRP***)

The partners in this EUREKA E! 2542 RENOVA-LASER project are research institutes for lasers, art universities and also companies involved in renovation of art monuments and historical buildings.

Our objective in the project is to establish new cleaning technologies for metals and stones using solid state Nd:YAG lasers. Our experience in solid state lasers as well as the interaction of lasers with matter allow the approach of cleaning methods on art objects.

Laser cleaning has many advantages: non-contact method, easy to perform, possibility of fine focusing. It is possible then to remove only a thin layer, generally the corrosion products on metal, or the crust on stone.

The main problems to be solved now are to reshape the laser pulse and to couple the laser by optical fibre to the handling device. A special regime for the Nd :YAG laser is proposed: multipulse Q-switched. In this regime we expect the train of pulses to be uniform in order to obtain a smooth interaction of the laser beam on the surface. The cleaning effect by laser ablation consists in the formation of a plasma coupled to the processed surface. The proposed regime is expected to have reasonable thermal effect, high productivity and reduced mechanical stress.

The preliminary tests show a promising application of this laser regime especially for stone and metal art objects. The cleaning of these is conducted by the restorer, who is able to assess the effect of laser cleaning in comparison to more traditional cleaning methods.

Training of end-users to that technique is planned in the future.

Contact: Clementina Timus (NILPRP)
Funding: Ministry for Education and Science

Ongoing research projects

A literature review of active corrosion phenomena on archaeological objects. Definition of the concept and characterisation of the symptoms (***UPS/IRRAP***)

The rapid degradation or active corrosion of archaeological iron objects after their excavation is commonly encountered by conservators. Active corrosion covers in fact different phenomena, which lead to many different aspects of corrosion but are not well known. The objective of this work is to revise both the different aspects and mechanisms of this corrosion.

A new denomination is proposed which seems more appropriate to account for the time and place of this corrosion mechanism: reactivated corrosion. As for the condition of the corroded artefact, the terms stable and unstable are used to describe its behaviour.

The term reactivated is used in chemistry and supposes that the corrosion occurs when a criteria changes in the system "object- environment". In the case of archaeological artefacts, we propose then the following definition for reactivated corrosion: revival of the corrosion of the metal due to the modification of parameters of the external environment. It is usually revealed by the formation of unstable corrosion products.

In the second part of this work, we propose a diagnosis of an archaeological iron object. It includes previous criteria like type of mineralization (for example corrosion depth), posterior major symptoms and minor symptoms (features revealing the presence of reactivated corrosion). The presence or absence of these characteristics in relation with the date of the apparition of damage gives an assessment of the risk for the object to develop a reactivated corrosion.

In the long term, this work will be developed and extended during a Master degree in conservation of Cultural Heritage.

Contacts: Marie-Anne Loeper-Attia (IRRAP)
Funding : no external funding

New research projects

 Development of a simple non-destructive method for the chemical characterisation of metal objects through corrosion potential measurements (***Ghent University***)

In this work the possibilities of corrosion potential (E_{corr}) measurements as a quick screening and identification technique for metals and their corrosion products will be considered. The benefits of this technique are its simple operation and its low cost. As a result conservators can conduct a first quick screening of the metals on the spot, and are able to suggest quite rapidly better storage conditions in view of preventive conservation. Another advantage is that the often unique and precious objects do not need to be transported anymore.

The project consists of different steps. Our first goal is to determine to which extent E_{corr} measurements are suitable for the differentiation of various alloys with minor differences in composition. The project will concentrate on three metal families often encountered in the conservation field: 1) copper and copper alloys (brass and bronze), 2) lead and lead alloys (including lead-tin alloys) and 3) iron and its alloys. Not only bare metals, but also artificially corroded metals will be examined. Using this information a database of E_{corr} versus time plots will be built up for the various alloys.

In what follows the project will concentrate on the practical use of this approach for the analysis of archaeological and historical artefacts. Immersion is often not possible in this case, therefore a micro test method will be developed using a capillary-based droplet cell. Time will be spent in developing and optimising this method.

Finally the developed technique will be applied to authentic artefacts and the possibilities of this new technique will be compared to existing ones.

Contacts: Annemie Adriaens, Karen Leyssens (Ghent University) & Christian Degrigny
Funding: Ghent University

General information

- Web-sites

Some sites offer interesting information on research applied to the conservation field. Specific studies on metals might be found.

- **Laboratories on Science and Technology for the conservation of European Cultural Heritage**
  http://www.chm.unipg.it/chimgen/LabS-TECH.html

- **Cost Action G8: Non destructive analysis and testing of museum objects**
  http://srs.dl.ac.uk/arch/cost-g8

- **Cost Action G7: Artwork conservation by laser**
  The previous address is no more correct. Please consult the following one:
  http://domino.datacenter.ro/cost/index.html

- **JEWELMED** (Comparison analysis of manufacturing technologies in Goldsmithing and Silversmithing form the VII to the I century BC. in the Mediterranean Area. Search from Google or Yahoo with the acronym name. You will find the EJTN site. Choose then project. You will get a powerpoint presentation of JEWELMED.

- Future seminars and conferences

- **La conservation des métaux archéologiques: entre manufacture, analyses et traitements** (20 November 2002, Sion, Switzerland). For more information contact Cyril Benoît (benoitC@fr.ch)

- **Archaeometallurgy in Europe** (24-26 September 2003, Milan Italy). For more information consult http://www.aimnet.it/archaeo.htm

- Abbreviations and acronyms

CWOCL: Colonial Williamsburg Objects Conservation Laboratory
EDTA: Ethyldiaminetetraacetic
ICN: Instituut Collectie Nederland
IRRAP: Institut de Restauration et de Recherches Archeologiques et Paléométallurgiques
MAC: Maryland Archaeological Conservation
NHC: US Navy Naval Historical Center
NILPRP: Nastional Institute for Laser,Plasma and Radiation Physics
SRAL: Stichting Restauratie Atelier Limburg
TDS: Total dissolved solids
UPS: University of Paris Sorbonne
VDHP: Virginia Department of Historical Preservation
WLCC: Warren Lab Conservation Center

- Contacts

Annemie Adriaens / Ghent University (+ 32.9.264.48.26 - annemie.adriaens@rug.ac.be)
Bart Ankersmit / ICN (+31.20.30.54.737 - bart.ankersmit@icn.nl)
Christian Degrigny (christian_degrigny@hotmail.com)
Gilberte Dewanckel / IRPA (+32.2.739.68.34 - gilberte.dewanckel@kikirpa.be)
Karen Leyssens (Karen.Leyssens@rug.ac.be)
Marie-Anne Loeper-Attia / IRRAP (+33.1.46.07.87.97 - philattia@wanadoo.fr)
Paul Mardikian / WLCC, USA (mardikian@hunley.org)
Clementina Timus / NILPRP (timus@ifin.nipne.ro)
Marina Van Bos / IRPA (marina.vanbos@kikirpa.be)
Howard Wellman / MAC Lab (+410.586.8577 - wellman@dhcd.state.md.us)

- Correspondents

Australia: David Hallam, Canberra (d.hallam@nma.gov.au)
Belgium: Patrick Storme, Antwerpen (Patrick.storme@skynet.be) & Gilberte Dewanckel, Brussels (gilberte.dewanckel@kikirpa.be)
Denmark: Karen Stemann Petersen, Copenhagen (karen.stemann.petersen@natmus.dk)
France: Jean-Bernard Memet, Nantes (arcantique.recherche@wanadoo.fr) & Régis Bertholon, Paris (bertholon7@aol.com)
Germany: Gerhard Eggert, Stuttgart (gerhard.eggert@abk-stuttgart.de)
Greece: Vasilike Argyropoulos, Athens (bessie@teiath.gr)
Italy: Paola Letardi, Genova (letardi@icmm.ge.cnr.it)
Latin America: Johanna Theile, Santiago de Chile (jtheile@abello.dic.uchile.cl)
Netherlands: Bart Ankersmit, Amsterdam (bart.ankersmit@icn.nl)
Norway: Birgit Wilster-Hansen, Oslo (b.w.hansen@ukm.uio.no)
Romania: Dorin Barbu, Sibiu (dorin.barbu@brukenthalmuseum.ro)
Russian Federation: Andrey Chulin, St Petersburg (andrey_chulin@yahoo.com)
South Africa: Jaco Boshoff, Cape Town, (jboshoff@iziko.org.za)
Spain: Emilio Cano, Madrid (ecano@cenim.csic.es)
Sweden: Helena Strandberg, Göteborg (helena.s@hem.utfors.se)
Switzerland: Valentin Boissonnas, La Chaux-de-Fonds (v.boissonnas@heaa-ne.ch)
United Kingdom: David Thickett, London (dthickett@thebritishmuseum.ac.uk)
USA: Paul Mardikian, Charleston (mardikian@hunley.org)

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