JERICO

Application for Transnational Access

to Coastal Observatories

National Research Council of Italy
OGS
cnrs
IBW PAN
hcmr
NIVA
Norwegian Institute for Water Research
Ifremer
Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung
CSIC
National Oceanography Centre

Description of the project (to be provided in pdf format)
Please contact the manager of the infrastructure/installation you wish to use before writing the proposal

PART 1: User group details

Indicate if the proposal is submitted by

O an individual
X a user group

Information about the applicants (PI and project partners)

Principal Investigator (user group leader)

Title Dr. Name and Surname Emilio Cano Diaz

Gender X Male O Female

Institution Consejo Superior de Investigaciones Científicas Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC)

Department / Research Group Departamento de Ingeniería de Superficies, Corrosión y Durabilidad

Address Avda. Gregorio del Amo 8
28040 Madrid

Country Spain

email ecano@cenim.csic.es

Telephone +34 91 5538900 ext 309

Fax +34 91 5347425

Project partners
(repeat for each partner of the group)

Partner # 1

Title Dr. Name and Surname Edith Joseph

Gender O Male X Female

Institution Swiss National Museum

Department / Research Group Collections Centre / Laboratory of research in conservation

Address	Lindenmoosstrasse 1
	8910 Affoltern am Albis
Country	Switzerland
email	edith.joseph@snm.admin.ch, edith.joseph@unine.ch

PART 2: Additional information about the applicant(s) expertise

Expertise of the group in the domain of the application

This joint research aims at developing and evaluating innovative protective treatments for metallic artefacts. This application is a great opportunity to start a long-term collaboration among the partners and also with the facility host, CMN-ISMAR. In fact, it is an unique occasion for partners to work together and share their competences in order to form an European team of experts in electrochemistry, spectroscopy and corrosion working for metal conservation-restoration.
The National Center for Metallurgical Research (CENIM) belongs to the Spanish Council for Scientific Research (CSIC) in the Area of Science and Technology of Materials. It has a staff of 131 members, 62 from them are researchers. The research line of the PI if focused on the corrosion and protection of metallic cultural heritage, indoor corrosion, electrochemical techniques applied to conservation science, XPS and corrosion inhibitors. The use of electrochemical techniques has been the main contribution of his group to the 6FP project PROMET ("Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean basin"). The PI is now starting a national project on the application of electrochemical techniques to the evaluation of coatings for cultural heritage (CREMEL).
The Collections centre of the Swiss National Museum (SNM) is the most important Swiss institution working in the field of research and conservation of museum collections. Its research laboratory relies on almost 50 years of experience in heritage conservation, archaeometry and analyses addressing the specific issues faced by conservators, curators and archaeologists. It is also actively engaged in different European research networks and cooperates in numerous European projects on material science (in total, 5 Projects). In particular, the 7th FP MUSECORR project is developing loggers for continuous measurement of the corrosion rate in atmospheric conditions. Recently, a closed collaboration has been established with the University of Neuchâtel (CH) in order to create biological patinas for archaeological and artistic metal artefacts (BAHAMAS, 7FP). In particular, a biological treatment using fungi resistant to copper is developed to transform unstable corrosion patinas into copper oxalates. The BAHAMAS project is following the EU-ARTECH (6FP) project where a joint research activity on outdoor bronze monuments was carried out.

Short CV of the PI

Emilio Cano is Tenured Scientist at the National Center for Metallurgical Research (CENIM) of the Spanish National Research Council (CSIC) in Madrid. He graduated in Fine Arts Conservation in 1996 from the Complutense University of Madrid, where he also obtained his PhD in 2001 with a thesis that focused on the effect of organic acids on the conservation of copper. After completing an internship at the Canadian Conservation Institute, he continued his research career at the CENIM. He has published more than 80 papers on corrosion and conservation science (60 of them in international scientific journals included in the ISI-SCI) and presented at more than 45 scientific

conferences on corrosion and conservation science. Since 1997, he has participated in 19 national and international research projects, and 21 research contracts with institutions or private companies, including *Patrimonio Nacional* (National Heritage), *Instituto del Patrimonio Cultural de España* (Spanish Cultural Heritage Institute), and Museo Guggenheim Bilbao. He is Member of several conservation-related institutions, including the ICOM (Voting member of the ICOM-CC), the IIC (International Institute of Conservation), the GE-IIC (Spanish Group of the ICC) and the "Grupo Latinoamericano de Restauración de Metales" (Latin american metal conservation group).
He is Assistant Coordinator of the ICOM-CC Metal Working Group and Spanish Co-editor of the BROMEC (Bulletin of Research on Metal Conservation) published by that group. Member of the Executive Board of the Joint Programming Innititative "Cultural Heritage and Global Change: a challenge for Europe" and member of the Experts Group for the elaboration and follow-up of the "Plan Nacional de Investigación en Conservación-PNIC" (National Plan for Research in Conservation) of the Spanish Ministry of Culture.

A list of 5 recent, relevant publications of the participant(s) in the field of the project

1. E. Cano, D. Lafuente, D.M. Bastidas."Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: a review." J. Solid State Electrochem., 14 (2010) 381-391.
2. E. Cano, D.M. Bastidas, V. Argyropoulos, S. Fajardo, A. Siatou, J.M. Bastidas, C. Degrigny "Electrochemical characterization of organic coatings for protection of historic steel artifacts." J. Solid State Electrochem. 14,(2010) 453-463.
3. Paterakis, A., Cano, E., Lafuente, D "The corrosive influence of acetic acid emissions on bronze and the efficacy of two protective coatings" In: Metal 2010, Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group, P. Mardikian et al, Eds. Charleston, South Carolina, USA,11-15 October 2010. ISBN 978098303990. pp.132-137.
4. E. Joseph, A. Simon, S. Prati, M. Wörle, D. Job, R. Mazzeo. Development of an analytical procedure for evaluation of the protective behaviour of innovative fungal patinas on archaeological and artistic metal artefacts. Analytical and Bioanalytical Chemistry 2011, 399 (9), 2899-2907. (Paper in forefront and cover image)
5. E. Joseph, P. Letardi, R. Mazzeo, S. Prati, M. Vandini. Innovative Treatments for the Protection of Outdoor Bronze Monuments. In Metal 07: Interim Meeting of ICOM-CC Metal WG Amsterdam, 17-21 September 2007. C. Degrigny, R. van Langh, I. Joosten and B.Ankersmit (Eds.), Rijksmuseum: Amsterdam, 2007; 71-77.

PART 3: Detailed scientific description of the project

List the main objectives of the proposed research

(one page maximum)

The main objectives of the project are to define advantages and limits of innovative protective treatments and to standardize a specially adapted electrochemical methodology for assessing their effectiveness in comparison with treatments nowadays used. Among the different treatments tested, a human- and eco-friendly biological treatment which creates protective patinas on copper artefacts will be evaluated. This project will contribute to a better conservation-restoration of metallic artefacts by means of the advance in the application of electrochemical techniques and to extend the knowledge on efficacy of biological interventions. Through this, the overall idea is to

enhance research in the field of metal conservation-restoration promoting a dialogue among conservators and scientists, to encourage the use of electrochemical techniques as well as new treatments based on clear scientific and ethical criteria (efficiency, harmless, respect of the aesthetic and historical values) and to enhance conservation activities in their social and economical aspects with the development of ready-to-use treatment kit for conservators-restorers. The following aspects will be investigated:

- Selection and characterization of metal standards to be used,
- Definition of the human- and eco-friendly innovative treatments and identification of the best conditions of application,
- Evaluation upon ageing of the developed method on standards coupons and comparison with the most commonly used treatments.
- Standardization of an electrochemical methodology for in situ assessment.

The analytical results will be integrated within a publication in Corrosion science, including a footnote, such as “This research has been carried out with the support of the European Union, within the VII Framework Program (Contract 262584: JERICO).The authors acknowledge the CNR ISMAR for access time to the experimental marine station”.

Give a brief description of the scientific background and rationale of your project

(one page maximum)

Electrochemical processes, chemical reactions with pollutants and physical phenomenon of deposit accumulation can lead to irreversible changes in the original appearance and structure of a metal artefact. A constant effort from the research community is necessary to overcome this continuous damage suffered by artefacts and to achieve outstanding advances in modern material science. Nowadays, waxes, acrylic resins (Incralac) and corrosion inhibitors (benzotriazole) are commonly used for the protection and corrosion inhibition of metal artefacts. The use of waxes is largely diffuse even if it represents some disadvantages such as surface darkening, frequent maintenance and incomplete reversibility[1,2]. Regarding Incralac, regular maintenance is also needed and other complications have been observed: shiny aspect assumed by the treated surface, brittleness of the film and its difficult removal over time[3]. Finally, benzotriazole is toxic and a well known human carcinogen. While organic coatings are applied in a non-selective way, improved protective systems should be developed so as to modify existing corrosion products, create more stable and less soluble compounds and maintain the surface’s physical appearance. In their design, some criteria should be taken into account in terms of effectiveness, durability, innocuousness for persons and environment. Here it is proposed an alternative treatment where the protection can be provided by naturally occurring microorganisms. In the literature, some species of fungi were reported for their ability to transform metal compounds into metal oxalates[4,5]. Moreover, the progress achieved in corrosion control using microbial films was already presented and their utilization was illustrated as a novel strategy for protecting metal substrates[6]. For example, the presence of copper oxalates on outdoor exposed bronzes has already been identified[7], but is not associated with the phenomenon of cyclical corrosion. Instead compact patinas of an attractive green color are created on the bronze surface. Moreover, with a high degree of insolubility and chemical stability even in acid atmospheres (pH 3), it provides the surface with good protection[8]. Within the EU-ARTECH and BAHAMAS projects, very promising results were obtained with almost 100% of conversion from copper hydroxysulfates and hydroxychlorides into copper oxalates, using a fungal strain isolated from vineyard soils highly contaminated with copper. This biological treatment is now further investigated. In particular, the

metal oxalates formed are in-depth characterized in order to define their properties (formation mechanisms, adhesion...) and optimize the application procedure. Particular attention is devoted to the efficacy, durability and impact on color to overcome the problems associated with the treatments in use nowadays. For the qualitative and quantitative assessment of the effectiveness of protective treatments, the utility of electrochemical impedance spectroscopy (EIS) have been demonstrated by pioneer works[9] However, as opposed to industrial applications, its use is not standardized[10]. Therefore, in parallel to the evaluation of innovative treatments mentioned above, a specific methodology will be assessed for applying electrochemical methods and testing protective treatments in situ, in particular during ageing.

1. Moffett, D. L. (1996) Journal of American Institute of Conservation, 35, 1-8.
2. Johnson, R. (1984) In Adhesives and consolidants (Eds. Brommelle, N. S., et al.). London: International Institute for Conservation of Historical and Artistic Works (IIC), 107-109.
3. Brostoff, L. B. 2003. Coating strategies for the protection of outdoor bronze art and ornamentation. Universiteit Amsterdam.
4. Sayer, J.A., M. Kierans, and G.M. Gadd. (1997) FEMS Microbiology Letters, 154, 29-35.
5. Gharieb, M.M., M.I. Ali, and A.A. El-Shoura. (2004) Biodegradation, 15, 49-57.
6. Zuo, R. (2007) Applied Microbiology and Biotechnology, 76, 1245-1253.
7. Nassau, K., et al. (1987) Corrosion Science, 27, 69–84.2.
8. Marabelli, M., R. Mazzeo. (1993) La metallurgia italiana, 85, 247–254.
9. Letardi, P. (2004) In Metal2004. (Eds. Ashton, J., Hallam, D.). Canberra: National Museum of Australia, 379-387.
10.Cano, E., et al, (2010) Journal of Solid State Electrochemistry, 14, 381-391.

Present the proposed experimental method and working plan

(one page maximum)

To achieve the general and specific objectives of the project, the following scientific and technologic research activities will be planned:

Task 1. Selection, preparation and characterization of samples to be used as standards.

It is known that active corrosion from chlorides (and in little part sulfates) is the main responsible for degradation of metal artefacts. In order to evaluate the efficiency of a novel treatment, copper,bronze and steel standards, which replicate the commonly found patinas in nature, are needed, as demonstrated by others studies in this field. The goal is to obtain at the end of the task, samples properly aged with typical natural patina, which is fully characterized in order to have a start point before treatment and understand the eventual modifications which will occur during the following treatment and ageing. Properly naturally aged metal coupons samples with typical occurring corrosion products, will be prepared. The patina will then be documented and fully characterized in order to assess its color, thickness, morphology, composition and protection efficiency before any treatment applied. A complement of analytical techniques such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Raman and Fourier transform Infrared (FTIR) spectroscopies, electron impedance spectroscopy (EIS), colorimetry and thickness measurements will be used.

Task 2. Definition of treatments (formation mechanisms and application protocols) and application.

The main objective is here the creation of relatively thick oxalates' patinas with no remains of fungi strains. The action mechanisms of *Beauveria bassiana* will be investigated in order to better reproduce and increase the formation of metal oxalates. The quantification of the metal oxalates crystals will be done by X-ray diffraction and the production of oxalic acid determined by high performance liquid chromatography. Particular attention will be dedicated to verify that all fungi

have been removed after treatment, using for example SEM. *Beauveria bassiana* will be inoculated on the different copper/bronze and steel standards to create biofilms of copper/iron oxalates, which will be characterized with the same analytical techniques used in task 1 for the original patina. For comparison, protective treatments (wax Cosmolloid H80, fluorosilane F8263, Paraloid B72…) used nowadays in bronze conservation will also be applied on similar copper and bronze coupons and characterized in the same way.

Task 3. Evaluation of their performance, efficiency and durability.

The performances of the treatments will be evaluated on the basis of their resistance, color, surface's morphology and protection behavior through color measurements, microscopy (optical, SEM, Raman, FTIR), as for tasks 1 and 2. These analyses will be carried out before and after exposure either non-destructively on sample's surface on micro-destructively in cross-sections. EIS measurements will be used to monitoring the protective performance during ageing tests. The ageing exposure is a key point to evaluate the protection performance of the treatments upon time, as confirmed elsewhere by numerous conservation research projects.

Indicate the type of access applied for

O remote	*(the measuring system is implemented by the operator of the installation and the presence of the user group is not required)*
X partially remote	*(the presence of the user group is required at some stage e.g. installing and un-installing)*
O in person/hands on	*(the presence of the user group is required/recommended during the whole access period)*

Indicate the proposed time schedule including expected duration of access time

(half a page maximum)

For task 1, we plan to expose in Genoa during one year 16 bare samples (60x60x3mm) made of copper, a modern bronze alloy (Cu85/Sn5/Zn5/Pb5) from a Swiss foundry and a weathering steel (such as CorTen steel) , for a total amount of 48 samples. The samples will be then properly aged with a natural urban-marine patina. In parallel, the facility will also be used during 4 months for evaluate the efficiency of a first selection of protective treatments on coupons already available at the SNM for a total amount of 60 samples. The most promising treatments will thus be individuated, then be applied on the coupons aged in task 1 and compared with traditional coatings used for conservation/restoration treatments. It's worth saying that this access of 130 days will allow us to obtain significant information for the implementation of our following tasks. As mentioned above, one-year exposure is planned and therefore users group will apply for further grants in order to achieve the tasks foreseen. The presence of one person for each partner-institution is requested at the beginning and end of the access as this will be the occasion to meet together with CNR-ISMAR and set the future collaboration together. In fact, SNM (Switzerland) will bring copper/bronze coupons and its expert in spectroscopy and corrosion and CENIM (Spain) will bring steel coupons and its expert in electrochemistry and corrosion.

Access time to JERICO facility	June 2012- t_0				October 2012- $t_{4months}$				June 2013- $t_{12months}$			
weeks	1	2	3	4	1	2	3	4	1	2	3	4
Installation of samples for pre-screening												
EIS measurements in situ – starting point												
EIS measurements in situ – end point												
Uninstallation of treated samples												
Installation of samples for ageing												
EIS measurements in situ – starting point												
EIS measurements in situ – monitoring												
EIS measurements in situ – end point												
Uninstallation of aged samples												

Host infrastructure

Indicate the type(s) of JERICO host facility(s) you are interested in
(Tick more than one if it is useful for your project)

O ferrybox X fixed platform O glider O calibration laboratory

Indicate the specific JERICO host facility(ies) you wish to choose

MPL Genoa

Explain briefly why you think your project will be best carried out at the specified host facility(ies)

The host facility available in Genoa is implemented in the Genoa harbor and represents a unique exposure site in an urban-marine environment. This site is therefore suitable for evaluating the corrosion behavior of treatments on urban and marine aged coupons together. Moreover, the estimated atmospheric corrosiveness is the max class C5 according to ISO 9223. This extremely aggressive atmosphere will allow a better evaluation of the different treatment's behaviors in a shorter exposure time. Moreover, these conditions will ensure the formation of an adequate urban-marine patina on the bare coupons. Finally, a meteorological station is collecting collected ongoing climatic data (temperature, relative humidity, pressure, precipitations, sunlight and Time of Wetness ToW). Our measurements could then be correlated with these meteorological data and a long-term predictive corrosion model for bronze artefacts could be designed. During the use of this facility, a closed collaboration will also be established with the host organization (CNR-ISMAR) for performing EIS measurements with a specially designed contact probe available at this institution. The pre-screening measurements are of the outmost importance to evaluate the corrosion behavior of the different treatments to be selected for this project.

If possible, list other JERICO facility(ies) where you think your experiment could alternatively be carried out

-

Additional information

Is there a facility similar to the one you wish to utilize in your country?

X Yes O No

If yes, please indicate your reasons for requesting access to the JERICO facility you have chosen

CENIM-CSIC has access to some atmospheric corrosion test sites, but none of them with the urban/marine character and the extreme aggressiveness of the JERICO facility. It is necessary to have such an aggressive environment in order to be able to assess the protectiveness of the coatings in a relatively low time.

Have you already submitted an Access Proposal to any of the participating facilities under this or previous EU Programs?

O Yes X No

If yes, please indicate the name of the institution, submission date and reference number for each such proposal

Is this a resubmission of a previously rejected proposal? *(Select "yes" if this application is a revised version of a proposal submitted to JERICO before that was rejected by the Selection Panel)*

O Yes X No

If yes, please give the exact reference number and submission date. Kindly describe briefly the changes made in comparison to the rejected version.

Is this a continuation of an earlier project funded under a previous call for Transnational Access in JERICO at the same facility?

O Yes X No

If yes, please give the exact reference number and submission date. Kindly indicate also what has been achieved in the previous experiment and the reasons why the objectives have not been fully met.

PART 4: Technical information

Wherever possible, please specify your requests regarding the use of your chosen facility's equipment/instruments/sensors, including any additional services, data or other requirements.

During the exposure in MPL Genoa, we need the meteorological data to be collected. Part of the EIS measurements will be performed with a specially designed contact probe (ST15) available at the CNR-ISMAR by Dr. Paola Letardi.

List all material/equipment you plan to bring to the JERICO facility (if any):

Bare samples to be aged:

- 16 copper coupons
- 16 bronze coupons (Cu85/Sn5/Zn5/Pb5 alloy- Swiss foundry)
- 16 steel coupons (CorTen alloy)

Treated samples to be aged:

- 12 urban naturally aged copper coupons (CUN)
- 12 urban artificially aged bronze coupons (UA)
- 12 marine naturally aged bronze coupons (QQ)
- 12 marine artificially aged bronze coupons (MA)
- 12 marine artificially aged copper coupons (CMA)

Nylon screws and nuts, cable ties for fixing the samples on the rack available.

Please provide a detailed and realistic budget for the expenses you expect to incur for travel/boarding and the shipment of equipment, if applicable in your case *(note that a maximum of two travel grants will be assigned to each user group, depending on the length of the requested period of stay)*.

As the beginning and the end of access will be the opportunity for partners to meet together with CNR-ISMAR, both institutions will be present at these periods of time.

Eligible expenses for the activities carried out by the users group - euro			
Partially remote access	*Travel allowance (flight AR Geneva/Madrid-Genoa)*	*Living allowance (15 days)*	*Accommodation allowance (14 nights)*
t_0	400.00	350.00	1000.00
$t_{4months}$	400.00	350.00	1000.00
TOTAL	800.00	700.00	2000.00
		TOTAL	**3500.00**

Please tick the appropriate boxes and give detailed information for the kind of risks associated with your proposed activity

☐ Chemical :-
☐ Biological :-
☐ Radiological :-
☐ Other :-

Date of compilation 23.03.2012

Signature of the PI

Signature of an appropriate authorised person
(e.g. Head of Department, Research Office)

DR. EMILIO CAMPO
HEAD OF DEPARTMENT

This section reserved to the JERICO TNA Office

Date of proposal receipt by email

Assigned reference number

Signature of receiving officer